

PHOTOCATALYTIC DEGRADATION EFFICIENCY OF AZO DYE IN AQUEOUS PHASE USING DIFFERENT PHOTO CATALYSTS

Nour Abd Alrazzak¹, Suad T. Saad¹, Hazim Y. Al-gubury¹, Mohanad M. Kareem^{2*} and Mawahib M. Assi¹

¹Department of Chemistry, College of Science for Women, University of Babylon, Hilla, Iraq

²Department of Chemistry, College of Science, University of Babylon, Hilla, Iraq

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ABSTRACT. The new azo dye [4-(4-hydroxy-2-methylnaphthyl)diazenyl]benzoic acid was synthesized by the reaction of 2-methyl-1-naphthol with *p*-amino benzoic acid. The photocatalytic degradation of azo dye has been investigated by using zinc oxide and cadmium sulfide. This degradation was carried out by the irradiation of aqueous suspended solutions containing different concentrations of this dye using 0.11 g/100 mL of metal oxide (semiconductors) ZnO and CdS. A mercury lamp 125 W in a Pyrex photoreaction cell of 100 mL at room temperature was used as an irradiation source. The effect of the catalyst on the photocatalytic degradation of the prepared dye was studied via several experiments at different conditions, where they involve the effect of the catalyst mass and the effect of the dye concentrations. The irradiated solutions were studied using UV-Vis spectrophotometer. It has been the performance of photocatalytic system that using ZnO was observed to be better than cadmium sulfide system for degrade the azo compound from its aqueous solution.

KEY WORDS: Photocatalytic, Degradation, Semiconductors, Zinc oxide; Cadmium sulphide, Azo dye

INTRODUCTION

Azo dyes are more interest field and important type of organic compounds due to their chemical structure which contains the -N=N- group that bridges one or more aromatic or heterocyclic systems [1-4]. The synthesis of these dyes is starting with the formation of the diazonium salt which is very important in the organic synthesis [5-7].

Several types of azo dyes are known, and a few classification frameworks exist. A few classes incorporate disperse dyes, metal-complex dyes, reactive and substantive dyes. Moreover called coordinate dyes, substantive dyes are utilized for cellulose-based materials, which incorporate for cotton. The dyes linked to the material by non-electrostatic powers. In another classification, azo colors can be classified agreeing to the number of azo groups [8, 9]. In addition, azo dyes are important in pharmaceutical, textile and cosmetics industries. Moreover, these dyes are difficult to be degraded when it is released to water sources [10-12] due to their resistance to light, oxidizing agents and many chemicals.

Many semiconductors such as metal oxides ZnO, TiO₂ and CdS are used in photocatalytic degradation to degrade many pollutants such as dyes and heavy metals in wastewater. If the semiconductor is irradiated by UV lamp, the electrons are promoted from the valence band to the conduction band of the semiconducting oxide to give electron-hole pairs. These electrons undergo photo reduction and that leads to leaving a positive hole in the valence band [13].

In addition, zinc oxide as a semiconductor has a wide-band gap, and it is used in many applicable fields due to this band gap, high electron mobility, intensive emission at room temperature and it is transparent. Therefore, it is used in light emitting diodes, electrodes and transistors fabrication [11-14].

In this work ZnO and CdS was used as catalysts for photocatalytic degradation process under ultra violet light for a prepared azo dye.

*Corresponding author. E-mail: sci.mohanad.mousa@uobabylon.edu.iq

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EXPRIMENTAL

Apparatus

The following apparatus were used to characterize the prepared dye. Melting point was measured using SMP30 melting point apparatus. The IR spectra was recorded with a Bruker spectrometer, UV/VIS double beam Spectrophotometer PG CECIL-CE7200 instrument was used to measure the dye solutions optical density. Microelemental analysis was investigated to estimate the content of C, H and N content for the dye using EuroEA3000 Elemental Analyzer, Italy. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were recorded on a Bruker AC 400 NMR spectrometer, operating at 400 MHz for $^1\text{H-NMR}$ and 100 MHz for $^{13}\text{C-NMR}$ at University of Al-albait, Jordon. All chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) as reference.

Chemicals

Catalysts and the other chemicals were purchased from Fluka AG and Sigma Aldrich.

