Uluslararası İleri Doğa Bilimleri ve Mühendislik Araştırmaları Dergisi
Sayı 8, S. 916-923, 11, 2024

Araştırma Makalesi

International Journal of Advanced Natural Sciences and Engineering Researches
Volume 8, pp. 916-923, 11, 2024

Research Article

https://as-proceeding.com/index.php/ijanser
ISSN:2980-0811

Photocatalytic activity of biosynthesized ZnO Nanostructures from Tilia extract against methylene blue, a water pollutant

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(Received: 11 December 2024, Accepted: 29 December 2024)

(5th International Conference on Scientific and Academic Research ICSAR 2024, December 23-24, 2024)

ATIF/REFERENCE: Altintas, B. Z., Oke-Altuntas, F., Altuntas, H., Saritan, S. & Colak, H. (2024). Photocatalytic activity of biosynthesized ZnO Nanostructures from Tilia extract against methylene blue, a water pollutant. *International Journal of Advanced Natural Sciences and Engineering Researches*, 8(11), 916-923.

Abstract – Numerous azo dyes, such as methylene blue, can trigger allergic responses and cancer. Most of these dyes are not biodegradable, harmful to the environment, and carcinogenic. Several techniques have been documented to eliminate these dyes, including oxidation through chemical action and reverse osmosis. These methods employ waste-producing, expensive, or non-biodegradable substances. To overcome this obstacle, inexpensive, non-toxic nanoparticles with potent photocatalytic activity for dye removal must be developed. It has been demonstrated that ZnO nanoparticles are efficient photocatalysts for the degradation of organic dyes due to their large surface area, high stability, and high electron binding energy. Tilia is indigenous to Western Asia and Europe. Flavonoids, mucilage, essential oil, phenolic acids, amino acids, and other substances are among its primary active components. Tilia flowers are used as an expectorant, to treat colds, and to relieve muscle spasms. In this research, zinc acetate and zinc nitrate were used as two different zinc sources in the synthesis of ZnO nanoparticles and Tilia extract was used as green stabilizer. The photocatalytic activity of the obtained nanoparticles against methylene blue dye under UV light was investigated and it was found that they showed excellent degradation activity of 99% and 91% for zinc acetate and zinc nitrate, respectively, after 180 min of UV illumination.

Keywords – ZnO nanostructures, Tilia, Photocatalytic activity, Water pollutant, Methylene blue

I. INTRODUCTION

Methylene blue is a cationic azo dye used as a chemical reagent in paper, silk fabric, printing, coloring and dyeing, causing vomiting, respiratory problems, hyperhidrosis and nervous disorders (Bukhari et al., 2022). Azo dyes are organic compounds that constitute two-thirds of all synthetic dyes used in textile dyeing and pharmaceutical industries (Gicevic et al., 2020). Water resources are exposed to high levels of pollution due to the disposal of large amounts of organic dyes in the textile industry. Many azo dyes are carcinogenic/mutagenic and cause allergic reactions. The toxicity of these dyes is mainly due to the presence of a large number of benzene rings in their structures. The products of many degraded dyes also show carcinogenicity; for example, benzidine, a degraded product of many azo dyes, is a known carcinogen for human urinary bladder (Gicevic et al., 2020). These dyes are mostly It is non-biodegradable, toxic to the ecosystem and carcinogenic. Since synthetic dyes such as methylene blue (MB) cause many diseases such as skin diseases, respiratory tract infections, eye irritation, it is very important to eliminate them and remove their colors from water sources. Because their mixing into water sources affects aquatic flora and fauna and disrupts the ecosystem. These dyes are resistant to biodegradation and last long in water, so they need to be converted into simple molecules; this is achieved by light-induced degradation of these dyes catalyzed by various photocatalysts (Patil and Shrivastava, 2016).

Nanomaterials exhibit high mechanical, optical, catalytic and biological properties due to their surface/volume ratio and are used in many application areas (Arumugam et al., 2021). Using chemicals in the synthesis of nanoparticles causes high amounts of toxic substances to be formed, therefore, a green and environmentally friendly method is required for their production (Gupta et al., 2018). Nanomaterials have attracted great attention because they have applications such as photocatalysis, environment, electronics, medicine, biology, and energy conversion.

