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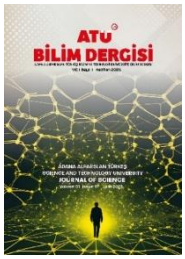

Green synthesis of ZnO nanoparticles using pine bark extract

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Abstract

In this study, zinc oxide (ZnO) nanoparticles (NPs) were synthesized by green synthesis technique using pine bark extract. ZnO NPs were synthesized in three different pine bark extract ratios, which acts as a reducing and stabilizing agent. The produced ZnO NPs were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrum analysis (EDS) and ultraviolet-visible light spectroscopy (UV-VIS). It was determined that the XRD diffraction peaks were consistent with the characteristic peaks of ZnO, and ZnO NPs were produced in the hexagonal wurtzite crystal phase. It was determined from the SEM images that the samples were produced homogeneously which have almost spherical geometry and the average particles were in the range of 20-30 nm. In the elemental analysis, only Zn and O elements were observed without any impurity atoms. Also, the degradation performance of methylene blue (MB) dye under UV light was determined to determine the photocatalytic activities of ZnO NPs. It was determined that MB reached almost 66% degradation efficiency after 80 minutes of UV illumination of ZnO NPs synthesized by using pine bark extract.

Keywords: ZnO; Green synthesis; Pine bark; Optical properties; Photocatalytic activity

Çam kabuğu ekstraktı kullanılarak ZnO nanopartiküllerinin yeşil sentezi

Öz

Bu çalışmada, çinko oksit (ZnO) nanoparçacıkları (NPs) çam kabuğu özütü kullanılarak yeşil sentez tekniği ile üretilmiştir. İndirgeyici ve dengeleyici bir madde olarak görev alan çam kabuğu özütü üç farklı oranda kullanılarak ZnO NP'leri sentezlenmiştir. Üretilen ZnO NP'leri X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM), enerji dağılımlı X-ışını spektrum analizi (EDS) ve ultraviyole-görünür ışık spektroskopisi (UV-VIS) kullanılarak karakterize edildi. XRD kırınım piklerinin ZnO'nun karakteristik pikleriyle uyumlu olduğu ve hekzagonal wurtzit kristal fazında üretildiği belirlendi. SEM görüntülerinden numunelerin homojen bir şekilde üretildiği, parçacıkların hemen hemen küresel geometriye sahip olduğu ve ortalama parçacık boyutunun 20-30 nm aralığında olduğu belirlendi. Elementel analizde sadece Zn ve O elementleri gözlenerek, safsızlık atomlarının bulunmadığı tespit edildi. Ayrıca, ZnO NP'lerinin fotokatalitik aktivitesinin belirlenmesi için UV ışığı altında metilen mavisi (MB) boyasının bozunma performansı incelendi. Çam kabuğu özütü kullanarak sentezlenen ZnO NP'lerinin 80 dakikalık UV aydınlatması sonrasında MB'yi yaklaşık %66 oranında bozunma aktivitesine ulaştırdığı belirlendi.

Anahtar Kelimeler: ZnO; Yeşil sentez; Çam kabuğu özütü; Optik özellikler; Fotokatalitik aktivite

1. Introduction

Nanotechnology, a field of intense interest today, traces its roots back to Michael Faraday's paper published in 1857 [1]. Nanotechnology has a wide range of applications, with primary uses in environmental and industrial sectors [2]. The sustainable use of natural resources is one of the most urgent environmental issues of our time. Increasing population and industrial activities are escalating environmental pressures, deepening pollution problems that threaten our water resources. Industrial waste, particularly harmful dyes such as the commonly used methylene blue, are among the primary pollutants. These dyes pose significant risks to both human health and ecosystems. Protecting water resources and effectively removing pollutants are vital for the continuation of healthy ecosystems [3].

All methods, except for green synthesis, have disadvantages such as high costs and the formation of toxic by-products. In contrast, the green synthesis method offers an environmentally friendly, non-toxic, and more cost-effective alternative, making it more advantageous compared to other chemical and physical methods [4].