Synthesis of [4-(4-hydroxy-2-methylnaphthyl)diazenyl]benzoic acid [14]

A *p*-amino benzoic acid (0.01 mol, 1.37 g) was dissolved in distilled water 10 mL and 5 mL of concentrated HCl at 0-5 °C. Then NaNO_2 (0.01 mol, 0.68 g) was dissolved in distilled water 10 mL and added as dropwise to the *p*-amino benzoic acid solution for 15 min. This diazonium solution was added dropwise to a mixture of 2-methyl-1-naphthol (0.01 mol, 1.58 g) in absolute ethanol and sodium hydroxide (1 g) in 10 mL distilled water. The orange dye precipitate was then filtered and washed with water. Molecular formula: $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_3$, colour: orange, yield 94%, m.p. = 227-230 °C. IR (ν , cm^{-1}): 3391 (O-H), 2986 ($\text{C-H}_{\text{Alph.}}$), 3020 ($\text{C-H}_{\text{Ar.}}$), 1681 ($\text{C=O}_{\text{carboxylic acid}}$), 1504 (N=N). $^1\text{H-NMR}$ (δ , ppm): 0.9 (3H, CH_3), 6.9-8 (H, Ar-H), 8.092 (H, Ar-OH), 11.2 (H, COOH); $^{13}\text{C-NMR}$ (δ , ppm): 16.0 (C, CH_3), 116.0-130.0 (C, Ar-C), 182.0 (C, C=O). CHN found: C, 70.778; H, 4.62; N 9.21%; calculated C, 70.588; H 4.575; N, 9.15.

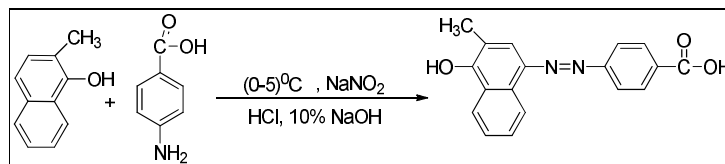
Photoreactor

All the experiments were done using the photochemical reactor, where its parts have been mentioned in the literature [15].

RESULTS AND DISCUSSION

Azo dye synthesis

The azo dye was synthesized by the reaction a diazonium salt of *p*-amino benzoic acid reacted as an electrophile with the nucleophile-coupling compound (2-methyl-1-naphthol) at (0 °C) as shown in Scheme 1.



Scheme 1. Azo dye synthesis.

The IR spectrum of the prepared dye exhibited absorption band of $-N=N-$ at 1504 cm^{-1} and absence of absorption band for (NH_2) at 3458 and 3359 cm^{-1} (Figure 1). The $^1\text{H-NMR}$ showed a single signal at δ 11.2 for (s, H, COOH) (Figure 2), while the $^{13}\text{C-NMR}$ showed signal of (C, COOH) at 182 (Figure 3).

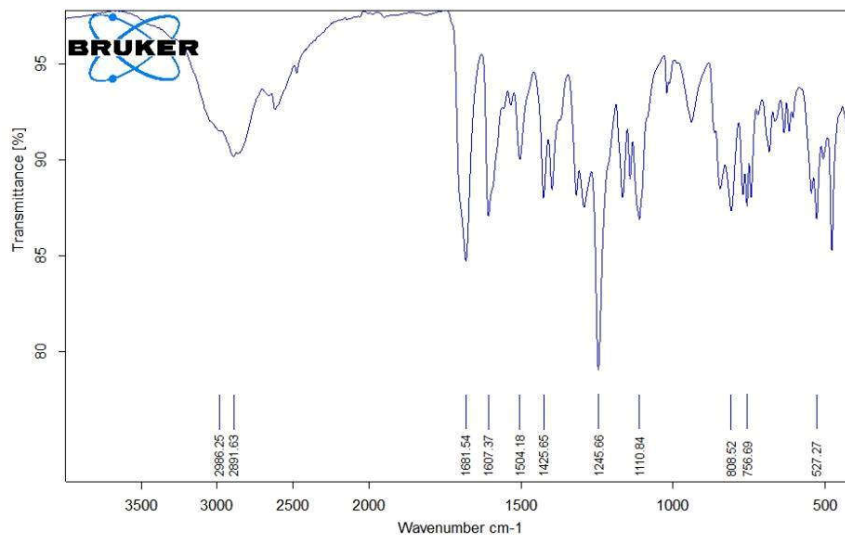


Figure 1. Infrared spectrum of the azo dye.

