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Full Length Research Article

SYNTHESIS AND PHOTOCATALYTIC DEGRADATION OF AN ACID DYE USING FACTORIAL DESIGN

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ABSTRACT
A new acid dye was synthesised from the reaction of 6-amno-2-(5-chloro-1,3-dioxoisoindolin-2yl)-*1H*-benzo[*de*]isoquinoline-1,3(*2H*)-dione with J-acid. The synthesised dye was characterised by melting point, UV-visible absorption, FT-IR and ^{1}H-NMR spectroscopy. The synthesised dye was stimulated and subjected to photodegradation using hydrogen peroxide (H_2O_2) as photocatalyst in the presence of ultraviolet light in a photo reactor. The rate of degradation of the dye solution was determined on the basis of absorbance measurement. Four factors such as dye concentration, pH of the solution, time of irradiation and catalyst loading were used as the operational parameters for the photo-degradation studies. The Minitab 17 software was used to determine the optimized conditions for the experiment. The main effects and interactions between factors were investigated and results analysed. The results for the optimization parameters in the photocatalytic degradation revealed the following conditions for the percentage degradation: Maximum degradation at 67.9 % with the desirability of 0.96462, dye concentration of 10 mg/L, catalyst loading of 2 mL, with the time of irradiation of 90 minutes at pH of 3.9 for the dye. This showed that (UV/H_2O_2) photocatalytic degradation of acid dyes using factorial design were effective and efficient technology which can be used in treatment of tannery and textile effluents.

Keywords: H_2O_2, Photocatalytic, Degradation, Acid Dye.

INTRODUCTION

Dyes are coloured compounds or mixtures capable of imparting their colour on a substrate such as leather, cloth, plastic and paper in a reasonably permanent fashion, or a coloured substance that has an affinity for the substrate to which it is being applied (Abubakar, 2020). The dye is generally applied from an aqueous solution and some dyes require a mordant to improve their fastness on the fibre. Dyes appear to be coloured due to their ability to absorb some wavelengths in the visible spectrum of light more than others. In contrast to dyes, pigments are generally insoluble and have no affinity for the substrates (Ashok *et al.,* 2021), furthermore, not all coloured substances are dyes. However, the true dye must be able to attach itself to material from solution or to be capable of being fixed on it. It must also be soluble in water or other medium, or form a stable and good dispersion in water. The substrate to be dyed must have an affinity for an appropriate dye and must be able to absorb it from solution or aqueous dispersion, in the presence of auxiliary substance under suitable conditions of concentration, pH and temperature. The dye must be fast to washing, dry cleaning, perspiration, light, heat and other agencies when fixed on the substrate. It must also be resistant to the action of water, acid or alkalis in particular (Omid, *et al.,* 2013).

Dyes are used in various industries as colouring agents. The discharge of dyes, specifically synthetic dyes, in wastewater represents a serious environmental problem; it causes public health concerns (Rahat and Umair, 2019). The implementation of regulations for wastewater discharge has forced research towards either the development of new processes or the improvement of available techniques to attain efficient degradation of dyes. Catalyst oxidation is one of the advance oxidation process (AOPs), based on the active radicals produced during the reaction in the presence of ultraviolet light (Rahat and Umair, 2019).
Synthetic dyes are colour substances obtained by chemical transformation. They offer a vast range of new colours and impact better properties to the dyed materials. Synthetic dyes have quickly replaced the traditional natural dyes, because they impact better properties to the dyed material (Virendra, 2019). Synthetic dyes have furnished the dye users with a colourful palette for over a century. Many different substrates which are either natural or synthetic polymer structure of all kinds can be dyed (Andrew, 2019).
The photocatalytic degradation method using design of experiment has 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 to be used 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 non-biodegradable contaminants into harmless products (Danladi *et al.,* 2014).

EXPERIMENTAL

MATERIALS AND METHODS

All the chemicals used in the synthesis were of commercial grade and were used as received. The melting points were determined in an open capillary tube using Barsntead electrothermal and were uncorrected. The purity of the intermediate and dye were determined by thin layer chromatography (TLC) using silica gel G-coated Al-plates. The UV-visible absorption spectrum was measure using Jenway Uv-visible spectrophotometer model 6305. The FT-IR spectra were determined using FTIR-84005.The ^{1}H-NMR was recorded on a 300 MHz bruker instrument using deuterated dimethylsulphoxide (DMSO-d_6) as solvent. Photo-degradation was done with photo-reactor and Minitab 17 software was used to determine the optimum conditions for the experiment.

