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RESEARCH PAPER

Photocatalytic Decomposition of Nigrosin Dye Using ZnO Nanoparticles Synthesized By Co-Precipitate Method

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ABSTRACT

Zinc Oxide nanoparticles (ZnO NPs) were produced in the form of a powder by co-precipitation synthesis method. The photocatalysts underwent characterization Employing X-ray diffraction (XRD), scanning electron microscopy, and Energy dispersive X-ray spectroscopy (EDX). The assessment of photocatalytic activity was conducted aqueous heterogeneous medium containing Nigrosin dye and ZnO NPs as photocatalyst in a batch reactor. An investigation was conducted to examine the many elements that influence. The efficacy of photocatalytic decomposition. These factors include amount of catalyst used, the initial concentration of dyes, the impact of H_2O_2, and the effect of temperature. The optimal concentration of Nigrosin dye equal 30 mg L^{-1}, and catalyst concentration of 0.13 g /100mL. The activation energy for the photo degradation process calculated using the Arrhenius equation was equal to (30.36 KJ/mol).

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INTRODUCTION

Wastewater from textile, paper, and agro-industries contains pollutants such as dyes, phenols, and pesticides. Due to their poisonous and carcinogenic properties, these substances pose a significant threat to human health and have a negative impact on the ecosystem. The persistent nature of these compounds, which do not readily decompose in nature, has raised significant concerns among society and regulatory agencies worldwide due to their continuous accumulation in water bodies. The majority of conventional water treatment procedures, such as membrane filtration, adsorption, and chemical treatment, are not efficient in completely eliminating dyes [1]. Various methods have been employed in recent years to eliminate various methods may be used to remove colors from wastewater, such as biological processes (aerobic and anaerobic), chemical precipitation, coagulation/flocculation, solvent extraction, membrane filtration, ion exchange, ozonation, electrochemical destruction, and adsorption. Advanced oxidative processes (AOPs) have been intensively explored as a more viable method for decolorization and degradation of textile dyes. The method of heterogeneous photocatalytic oxidation is now being extensively studied, leveraging nanotechnology. Nanoparticles are mostly utilized because to their significant surface area and simplicity of production. Titanium dioxide is the most significant nanoparticle because of its exceptional photocatalytic activity, affordability, lack of toxicity, and strong stability in water-based solutions [2]. Advanced -oxidation procedures (AOPs), such as photocatalysis decompostion, are a sustainable technique that

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breaks down pollutants into less harmful or harmless substances. Plasma deposition (PD) is distinguished by its cost-effectiveness, as it operates at normal pressure and temperature and may achieve full mineralization of colors. The photocatalytic approach utilizes the production of hydroxyl free radicals (•OH), superoxide anion ($•O_2^-$), singlet oxygen ($1O_2$), and (H_2O_2) to break down inorganic dye molecules. [3]. The photocatalysis process Due to its rapid breakdown rate [4], has been suggested as a feasible approach for treating dye wastewater. This procedure also employs a cost-efficient photocatalyst that is both non-toxic and ecologically friendly, setting it apart from past techniques. ZnO has a semiconducting characteristic and possesses a structure with a hexagonal shape, similar to the wurtzite crystal structure. .Zinc oxide (ZnO) is a chemical that acts as an oxidizing agent and possesses a wide bandgap semiconductor property, with a value of around 3.3 electron volts [5]. Zinc oxide (ZnO) possesses several unique characteristics that make it highly suitable as a nanomaterial for a wide range of applications. These include its ability to undergo surface modifications, its capacity for low-temperature regeneration, its affordable cost, its ease of operation at lower temperatres, and its high occurrence of Lattice flaws and imperfections. Oxygen vacancies in its crystalline structures [6]. For the first time in this study, we have produced zinc oxide nanoparticles by employing Zinc nitrate is used as the zinc supply, while water serves as the solvent. Through a chemical co-precipitation technique. The acquired sample was analyzed using and its X-ray diffraction pattern (XRD) was examined. The photocatalytic efficiency ZnO nanoparticles (Zn0-NPs) has been assessed for the decomposition of Nigrosin dye.

