



ORIGINAL ARTICLE

Photocatalytic decolourization of a new water-insoluble organic dye based on phenothiazine by ZnO and TiO₂ nanoparticles



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Abstract A new water-insoluble organic dye, namely, 2-((10-decyl-10H-phenothiazin-3-yl)methylene)malononitrile, was synthesized and fully characterized. It was envisioned that photocatalytic decolourization of a dye-containing long chain would pave the way for the photocatalytic remediation of wastewater containing toxic hydrophobic organic pollutants. Two commercially available nanoparticles, ZnO and TiO₂, were selected, and their photocatalytic decolourization of the dye from aqueous medium were compared. The black UV light irradiation of the colored samples in the presence of TiO₂ (P25) or ZnO resulted in their decolourization and the photocatalytic activity observed for TiO₂ (P25) was better than that of ZnO. The kinetic of decolourization indicated that the process was first-order from which the rate constant was calculated. Also, the effect of pHs on the kinetic of decolourization revealed a negligible effect, indicating that the pH, although it affects the catalysts but has no effect on the organic-based hydrophobic dye and thus no effect on the photocatalytic process.

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1. Introduction

Dyes are conventionally used in textile coloration and coating of polymers. Hi-tech functional dyes, on the other hand, are being manufactured for optoelectronic and medicinal applications (El-Shishtawy, 2009; El-Shishtawy et al., 2017). Parallel to this growing interest in dyes and their application, a severe environmental impact is being a challenge for scientists due to

the waste of toxic organic dyes in industrial effluents that damage the aquatic life. It is estimated that about 10^5 of various commercial dyes and pigments amounted to 7×10^5 tons are produced annually worldwide (Zollinger, 2001). Ultimately, about 10–15% of these chemicals are wasted into the effluents of the textile industry (Pagga and Taeger, 1994). Considerable research activities have been paid for the decolorisation of organic dyes from industrial effluents. These activities include decolorisation by sonocatalytic degradation (Salavati et al., 2012; Li et al., 2014; Taghizadeh and Seifi-Aghjekohal, 2015), ozonation (Hu et al., 2016), chemical oxidation (Esteves et al., 2016; Al Angari et al., 2019), adsorption (Hashem and El-Shishtawy, 2001; El-Shishtawy and Melegy, 2001; El-Shishtawy and Soltan, 2001; Sathian et al., 2014; El-Zahhar and Awwad, 2016; Patra et al., 2016), photocatalytic degradation (Cai et al., 2015; Chandra et al., 2016; Elango and Roopan, 2016; Kumar et al., 2016.), coagulation (Wei et al., 2015; Huang et al., 2015), microbiological decomposition (Kumar et al., 2016.), and adsorption processes (Hao et al., 2000). Each process has its advantages and disadvantages, as summarized in the literature (Pekkuz et al., 2008). However, in some of these, dye pollutants are only transferred from one phase to another, leaving the problem mostly unsolved.

Photocatalytic degradation is generally believed to proceed by the excitation with photons of energy higher than the bandgap of a semiconductor. This process results in the formation of a hole-electron pair in which the hole presents the valence band and the electron in the conduction band and. The generation of such an exciton pair would degrade the organic pollutants by a redox mechanism (Rochkind et al., 2015).

Zinc oxide, with its characteristic features such as low toxicity, abundance, chemical, and photochemical stability, renders this semiconductor as one of the most photocatalysts. However, ZnO has a high bandgap (3.37 eV), and its photocatalytic efficiency remains low as a result of electron-hole pair recombination (Becker et al., 2011; Umar et al., 2011; Li and Wang, 2010; Zhang et al., 2015). Titanium dioxide (TiO₂) has several advantages similar to ZnO but with more efficiency as photocatalyst as its bandgap energy (3.20 eV) is lower than that of ZnO (Hoffmann et al., 1995; Chen and Mao, 2007; Wang et al., 2014).

The above information concluded some successes in the degradation of water-soluble dyes; however, water-insoluble dyes that hazard the environment are scarcely investigated. Water-insoluble dyes are class of dyestuffs that are widely used in the coloration of textile industries as well as in the recent application of functional dyes. The use of an electron donor such as phenothiazine moiety in the construction of optoelectronics and dye-sensitized solar cells has been growing (Luo et al., 2016; El-Shishtawy et al., 2018; El-Shishtawy et al., 2016; Kafafy et al., 2014). It was envisioned that paving the way towards photocatalytic decolorization of such an important class of water-insoluble organic dyes would inspire scientists for further developments in this field. In this paper, a new water-insoluble dye derived from phenothiazine as electron donor and malononitrile as electron acceptor as a model dye of functional dyes was synthesized. The photocatalytic decolorization of aqueous solutions of the dye using TiO₂ and ZnO and at different pHs was investigated.