ZnO nanoparticles are widely utilized in various fields such as electrochemistry, medical devices, and the textile industry due to their high specific surface area, ultraviolet light absorption, and scattering properties. The synthesis of ZnO nanoparticles is typically categorized into physical and chemical methods, which often involve high energy consumption, low purity, irregular particle size distribution, high production costs, substantial secondary waste generation, and irreversible environmental pollution. As the applications of ZnO nanoparticles continue to expand, their synthesis through environmentally friendly methods has become a significant concern, primarily due to the increasing importance of environmental protection in societal expectations. Green synthesis methods are eco-friendly alternatives that utilize natural resources, such as plant extracts, during the production process. Plant extracts provide a sustainable and eco-friendly substitute for conventional chemical approaches in green synthesis processes. Because of its abundance of bioactive components, pine bark extract is a noteworthy natural reducing and stabilizing agent in this context. Pine bark, which is rich in phenolic compounds, supports the reduction of metal ions through its strong antioxidant activity, which aids in the creation of nanoparticles. Pine bark's organic components, which include functional groups like hydroxyl and carbonyl, allow it to bind metal ions and serve as a stabilizing and reducing agent in green synthesis. Taking all these elements into account, the application of pine bark extract in green synthesis is thought to be a creative and sustainable method from an economic, scientific, and environmental standpoint [5].

Plants and their extracts are readily accessible resources, and the process requires only the use of a zinc salt solution as the metal precursor. ZnO nanoparticles are synthesized through the reaction of plant extracts with a zinc salt solution. This method offers a highly suitable approach for the green synthesis of ZnO nanoparticles. In addition, studies in the literature were reviewed. Karnan et al. synthesized ZnO nanoparticles using *Nephelium lappaceumL.* plant extract and achieved 83.99% successful reduction to methylene blue dye [6]. Soto-Robles et al synthesized ZnO nanoparticles using Corymbia *Hibiscus sabdariffa* extract and achieved 98.6% successful reduction to methylene blue dye [7]. Zheng et al. synthesized ZnO nanoparticles using *Corymbia citriodora* plant extract and achieved 83.45% successful reduction to methylene blue dye [8].

In this study, we report the synthesis of ZnO nanoparticles using pine bark extract and zinc salt as precursors as an original and unprecedented study among numerous studies. The structural properties of the synthesized ZnO nanoparticles were verified using UV-Vis, XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray Analysis) techniques [7].

2. Methods

2.1 Materials

Pine bark extract was utilized instead of reducing and stabilizing agent chemicals for the green synthesis of the ZnO samples. Distilled water was employed for the synthesis. The zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich, 99%) was used as Zn source.

2.2 Synthesis of particles

ZnO particles were produced by the green synthesis method as shown in Figure 1. 1.0 gr of zinc nitrate hexahydrate salt was completely dissolved in 15 ml of distilled water within a 50 ml beaker using an ultrasonic

bath. 1.0 gr of pine bark extract was also dissolved in 13 ml of distilled water within a 50 ml beaker using an ultrasonic bath. Subsequently, the well-mixed solutions were combined by placing the beaker containing the zinc nitrate salt on a magnetic stirrer and adding the pine bark extract drop by drop. The mixture was stirred at 150 °C until the solution reached a gel-like consistency. The gel was then subjected to calcination by placing it in an oven at 500 °C for 2 hours. After the calcination process, the samples were ground with an agat mortar for a total of 20 minutes and then placed into tubes for measurements. The sample produced as explained above is labelled as ZnO-PB2. The same process was repeated two more times to change the concentration of pine bark extract. Changing the concentration in the samples is intended to have a direct impact on the physicochemical characteristics of the nanoparticles in the green synthesis process, which may result in notable modifications. The reduction rate of metal ions increases with extract concentration, perhaps resulting in the production of smaller nanoparticles. On the other hand, the growth process moves more slowly at lower concentrations, producing larger and more asymmetrical structures. Samples were made at varying concentrations as a result. Other samples were prepared by dissolving the pine bark extract in 7.0 ml of distilled water (ZnO-PB1) and 19 ml of distilled water (ZnO-PB3).