MATERIALS AND METHODS

Materials

zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), provided by Fluka AG, Nigrosin The dye is provided by Sigma-Aldrich, sodium hydroxide is provided by Fluka, whereas the hydrochloric acid is authored by Fluka, e-Hydrogen peroxide supplied by Fluka. All compounds were used without further purification.

Photocatalytic Reactor Set up

Fig. 1 shows the photocatalytic degradation system that was used to carry out all experiments.

Photocatalytic degradation experiment

The liquid solution of Nigrosin dye was subjected to photocatalytic degradation studies. During this

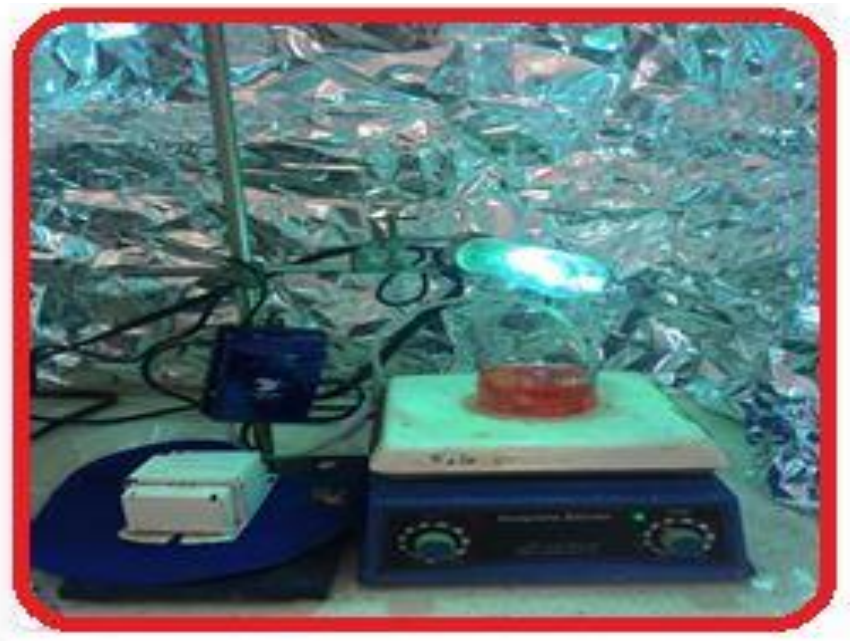

Fig. 1. Optical photo for main parts of the Photocatalytic degradation system.

experiment, the pigment was subjected to solar radiation and zinc oxide in a batch reactor with the purpose of teaching about their interaction. This reactor comprises a cylindrical annular-type reactor that is divided into two halves. The initial component consisted of an external thimble, where a flow a stream of water was diverted through the thimble in order to decrease the temperature of the reaction solution. The temperature of the reaction solution was affected by the continuous cooling process. Kept at the ambient temperature. The second component consisted of an internal thimble containing the reaction solution, which was precisely measured to be 100 cm3, and placed within the reaction chambers. Dye was subjected to photocatalytic degradation using sun light. The photocatalytic decompostion tests Nigrosin dyes were conducted by combining 0.13 g/1oo mL of the catalyst with a 30 ppm solution of the Nigrosin dye. To verify the equilibrium of adsorption on the surface of the catalyst.

Initially, the suspension solution containing ZnO NPs and the Nigrosin dye solution were mixed vigorously in the absence of light for a duration of 30 minutes to achieve equilibrium in the dark adsorption process. Subsequently, the dye solution underwent bubbling with air at a rate of 10 mL per minute while being exposed to irradiation. Subsequently, a volume of 2 mL from the suspension reaction mixture was extracted at 10-minute intervals. Subsequently, centrifugation was performed at a speed of 4000 revolutions per minute to eliminate any remaining particles of antimony trioxide. Ultimately, all samples were subjected to analysis at the peak absorption wavelength using a UV-Vis spectrophotometer.

