



Science Forum (Journal of Pure and Applied Sciences)



Journal Homepage: <https://atbuscienceforum.com.ng/index.php/jpas>

Synthesis, Characterization and Photocatalyticdegradation of Acid Dyes Using Hydrogen Peroxide (H₂O₂) As A Catalyst.

Etafiemor Jacob, Umar Salami Ameuru, Abdulraheem Giwa

Department of Polymer and Textile Engineering, Ahmadu Bello University, Zaria

Abstract

This study reports the synthesis, characterization, and photocatalytic degradation of a novel azo dye derived from 6-amino-2-(5-chloro-1,3-dioxoisindolin-2-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione as a key intermediate. The intermediate was diazotized and subsequently coupled with H-acid (4-amino-5-hydroxynaphthalene-2,7-disulfonic acid) to yield the target dye. Structural and physicochemical characterization of the synthesized dye was carried out using melting point determination, UV-Visible spectroscopy, Fourier Transform Infrared (FT-IR) spectroscopy, and proton nuclear magnetic resonance (¹H-NMR) spectroscopy. The dye was further evaluated for photocatalytic degradation using a UV/H₂O₂ advanced oxidation system in a photoreactor. The degradation process was systematically investigated by varying four operational parameters: solution pH, initial dye concentration, catalyst (H₂O₂) loading, and irradiation time. Experimental design, optimization, and statistical analysis of main and interaction effects were performed using Minitab 17 software. Optimization results indicated that maximum degradation efficiency of 72.1417% (desirability = 0.73063) was achieved under the following conditions: dye concentration of 10 mg/L, H₂O₂ loading of 2 mL, irradiation time of 90 minutes, and acidic medium at pH 3.0. The findings demonstrate that the UV/H₂O₂ photocatalytic system is effective for the degradation of the synthesized acid dye. Consequently, this approach shows significant potential for application in the treatment of tannery and textile wastewater containing recalcitrant dye pollutants.

Keywords

Synthesis,
Analytical techniques,
photocatalyticdegradation,
Effluents

ISSN 1119-4618



1119-4618

JPAS



— Faculty of Science, ATBU Bauchi —

INTRODUCTION

Leather and textile are dyed to improve their appearance and make them saleable in a finished form. Some colours may be imparted by the producer's agent, but usually these are supplemented with synthetic dyes or pigments, which make attainment of uniformity of shade throughout the piece difficult, if not impossible to attain, but these make leather and textile difficult to duplicate synthetically, and is one of the factors that gives them psychological appeal. The application of dyes on leather involves: drum, spray, paddle, brush and solvent dyeing. The dyeing temperature is controlled within the range of 25 - 60 °C and the pH is set in the range of 3.8 - 5.5. Liquor ratio is generally low e.g. in drum dyeing, 2 - 5 times the weight of leather (Ameuru et al., 2014).

The water solubility is as a result of the presence of sulphone acid group or in rare cases carboxylic acid groups. Acid dyes are found in nitrophenols and azo compound; Acid dyes are water soluble dyes which are applied basically from acid solution onto fibres possessing basic nitrogen group e.g. leather, wool, silk and nylon triphenyl methane, anthraquinoids or indigoid compound. There are three kinds of acid dyes which are in accordance to their molecular mass and ease of leveling. Those of high molecular mass, which do not level easily (group 2 and 3) are known as acid milling and neutral milling dyes (Pratima, 2018).

Effluent from leather plants is classified as one of the most polluting of all industrial sectors, considering the volume generated as well as the effluent components (Manjushree et al., 2013). In addition, the increase demand for leather products and the proportional increase in their production and the use of

synthetic dyes have contributed to dye effluent becoming one of the substantial sources of several pollutions problem in current times (Ahmed and Prol, 2019). The effluent causes serious environmental problem due to its high colour, large number of suspended solids (SS) and high chemical oxygen demand (COD) (Muhammad et al., 2019).

The impact of these dyes on the environment is a major concern because of the carcinogenic properties of the chemicals (Selma and Quahib, 2021). Also, some dyes can undergo anaerobic decolouration to form potential carcinogens (Raja et al., 2021). One of the most difficult tasks confronted by the leather and textile effluent treatment is the removal of the colour of these compounds, mainly because, dyes and pigments are designed to resist biodegradation such that they remain in the environment for a long period of time (Hettige and Mowjood, 2015).

Consequently, there is a considerable need to treat these coloured effluent before discharging them into various water bodies. The increase of public concern as well as tighter regulations have challenged the environmental problem associated with such effluent. At present, the industrial methods for dye effluent treatment includes: adsorption, precipitation, electrical remediation, oxidation and biological degradation. But all these methods cost much money and /or create secondary contamination (Joshua et al., 2017).

The photocatalytic degradation method using experimental design of has been shown to be efficient for degradation and mineralization of various organic pollutants in waste water at room temperature and normal pressure. The

method has potential for treatment of industrial or domestic waste water on a large scale (Wibawa et al., 2021). Treatment of hazardous effluents is one of the growing needs of the present time. Advanced Oxidation Processes (AOPs) have been developed to convert nonbiodegradable contaminants into harmless products (Danladi et al., 2014).