2. Experimental

2.1. General

Reagent grade chemicals purchased from Sigma-Aldrich and used without further purification. Aqueous solutions of the dye were prepared by using distilled water. ¹H and ¹³C NMR spectra were measured on a Bruker Avance 600 MHz spectrometer using in CDCl₃-d₆ solution. Infrared spectra and mass spectrometry were measured on a PerkinElmer spectrum 100 FTIR spectrometer and Agilent GC 7000 mass spectrometer, respectively. LC-mass spectrometry was performed using Agilent LC 6320 Ion Trap Mass Spectrometer. UV-Vis absorption spectra were determined in DMF/water (90/10, v/v) on Shimadzu UV-Vis Spectrophotometer. The melting points were measured with a Stuart Scientific melting point apparatus and uncorrected. ZnO nanoparticle (particle size < 100 nm) and TiO₂ (P25) of particle size < 25 nm were purchased from Sigma-Aldrich.

2.2. Synthesis of compound I

Into a round-bottomed flask containing a mixture of phenothiazine (2.4 g, 12 mmol), 1-bromodecane (4.48 g, 18 mmol), and KI (catalytic amount) in 50 ml DMSO, KOH (2 g, 35.71 mmol) was added portion-wise with stirring at room temperature. The reaction was completed after 5 h, as judged by the TLC, then 250 ml of water was added, and the organic product gets extracted with CHCl₃ (4 × 40 ml). The combined extracts were collected, washed with 20% (w/w) NH₄Cl (50 ml), and water. Drying the combined extracts with anhydrous Na₂SO₄, filtrated and finally dried in vacuo. Column chromatography (SiO₂) of the crude product using hexane as eluent gives I as oil product, TLC System: Petroleum ether: Ethyl acetate (PE/EtOAc, 8/2), Yield 78%, ¹H NMR (600 MHz, CDCl₃) δ 0.90 (3H, t, *J* = 7.2 Hz, CH₃), 1.3 (12H, m, CH₂), 1.45 (2H, m, CH₂), 1.82 (2H, m, CH₂), 3.86 (2H, t, *J* = Hz, N-CH₂), 6.90 (2H, d, *J* = 7.8 Hz, Ar-H), 6.93 (2H, t, Ar-H), 7.16 (2H, d, *J* = 7.2 Hz, Ar-H), 7.18 (2H, t, H-Ar). ¹³C NMR (125 MHz, CDCl₃) δ 14.33, 22.89, 27.12, 27.18, 29.47, 29.50, 29.70, 29.76, 29.93, 32.10, 47.73, 115.68, 122.57, 125.12, 127.38, 127.63, 145.47 FTIR, ν, cm⁻¹: Aliphatic and olefinic C-H appears at 2922, 2852 and 3064, respectively. The peaks at 1594, 1572, 1457 are due to C=C stretch vibrations.

2.3. Synthesis of compound II

A cooled POCl₃ (15 ml) was dropwise into an ice-cooled DMF (40 ml) at 0 °C with stirring. Afterward, the reaction temperature raised gradually to room temperature, where the reaction continued for 90 min with stirring to be completed. The flask of the reaction was cooled to 0 °C, and compound I (66 mmol) was added, followed by removing the ice-bath to allow the reaction mixture to get warm gradually to reach 80 °C, where it kept running with stirring for 2 h. The mixture was then quenched after being cooled and mixed with ice-water and basified (sat. aqueous K₂CO₃ solution). The product was extracted from the mixture with CHCl₃ (4 × 40 ml) washed with brine and water. Drying the combined extracts with anhydrous Na₂SO₄, filtrated and finally dried in vacuo. Column