Preparation of ZnO NP$_s$ Using The co-precipitation technique

ZnO nanoparticles were The synthesis was performed utilizing a chemical co-precipitation approach with zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and sodium hydroxide (NaOH) as the initial substances. To prepare ZnO nanoparticles, a solution comprising 0.5 M of $Zn(NO_3)_2.6H_2O$ was dissolved in 100 mL of deionized distilled water. Additionally, a solution of 1mM NaOH was separately dissolved in 1oo mL of deionized distilled water. The NaOH solution was gradually added drop by drop into the precursor solution of ($Zn(NO_3)_2.6H_2O$) while vigorously stirring, resulting in the development of a white precipitation product (ZnO). The precipitate underwent many washes with deionized distilled water and ethanol to remove contaminants. Subsequently, the ZnO powder was subjected to a drying process in a hot air oven at a temperature of 70 °C for a duration of 6 hours, with the purpose of eliminating any water molecules that were adsorbed on the surface. Following this, the powder was annealed a muffle furnace at a temperature of 400 °C a period of 2 hours, aiming to enhance its crystalline structure

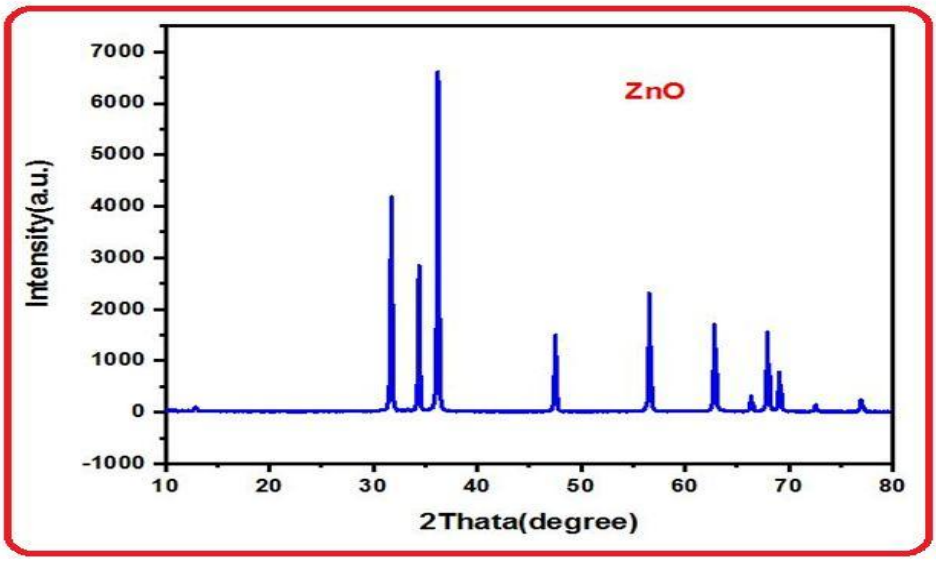

Fig. 2. XRD patterns of ZnO nanoparticles.

[7].

RESULTS AND DISCUSSION

The measurement conditions were configured using 45 the radiation used is Cu-Kα with a wavelength of (λ = 1.54056 Å) at 40kV, 30mA with a rate of 5 deg/min and ran at the 2θ range (3-90˚). In Fig. 2 the peaks positions of ZnO nanoparticle appearing at 2θ 31.837˚, 34.502˚, 36.334˚, 47.650˚, 56.726˚, 63.012˚, 68.114˚, 69.254˚ and 89.860˚), which agrees with the standard data of zinc oxide could be indexed to the hexagonal (JCPDS 38–1479) [9].

The SEM analysis revealed the morphologies of the ZnO powder, as seen in Fig. 3. The micrograph of ZnO NPs confirms the presence of semi-spherical particles with a non-uniform distribution. These particles can exist as individual entities or as clusters, forming aggregated Zinc Oxide nanoparticles. It indicates that the powder particles have formed little clusters. The use of heat treatment caused the powder particles to clump together as a result of the interaction between the nanoparticles. [10].

The EDX spectrum of ZnO nano particles generated using the co-precipitation method is displayed in Fig. 4. (EDAX) examination was conducted to determine the presence of components in the produced ZnO NPS. The EDAX spectrum of the generated ZnO nanoparticles revealed the existence of Zn and O atoms, indicating their purity and providing information on the weight % of Zn and O. This suggests that the chemical co-precipitation approach is particularly advantageous for the production of ZnO nanoparticles [11].