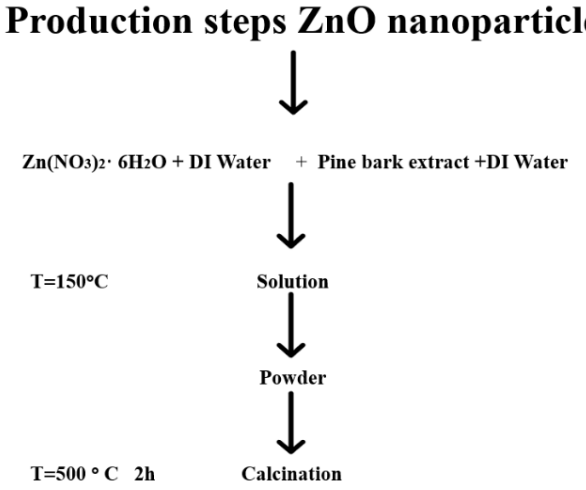


Figure 1. Production scheme of ZnO nanoparticles.

2.3 Characterization techniques

The structural properties of ZnO NPs synthesized via green synthesis were investigated using a Rigaku MiniFlex 600 model XRD system with Cu-Kα radiation (wavelength λ = 1.5406 Å). Subsequently, the morphology, surface properties and elemental analysis of the ZnO nanoparticles were examined using a SEM and EDS with an FEI-QUANTA650. The UV-VIS spectrophotometer, which measures in the wavelength range of 300-800 nm, was used to examine the optical characteristics of ZnO nanoparticles.

3. Results and Discussion

The X-ray diffraction technique was used to identify and describe the crystalline phase of the ZnO nanoparticles (Fig.2). The diffraction patterns of the ZnO-PB1, ZnO-PB2, and ZnO-PB3 samples exhibit sharp and well-defined peaks, indicating their highly crystalline structure. Although the concentration of pine bark extract was different in ZnO-PB1, ZnO-PB2, and ZnO-PB3 samples, the diffraction peaks of them are almost same. This means that the working concentration of pine bark extract were not affected the crystal formation of ZnO NPs. However, the peak intensities changes by the concentration of pine bark extract. The maximum peak intensity was seen in ZnO-PB2 sample. Different diffraction peaks at the 2θ values of 32.11°, 34.76°, 36.59°, 47.85°, 56.91°, 63.16°, 66.68°, 68.24°, 69.38°, 72.54°, and 76.92° are visible in the X-ray diffraction patterns of the green synthesis nanoparticles. These peaks are indexed to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes, respectively. The hexagonal wurtzite crystal structure that characterizes ZnO nanoparticles is represented by these peaks [9].