chromatography (SiO₂) of the crude product (eluent: PE/EtOAc, 8:2) on silica gel gives a yellow solid product. Yield 91%. ¹H NMR (600 MHz, CDCl₃) δ 3.91 (t, 3H, N-CH₂), 6.91 (d, 1H, *J* = 8.4 Hz, Ar-H), 6.92 (d, 1H, *J* = 9.0 Hz, Ar-H), 6.99 (td, 1H, *J* = 7.2 Hz, Ar-H), 7.14 (dd, H, *J* = 7.8, 1.2 Hz), 7.19 (td, 1H, *J* = 7.5, 1.2 Hz, Ar-H), 7.61 (d, 1H, *J* = 1.8 Hz, Ar-H), 7.67 (dd, 1H, *J* = 8.4, 1.8 Hz, Ar-H), 9.82 (s, 1H, CHO). ¹³C NMR (125 MHz, CDCl₃) δ 14.30, 22.82, 26.96, 27.03, 29.35, 29.39, 48.23, 115.01, 116.16, 123.78, 124.04, 125.25, 127.76, 127.78, 128.64, 130.27, 131.26, 143.67, 150.99, 190.26. FTIR, ν, cm⁻¹: Aliphatic and olefinic C—H bands appear at 2923, 2852 and 3061, respectively. The peaks at 2724 and 1686 are due to C—H and C=O stretching vibration of aldehyde group, respectively.

2.4. Synthesis of 2-((10-decyl-10H-phenothiazin-3-yl)methylene)malononitrile III

A mixture of malononitrile (0.2 g, 3 mmol) and compound II (1.1 g, 3 mmol) and in 7 ml of basic ethanol solution (composed from mixing 1:3:96 by volume of piperidine, glacial acetic acid, and absolute ethanol, respectively) was reacted overnight with stirring at room temperature, filtered off and recrystallized from ethanol to produce dye III, Yield 52%, M.P. 65–57 °C. ¹H NMR (600 MHz, CDCl₃) δ 3.91 (t, 2H, N-CH₂), 6.88 (d, 1H, *J* = 9.0 Hz, Ar-H), 6.91 (d, *J* = 8.4 Hz, Ar-H), 7.01 (td, 1H, *J* = 7.8 Hz, Ar-H), 7.11 (dd, 1H, *J* = 7.5, 1.2 Hz, Ar-H), 7.20 (td, 1H, *J* = 7.8, 1.8 Hz, Ar-H), 7.51 (s, 1H, H-C=C), 7.57 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.78 (dd, 1H, *J* = 9.0, 2.4 Hz, Ar-H) ¹³C NMR δ 14.33, 22.88, 26.90, 26.98, 29.36, 29.47, 29.66, 29.72, 32.08, 48.42, 113.76, 114.88, 115.12, 116.28, 123.21, 124.38, 125.20, 125.39, 127.84, 128.00, 129.75, 131.55, 142.69, 151.05, 157.54.

FTIR, ν, cm⁻¹: Aliphatic C—H bands appear at 2923, 2851. The peak at 2224 is due to CN group and the bands at 1600, 1581, 1563 are due to C=C. MS (ESI): M⁺; found: 415.1, C₂₆H₂₉SN₃ requires 415.6.

2.5. The photocatalytic method

The photocatalytic decolorization of the dye was made following the method reported in the literature (Hamdy et al., 2014). In this method, black UV light (λ > 367 nm) was used as the light source for the irradiation of the sample. The dye sample aqueous solution (50 ml, 8.02 × 10⁻⁵ M) was prepared by dilution of a concentrated DMF solution of the dye in DMF/water, 1/9 v/v. Two catalysts, namely TiO₂ (P25) and ZnO, were used for the photocatalytic decolorization of the dye. Typically, the catalyst (TiO₂ (P25) or ZnO, 100 mg) and 50 ml of the aqueous dye solution (8.02 × 10⁻⁵ M) were mixed in a beaker. The sample was subjected to sonication for about 10 min and then placed into the photoreactor. Dark chemisorption of the catalyst was firstly allowed by stirring the samples (700 rounds per minute (rpm)) for 15 min at room temperature. Afterward, an aliquot of the dye sample was taken, and the remaining dye solution was subjected to the irradiation. For the kinetic studies, several aliquots were taken every 10 min, filtered (0.2 mm PTFE Millipore membrane filter) to remove the catalyst, and finally analyzed optically at the maximum wavelength of absorption of the dye at 538 nm to determine

the remaining concentration of the dye (Fig. 1-a). Assuming that the photocatalysis proceeds via first-order kinetics, then the reaction rate constant (K) can be obtained from the following equation:

$\ln(C_0/C) = -Kt$, where C₀ and C are the dark chemisorption concentration and the concentration at time t, respectively. K is the reaction rate constant. Thus, plotting ln(C₀/C) versus t results in a straight line with a slope equal -K. Two or three runs of photocatalysis were repeated using a fresh catalyst, and the standard deviation obtained was about 5%.