The effect of catalyst dose on photolysis of Nigrosin dye using ZnO nanoparticles is shown in Fig. 5. This catalyst changed from 0.05 - 0.30 G/100mL to prepared ZnO nanoparticles. The observed enhancement in ZnO's photocatalytic activity, upon increasing the catalyst dosage, can be attributed to the presence of more active sites and a larger adsorption area. These factors facilitate the formation of active radicals, which effectively destroy the dye. The catalyst dosages of o.13 g/100mL were shown ideal for the process of photocatalytic degradation of Nigrosin dye [12-14].

In order to investigate the impact of varying starting concentrations of Nigrosin dye on photodegradation activity, the concentrations

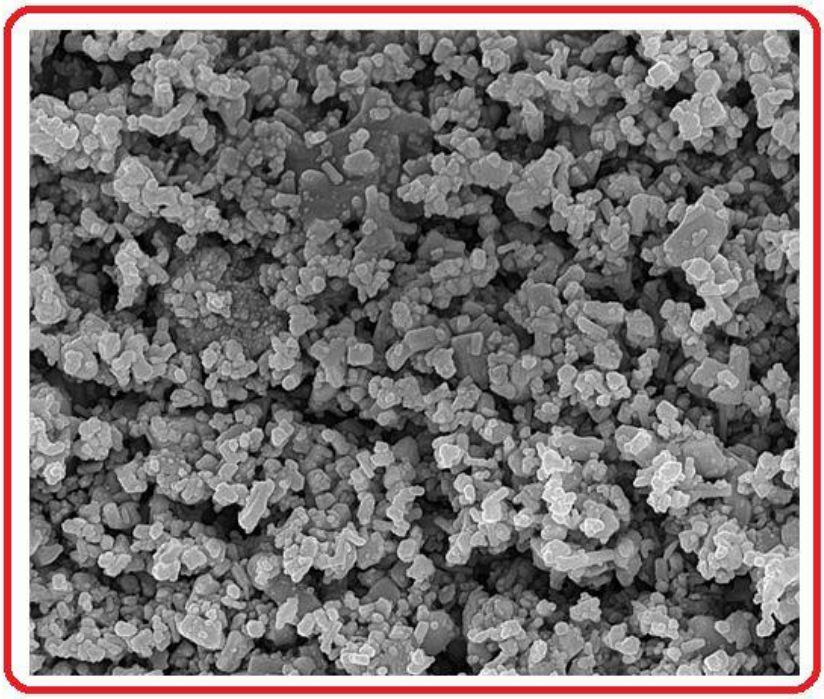

Fig. 3. Scan electron microscopy pattern of zinc oxide nanoparticles.

were altered within the range of 30 to 60 mg/L. The results depicting the rate at which the dye is removed are displayed in Fig. 6. Under constant circumstances, the clearance rate of [substance]

