

Decolorization of textile dyes by TiO₂-based photocatalyst using polyol as electron donor

Pham Thi Bich Van¹, Hoang Minh Hao², Nguyen Thi Thanh Thuy¹, Cao Thi Hong Xuan¹

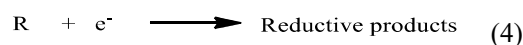
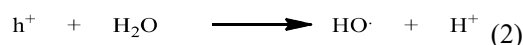
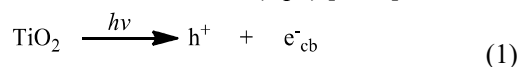
Abstract—Decolorization of textile dyes including 2,6-dichlorophenolindophenol (DCIP), congo red (CR) and methyl orange (MO) by using TiO₂-based photocatalyst in the presence of polyols such as glycerol and ethylene glycol was investigated. Polyols were used as sacrificial electron donors (SEDs). The results showed that the polyols improved the rate and yield of a light-induced decolorization of dyes in comparison with a photocatalytic reaction without polyols. A possible reaction mechanism of dye decolorization by the photocatalyst in the presence of electron donors was proposed. TiO₂ photocatalyst absorbed light to generate electrons (e⁻) and holes (h⁺). The electrons and holes were prevented from recombining by the presence of SEDs. The free electrons and holes then involved in decolorization processes through reduction or oxidation reactions. The effects of TiO₂ catalyst amounts, irradiation time and polyol concentrations on dye decolorization were investigated. The decolorization efficiency significantly increased with the increasing irradiation time, SED concentrations and certain amounts of TiO₂.

Keywords—Congo red, 2,6-dichlorophenolindophenol, methyl orange, polyol, TiO₂ photocatalyst

1. INTRODUCTION

Photocatalyst causes an increase in the rate of a light-induced reaction by a catalyst. One of the applications of photocatalysis that is receiving current attention is the decolorization/degradation of organic pollutants [1-7]. The interest in this area will become more intense as inhabitants have been seriously influenced by organic pollutants in wastewaters of factories. The use of sunlight to drive the decolorization of dyes requires a

photochemical system into which the energy enters *via* the absorption of light with a certain wavelength by one of the components such as colored organic dyes or photocatalyst [1, 7]. These systems generally consist of a semiconductor and a colored dye that adsorbs on the surface of the semiconductor. Titanium dioxide (TiO₂) is a best semiconductor material for the photocatalytic decolorization/degradation of organic pollutants, being inexpensive and capable of decolorizing a variety of dyes [1, 7-11]. In the photocatalytic reaction, TiO₂ absorbed the UV light to excite an electron from the valence band (VB) to the conduction band (CB). This band-band excitation produced the reductive conduction band electrons (e⁻) and the oxidative valence band holes (h⁺) (eq 1). The holes could react with surface adsorbed H₂O to produce HO· surface-absorbed radicals (eq 2). The subsequent radicals HO· directly oxidized the organic pollutants (R) into their oxidative products (eq 3). The photogenerated electron from CB decolorized R into reductive products *via* a chemical reduction (eq 4) [1, 11].



However, the efficiency of the photo-induced decolorization of dyes was in general low due to the recombination of the electrons and holes. In order to inhibit this disadvantage, an electron donor could be added into the reaction mixture as a hole scavenger to achieve high efficiency of decolorization process of colored organic dyes [12]. Polyols were well-known as electron donors. They were extensively used in organic

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synthesis, food and industry. In this study, polyols including glycerol and ethylene glycol were used as sacrificial electron donors (SEDs) to prevent the recombination of the electrons and holes in TiO₂ photocatalyst. This resulted in more electrons (e⁻) and holes (h⁺) becoming free to reduce or oxidize organic dyes into colorless forms. The dyes of 2,6-dichlorophenolindophenol (DCIP), congo red (CR) and methyl orange (MO) were used to investigate the photo-induced decolorization by TiO₂ photocatalyst in the presence of polyols.