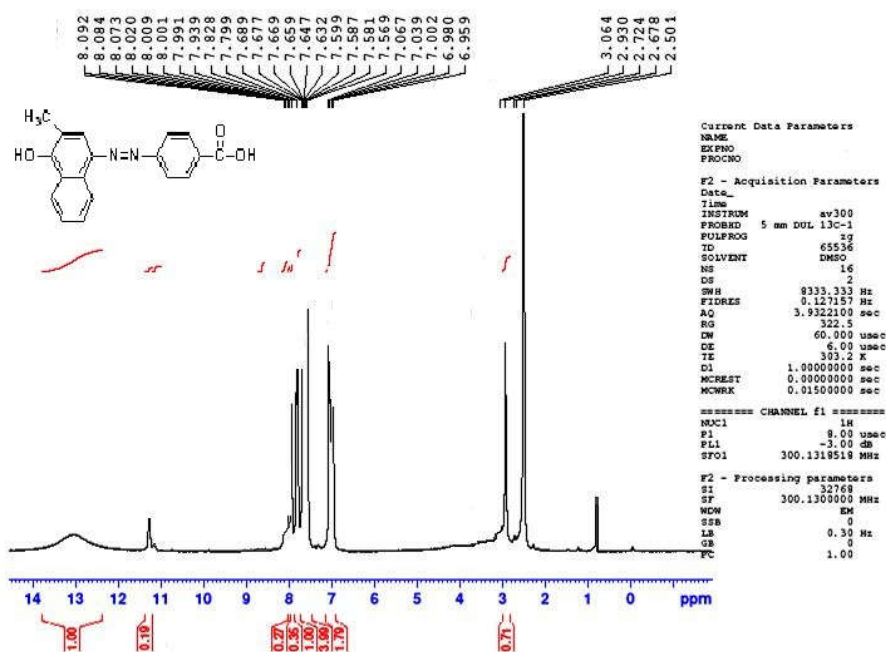


Figure 2. $^1\text{H-NMR}$ of the azo dye.

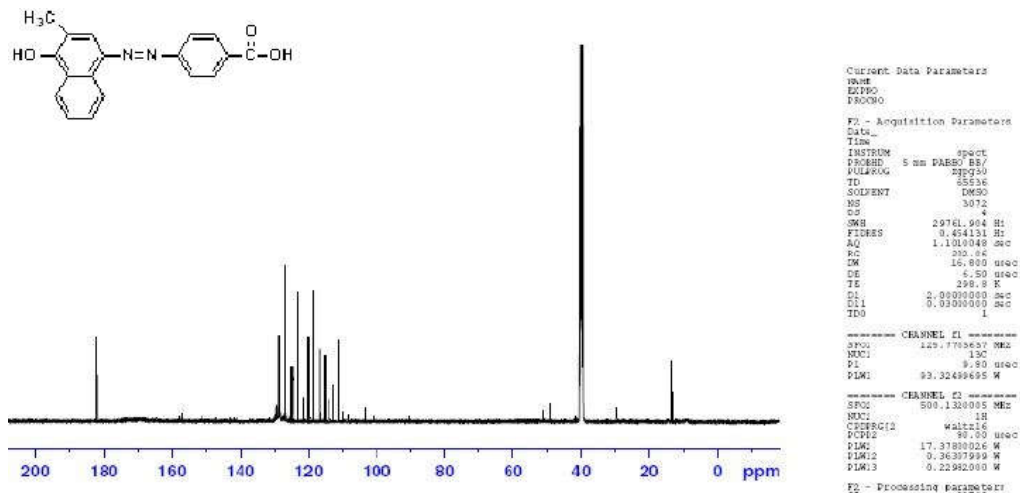
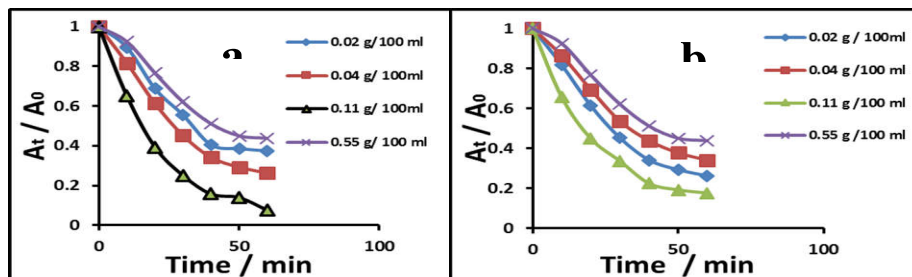