EXPERIMENTAL

MATERIALS AND METHODS

The chemicals used in this experiment were of commercial grade and were used as received. The melting point of the synthesised dye was determined in an open capillary tube. The purity of the dye was determined by thin layer chromatography (TLC). The Uv-visible absorption spectrum was measured, using 6305 Jenway spectrophotometer model. The FT-IR was determined using FT-IR -84005. The ¹H-NMR was recorded on a 300 MHz Bruker instrument using deuterated dimethylsulphoxide (DMSO-d₆) as solvent. The photodegradation was carried out in a reactor and Minitable 17 software was used to determine the optimum conditions for the research work.

Synthesis of Intermediate

Synthesis of Intermediate was carried out according to the procedure (Ukanah et al., 2021)

Synthesis of 6-Amino-2-(5-Chloro-1,3-Dioxoisindolin-2-yl)-1H-Benzo[de]Isoquinoline-1, 3(2H)-Dione.

Dry sodium nitrite (1.5 mmol, 0.104 g) was added to cold conc. H₂SO₄ (98 %, 1.1 ml) at such a rate that yellow fume was not evolved.

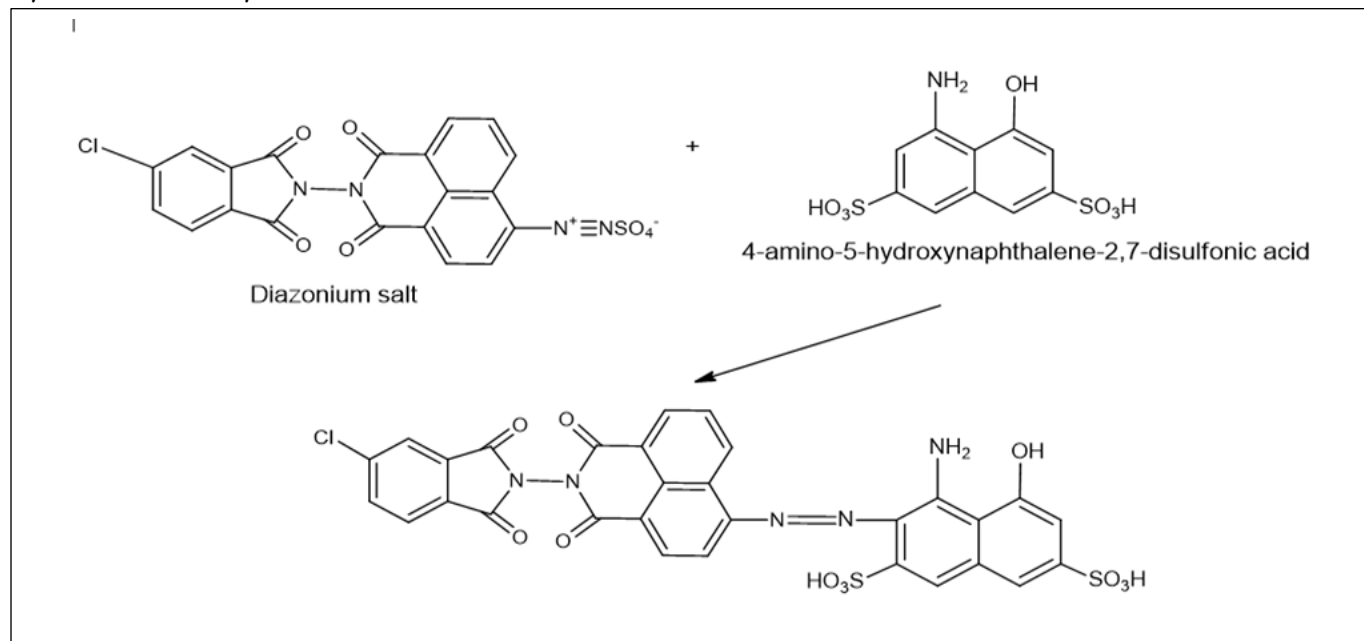
The reaction temperature was gradually increased to 65 °C, using water bath until all

the sodium nitrite was completely dissolved. The solution was cooled to 0 - 5 °C and added drop wise at 5 - 20 °C with the mixture of propionic acid and acetic acid (10 ml, 1.5:8.5). The final ground powder of (1.5 mmol) of 6-amino-2-(5-chloro-1, 3-dioxoisindolin-2-yl)-1H-benzo [de]isoquinoline-1, 3(2H)-Dione, was added in portion wise at less than 10 °C, then the solution was stirred for 180 minutes. The obtained clear diazotization salt solution was used immediately in coupling with H-acid to obtain the dye (Ameuru et al., 2014).

