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Photocatalytic degradation of textile dyeing wastewater Using ZnO as photocatalyst

[1]M. Asha Berlin, [2]J. Mary Juli Jenisha, [3]N.S. Sushmi, [4*]T. Sumitha Celin, [5]R. Leena, [6]G. Allen Gnana Raj

[1]Research Scholar(20213162192009), [2]Research Scholar (21113162032011), [2]Research Scholar (21113162032010),
[4,5]Assistant Professor, [6]Associate Professor*
[2,3,4,6]Department of Chemistry & Research Centre,
[1,5]Department of Zoology & Research Centre,
Scott Christian College (Autonomous), Nagercoil-629003
(Affiliated to ManonmaniamSundaranar University, Tirunelveli).
[4]Email: sumithaezhil77@gmail.com*

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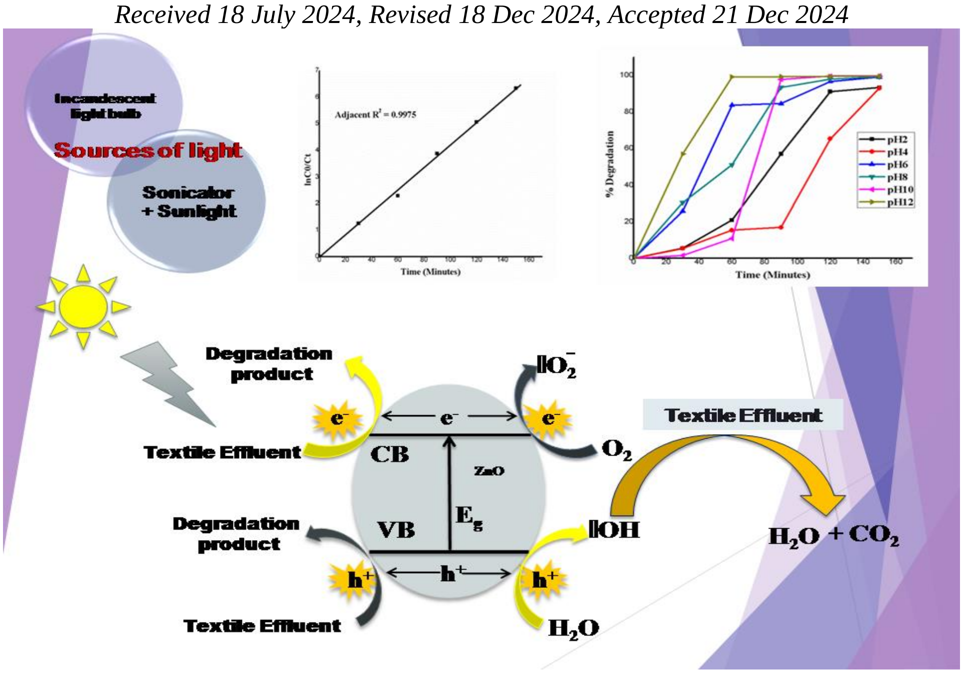

Abstract

Photocatalytic degradation is a new and cost-efficient method for cleaning water tainted with dyes, which may harm the environment and human health. In this context, the sol-gel technique was used to generate a preparation of zinc oxide. This strategy was shown to be cost-effective and user-friendly. Optimal parameters were studied for the photodegradation of textile dyeing effluent using ZnO as a catalyst. An elevation in ZnO dosages and a basic initial pH value resulted in a discernible escalation in the rate of direct dye photodegradation at lower

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concentrations of dye. The best conditions for ZnO dose, pH, and dye concentrations were found to be 0.02 g, 10, and 5 mg/L, respectively, at room temperature. The direct dye removal effectiveness reached 99.8% within 150 minutes in the batch testing. This research also shown that elevated temperatures may enhance the effectiveness of dye elimination.