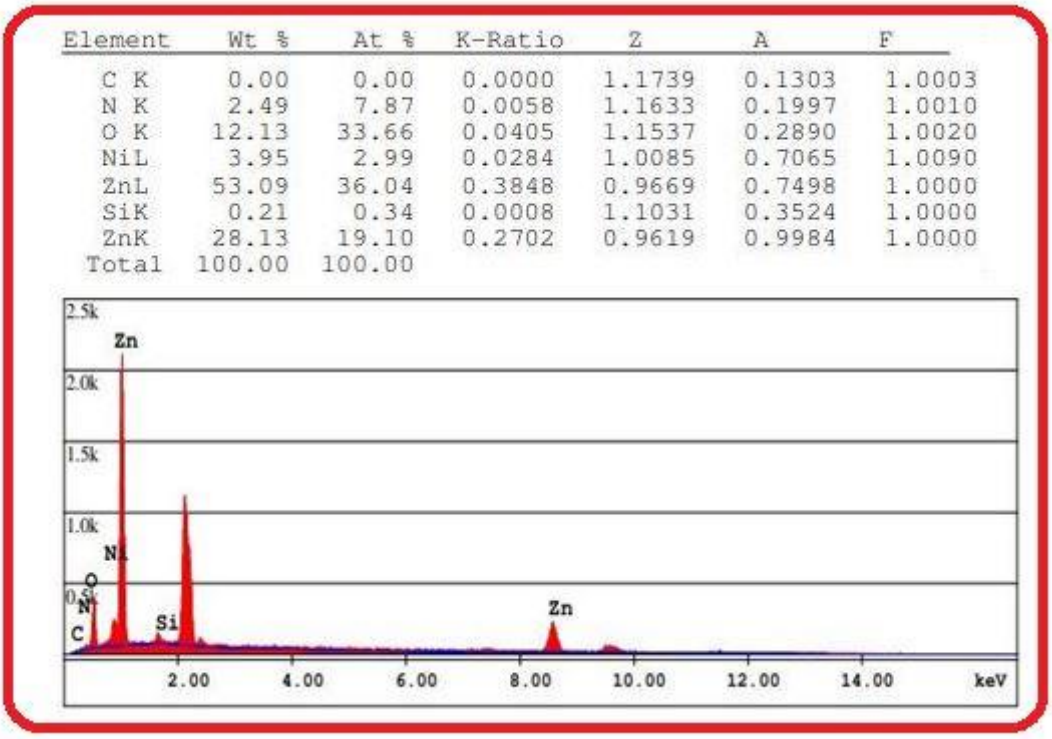

Fig. 4. Spectrum of ZnO NPS obtained by energy-dispersive X-ray spectroscopy (EDX).

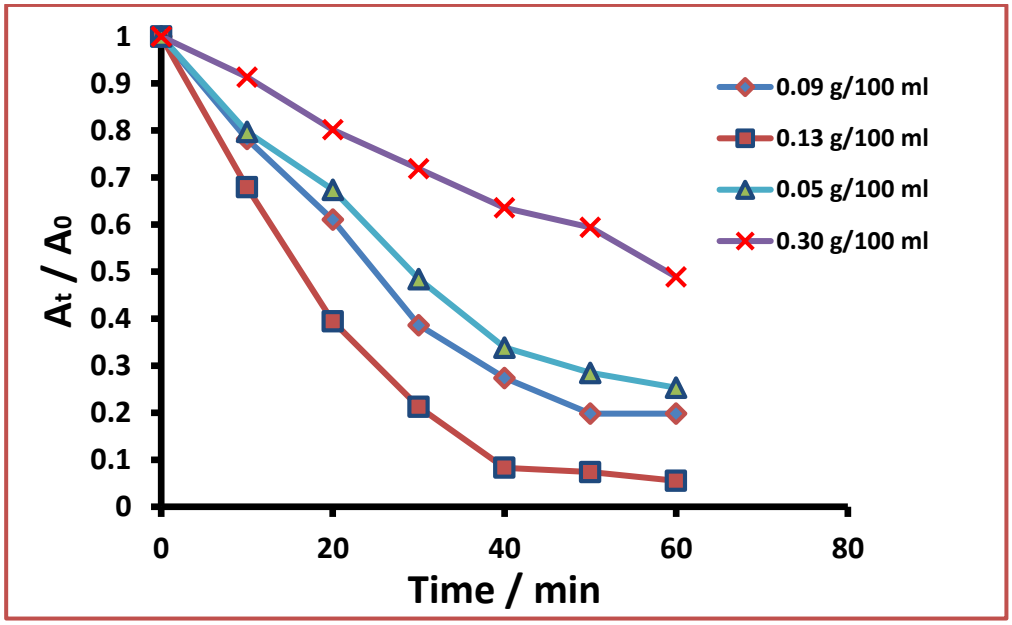

Fig. 5. Photocatalytic degradation process using (30mg/L) of Nigrosin dye at differense mass of ZnO NPs.

increased as the original concentration increased. Nigrosin dye decreased significantly from 90.80%, 43.36%. Consequently, reducing the initial concentration of the dye can improve the effectiveness of dye removal. When the initial concentration of the dye was raised, a greater number of dye molecules were adsorbed onto the surface of the photocatalyst. Due to the presence of photons before reaching the photocatalyst surface The clearance rate decreased when the