The Yield = 75%, Melting point = 391°C, FT-IR(KBr,cm⁻¹) 3358, 3232, 3083, 1428, 1741, 1525, 753, 828, 1275. (¹³C-NMR spectrum). 77.2, 104.8, 108.9, 119.6, 120.1, 124.3, 124.7, 126.2, 127.5, 130.2, 130.9, 131.3, 132.7, 135.5, 135.8, 140.9, 154.5, 159.5, 161.2, 162.8, 163.1. (¹H NMR (400 MHz, DMSO-d₆), δ (ppm)) 6.90 (1H, d, J = 8.5 Hz, -NH₂), 7.71 (2H, t, J = 8.3 Hz, 3-H), 7.90 (2H, s), 8.05 (2H, dd, J = 4.9, 6.0 Hz, 7-H), 8.22 (2H, t, J = 8.5 Hz, 4-H), 8.51 (1H, d, J = 7.2 Hz, 2-H), 8.74 (1H, t, J = 8.3 Hz, 3-H)

RESULTS AND DISCUSSION

Synthesis of the dye



Scheme 1: Schematic route for the synthesised dye

As mentioned in (Ukanah *et al.*, 2021). Synthesis of Intermediate 6-amino-2-(5-chloro-1, 3-dioxoisindolin-2-yl)-1H-benzo [de]isoquinoline-1, 3(2H)-Dione, was determined and characterized. Yield = 75%, Melting point = 391°C The ^1H NMR (300 MHz, DMSO- d_6 spectrum of Intermediate (figure....) showed peaks at 6.90 ppm which correspond to the proton on the amino group (NH_2) while the (8H) at aromatic region is shown by the peaks at 7.24-8.78 ppm. The synthesis of 4-amino-3-((2-(5-chloro-1, 3-dioxoisindolin-2-yl)-1, 3-dioxo-2, 3-dihydro-1H-benzo [de]isoquinolin-6-yl)diazenyl)-5-hydroxynaphthalene-2, 7-disulfonic acid dye was carried out using 6-amino-2-(5-chloro-1, 3-dioxoisindolin-2-yl)-1H-benzo [de]isoquinoline-1, 3(2H)-Dione with H-Acid to give the dye (Scheme 2). The Yield = 45.2%, Melting point = $>300^\circ\text{C}$.

The UV-visible of the absorbed maximum Wavelength at ($\lambda_{\text{max}} = 440 \text{ nm}$). It shows within the yellow region of the spectrum and compound appears blue violet to the eyes. The FT-IR (KBr, cm^{-1} spectrum of the dye (Figure 5), showed -N-H stretching vibration at 3358, -OH stretching vibration at 3232, -C-H aromatic stretching vibration at 3083, C=O stretching vibration at 1741, C=C stretching vibration at 1525, -N=N stretching vibration at 1428, C-N stretching vibration at 1275, -C-H aromatic bending vibration at 828 and -C-Cl stretching vibration at 753. The ^1H -NMR (300 MHz, DMSO- d_6) spectrum of the Dye (Figure 7), showed peak at 3.43 ppm which account for the hydrogen with the NH_2 substituent, the peak at 3.86 ppm correspond to the hydroxyl group (OH) of the H-acid. The aromatic protons showed signal at 6.92–5.78 ppm and the number of protons is in agreement with the aromatic protons in the structure of the dye.

The peak at 10.30 ppm correspond to the (OH) in the sulphonic group substituent of the dye.

The photo-catalytic-degradation of the synthesized acid dye was carried out successfully, using factorial design experiment with hydrogen peroxide (H_2O_2) as catalyst, minitab17 software, photo reactor and spectrophotometer as source of ultra violet light. The effects of operational parameters in Photodegradation of the dye were determined on the basis absorbance measurements. Four factors such as pH, dye concentration, catalyst loading, and time of irradiation had been determined and results analysed.

(Soroosh and David, 2019). The Optimization parameters in the photocatalyticdegradation of the dye, shows the maximum degradation at 85.3 % with the desirability of 0.86755 at dye concentration of 10 mg/L and catalyst loading of 2 ml with irradiation of 90 mins at pH of 2.9 of the dye. This gives the best suitable conditions to get the best predicted result for the percentage degradation of the dye, which shows that the photocatalytic degradation of the acid dyes used in this research work, has shown good value results of (68.0 - 85.4 %) for effective treatment of tannery and textile effluents.