Keywords: catalyst, effluent, pH, sol-gel, ZnO

*Corresponding author.
E-mail address: sumithaezhil77@gmail.com

1. Introduction

The wastewater generated by textile, dye, and dyestuff industries consists of a diverse mixture of inorganic and organic substances (Roy *et al.*, 2018; Akartasse *et al.*, 2022; Al-Tohamy *et al.*, 2022). Dyes often originate synthetically and possess intricate aromatic molecular structures, making them more durable and less prone to biodegradation. Textile industries use the most dyestuffs, accounting for approximately 60-70%. Dyestuffs are crucial for preparing raw materials, pretreatment materials, dyeing, and finishing textile materials. It has been shown that a significant quantity of dye-stuffs, ranging from 10 to 90%, were discharged into the sewage treatment system or ambient water during the dyeing operations. This is because there is a broad variety of fibres, process auxiliaries, dyes, and end products involved (Benkhaya *et al.*, 2017; Khan & Malik, 2014; N'daye *et al.*, 2022; Periyasamy, 2024). Dye wastes are a challenging category of pollutants due to their visibility to the human eye and non-biodegradable nature (Lellis *et al.*, 2019).

The textile industry produces large quantities of vividly coloured pollutants that are often toxic and resistant to decomposition using biological treatment methods (Lellis *et al.*, 2019; Rais *et al.*, 2008; Al-Rueda-Marquez *et al.*, 2020). Due to the substantial organic content and the resilience of modern textile dyes, conventional biological treatment methods are ineffective in eliminating their colour and decomposing them. Later, more effective methods were explored. In recent years, Advanced Oxidation Processes (AOPs) have been developed to meet the increasing need for effective wastewater treatment (Jaafar *et al.*, 2016; Gopalakrishnan *et al.*, 2023; Hübner *et al.*, 2024). Extensive study has focused on advanced oxidation processes (AOPs) via the utilisation of ultraviolet (UV) and visible light (Zawadzki *et al.*, 2022; Melliti *et al.*, 2013). Sunlight offers limitless energy that can be used to activate photocatalysts, but it covers a wide variety of wavelengths (Zhang *et al.*, 2024; Jalal *et al.*, 2020). Visible light-emitting diodes (LEDs) provide specific wavelength selection, reactor construction capability, and cost-effective controlled irradiation delivery (Hassaan *et al.*, 2023; Zondag *et al.*, 2022). Several semiconductor materials, such as titanium dioxide (TiO_2) and zinc oxide (ZnO), are considered promising because to their abundance, lack of toxicity, and resistance to light-induced degradation. Yet, these materials have several disadvantages, including a high band gap energy (3.3–3.5eV), restricting their use to the UV region of sunlight, representing only 4% of solar energy, and a high rate of electron-hole recombination, which hampers material efficiency (Haque *et al.*, 2024; Elafia *et al.*, 2023; Abhishek *et al.*, 2024).

The need of potable water and safe environment is the main goal of humanity and governments. The numerous published papers in this field can be analysed using Scopus which shows more 5800 documents using the 2 keywords "catalyst AND effluent" reaching 857 documents at 2024 (Figure 1). We see the importance of this vital water via the interest of industrialist countries and highly concentrated population as China, India, United State … (Figure 2)

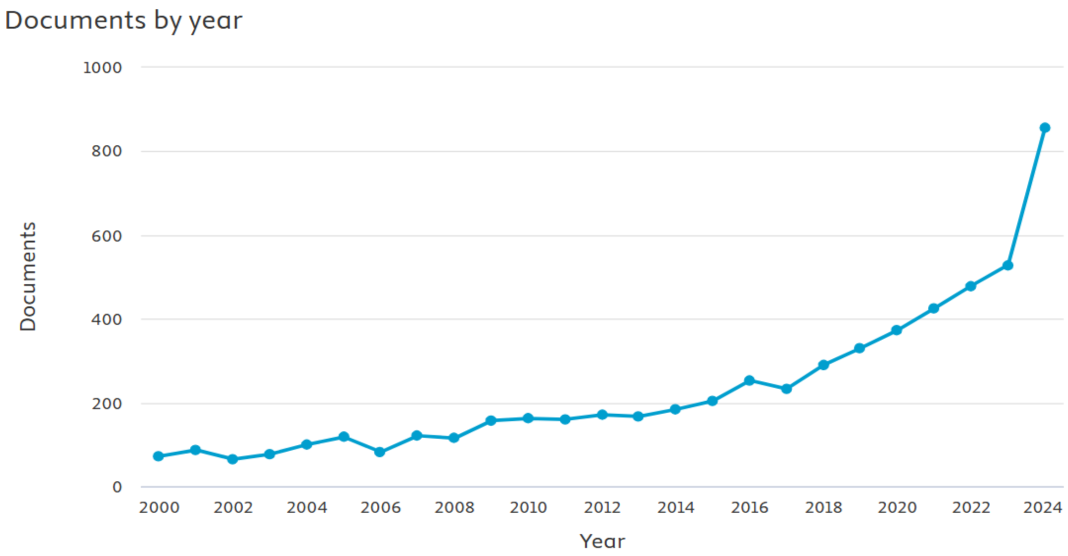


Figure. 1. Evolution of publication production on "catalyst AND effluent" With time