2. MATERIALS AND METHODS

Materials

Titanium (IV) dioxide (AEROXIDE® TiO₂ P25, nanopowder, 21 nm, Sigma Aldrich, 99.5%) was used as photocatalyst. Glycerol (Merck 98%) and ethylene glycol (Merck 98%) were used as electron donors in decolorization reactions. 2,6-dichlorophenolindophenol (DCIP, Merck), congo red (CR, Fluka) and methyl orange (MO, Fluka) were used as dyes. Chemical structures of dyes were given in Fig. 1. Silica gel (Merck 99%), which is the same color as the TiO₂ catalyst, was used as a non-photocatalytically active powder. The Suntest was equipped with a 70 W B22 IL0132 Halogen lamp. Absorption spectra of dye solutions were measured by UH5300 UV-Vis spectrophotometer.

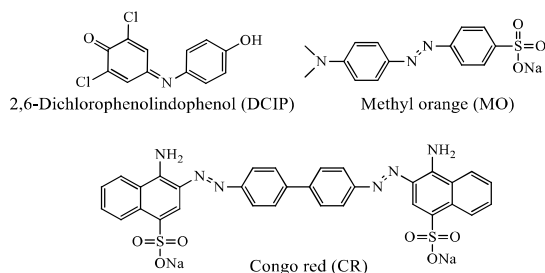


Fig. 1. Chemical structures of dyes were used in experiments

Sample preparations

To demonstrate the efficiency of polyols on the dye decolorization by using TiO₂ P25, it was important to have two controls: one with no photocatalyst (control 1) to show that the light could not decolorize dye solutions and another (control 2) to have a test tube with a white powder of silica gel to show that the color change came from the photocatalyst acting on dyes rather than from the powdered sample. A third control (control 3) contained photocatalyst but was kept in the dark

to confirm that it was the action of the light combining with the photocatalyst that caused the color change. Stock solutions were prepared by dissolving dyes in double distilled water. Concentrations of stock solutions of DCIP, CR and MO were 5.0, 2.0 and 2.5 g L⁻¹, respectively. Samples were prepared as follows:

Effects of TiO₂ amounts on dye decolorization

Concentrations of dyes and polyols were kept constant. The amounts of TiO₂ were varied in a range from 1.0 to 10.0 mg.

Control 1: Each dye of 1 mL, 5 mL double distilled water, 2.4 mg glycerol (or 3.6 mg ethylene glycol), 0 mg TiO₂.

Control 2: Each dye of 1 mL, 5 mL double distilled water, 2.4 mg glycerol (or 3.6 mg ethylene glycol), silica gel (the same amount with TiO₂ used).

Control 3: Each dye of 1 mL, 5 mL double distilled water, 2.4 mg glycerol (3.6 mg ethylene glycol), TiO₂ (kept in the dark).

Photocatalyst: Each dye of 1 mL, 5 mL double distilled water, 2.4 mg glycerol (3.6 mg ethylene glycol), (1.0–10.0) mg TiO₂.

Control 1, control 2 and photocatalyst tubes were continuously irradiated under halogen lamp.

Effects of irradiation time on dye decolorization

Dye, polyol concentrations and TiO₂ amount were fixed while the irradiation time had been changed. The irradiation time on DCIP solutions were 15, 30 and 45 min, respectively. CR and MO solutions were irradiated for 60, 90 and 120 min.

Effects of polyol concentrations on the dye decolorization

TiO₂ amount (5 mg), dye concentrations and irradiation time were kept constant. The polyol concentrations were changed in a range from 0.1 to 0.5 g L⁻¹ in DCIP solutions while those were varied between 0.3 and 0.7 g L⁻¹ in CR and MO solutions.

After dye solutions were irradiated, all suspension solutions were centrifuged in three repetitions to completely remove TiO₂. Dye solutions were then measured their absorption spectra to obtain the absorbance values at maximum absorption wavelengths. Dye water-solutions were conducted at room temperature. Experimental procedures followed the order: (1)

The effects of the amounts of TiO_2 on dye decolorization, (2) the examination of the photocatalytic efficiency of TiO_2 for decolorization of dyes in the presence of polyols in comparison with the results of TiO_2 catalyst without polyols, (3) the irradiation time, and (4) the effects of polyol concentrations on dye decolorization.