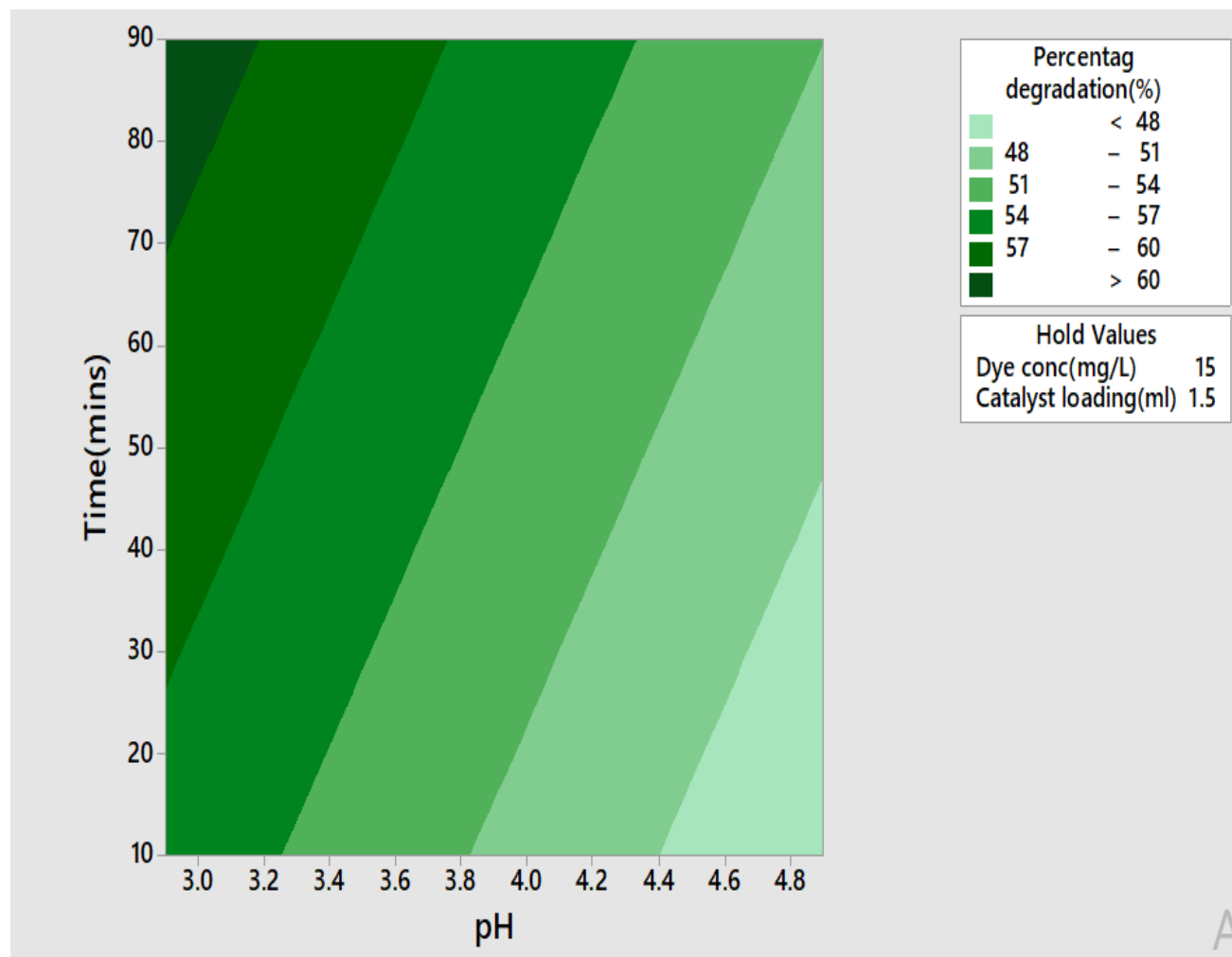


Figure 1: Contour Plot of Percentage Degradation versus Time and pH of Dye

This indicates the contour plot of percentage degradation of time versus pH for dye concentration of 15 mg/L and catalyst loading of 1.5 ml. The percentage degradation is greater than 60 % at a steady increase in time from 70 to 90 mins with a responding increase of the pH from 3.0 to 3.2. This shows that with slightly increases in the pH and the time, degradation occurs fully in that region. This could be attributed to the fact that surface

activity of the photo-catalyst is affected by the acidic medium as it lies with this assumption of the isolines on the contour plot represent distinct level of design parameter. The darker portion of the plot which is within the pH range, represent the area where there is highest probability of finding the optimum response and percentage degradation (Muktar and Umar, 2019).