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-Dioxoisoindolin-2-yl)-1*H*-

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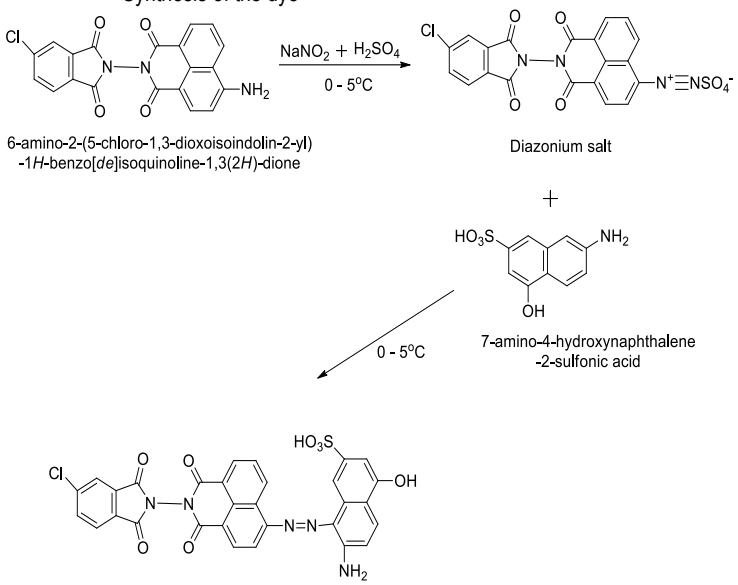
Benzo [*de*] Isoquinoline-1, 3(2*H*)-Dione.

Dry sodium nitrite (1.5 mmol, 0.104 g) was added to cold conc. H_2SO_4 (98%, 1.1mL) 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-dioxoisoindolin-2-yl)-1*H*-benzo [*de*]isoquinoline-1, 3(2*H*)-Dione, was added in portion wise at less than 10 °C then the liquor was stirred for 3hr. The obtained clear diazonium salt solution was used immediately in coupling reaction. The crude product was purified by recrystallization from ethanol several times to afford the product as yellow (Ameuru *et al.,* 2014). Yield = 49.2 %; Melting point = >300 °C, FT-IR (KBr, cm^{-1}) 3358, 3235, 3083, 1428, 1741, 1528, 753, 828, 1275; ^{1}H-NMR (300 MHz, DMSO-d_6): (ppm) 2.48 (2H, s, NH_2), 3.41 (1H,s, OH), 6.89 (1H, d, J = s.4 Hz), 7.09 (1H, s), 7.24 (1H, d, J = 8.8 Hz), 7.54 (1H, s), 7.62 (1H,s), 7.72 (1H, d, J = 8.4 Hz), 7.93 (1H, s), 8.09 (1H, d, J = 8.0 Hz), 8.14 (1H, d, J = 8.4 Hz), 8.23 (1H, d, J = 5.6 Hz), 8.53 (1H, d, J = 7.2 Hz), 8.77 (1H, d, J = 8.4 Hz),10.32 (1H, OH).