3. RESULTS AND DISCUSSION

UV-Vis spectra of dye solutions

Fig. 2 showed UV-Vis absorption spectra of dye solutions in a range of wavelength from 400 to 700 nm. The results showed that the positions of the maximum absorption peaks of DCIP, CR and MO were 600, 498 and 464 nm, respectively. The absorbance values at maximum absorption wavelengths of dyes were measured to investigate the effects of the TiO_2 catalyst amounts, the efficiency of polyols, polyol concentrations and irradiation time on dye decolorization.

Effects of amounts of TiO_2 on the dye decolorization

For examining the effects of amounts of TiO_2 catalyst on dye decolorization, several amounts of TiO_2 (a range from 1.0 to 10.0 mg, corresponding to a concentration range from 0.17 to 1.67 g L^{-1}) were dispersed in 6 mL of dye solutions. Concentrations of dye solutions and irradiation time were kept constant. Depending on dyes, the irradiation time on DCIP solutions was 45 min while CR and MO solutions were irradiated for 90 min. Glycerol concentration (0.4 g L^{-1}) was also fixed. Fig. 3 showed that the absorbance values at maximum absorption wavelengths decreased with increasing the amount of TiO_2 catalyst from 0.17 to 0.83 g L^{-1} , i.e., the decolorization efficiency increased. However, the higher amounts ($> 0.83 \text{ g L}^{-1}$) showed a decrease in decolorization. These results could be explained in terms of availability of active sites on TiO_2 surface and light penetration of photoactivating light into dye solutions. The availability of active sites increased with the suspension of TiO_2 catalyst, but the light penetration decreased due to increased opacity of the suspension, brought as a result of excess of TiO_2 particles. Moreover, the decrease in the dye decolorization at higher catalyst loading might be also due to deactivation of activated molecules by collision with ground state molecules [2, 13, 14]. In

addition, the decrease in dye concentrations with increasing TiO_2 amounts could be attributed to the adsorption of dye-adsorbed TiO_2 [15]. TiO_2 P25 (21 nm) was a fine white powder with hydrophilic character caused by hydroxyl groups on the surface [16]. This surface adsorbed dyes *via* hydrogen bonds between catalyst surface and dyes [15, 17]. In our experiments, the control samples were always attached. Therefore, the decolorization of TiO_2 catalyst in the presence of polyols was more significant than without polyols. The optimum concentration of TiO_2 was 0.83 g L^{-1} (5 mg). This amount was selected for the next experiments.

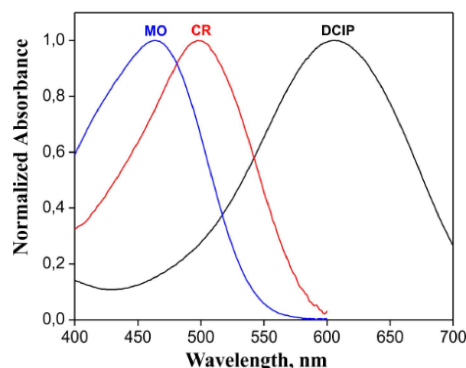


Fig. 2. The normalized absorption spectra of dye solutions. The concentrations of DCIP, CR and MO were 0.83, 0.33 and 0.41 g L^{-1} , respectively

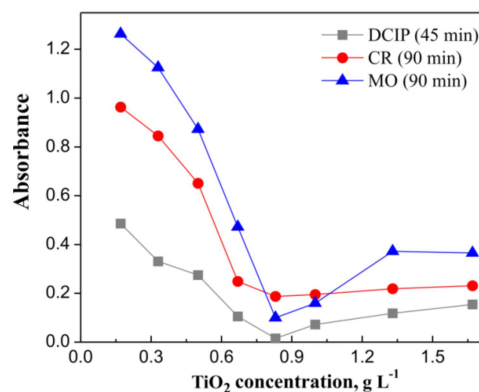


Fig. 3. The effects of TiO_2 concentrations on dye decolorization. Absorbance values of dye solutions were determined at maximum absorption wavelengths from their absorption spectra. Irradiation time on DCIP solutions were 45 min while CR and MO solutions were irradiated for 90 min. Glycerol was used as an electron donor with a concentration of 0.4 g L^{-1}