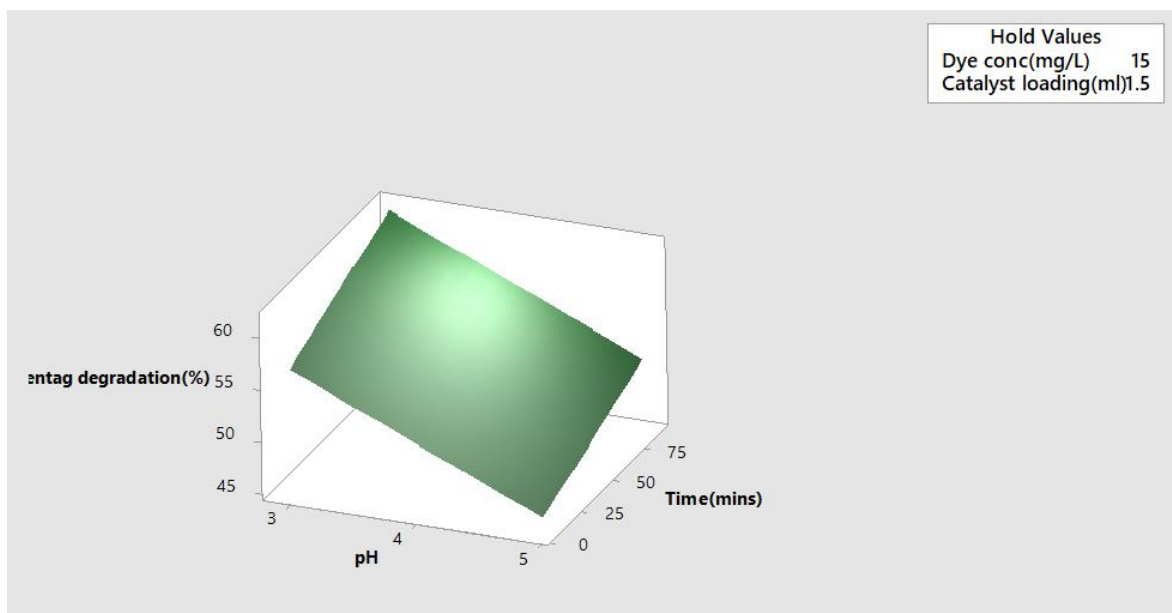


Figure 2: Surface Plot of Percentage Degradation versus Time and pH of Dye

This illustrates the surface plot of percentage degradation of time and pH in three-dimensional view at the dye concentration of 15 mg/L and catalyst loading of 1.5 ml. This shows that with increase in the pH from 3 to 5 downward, there is a steady increase in the irradiation time from 0 to 75 upward trend.

This is a pointer that the reaction is in acidic medium. This implies that as the pH increases, there is responding increase in the degradation, as demonstrated in the graphical representations of 3D regression response surface plots (Lezhuo et al., 2018).

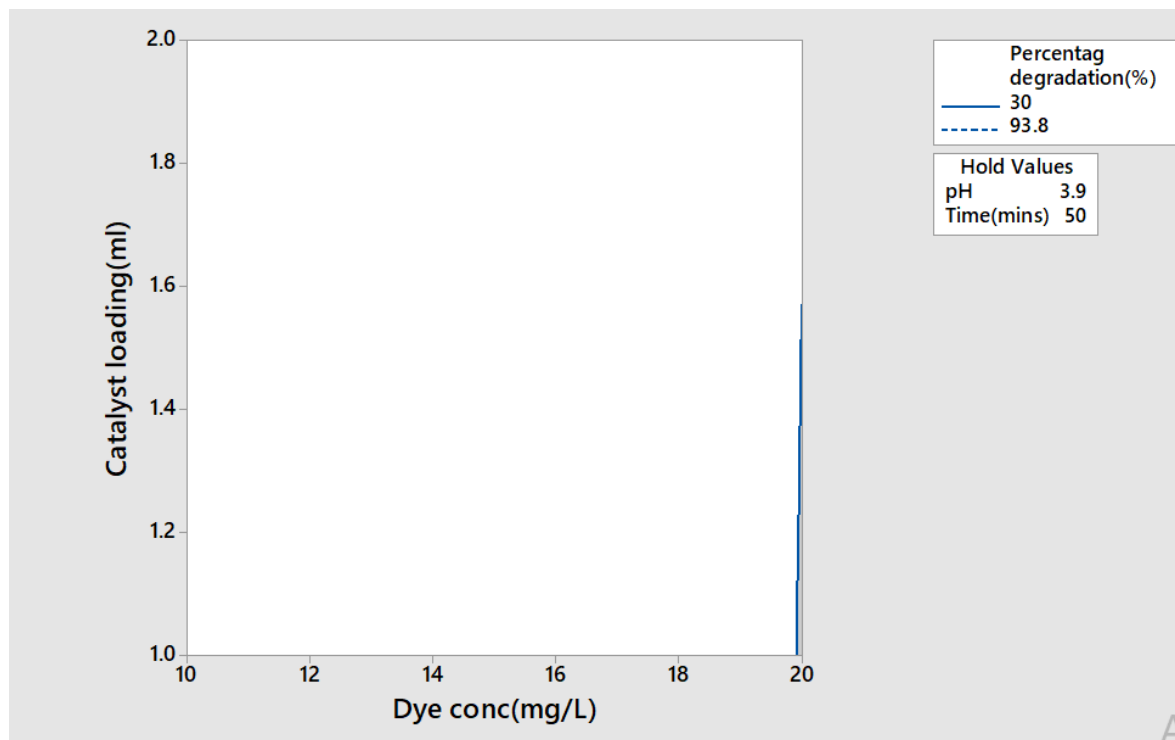


Figure 3: Contour Plot of Percentage Degradation of Dye

This illustrates the feasibility of percentage degradation at time of irradiation of 50 mins with pH of 3.9, the dye concentration approaches 20 mg/L and catalyst loading didn't affects percentage degradation negatively and the percentage degradation is 93.8 %. This shows that degradation is possible

up to concentration close to 20 mg/L, this can be attributed to the hydroxyl radical (OH^\cdot) generated from catalyst loading (H_2O_2) called sonoluminescence mechanism. Sonoluminescence involves an intense UV-light, which excites the (H_2O_2), thereby leading to degradation efficiency (Alireza et al., 2017).