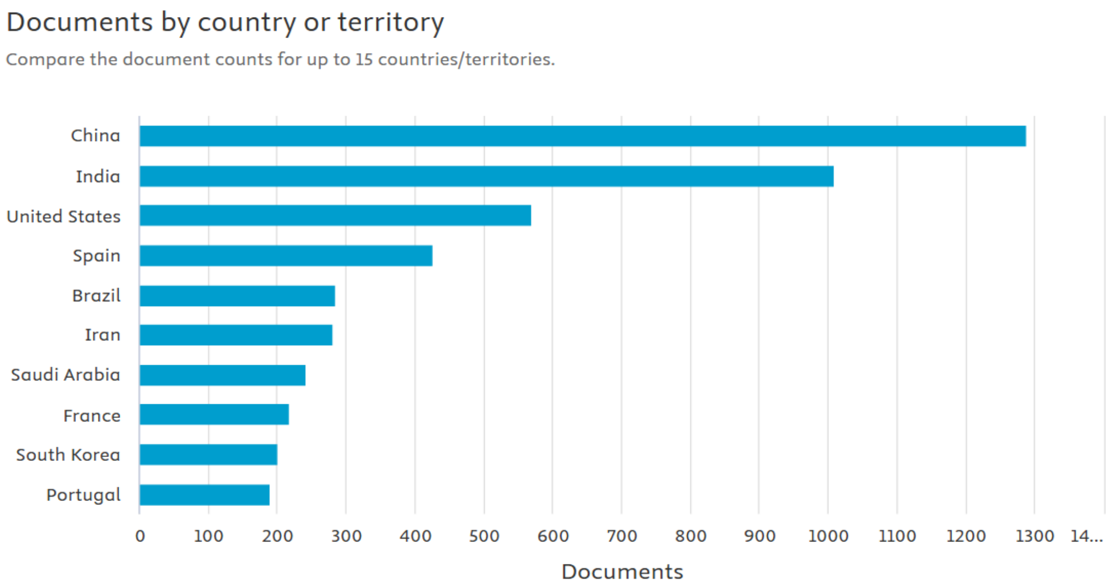


Figure 2. Distibution of publication production on "catalyst AND effluent" per Country

2. Materials and methods

2.1. Material

Zinc Acetate (Zn Ac, purity > 98 %); absolute ethanol; Hydrochloric acid; Deionized water. The chemicals used were purchased from Sigma Aldrich