Zinc oxide (ZnO) nanoparticles are important metal oxide materials due to their easy synthesis, low-cost production, non-toxicity, safety and applications in biomedical systems, electronics and optics (Anbuvannan et al. 2015). ZnO nanoparticles are characterized by wide band gap (3.37 eV), high binding energy (60 meV), photocatalytic and photo-oxidation activity, optical and UV filtering properties (Agarwal, Kumar, Rajeshkuma, 2017; Deepali Sharma et al. 2010). Synthesis of ZnO nanostructures is usually carried out by chemical methods. However, these methods have disadvantages such as low purity, high energy and cost, and formation of toxic substances. Therefore, green synthesis method, which is an environmentally friendly method, is gaining importance (Xu et al., 2021).

Green synthesis is an easy, fast and environmentally friendly method in which ZnO nanoparticles are synthesized using bio-renewable resources. Additionally, nanomaterials synthesized by this method are biocompatible and non-toxic (Mina Zare et al. 2019). Photocatalytic activity is the ability of nanostructures that can act as photocatalysts to break down dyes by interacting with UV light to produce hydroxyl radicals that can react with various dyes. For this purpose, it has been reported that ZnO nanostructures can be used in the degradation of dyes thanks to their electron binding energy and high stability (Sanna et al., 2016; Pavithra et al., 2017).

Tilia is a plant native to Europe and Western Asia. Its main active ingredients include flavonoids, mucilage, essential oil, phenolic acids, amino acids and others. Tilia flowers are used to treat muscle spasms, as an expectorant, and to cure colds. (Corciova, A.et al. 2018).

In this study, it was aimed to determine the photocatalytic activities of ZnO nanostructures produced by green synthesis from tilia plant using different zinc sources.

II. Materials and Method

Materials

Zinc acetate dehydrate (Zn $(Ac)_2.2H_2O$) and zinc nitrate hexahydrate (Zn $(NO_3)_2.6H_2O$) used in this study were purchased from Sigma-Aldrich. Tilia was collected from Ankara Nallıhan region. Methylene blue dye (AFG Bioscience) were used in the photocatalytic activity study. pH of methylene blue dye was 7.95.

Methods

Synthesis and Characterization

Our previous study was taken as a reference in the synthesis of nanoparticles from the Tilia plant and in checking whether nanostructures were formed (Altintas, B. Z. et al., 2024).

Photocatalytic Activity

Photocatalytic activity of ZnO nanostructures synthesized by green synthesis method was investigated by photodegradation of MB dye under UV lamp. For dye solution, 5 mg MB dye was added to 500 ml distilled water and mixed in the dark. For each sample, 10 ml nanoparticles and 10 ml dye solution were taken into a beaker and mixed in the dark. After the first measurement (0th minute), the samples were mixed with a magnetic stirrer under UV lamp.

The wavelength absorptions of each sample between 400-800 nm were measured in UV-vis spectrophotometer at 30-minute intervals. Measurements were made up to 180th minute.

III. RESULTS

The photocatalytic activity of ZnO nanostructures was examined according to the degradation process of MB dye under UV light at different time intervals. The absorbance values of MB measured at different time intervals in the presence of green synthesized ZnO nanostructures are shown in Figure 1. As seen in Figure 1, as the exposure time to UV light increased, the absorbance value decreased and MB degraded.