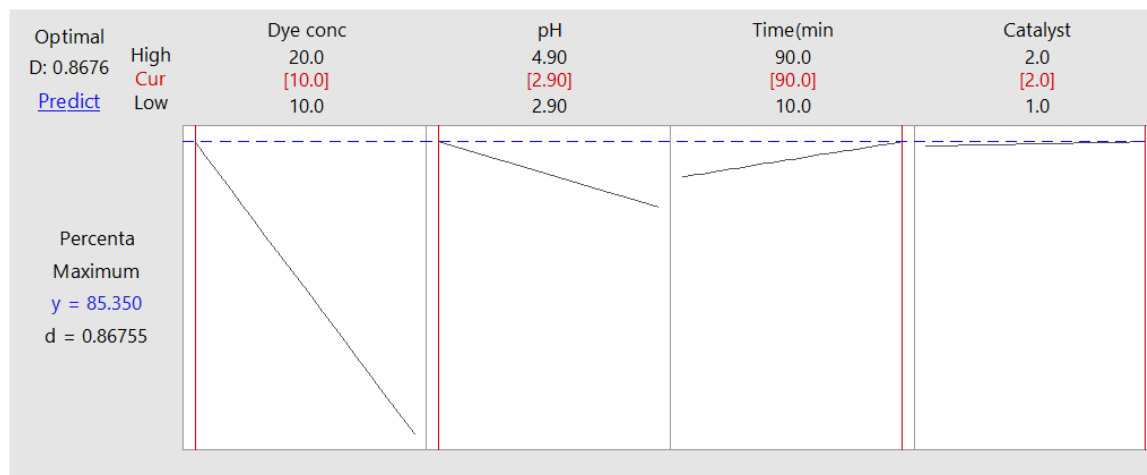


Figure 4: Response Optimization of Dye

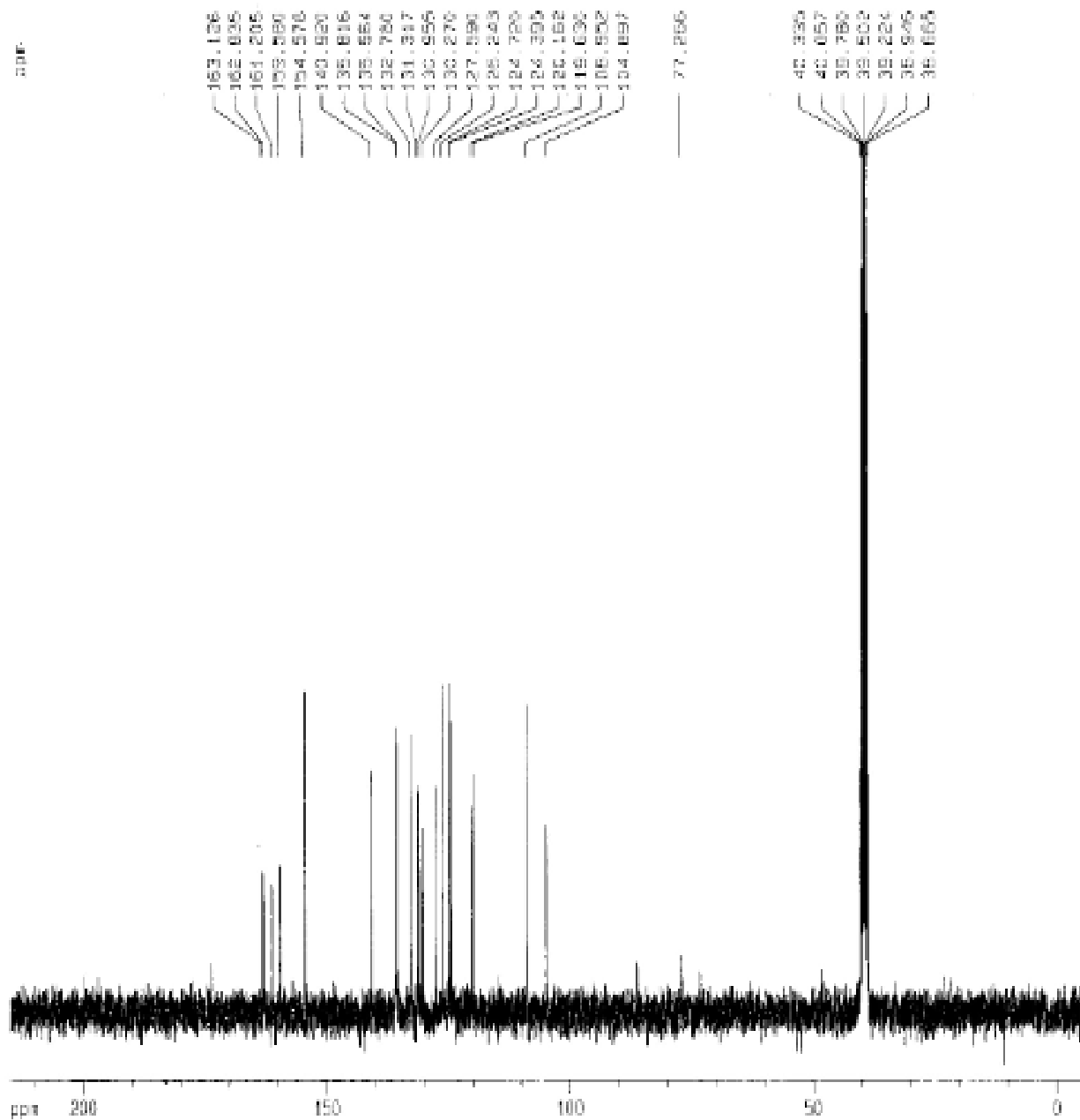


Figure 7: ¹³C-NMR Spectrum of the Intermediate

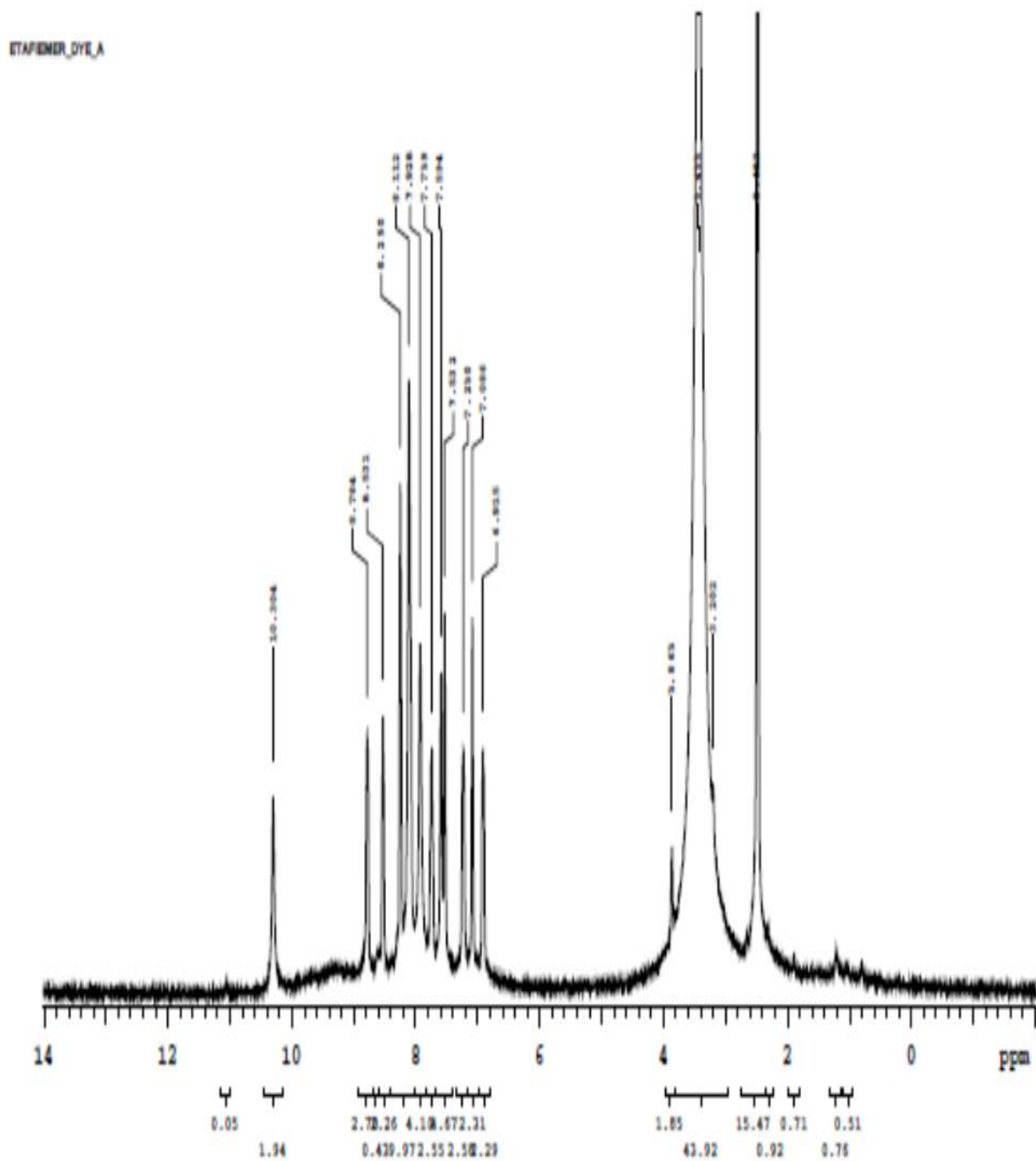


Figure 8: H-NMR Spectrum of the Synthesised Dye

Reference

- Ahmed, A., Hongbo, Y., Xiaoyu, Z. and Fuying, M. (2019). Highly Efficient and Sustainable Spent Mushroom Waste Adsorbent Based on Surfactant Modification for the Removal of Toxic Dyes. *Int J Environ Res Public Health*. 15(7), 1421-1436. Doi: [10.3390/ijerph15071421](https://doi.org/10.3390/ijerph15071421)
- Alireza, K., Berkant, K., Peyman, G., Dimitrios, K. and Sema, A. (2017). Sonocatalytic Degradation of an Anthraquinone Dye Using TiO₂-Biochar Nanocomposite. *Ultrasonics Sonochemistry*, 39, 1-15. doi.org/10.1016/j.ultsonch.2017.04.018.
- Ameuru, U., Yakubu, M. K. and Bello, K. A. (2014). Synthesis and Characterization of Nitrosonaphthol Dyes Based on 1-Naphthol and Their Dyeing Properties on Tanned Leather. *Open Journal of Applied Sciences*, 4, 354-359. Doi: 10.4236/ojapps.2014.46032.pp5.
- Danladi, E., Giwa, A. and Nkeonye, O. P. (2014). Optimizing Processes Using Response Surface Method for the Photodegradation (If Asynthesised Disperse Dye Derived from 2-Amino-4-Methyl-5-Carboxythiazole; *Nigerian Journal of Scientific Research*, 13(2), 18.