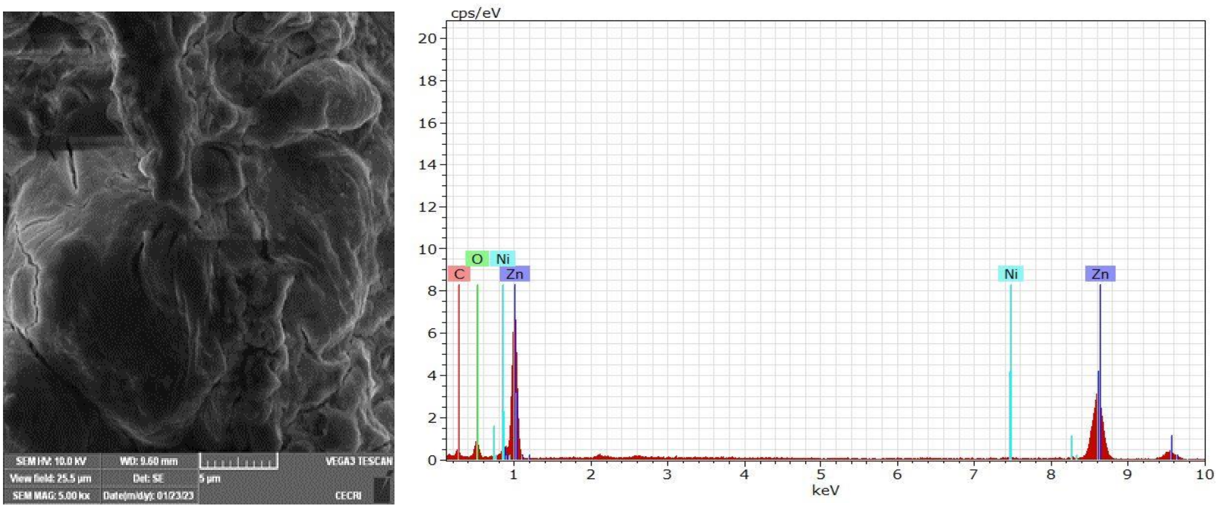
2.2. Preparation of the extracts

The sol-gel process was employed to synthesis zinc oxide nanoparticles. The solution was prepared by mixing 20 grams of zinc acetate (ZnAc), 23 milliliters of ethanol, and 18 milliliters of a hydrochloric acid (HCl) solution with a concentration of 4.4 moles per liter. The mixture was vigorously stirred for a duration of 15 minutes. Next, the mixture underwent Sonication for approximately 15 minutes. The composites obtained were dried in a forced-air oven at a temperature of 100°C for a duration of roughly two hours. The desiccated nanoparticle was subjected to calcination at a temperature of 400°C in a muffle furnace, and thereafter stored in a hermetically sealed container for future utilization.

2.3. Characterization

2.3.1SEM & EDAX

Figure 3. (a) and (b) depict the Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX) techniques, respectively. The SEM image shows that the nanoparticles have a morphology resembling flakes. The EDAX spectrum confirms the presence of Zn and O. Oxygen and zinc are the main components of the photocatalyst. This is apparent from their substantial weight proportion. Zinc (Zn) has characteristic peaks at energy levels of 1.2 and 8.6 kiloelectron volts (KeV), while Oxygen (O) displays a peak at 0.5 KeV. The presence of Ni and C may be attributed to impurities. Therefore, the existence of elemental composition provides evidence for the production of ZnO.



(a) (b)

Figure. 3. SEM (a) & EDAX (b) Spectrum of ZnO nanoparticles

2.3.2. XRD

The X-ray diffraction technique was employed to analyze the level of crystallinity and the crystal phases of the synthesized nanoparticles. The observed pattern exhibited distinct diffraction reflections that corresponded to the pure wurtzite hexagonal phase of ZnO (Figure 4). The most intense peak occurs at 2 thetas = 20.21, 22.31, and 30.67. The sharpness, prominence, and confined width of the ZnO diffraction peaks in the pattern of XRD suggest that the produced ZnO particle is well crystalline (Al-Kandari *et al.*, 2017; Greeshma *et al.*, 2021). These reflections were accurately aligned with the reference JCPDS Data Card no. 36-1451.