Figure 3. ^{13}C -NMR spectra of the azo dye.

Effect of ZnO and CdS masses on photo catalytic degradation of the azo dye

The effect of the catalysts ZnO and CdS masses on the photocatalytic degradation of azo dye was studied using 40 mg/L of the dye with 10 mL/min flow rate of air at room temperature.

As shown in Figure 4, the photocatalytic degradation process of the azo dye at different loaded masses of ZnO and CdS gradually increased as the masses of ZnO and CdS increased. When the catalysts mass reached 0.11 g/100 mL the photocatalytic degradation gradually decreased. At this weight, the semiconductors ZnO and CdS can provide high light absorption. The less photodegradation efficiency PDE% at high masses of the catalysts is due to the light absorption and will be limited only to the first layers of prepared dye. Other layers of solution do not receive light photons [16, 18]. When the loading masses of catalysts is less than that concentration, the rate of photo degradation of the azo dye also decreased. The reason of that is from the decrease in the catalyst. That means the surface area decreased and that lead to decreasing of light absorption by the catalyst, which caused low photo degradation rate of azo dye. The ZnO was found to be more efficient than CdS from the increase in the effective surface area, as shown in Figure 4. However, the percentage of percentage of photocatalytic degradation efficiency (PDE %) of ZnO was 92.41%, while that of CdS was 62.56% (Figure 5).



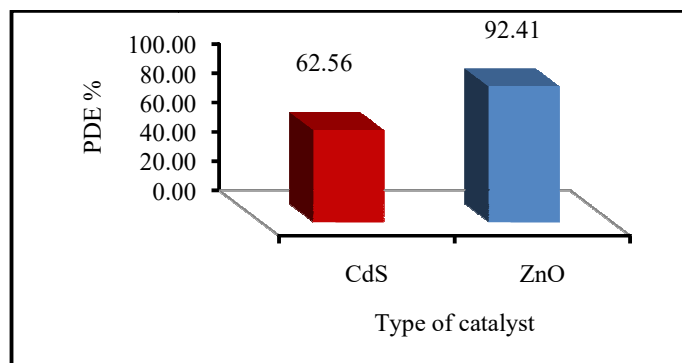


Figure 5. Photocatalytic degradation efficiency (PDE %) using ZnO and CdS with 40 mg/L of the azo dye.

Photocatalytic degradation process

The effect of the initial dye concentration on the photocatalytic degradation process was studied using different dye concentrations 40–80 mg/L with 0.11 g/100 mL of the catalysts, 8.22 mW/cm² light intensity at room temperature. The results are plotted in Figure 6 and it is obvious that the degradation rate gradually decreased when the initial azo dye concentration increased.

The optimum concentration of the dye was 40 mg/L, which it covers the large area of the catalyst. It also was absorbed the largest number of exciting photons to get the higher concentration of the activated catalyst, while the excess of the azo dye prevented the light to go through the other layers of azo dye on the catalyst surface. It was generated the excited photocatalytic degradation efficiency dye state, which it was adsorbed on the catalyst [16]. However, it was found that ZnO more efficient than CdS, as shown in Figures 6 and 7.