- Hettige, A. and Mowjood, M. (2015). Reduction of Colour Interacted Waste Water from Textile Industry Using Sawdust as Bio-Sorbents. *Tropical Agricultural Research*, 26 (4), 666-676
- Joshua, N. E., John, O. O. and Olatunde, S. D. (2017). Impact of Wastewater on Surface Water Quality in Developing Countries: A Case Study of South Africa; *Open access peer-reviewed chapter*, 61. DOI: 10.5772-66561.
- Lezhuo, L., Qiuling, M., Sanfan, W., Sanxiang, S., Bo, L., Ruonan, G., Xiuwen, C., and Qingfeng, C. (2018). Photocatalytic Performance and Degradation Mechanism of Aspirin by TiO₂ through Response Surface Methodology, *Catalysts*, 8 (118), 2-14. doi:10.3390/catal803011.
- Manjushree, C., Tapan, B. M. G. and Mostafa, A. K. S. (2013). Treatment of leather Industrial Effluents by Filtration and Coagulation Processes, Project: Treatment of Textile Dyeing Effluent, *Water Resources and Industry*, 3, 11-22. Doi: 10.1016.
- Muhammad, I., Waqas A. H., Saeeda, Y., Muhammad, Y. and Anwarzeb, K. (2019). Environmental and Health Impacts of Industrial Wastewater Effluents in Pakistan, *Journal Reviews on Environmental Health*, 16-20. Doi: 10.1515-2018-0078.