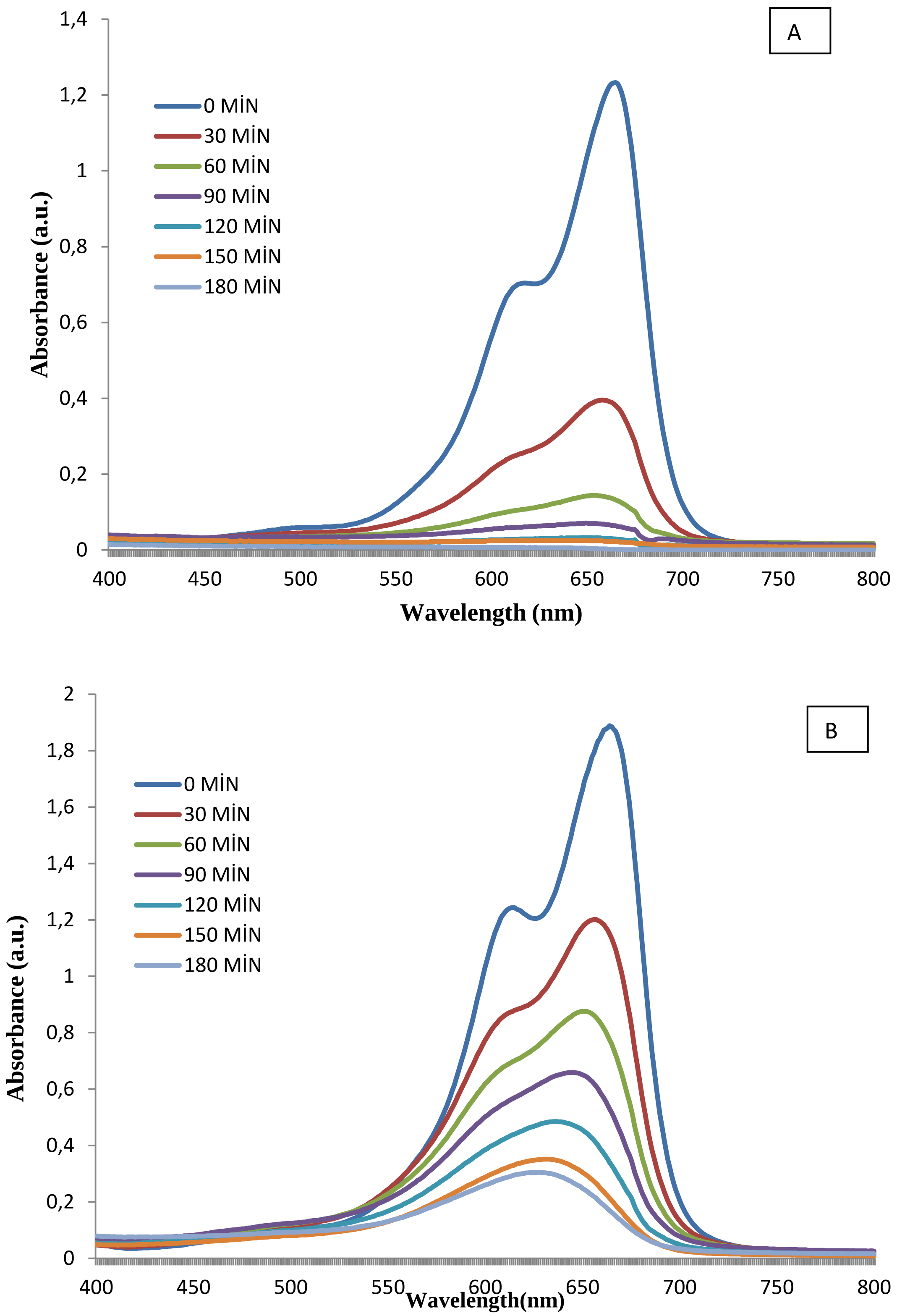

Figure 1. Degradation absorption values of MB dye at different time intervals in the presence of green synthesized ZnO nanoparticles a; ZnAc, b; ZnN

The degradation percentage of MB dye at 664 nm was calculated using the following formula.

$$\%\text{Degradation} = (A_0 - A_t)/A_0 \times 100$$

where, A_0 is the initial absorbance value of the MB dye solution and A_t is the absorbance value of the MB dye and ZnO nanostructure solution obtained after each measurement time interval.

The % degradation results of MB dye are shown in Figure 2. As seen in Figure 2, the % degradation of ZnAc-based nanostructures is 99.89%, the % degradation of ZnN-based nanostructures is 91.47% at 180 minute.