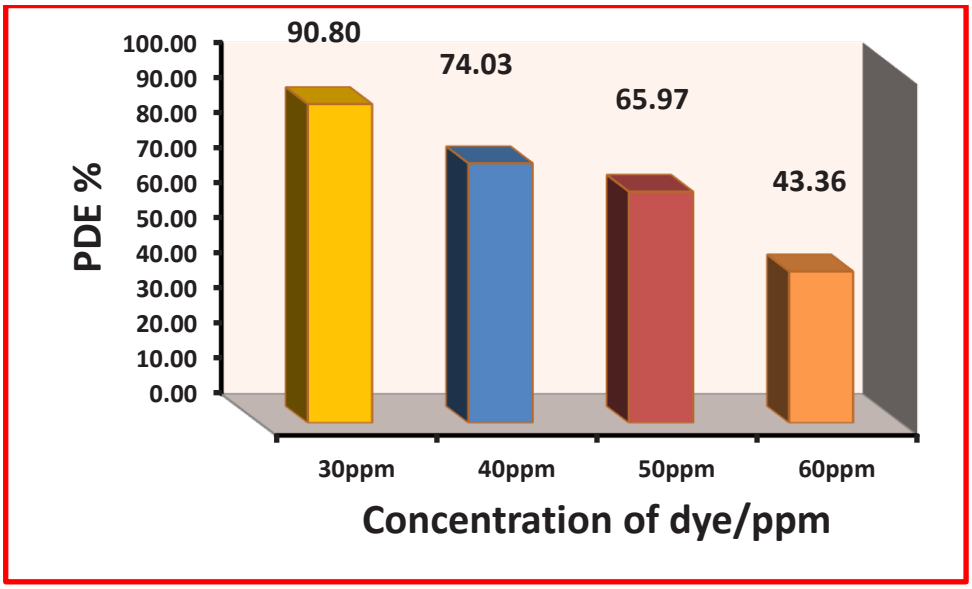

Fig. 6. Photolysis of efficiency using 0.13 g / 100 ZnO -NPs and 30 ppm of Nigrosin dyes.

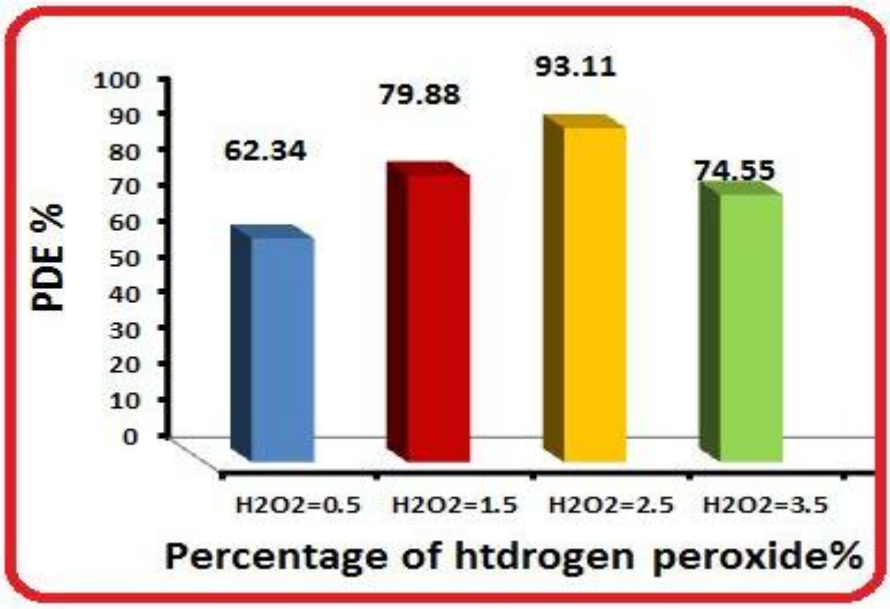

Fig. 7. Photocatalytic degradation efficiency at different percentage of hydrogen peroxide using 0.13 g / 100 mL ZnO NP_s and 30 ppm of Nigrosin dye.

original dye concentrations were high [16,17].