- Mukhtar, M. and Umar, I. G. (2019). Synthesis of Eosin Y-Sensitized Ag-TiO₂ Nano-Hybrid for Optimized Photocatalytic Degradation of Aqueous Caffeine. *Journal of the Chilean Chemical Society* 64(1), 5-19. Doi: [10.4067/s0717-97072019000104275](https://doi.org/10.4067/s0717-97072019000104275)
- Pratima, B. (2018). Biermann's Handbook of Pulp and Paper (Third Edition), Additives for Papermaking, 2, 77-94. Doi:10.1016/B978-0-12-814238-7.00004-0.
- Raja, S. A., Zeeshan, A. S., Rehman Gulzar, M. A., Muhammad, A. R. (2021). Methods for the Treatment of Wastewaters Containing Dyes and Pigments. *Water Pollution and Remediation: Organic Pollutants*, Project Work, pp 597-661

- Soroosh, M., Ali, S. and David, E. J. (2019). Optimization of Photocatalytic Degradation of Acid Blue 113 and Acid Red 88 Textile Dyes in a UV-C/TiO₂ Suspension System: Application of Response Surface Methodology (RSM), *Catalysts*, 9, 360; doi:10.3390/catal9040360 pp6-9.
- Ukanah, S. P., Bello, K., Yakubu, M. K., Giwa, A and Azim, Z. (2021). Synthesis And Application of Monoazo Disperse Dyes Based on Asymmetric Bisimide on Polylactic Acid Fabrics. *Science World Journal*, Vol. 16(3), 301-307. ISSN: 1597- 6343..
- Wibawa, H. S., Aryan, F. A., Rahman, D. and Dwiwahju, S. (2021). Review Photocatalytic Technology for Palm Oil Mill Effluent (POME) Wastewater Treatment: Current Progress and Future Perspective. *Journal of Materials*, 14, 2846. Doi: 10.3390-14112846,