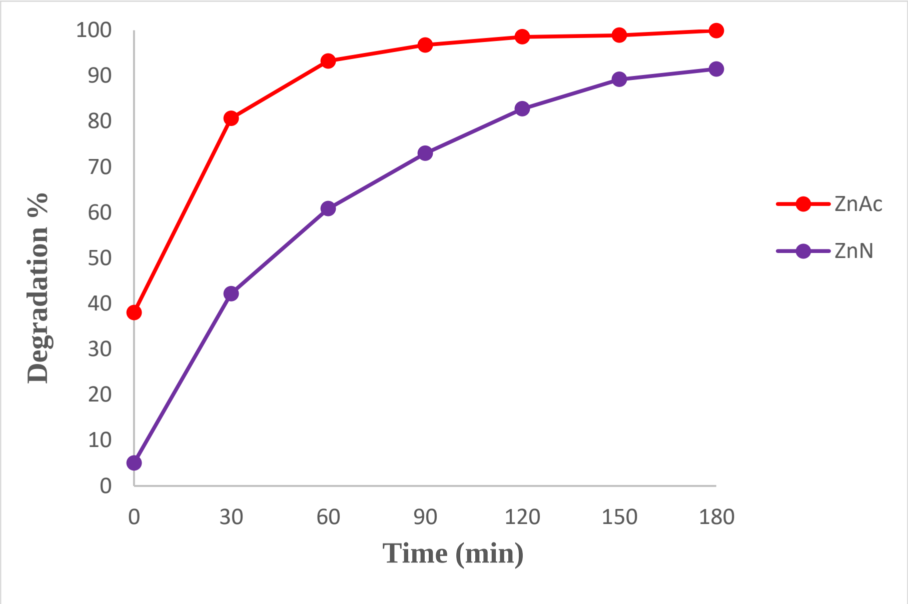

Fig 2: Photocatalytic activity % degradation results

As seen in Table 1, zinc acetate nanoparticles showed 80% photocatalytic activity in 30 min, while zinc nitrate nanoparticles showed 42% activity.

Table1: Degradation percentages (%) at each time interval

	0 Min	30 Min	60 Min	90 Min	120 Min	150 Min	180 Min
ZnAc	38,02	80,64	93,22	96,73	98,52	98,88	99,89
ZnN	5,03	42,18	60,81	72,97	82,71	89,17	91,47

In addition, it is shown in Figure 3 that nanoparticles using zinc acetate as the zinc source degrade methylene blue dye faster.