3. Results and discussion

3.1. Synthesis

The synthesis of dye III was made, as shown in Scheme 1. Thus, the N-alkylation of phenothiazine via SN₂ reaction afforded the corresponding product I, which underwent Vilsmeier formylation reaction to give the corresponding aldehyde II in high yield. Condensation of compound II with malononitrile via Knoevenagel reaction afforded the corresponding dye III in good yield. The chemical structure of these synthesized compounds was confirmed by IR, NMR, and high-resolution mass spectra (see supplementary file).

3.2. Photocatalytic studies

The photocatalytic decolorization of water-insoluble dyes is not common, and to the best of our knowledge, as yet, no report for such an approach has appeared. It is believed that the success in the decolorizing organic-based hydrophobic dye, such as the presented one, would pave the way for the decontamination of water-insoluble organic pollutants. Thus, the title dye was subjected to photodecolorization from aqueous solution (1:9, DMF/water v/v). It was observed that at zero time (dark chemisorption), the dye concentration remains almost constant, indicating the absence of chemisorption. Having been informed by that, it was necessary to study whether TiO₂ (p25) would catalyze the decolorization of the dye. Fig. 1 top (right) reveals the gradual decreases in the dye absorption upon irradiation time to reach almost complete decolorization after 30 min. Fig. 1 top (left) reveals the time curve of the decolorization of the dye in the absence of catalyst and in the presence of TiO₂ (p25) and ZnO. It is clearly observed that the dye is almost stable during all tested irradiation time in the absence of catalysts, whereas in the presence of catalysts, TiO₂ (p25) shows superior efficiency at a higher rate than ZnO. Analyzing the data, as shown in Fig. 1 bottom (left) and bottom (right), the rate using TiO₂ (0.095 min⁻¹) is higher than the rate constant using ZnO (0.055 min⁻¹). The effect of solution pH on the rate of photocatalytic decolorization of the dye was performed at three different pHs of 5, 7, and 9. The colour of the dye did not change, and the obtained first-order rate constant did not change a lot (only negligible difference), indicating that the pH, although it affects the catalysts but has no effect on the organic-based hydrophobic dye and thus no effect on the photocatalytic process. The results of pH effect are presented in the supplementary file.