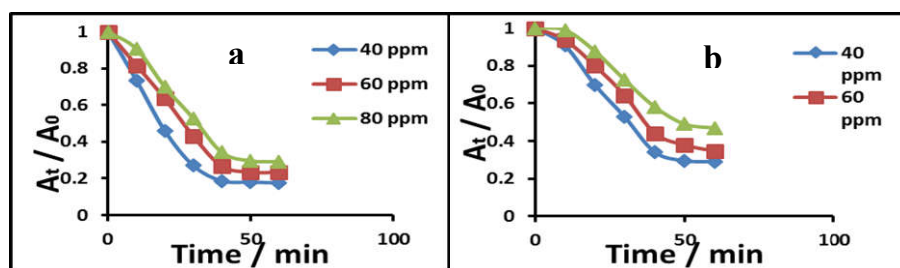


Figure 6. Variation in (A_t/A_0) with irradiation time at different concentrations of the dye with (a) ZnO and (b) CdS.

A comparison between zinc oxide better than cadmium sulfide as a catalyst on the azo dye degradation was performed using the optimum conditions as 0.11 g/100 mL of the catalyst with 40 mg/L of the azo dye. It can be observed that the ZnO exhibited a higher photocatalytic activity when compared with CdS. This can be attributed to the increase in the effective surface area of the catalyst which led to enhance its photocatalytic activity for the dye degradation. As shown in Figure 8, the photocatalytic degradation efficiency was found to be 95.20% for ZnO and 67.40 % for CdS [18, 19].

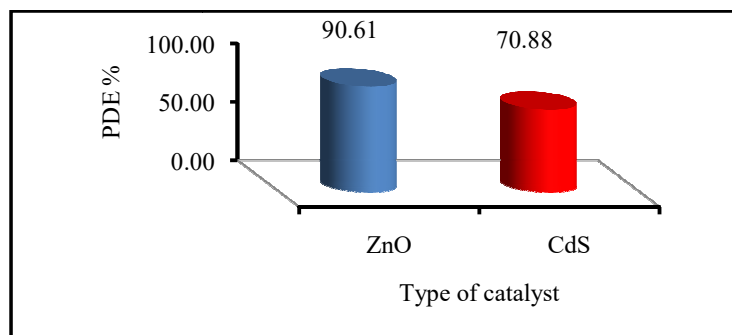


Figure 7. Photocatalytic degradation efficiency (PDE %) using 0.11 g/100 mL of each ZnO and CdS with 40 mg/L of the azo dye.

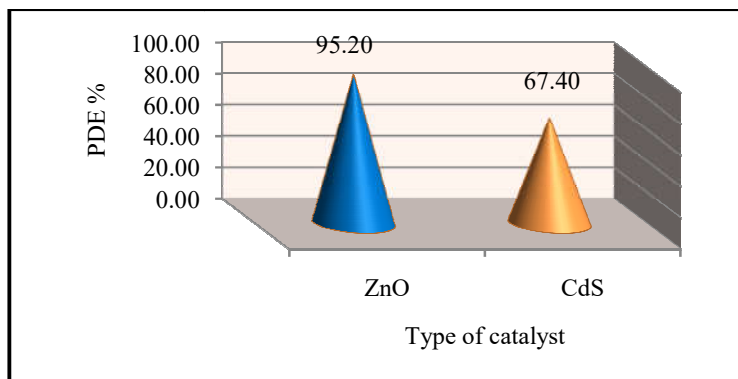


Figure 8. Comparison in photocatalytic degradation efficiency (PDE %) using ZnO and CdS 0.11 g/100 mL of each ZnO and CdS with 40 mg/L of the azo dye.

CONCLUSION

Photocatalytic degradation process under ultra violet light for a prepared azo dye was performed using two catalysts ZnO and CdS. Several experiments were carried out to reach the optimum conditions for the azo dye degradation. These experiments included the effect of the catalyst mass and the effect of dye concentrations. It was found that ZnO is more effective than CdS with 92.41 and 62.56 PDE%, respectively. The effect with the impact of starting dye concentration was found that the photocatalytic degradation productivity utilizing ZnO was 90.61% whereas with CdS was 70.88%. In addition, the photocatalytic degradation efficiency was studied under the optimum conditions. It was 95.205% for ZnO and 67.40% for CdS. It could be concluded from this work that the photodegradation of the azo dye using ZnO is more effective than CdS.