Effects of polyol and irradiation time on dye decolorization

Left panels of Fig. 4 gave the absorption spectra of dye solutions while the right ones depicted the absorbances of dyes at their maximum absorption wavelengths at different irradiation time in the absence and the presence of glycerol (Gly). The absorbances at maximum wavelengths of dyes significantly decreased in the presence of polyol under different irradiation time. Color of dye solutions had changed to colorless with increasing irradiation time. The experimental results showed that absorbance values at maximum absorption wavelengths decreased as irradiation time was increased. The color of dye solutions completely disappeared within 45 min for DCIP and 120 min for CR and MO. It was observed that the

photodecolorization increased with an increase of in the irradiation time. Fig. 4 showed that in the presence of glycerol (0.4 g L^{-1}) and photocatalyst of TiO_2 (0.83 g L^{-1}) and under 45 min of irradiation, 99.14% of the DCIP solution (0.83 g L^{-1}) was decolorized. The decolorization yields of CR (0.33 g L^{-1}) and MO (0.41 g L^{-1}) under 120 min of irradiation were 99.86% and 99.18%, respectively. In the absence of glycerol, 48.63% of the DCIP solution was decolorized by TiO_2 catalyst after 45 min while the photodecolorization yields of 74.08 and 77.30% obtained for CR and MO solutions respectively after 120 min of irradiation.

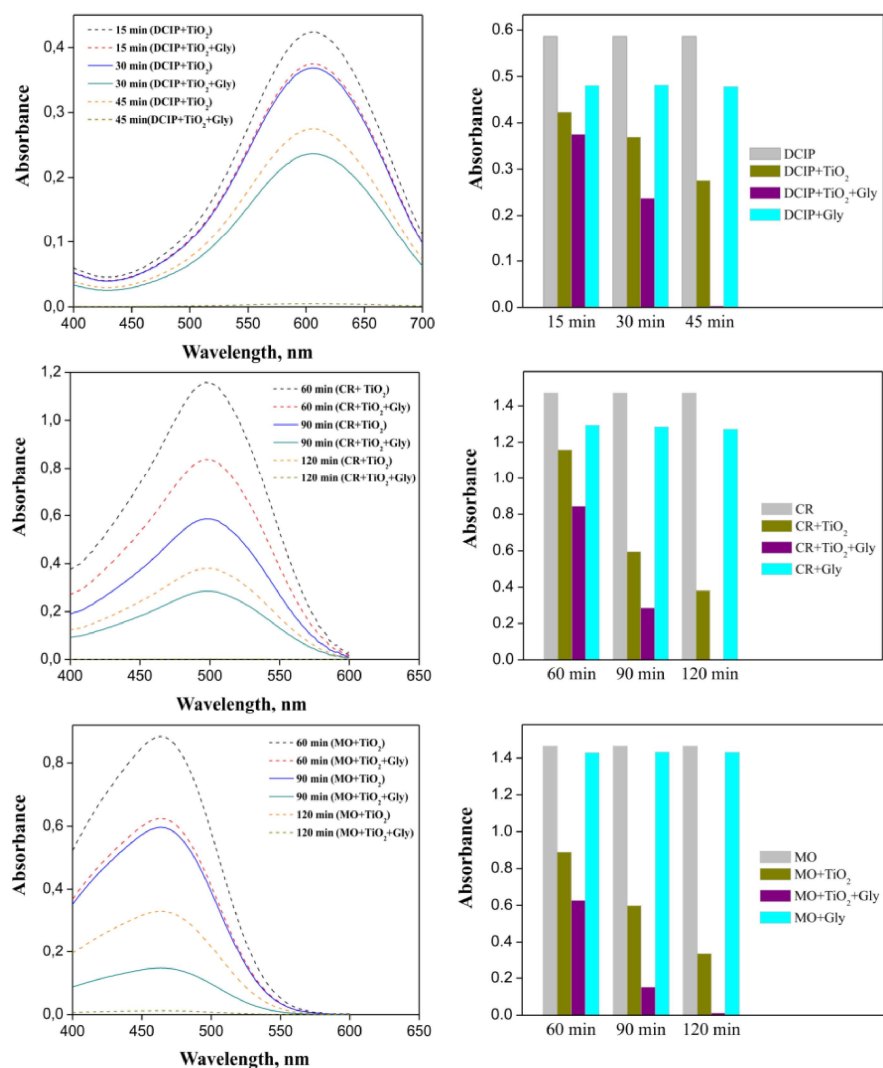


Fig. 4. The absorption spectra (left panels) and the absorbance values (right panels) at maximum absorption wavelengths of dye solutions at different irradiation time in the absence and the presence of glycerol (Gly)