Several experiments have been performed To investigate the impact of hydrogen peroxide on the process of photocatalytic degradation of Nigrosin dye at 30ppm using 0.13 g/100mL prepared ZnO NPs. As shown in Fig. 7. The inclusion of H_2O_2 in photocatalytic processes often yields favorable outcomes in terms of contaminant removal efficiency. This is due the production of strong hydroxyl free dradicals, which

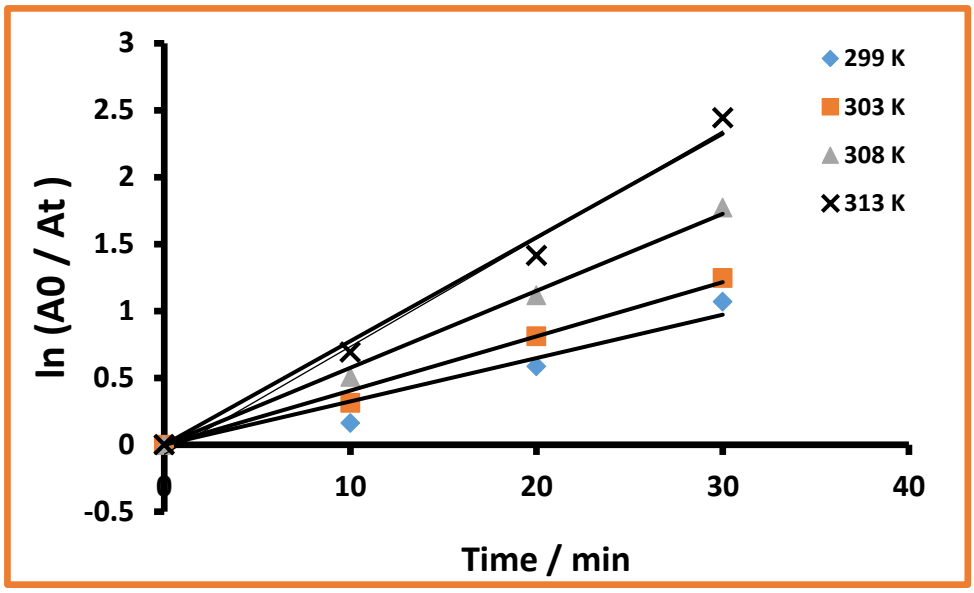

Fig. 8. The changed of ln (A_o / A_t) with irradiation time at different tempe using solar radiation, initial Nigrosin dye conc = 30 ppm, amount of photo catalyst = 0.13 g / 100 mL.