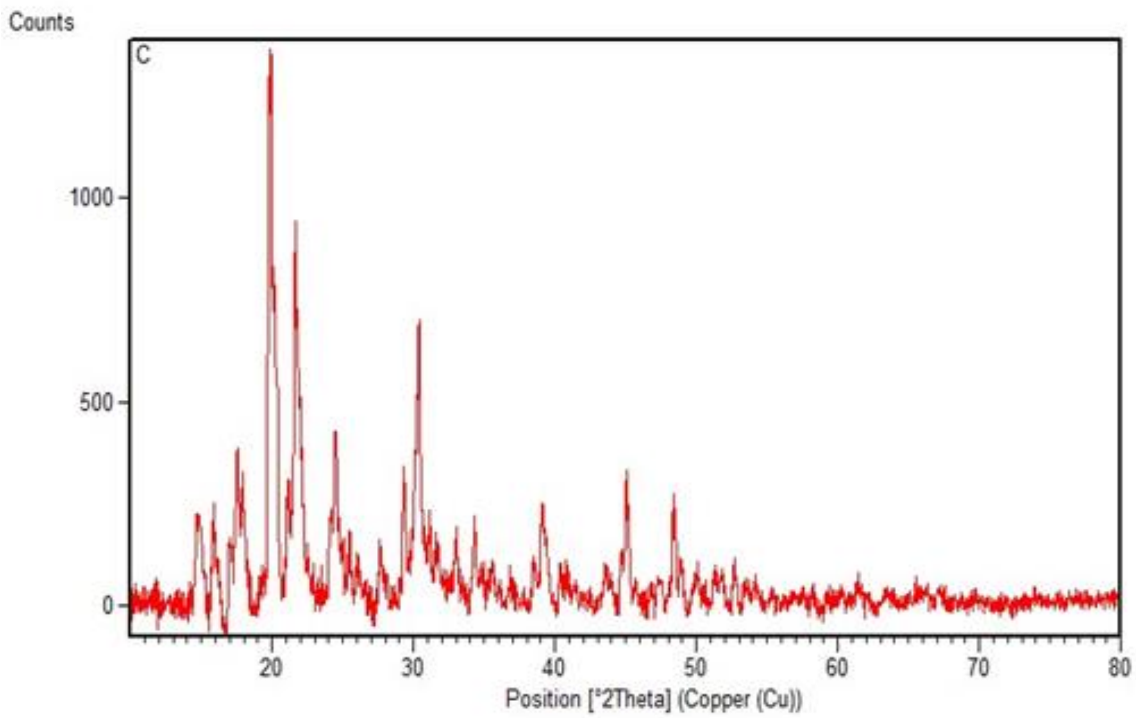


Figure. 4. XRD Spectrum of ZnO nanoparticles

2.3.3. FT-IR

The synthesized ZnO nanoparticle's FT-IR spectrum is illustrated in Figure 5. The FT-IR study demonstrates the presence of stretching vibrations at distinct wavenumbers ranging from 400 to 4000 cm^{-1}. The presence of vibrations at specific wavenumbers, namely 2923.53 cm^{-1}, 2361.05 cm^{-1}, 1625.99 cm^{-1}, and 1014.91 cm^{-1}, provides evidence that ZnO nanoparticles have indeed been formed. The peak observed at 3413.93 cm^{-1} signifies the elongation of the O-H bond, which suggests the existence of the aqueous phase and the reduction of $ZnSO_4$. The prominent peak observed at 575.71 cm^{-1} and 449.04 cm^{-1} indicates the elongation of the Zn-O-H bond. The peaks seen at 2341.40 cm^{-1}, 1746.21 cm^{-1}, 1459.90 cm^{-1}, and 1384.32 cm^{-1} correspond to the bending of the O-H bond (Dobrucka *et al.*, 2016; Taufiq *et al.*, 2018).