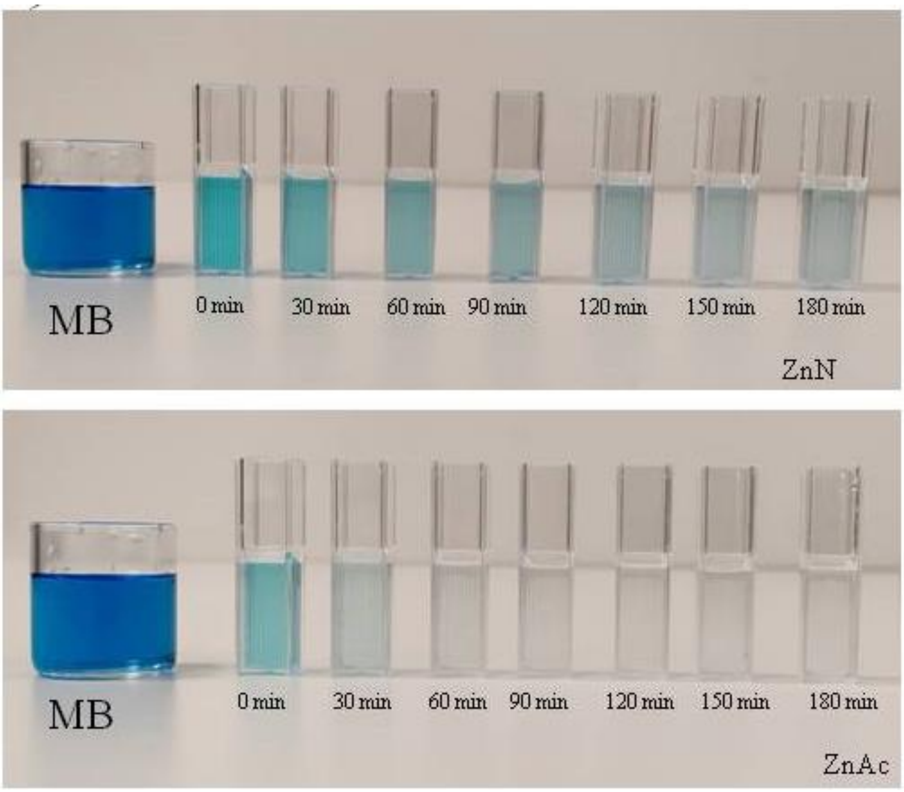

Fig 3: Color change of methylene blue with different zinc sources in the range of 0-180 minutes a:ZnN, b:ZnAc

IV. DISCUSSION

In this study, the photocatalytic activities of ZnO nanoparticles synthesized using zinc acetate and zinc nitrate as different zinc sources and tilia extract as green source against methylene blue dye were investigated. After 180 minutes of UV illumination, it was observed that nanoparticles using zinc acetate showed 99% degradation activity and nanoparticles using zinc nitrate showed 91% degradation activity. According to this result, it was seen that both nanoparticles can be used in cleaning methylene blue dye, but it can be said that the nanoparticles using zinc acetate showed higher activity than those using zinc nitrate and cleaned the methylene blue dye faster.

Fouda et al. used different ratios of biosynthesized CuO/ZnO, 80/20, 50/50 and 20/80, to study the degradation of MB dye under visible light. They showed that CuO/ZnO20/80 photocatalyst has higher photocatalytic activity than other photocatalysts and as the percentage of ZnO in the nanocomposite increases, the degradation percentage of MB dye increases with the decrease of contact time. This is because the band gap decreases with the increase of ZnO ratio (Fouda et al., 2020).

Hemalatha et al. investigated the photocatalytic activity of ZnO photocatalysts fabricated using sol-gel process for methylene blue dye degradation. It was studied under UV light and the results showed that at the optimum dye concentration of 20 ppm, the catalyst dose concentration varied from 0.2 g/L to 2.4 g/L and the degradation efficiency increased up to 0.6 g/L. This was because the active site on the surface of the photocatalyst increased with the increase in catalyst dose. When a catalyst was overdosed, the degradation rate decreased, which could be attributed to more suspended catalyst particles blocking the light (Hemalatha et al. 2016).

Chanu et al. tested the photocatalytic activity of ZnO photocatalyst produced by chemical co-precipitation by exposing methylene blue dye to UV light. They found that at catalyst concentrations of

0.25 g/L, 0.30 g/L and 0.35 g/L, the highest degradation rate was observed at 0.30 g/L, and as the concentration increased, the degradation rate decreased, which was probably due to the decrease in catalyst activity. The researcher also found that when a fixed catalyst dose of 0.30 g/L was used and the dye concentration was changed from 8 ppm to 12 ppm, the maximum degradation of MB was observed at 10 ppm, and the rate increased as the dye concentration increased (Chanu et al., 2019).

Gnanamozhi et al. investigated the effect of nickel doping concentration on the activity of ZnO photocatalyst for methylene blue dye degradation. 3% Ni/ZnO and 5% Ni/ZnO prepared by co-precipitation method were used. It was revealed that 5% Ni/ZnO photocatalyst performed better than 3% Ni/ZnO photocatalyst. This may be because 5% Ni/ZnO has more oxygen vacancies, which inhibits electron-hole pair recombination and enhances photocatalytic activity; a higher Ni/ZnO ratio has a lower band gap, which allows the photocatalyst to increase photogenerator carriers and light absorption, which positively affects the photocatalyst activity (Gnanamozhi et al., 2020).

Our study is compatible with these studies in the literature.

V. CONCLUSION

As a result, the photocatalytic activity of ZnO nanostructures synthesized by green synthesis method using tilia extract in MB degradation was found to be consistent and comparable with previous studies in the literature. As a result of previous studies and our study, zinc oxide is expected to be used as an important factor in water pollution and more detailed research is expected.

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