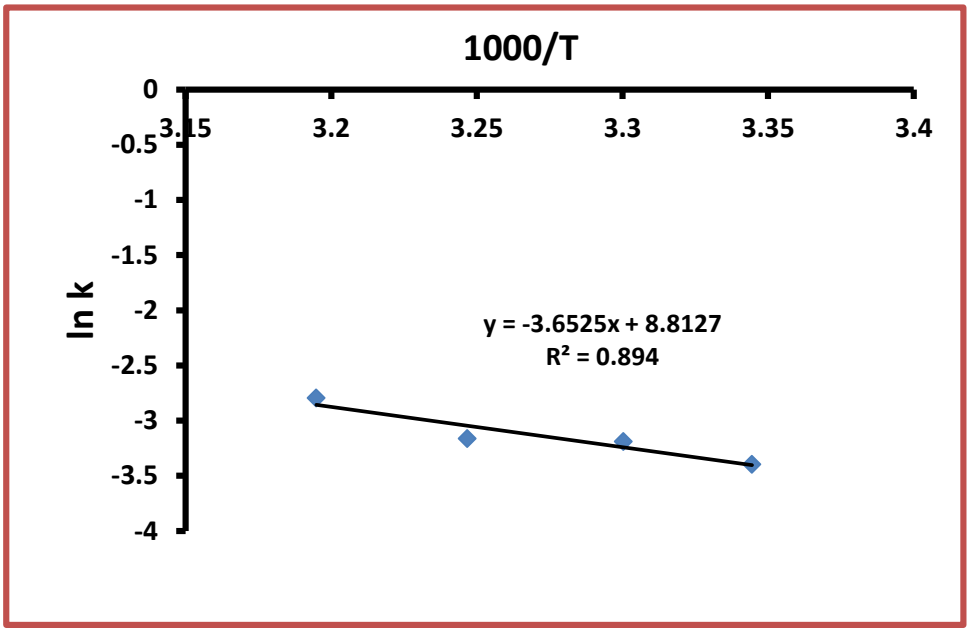

Fig. 9. Arrheneius plot of Nigrosin dyes.

increase the oxidation process and contribute to the degradation of pollutants. However, H_2O_2 can impede the recombination of electrons and holes by capturing the generated electrons in the conductive band. The involvement of H_2O_2 molecules in the degradation process can occur through the following three mechanisms:

1) Through the absorption of radiation energy, which leads to the generation of hydroxyl radicals according to Eq. 1. 2) By acting as an electron acceptor and taking the place of oxygen, as described in Eq. 2. This process generates hydroxyl radicals with strong reactivity, while simultaneously reducing the electron-hole recombination rate. 3) The reduction through of H_2O_2 by superoxide ($-\bullet O_2$) and result of ($OH\bullet$) radicals (Eq. 3).

$$H_2O_2 + h \rightarrow 2OH\bullet \quad (1)$$

$$e^-_{CB} + H_2O_2 \rightarrow OH\bullet + OH^- \quad (2)$$

$$^\bullet O_2 + H_2O_2 \rightarrow OH^\bullet + OH^- + O_2 \quad (3)$$

Nevertheless, elevated levels of H_2O_2 would detrimentally impact the effectiveness of the photocatalytic process by functioning as a radical scavenger (as shown in Eqs. 4 and 5 and as a scavenger for holes (h+) as described in Eq. 6:

$$OH\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet \quad (4)$$

$$HO^\bullet_2 + OH\bullet \rightarrow H_2O + O_2 \quad (5)$$

$$H_2O_2 + h^+ \rightarrow HO\bullet_2 + H^+ \quad (6)$$

Due to the lower reactivity of $HO\bullet_2$ radicals compared to hydroxyl radicals, the presence of significant amounts of H_2O_2 will hinder the primary process of contaminant oxidation by $OH\bullet$ radicals. [18].

A series of studies were conducted to investigate the impact of temperature on the photocatalytic degradation of Nigrosin dye within the temperature range of 299 to 313 Kelvin. Under the condition of conservation, the starting concentration of Nigrosin dye was 30 parts per million (ppm), and the dosage of ZnO nanoparticles (NPs) catalyst was 0.13 grams per 100 cubic centimeters (cm^3). The results depicted in Fig. 8 indicate a progressive rise in the degradation process of dye at higher temperatures. This can be attributed to the heightened presence of reactive hydroxyl radicals [19,20].

The activation energy for the photodegradation of dye was determined using the Arrhenius equation through a plot of the natural logarithm of the rate constant (k) against the reciprocal of the temperature (1/T). Fig. 9 shows a value of 30.34 ±1 $kJ.mol^{-1}$.

CONCLUSION

This article describes the synthesis of zinc oxide nanoparticles using the co-precipitation technique. The degradation processes of Nigrosin dye by photocatalysis were found to be dependent on the dose of catalyst, with the best value being 0.13 gm / 100 mL of ZnO NPs. An investigation has been conducted on the impact of dye concentration. The optimal concentration of Nigrosin dye is 30 parts per million (ppm). The photocatalytic degradation diminishes as the concentration of Nigrosin dye increases, as a result of the reduction in the concentration of OH- adsorbed on the catalyst surface. The degradation of Nigrosin dye by photocatalysis is enhanced as the concentration of hydrogen peroxide increases. The photocatalytic degradation of Nigrosin dye achieved an efficiency of 93.11%.The value for the activation energy has been computed =30.36kJ. mol^{-1}.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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