RESULTS AND DISCUSSION

Synthesis of the dye



Scheme 1: Schematic route for the synthesized dyes

As mentioned in (Ukanah *et al.,* 2021). Synthesis of intermediate, 6-amino-2(5-chloro-1,3-dioxoisoindolin-2-yl)-1*H*-benzo [*de*] isoquinoline-1,3-(2*H*)-dione was obtained and characterized. Yield = 75 %; Melting point = 391 °C. The ^{1}H-NMR (300 MHz, DMSO-d_6 spectrum of intermediate (Figure 6), 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 7-amino-8-(2-(5-chloro-1,3-dioxoisoindolin-2-yl)-1,3-dihydro-1*H*-benzo[*de*]isoquinolin-6-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonic acid dye was carried out using 6-amino-2(5-chloro-1,3-dioxoisoindolin-2-yl)-1*H*-benzo [*de*] isoquinoline-1,3-(2*H*)-dione and coupled with J-acid to give the dye (Scheme 1). Yield = 49.2 %; Melting point = >300 °C. The UV-visible of the dye absorbed maximal wavelength at (λ_{max} = 438 nm). It falls within the blue region of the spectrum, the compound appears yellow to eyes. The FT-IR (KBr, cm^{-1} spectrum of dye Figure 5), showed -N-H stretching vibration at 3358, -OH stretching vibration at 3235, -C-H aromatic stretching vibration at 3083, C=O stretching vibration at 1741, C=C stretching vibration at 1528, -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 75. The ^{1}H-NMR (300 MHz, DMSO-d_6 spectrum of dye (Figure 7), showed peak at 2.48 ppm which account for the hydrogen with the NH_2 substituent, the peak at 3.41 ppm showed the hydroxyl (OH) of the J–acid. The peak at 6.59–8.77 ppm correspond to aromatic region of the dye structure. The peak at 10.32 ppm account for the (OH) in the sulphonic group substituent The synthesised dye was stimulated and subjected to photodegradation using hydrogen peroxide (H_2O_2) as photocatalyst in the presence of ultraviolet light in a photo reactor. The rates of degradation of the dye solution were determined on the basis of absorbance measurement. Four factors such as dye concentration, pH of the solution, time of irradiation and catalyst loading were used as the operational parameters for the photo-degradation studies. The conditions were optimised using Minitab 17 software, the main effects and interactions between factors were investigated and results analysed (Eid *et al*., 2017). The results for the optimisation parameters in the photocatalytic degradation, revealed the following conditions for the percentage degradation: Maximum degradation at 67.9 % with the desirability of 0.96462, dye concentration of 10 mg/L, catalyst loading of 2 ml, with the time of irradiation of 90 minutes at pH of 3.9 for the dye. This showed that (UV/H_2O_2) photocatalytic degradation of acid dyes using factorial design were effective and efficient technology which can be used in treatment of tannery and textile effluents.

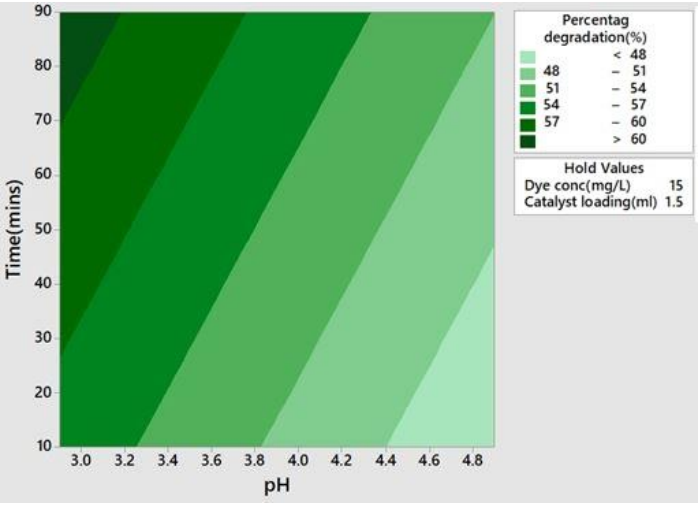


Figure 1: Contour Plot of percentage degradation versus Time and pH of the dye.

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 occur fully in that region. This could be attributed to the fact that surface activity of

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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).

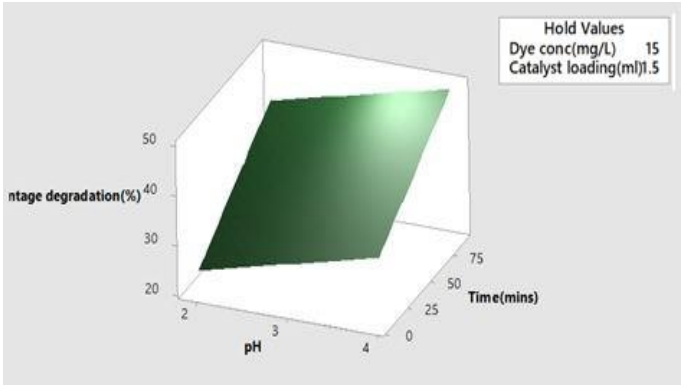

Figure 2: Surface plot of percentage degradation versus Time and pH of the dye

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 increased in the pH from 2 to 4 upward, there is a steady increase in the irradiation time from 0 to 75 upward trends. 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).