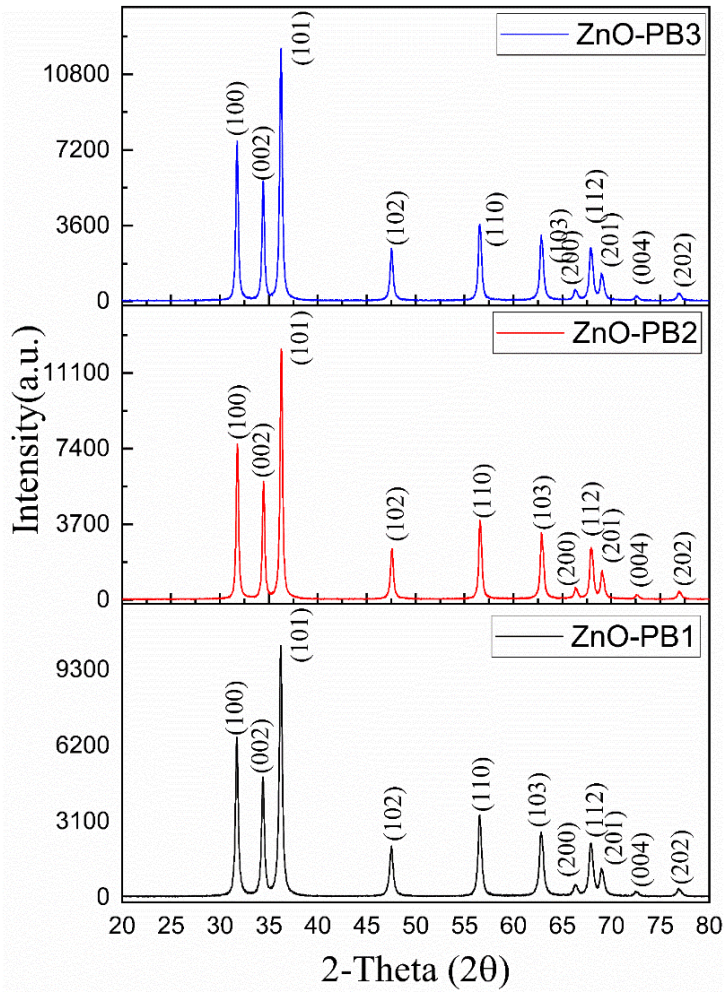


Figure 2. XRD patterns of the ZnO samples.

The Debye-Scherrer formula can be used to determine the crystal size:

$$D = \frac{\kappa\lambda}{\beta cos\theta} \quad (1)$$

where θ is the Bragg angle, β is the full width at half-maximum peak intensity (FWHM), λ is the x-ray wavelength, D is the average crystallite size, and κ is a dimensionless value that is about equal to 0.9 [10]. The average crystallite sizes of samples calculated from the XRD data were found as 24, 39, and 27 nm for ZnO-PB1, ZnO-PB2, and ZnO-PB3, respectively. These results show that the amount of extract used affects the crystal size of ZnO NPs.

2.1 Surface morphology and elemental analysis

Since the crystal property of samples are similar, the ZnO-PB2 sample was selected for surface morphology and elemental analysis measurements. SEM images taken at various magnifications for ZnO-PB2 sample are shown in Fig.3(a-d). SEM images were taken at 50kx, 100kx, 200kx, 400kx magnifications under 20kV. It was observed that the surface morphology of the ZnO nanoparticles was close to spherical grains and exhibited a homogeneous distribution. The morphology of our green-synthesized sample is consistent with the literature [11]. In addition, the grain size distribution of ZnO-PB2 sample was drawn by randomly selected 100 grains in the SEM images.. Figure 3(e) shows t grains size distribution of ZnO-PB2 sample. The average grain size of the ZnO-PB2 sample was found in the range of 20-30 nm.

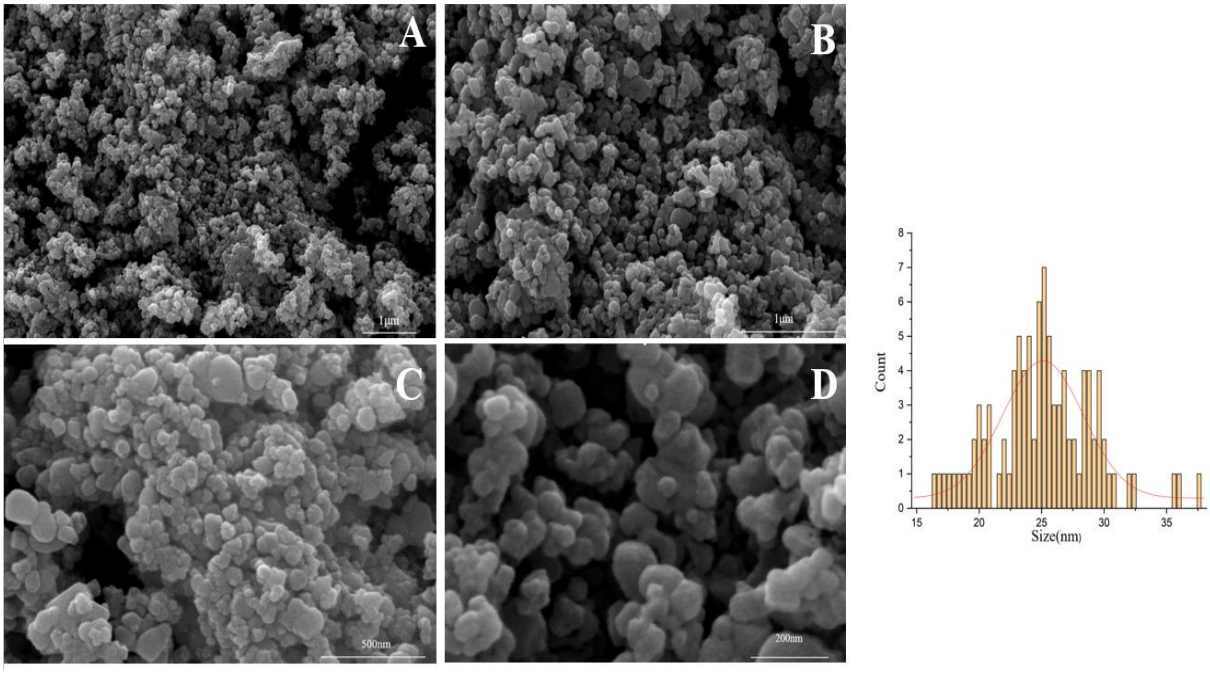
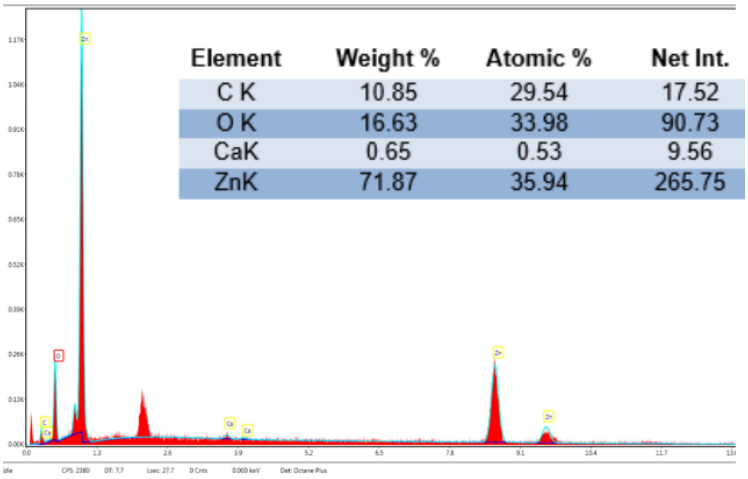