The experimental observations confirmed the effect of polyol on the dye decolorization. A possible photocatalytic mechanism in the presence of polyol was suggested [7]. In the photocatalytic reaction, light generates electrons (e^-) and holes (h^+) in TiO_2 (eq. 1). The electrons and holes were prevented from recombining by the presence of a sacrificial electron donor (SED). In this experiment, glycerol was oxidized. This left the photogenerated free electrons and holes to reduce or oxidize dyes to its colorless forms. The schematic of this process was shown in Fig. 5. The experimental results also confirmed that dye solutions were not considerably reduced by SED in solution including dye and SED (the cyan columns in right panels in Fig. 4). The photodecolorization was mainly caused through a possible mechanism suggested in Fig. 5. Carbon dioxide and water were the final oxidation products of glycerol *via* intermediates including glyceraldehyde, glycolaldehyde, glycolic acid, and formaldehyde [8, 12].

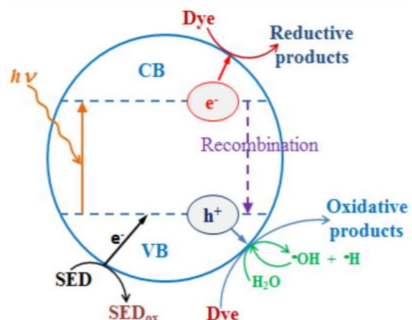


Fig. 5. A possible photocatalytic mechanism in the presence of a sacrificial electron donor (SED)-polyol

Effects of polyol concentrations on dye decolorization

In order to investigate the effects of polyol concentrations on dye decolorization, the amount of TiO_2 (5 mg , 0.83 g L^{-1}) and dye concentrations (DCIP: 0.83 g L^{-1} ; CR: 0.33 g L^{-1} ; MO: 0.41 g L^{-1}) were kept constant while polyol concentrations were varied. After centrifugation, dye solutions were then measured their absorption spectra to obtain the absorbance values at maximum absorption wavelengths. It is noted that the increase in polyol concentrations leads to increase in decolorization (Fig. 6). The optimized concentrations of glycerol and ethylene glycol to decolorize dye solutions are 0.4 g L^{-1} for DCIP, 0.6 g L^{-1} for CR and 0.5 g L^{-1} for MO, respectively. The decolorization efficiency relates to the prevention from recombining between electrons (e^-) and holes (h^+) of sacrificial electron donor. As concentrations of polyols increase, the probability of reaction between holes (h^+) and reducing species (polyols) also increases. The decolorization thus increases.

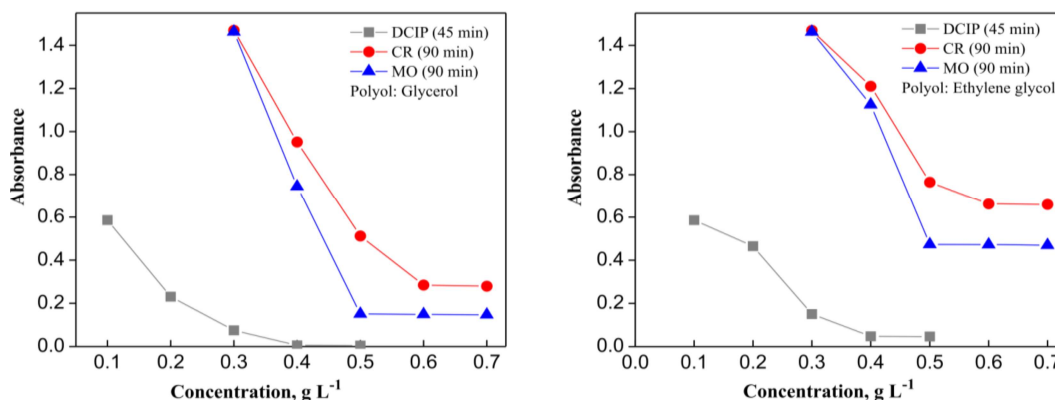


Fig. 6. Effects of polyol concentrations on decolorization of dye solutions. DCIP solution was continuously irradiated for 45 min while the irradiation time for CR or MO solutions was 90 min