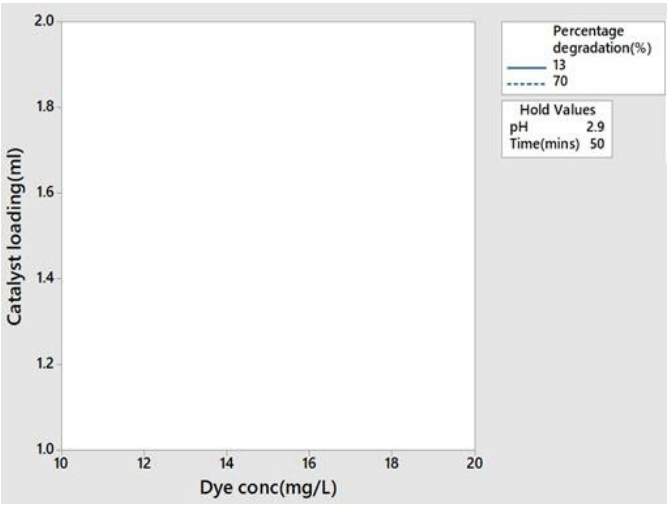

Figure 3: Contour plot of percentage degradation of the dye

This illustrates the feasibility of percentage degradation at time of irradiation of 50 mins with pH of 2.9, the dye concentration approaches 20 mg/L and catalyst loading didn't affects percentage degradation negatively and the percentage degradation is 70 %.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).

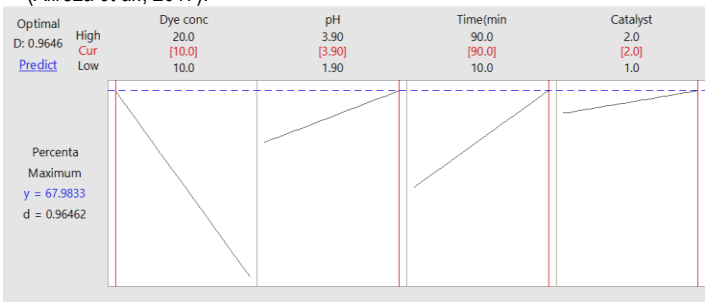

Figure 4: Response optimization of the dye

This illustrates the response optimisation parameters in photo catalytic degradation of the dye; it determines the maximum degradation at 67.9 % with the desirability of 0.96462, dye concentration of 10 mg/L, catalyst loading of 2 mL, with irradiation of 90 mins at pH of 3.9. The significance of the percentage degradation as evaluated based on computed F-statistic values and their associated p-values of the regression models (Soroosh *et al*., 2019). This shows the best suitable conditions to get the best predicted result for the percentage degradation of the dye.

Conclusion

In this research work, a new acid dye was synthesised from 6-amno-2-(5-chloro-1,3-dioxoisoindolin-2yl)-*1H*-benzo[*de*]isoquinoline-1,3(*2H*)-dione in good yield. The intermediate and the dye structures were confirmed using FT-IR, ^{1}H-NMR, UV-visible spectroscopic techniques. The photo degradation of the dye was carried out using factorial design experiment. The effects of operational parameters such as pH, dye concentration, catalyst loading, and time of irradiation were determined. The results revealed the following conditions for the percentage degradation: Maximum degradation at 67.9 % with the desirability of 0.96462, dye concentration of 10 mg/L, catalyst loading of 2 ml, with the time of irradiation of 90 minutes at pH of 3.9 for the dye. This showed that (UV/H_2O_2) photocatalytic degradation of acid dyes using factorial design were effective and efficient technology which can be used in treatment of tannery and textile effluents.

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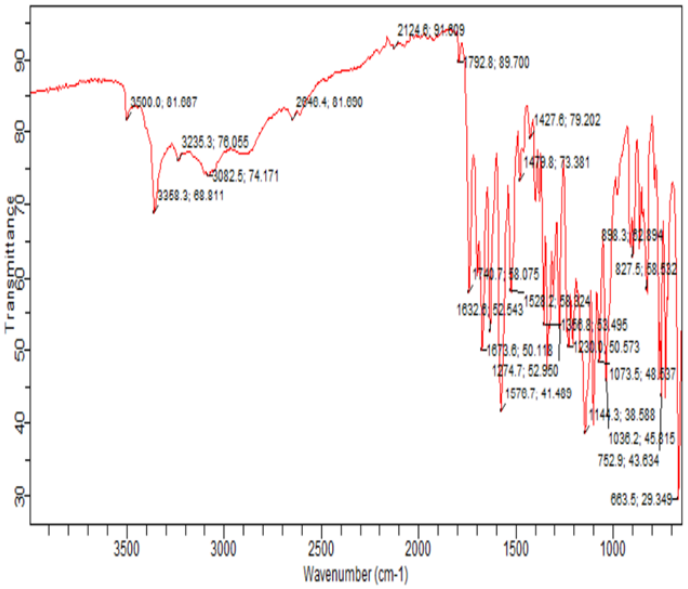

Figure 5: FTIR spectrum of the dye.