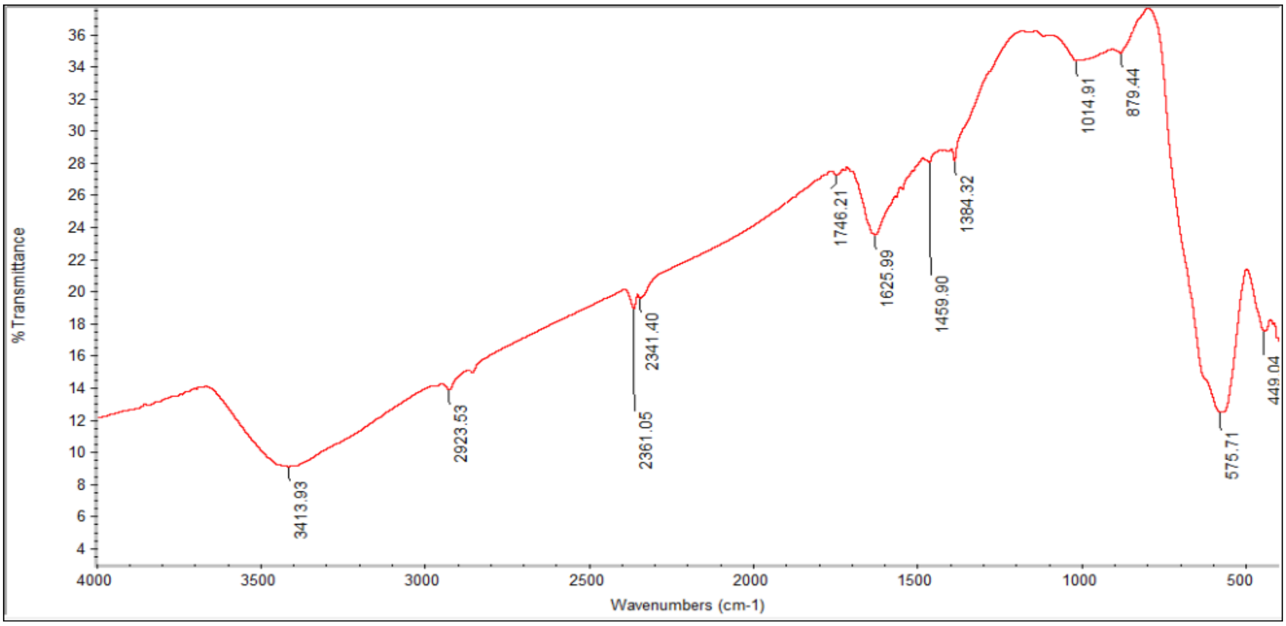


Figure. 5 FT-IR Spectrum of ZnO nanoparticles

3.Result& Discussion

3.1Effect of pH

pH is an important element in the photocatalytic process and may affect effluent adsorption on the photocatalyst surface. Figure 6 depicted the link between pH and effluent adsorption capacity using ZnO. Photocatalytic degradation of effluent was conducted in a suspension of water with a ZnO catalyst at various pH levels to assess its photocatalytic efficiency.

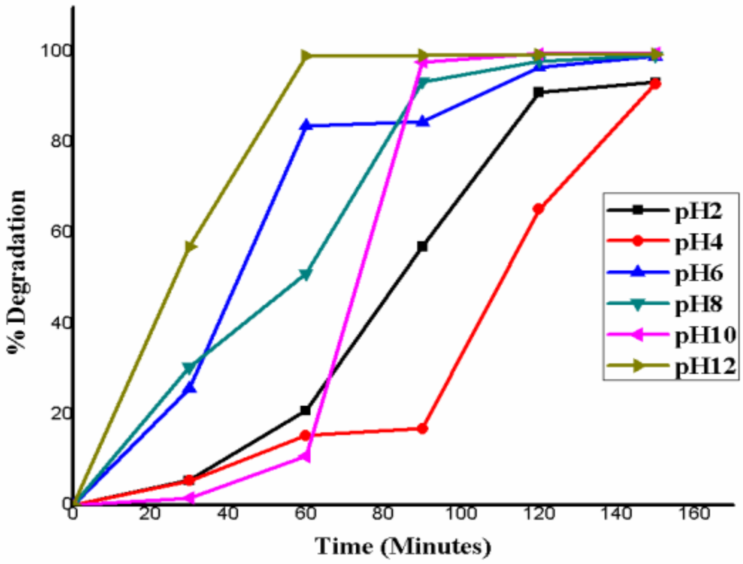


Figure. 6 Percentage degradation rate of effluent by ZnO

The effluent solution was first adjusted to various pH settings and analysed using an ultraviolet-visible spectrophotometer to eliminate the impact of pH on the highest absorption peak. The effluent's greatest absorption peak can be consistently kept at 556 nm within the specified pH ranges. ZnO catalysts have great efficiency when tested at pH 10 (99.8%), due to the negative charge present on their surfaces. The positively charged cationic effluent can be attracted to the highly negatively charged ZnO catalyst surface through strong electrostatic forces. This electrostatic interaction improves the adsorption properties, leading to increased degradation efficiencies. Conversely, the ZnO catalyst tested at pH 2 showed lesser effectiveness (93%) because of electrostatic repulsion between the positively charged nanoparticles and the cationic effluent. The effluent's degradation rate showed a strong preference for basic conditions. The clearance rate was notably increased at pH 10 and 12 compared to pH 2 (Yang *et al.*, 2017; Greeshma *et al.*, 2021).

3.2 Photocatalytic degradation

An experiment was conducted to degrade effluent using ZnO as a photocatalyst with 200 W light and a sonicator under sunlight. Photodegradation was conducted in a specially designed photoreactor. The photoreactor comprises a magnetic stirrer and a 200 W light source encased inside a sealed container. 0.02g of catalyst was added to the model wastewater in a standard procedure. Incubating the solution in darkness for 30 minutes achieved absorption-desorption equilibrium (Figure 7). Then The solution was continuously agitated using a magnetic stirrer and exposed to light, with samples being taken at certain time intervals.