4. CONCLUSION

A simple demonstration of photocatalysis was presented. The procedure was simple to perform, and could easily be modified into a laboratory experiment. The mechanism of dye decolorization by TiO₂ photocatalyst in the presence of polyols was discussed. The decolorization efficiency by TiO₂ photocatalyst on textile dye solutions significantly increased in the presence of polyols as electron donors. The effects of TiO₂ amounts, irradiation time and polyol concentrations on decolorization were examined. It was found that the DCIP solution (0.83 g L⁻¹) containing TiO₂ photocatalyst (0.83 g L⁻¹), glycerol or ethylene glycol (0.4 g L⁻¹) was completely decolorized (yield: 99.14%) after irradiation for 45 min. The decolorization yield of CR solution (0.33 g L⁻¹) consisting of TiO₂ photocatalyst (0.83 g L⁻¹), glycerol or ethylene glycol (0.6 g L⁻¹) under 120 min of irradiation was 99.86%. The one of MO solution (0.41 g L⁻¹) was 99.18% after irradiation for 120 min. The electron donors such as glycerol or ethylene glycol prevented from recombining of the electrons and holes being generated by light absorption of TiO₂ catalyst. They became free to easily involve in reductive or oxidative reactions in solution to change dyes into colorless forms. Therefore, the decolorization yields increased with the presence of polyols.