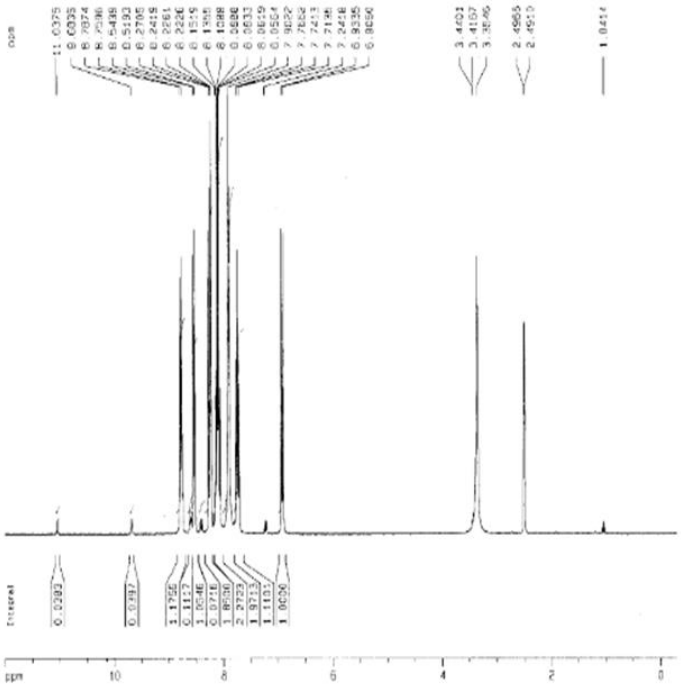

Figure 6: [1]H-NMR spectrum of the intermediate

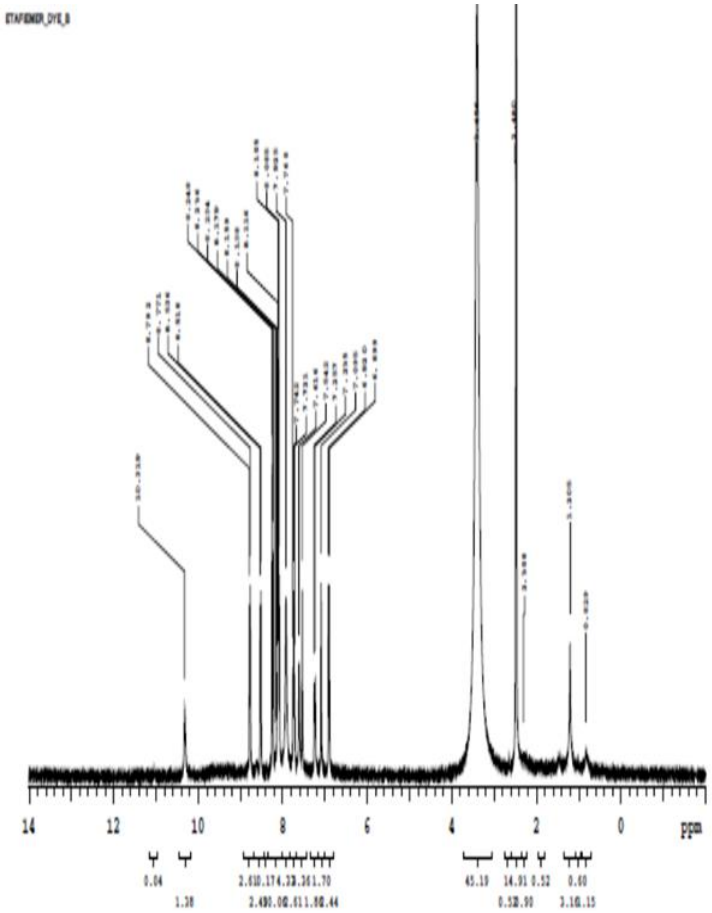

Figure 7: [1]H-NMR spectrum of the synthesized dye

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