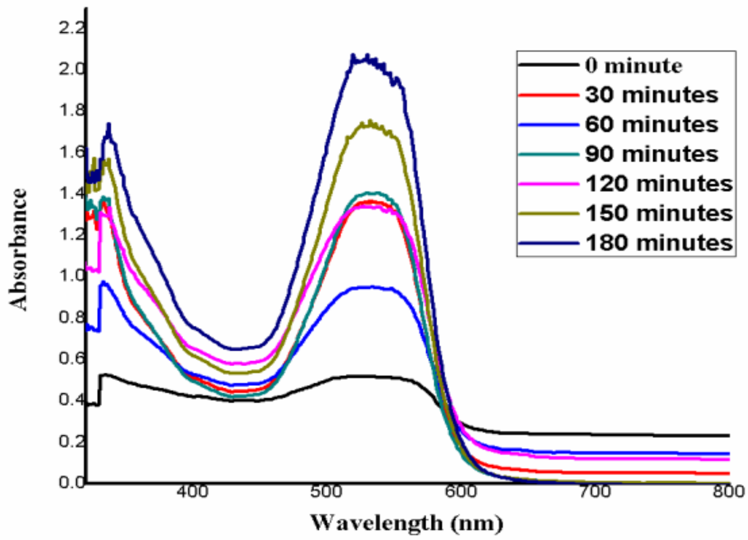


Figure. 7 Photocatalytic degradations of effluent by ZnO

The effluent degradation was monitored by analysing the absorbance spectrum of the solution. The highest photocatalytic efficiency was observed in the degradation process in the presence of a sonicator under sunlight at pH 10 (Mohamed *et al.*, 2016; Greeshma *et al.*, 2021):

$$\% \, Degradation = \frac{A_o - A_t}{A_o} x100$$

where A_0 and A_t correspond to the initial absorbance and absorbance after irradiation, respectively.

3.3 Kinetics plot for the degradation of effluent

The photodegradation process adheres to a pseudo-first-order reaction. The equation for calculating the decomposition rate constant for the reaction is $\ln(C_0/C)=kt$ (Figure 8), where k represents the apparent first-order rate constant and C_0 and C represent the initial concentration and concentration at time t, respectively. A graph of the natural logarithm of the concentration ratio C_0/C against time shows a linear relationship, as seen in Figure.6 The slope of this line, calculated using linear regression, corresponds to the perceived first-order rate constant k. The R^2value was determined to be 0.9975.

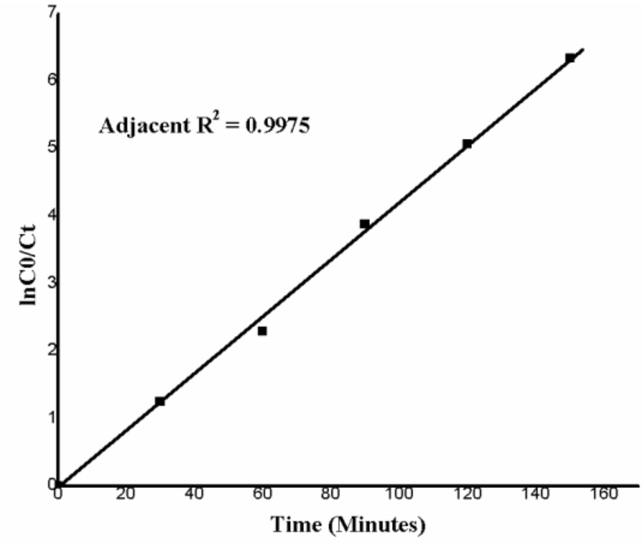


Figure. 8 Kinetic plot for the degradation of effluent

Conclusion

Zinc oxide (ZnO) nanoparticles were prepared using an adaptable sol-gel process and used as a very effective photocatalyst for textile effluent degradation. The delineations confirm the significant amount of crystalline structure and the presence of the wurtzite hexagonal shape in the synthesized nanoparticles. The photocatalytic effectiveness of ZnO nanoparticles was determined by the breakdown of effluent under sunlight irradiation. The degradation of photocatalytic catalysts was assessed by regularly monitoring the absorbance at a wavelength of 556 nm. The absorption intensity drastically decreased as the light irradiation duration increased, which was consistent with a lower pollutant concentration. Under bright sunlight at pH 10, the degradation process showed the greatest photocatalytic efficiency in presence of sonicator. The linear regression-derived slope represents the pseudo first-order rate constant k. R^2 was determined to be 0.9975.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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