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REFERENCES

- Robert, T.M.; Robert, N.B.; Bhattacharjee, S.K. *Organic Chemistry*, 6th ed., Pearson Prentice Hall: New Delhi; **2011**; pp 1096-1097.
- Abrahart, E.N. *Dyes and Their Intermediate*, Chemical Publishing: New York; **1977**, pp 1-12.
- Bindu, R.L.; Reghunadhan, C.P.; Ninan, K.N. Phenolic resins bearing maleimide groups: Synthesis and characterization. *J. Appl. Polym. Chem.* **2000**, 38, 641-652.
- Al-janaby, K.M.; AL-Jobory, M.A.M. Synthesis and biological testing of new 1,3-oxazepine derivatives of pharmaceutical interest. *Karbala J. Pharm.* **2014**, 5, 21-30.
- Ameen, S.T.; Khalil, A.I.; Mohammed, A.A. A new method for ISE construction for methyl orange dyes and using for indirect determination of amitriptyline hydrochloric drug. *Baghdad Sci. J.* **2015**, 12, 188-196.
- Sudha, M.; Saranya, A.; Selvakumar, G; Sivakumar, N. Microbial degradation of azo dyes: A review. *Int. J. Curr. Microbiol. App. Sci.* **2014**, 3, 670-690.
- Crini, G. Non-conventional low-cost adsorbents for dye removal: A review. *Bioresour. Technol.* **2006**, 97, 1061-1085.
- Fosso-Kankeu, E.; Waanders, F.; Geldenhuys, M. Photocatalytic degradation of dyes using TiO₂ nanoparticles of different shapes. 7th International Conference on Latest Trends in Engineering & Technology (ICLTET'2015), Irene, Pretoria (South Africa), November 26-27, **2015**, pp 84-89.
- Ahmad, T.; Kandil, F.; Moustapha, C. Preparation and characterization of some new azo dyes, azomethine dyes and heterocyclic Schiff bases derivatives. *AASCIT J. Chem.* **2015**, 2, 24-31.
- Gaffer, H.E.; Fouda, M.M.G.; Khalifa, M.E. Synthesis of some novel 2-amino-5-arylazothiazole disperse dyes for dyeing polyester fabrics and their antimicrobial activity. *Molecules* **2016**, 21, 122.
- Wankhede, S.B.; Patil, A.B. Studies on Ti(III), Cr(III) and Fe(III) complexes with 1-(1-hydroxynaphthalen-2-yl)ethanone-4-chlorobenzoylhydrazone ligand: Synthesis, Physico-chemical and Antimicrobial activity. *J. Pharm. Chem. Biol. Sci.* **2018**, 6, 25-33.
- Kadhim, M.Y.; Abdulsada, A.M.; Alshawi, M.S. Synthesis, identification and the study of some new azo dyes as corrosion inhibitors for copper in (1 M) HCl. *J. Basrah Res.* **2014**, 40, 108-127.
- Jabbar, A.Z.; Hadi, A.G.; Sami, F. Removal of azo dye from aqueous solutions using Chitosan. *Oriental J. Chem.* **2014**, 30, 571-575.
- Abd Alrazzak, N.; Abdulla, S.; Jassim, A. Synthesis and characterization of new 1,2,4-triazole derivatives from 2-naphthol. *JUBPAS* **2018**, 26, 234-252.
- Al-gubury, H.Y. Study the activity of titanium dioxide nanoparticle using orange G dye. *Malaysian J. Sci.* **2016**, 35, 319-330.
- Al-Gubury, H.A.; Mohammed, Q.Y. Prepared coupled ZnO-Co₂O₃ then study the photocatalytic activities using crystal violet dye. *JCHPS* **2016**, 9, 1161-1165.
- Al-Gubury, H.Y.; Alteemi, H.S.; Saad, A.M.; Al-Shamary, R.R. Removal of hazardous brilliant cresyl blue dye utilizing aluminum oxide as photocatalyst. *Indonesian J. Chem.* **2019**, 19, 292-297.
- Yadollah, A.; Abdul, H.A.; Zulkarnain, Z. Photodegradation of *o*-Cresol by ZnO under UV irradiation. *J. Am. Sci.* **2011**, 7, 165-170.
- Krishnakumara, B.; Swaminathan, M. Influence of operational parameters on photocatalytic degradation of a genotoxic azo dye Acid Violet 7 in aqueous ZnO suspensions. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2011**, 81, 739-744.