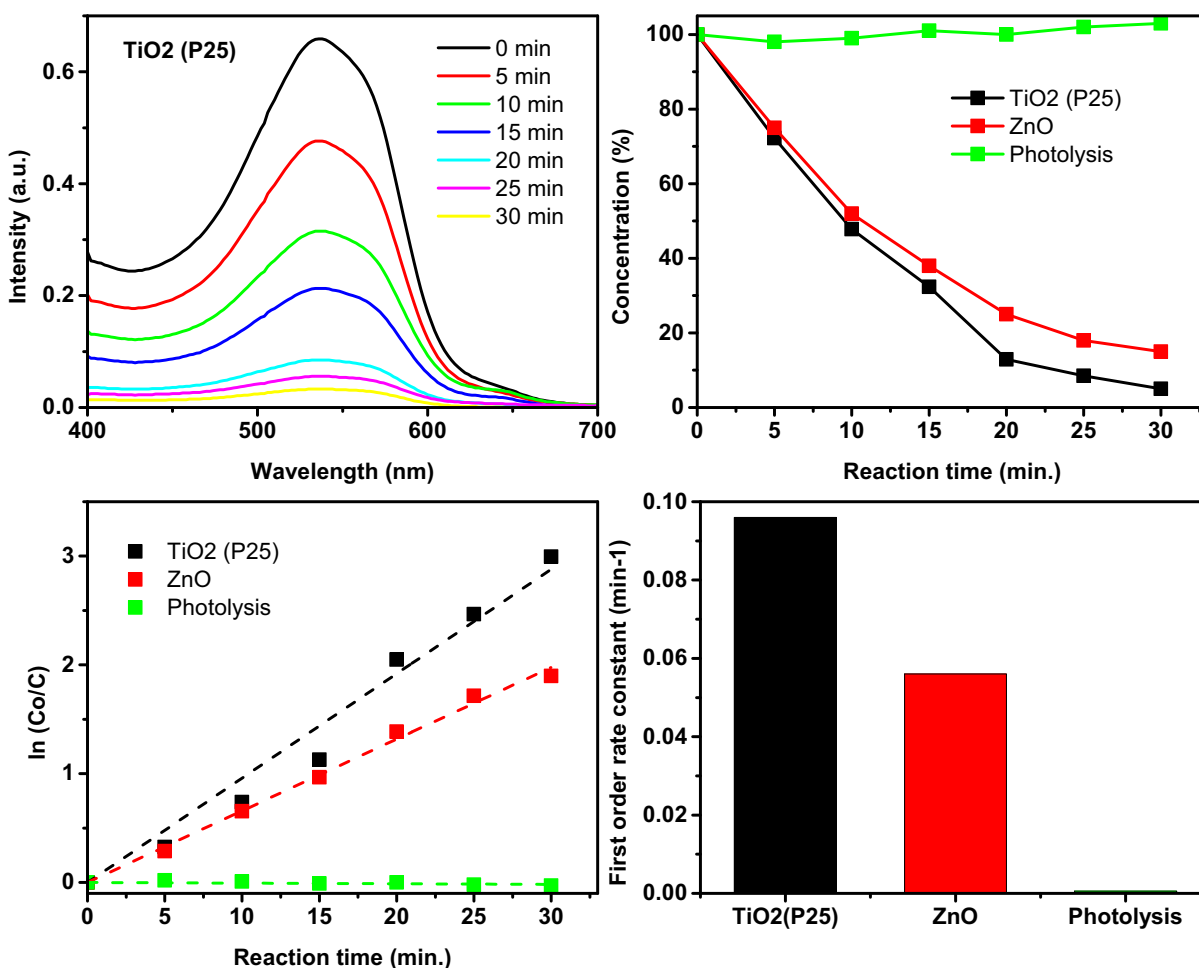
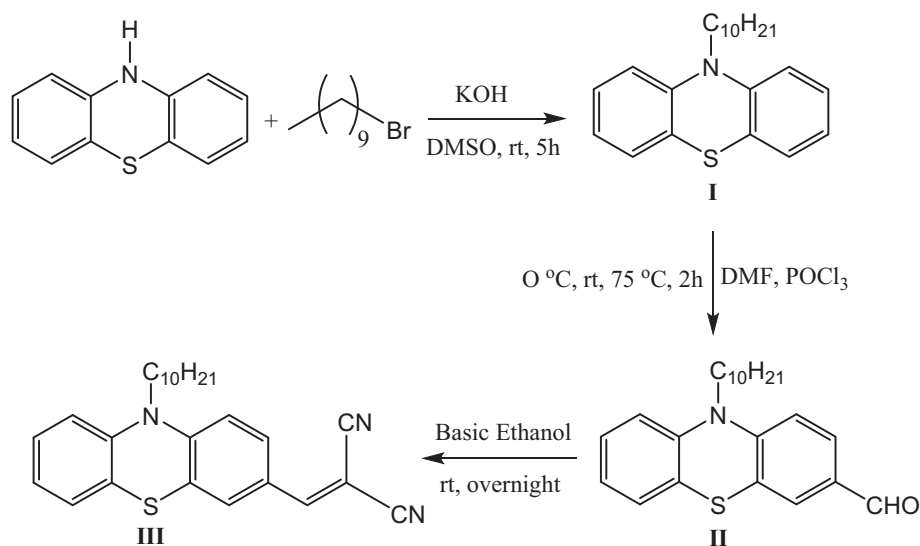


Fig. 1 (Top left) the UV-Vis spectra obtained as a results of 2-((10-decyl-10H-phenothiazin-3-yl)methylene)malononitrile dye degradation over TiO₂ (P25) under UV-Vis illumination. (Top right) the degradation profile of 2-((10-decyl-10H-phenothiazin-3-yl)methylene)malononitrile dye over TiO₂ (P25), ZnO, and without catalyst (photolysis). Bottom left) the kinetics of the 2-((10-decyl-10H-phenothiazin-3-yl)methylene)malononitrile dye degradation. Bottom right) the first order rate constants of the 2-((10-decyl-10H-phenothiazin-3-yl)methylene)malononitrile dye degradation.



Scheme 1 The synthetic route of the dye.

4. Conclusion

Heterogeneous photocatalytic decolorization of water-insoluble dye present in an aqueous solution made from 1:9, DMF: water was successfully made in a short time. The title dye showed photostability without catalysts and could be decolorized in a short time using both catalysts (TiO₂ (p25) and ZnO), although with a faster rate using TiO₂ (P25) compared with ZnO. In addition, the results of pH effect on the photocatalytic decolorization indicate that the process is independent of the pH as the dye used is an organic-based hydrophobic dye. These results suggest that the photocatalytic decolorization of water-insoluble organic pollutants is a viable process for environmental remediation and will inspire further work using different oxide nanoparticles for the photocatalytic decontamination of organic pollutants.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.arabjc.2019.12.007>.

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