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REFERENCES

- [1] C. Chen, W. Ma, J. Zhao, "Semiconductor-Mediated Photodegradation of Pollutants Under Visible-Light Irradiation", *Chemical Society Reviews*, vol. 39, no. 11, pp. 4206–4219, 2010.
- [2] S. Erdemoglu, S.K. Aksub, F. Sayilkan, B. Izgi, M. Asilturk, H. Sayilkan, F. Frimmel, S. Gucer, "Photocatalytic degradation of congo red by hydrothermally synthesized nanocrystalline TiO₂ and identification of degradation products by LC-MS", *Journal of Hazardous Materials*, vol. 155, no. 3, pp. 469–476, 2008.
- [3] M. Thomas, G.A. Naikoo, M.U. DinSheikh, M. Bano, F. Khan, "Effective photocatalytic degradation of congo red dye using alginate/carboxymethyl cellulose/TiO₂ nanocomposite hydrogel under direct sunlight irradiation", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 327, no. 15, pp. 33–43, 2016.
- [4] X. Shang, B. Lia, T. Zhanga, C. Li, X. Wang, "Photocatalytic degradation of methyl orange with commercial organic pigment sensitized TiO₂", *Procedia Environmental Sciences*, vol. 18, pp. 478–485, 2013.
- [5] Y. Su, Y. Yang, H. Zhang, Y. Xie, Z. Wu, Y. Jiang, N. Fukata, Y. Bando, Z. L. Wang, "Enhanced photodegradation of methyl orange with TiO₂ nanoparticles using a triboelectric nanogenerator", *Nanotechnology*, vol. 24, no. 29, pp. 1–6, 2013.
- [6] H.M. Hadi, H.S. Wahab, "Visible light photocatalytic decolorization of methyl orange using n-doped TiO₂ nanoparticles", *Journal of Al-Nahrain University*, vol. 18, no. 3, pp. 1–9, 2015.
- [7] D. Ravelli, D. Dondi, M. Fagnonia, A. Albini, "Photocatalysis: A multi-faceted concept for green chemistry", *Chemical Society Reviews*, vol. 38, no. 7, pp. 1999–2011, 2009.
- [8] A. Bozzi, T. Yuranova, I. Guasaquillo, D. Laub, J. Kiwi, "Self-cleaning of modified cotton textiles by TiO₂ at low temperatures under daylight irradiation", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 174, no. 2, pp. 156–174, 2005.
- [9] K.T. Meilert, D. Laub, J. Kiwi, "Photocatalytic self-cleaning of modified cotton textiles by TiO₂ clusters attached by chemical spacers", *Journal of Molecular Catalysis A: Chemical*, vol. 237, no. 1–2, pp. 101–108, 2005.
- [10] T. Yuranova, R. Mosteo, J. Bandata, D. Laub, J. Kiwi, "Self-cleaning cotton textiles surfaces modified by photoactive SiO₂/TiO₂ coating", *Journal of Molecular Catalysis A: Chemical*, vol. 244, no. 1–2, pp. 160–167, 2006.
- [11] M.R. Hoffmann, S.T. Martin, W. Choi, W.D. Bahnemann, "Environmental applications of semiconductor photocatalysis", *Chemical Reviews*, vol. 95, no. 1, pp. 69–96, 1995.
- [12] M.W. Pitcher, S.M. Emin, M. Valant, "A simple demonstration of photocatalysis using sunlight", *Journal of Chemical Education*, vol. 89, no. 11, pp. 1439–1441, 2012.
- [13] K.I. Konstantinou, A.A. Triantafyllos, "TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations", *Applied Catalysis B: Environmental*, vol. 49, no. 1, pp. 1–14, 2004.
- [14] J. Bandara, V. Nadrochenko, J. Kiwi, C. Pulgarin, "Dynamics of oxidant addition as a parameter in the modelling of dye mineralization (Orange II) via advanced oxidation technologies", *Water Science and Technology*, vol. 35, no. 4, pp. 87–93, 1997.
- [15] N.Q. Tuan, N. Tri, H.C. Hoai, L.C. Loc, "Ảnh hưởng của kích thước hạt tio₂ đến tính chất và hoạt độ xúc tác trong phản ứng quang oxy hóa p-xylene", *Tạp Chí Khoa Học, ĐHQGHN, Khoa Học Tự Nhiên và Công Nghệ*, vol. 26, pp. 57–63, 2010.
- [16] H.P. Boehm, "The chemistry of the surface of solids", *Kolloid-Zeitschrift und Zeitschrift für Polymere*, vol. 227, no. 1–2, pp. 17–27, 1968.
- [17] V. Augugliaro, L. Palmisano, A. Sclafani, C. Minero, "Photocatalytic degradation of phenol in aqueous titanium dioxide dispersions", *Toxicological & Environmental Chemistry*, vol. 16, no. 2, pp. 89–109, 1988.

Khử màu các chất màu dệt nhuộm bằng xúc tác quang TiO₂ dùng polyol làm chất cho electron

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Tóm tắt—Trong nghiên cứu này, hỗn hợp gồm xúc tác quang TiO₂ và polyol (glycerol hoặc ethylene glycol) đã được sử dụng để khử màu các chất dệt nhuộm 2,6-dichlorophenolindophenol (DCIP), congo đỏ (CR) và methyl cam (MO). Các polyol đóng vai trò là các chất cho electron. Kết quả cho thấy rằng với sự có mặt của polyol, tốc độ và hiệu suất khử màu của TiO₂ tăng lên đáng kể so với quá trình khử màu chỉ dùng TiO₂. Cơ chế khử màu bằng xúc tác quang TiO₂ với sự tham gia của polyol đã được đề nghị. Xúc tác quang hấp thu năng lượng từ nguồn sáng đã tạo ra các electron (e⁻) và các lỗ trống (h⁺). Với vai trò là các chất cho electron,

polyol đã ngăn chặn sự kết hợp lại giữa e⁻ và h⁺. Điều này tạo điều kiện cho các e⁻ và h⁺ tham gia các phản ứng khử hoặc oxy hóa tạo ra các dạng không màu của chất màu dệt nhuộm. Ảnh hưởng của lượng TiO₂, thời gian chiếu xạ và nồng độ của polyol lên hiệu suất khử màu cũng được khảo sát. Quá trình khử màu tăng lên đáng kể khi tăng thời gian chiếu xạ và nồng độ polyol trong một lượng nhất định TiO₂.

Từ khóa—Congo đỏ, 2,6-dichlorophenolindophenol, methyl cam, polyol, xúc tác quang TiO₂