Figure 3. SEM images and nanoparticle size analysis of the sample coded ZnO-PB2.

To determine the elemental composition of the ZnO nanoparticles, EDS analysis was performed. Figure 4 shows the EDS spectrum and elemental analysis results of the ZnO-PB2 sample. In the spectrum, Zn, O, ca and C elements were detected. The C peak might come from the carbon sample holder. The reason of observing Ca peaks might be related to the insufficient washing procedure. Zn and O elements are almost equal atomic % that it confirms the formation of ZnO structure.



Element	Weight %	Atomic %	Net Int.
C K	10.85	29.54	17.52
O K	16.63	33.98	90.73
CaK	0.65	0.53	9.56
ZnK	71.87	35.94	265.75

Figure 4. EDS images sample coded ZnO-PB2.

2.2 Photocatalytic activity

The photocatalytic activity of ZnO nanoparticles synthesized using green methods with pine bark extract was examined the degradation of methylene blue under ultraviolet light irradiation. All experiments were performed at room temperature and the spectrum was taken every 10 minutes up to total 80 minutes. The UV–VIS adsorption variations in the presence of ZnO-PB1, ZnO-PB2, and ZnO-PB3 photocatalysts are depicted in Figure 5(a–c), respectively. In the spectra, an absorbance peak originating from the MB solution was observed at 664 nm. The majority of the methylene blue solutions' discoloration happens in the presence of the photocatalyst within 80 minutes, based on variations in absorbance intensity during the course of the reaction. Figure 5(d) displays the

percentages of photocatalytic methylene blue dye degradation for each of the ZnO-PB1, ZnO-PB2, and ZnO-PB3 samples in a reactor over an 80-minute period. The degradation process was split into two stages. The first stage involved keeping the dye/catalyst solution at a steady temperature for 20 minutes without using the UV lamp. During an 80-minute reaction time in the second stage (with the UV lamp turned on), the ZnO-PB3 sample is found to have the maximum photocatalytic activity (33%), in contrast to the ZnO-PB1 and ZnO-PB2 samples (6% and 7%, respectively).

In contrast to ZnO nanoparticles made with other green reducing agents, these results validate the partially effective synthesis of ZnO nanoparticles employing pine bark extract. A comparison with other ZnO research conducted for the degradation of organic contaminants is presented in Table 2.

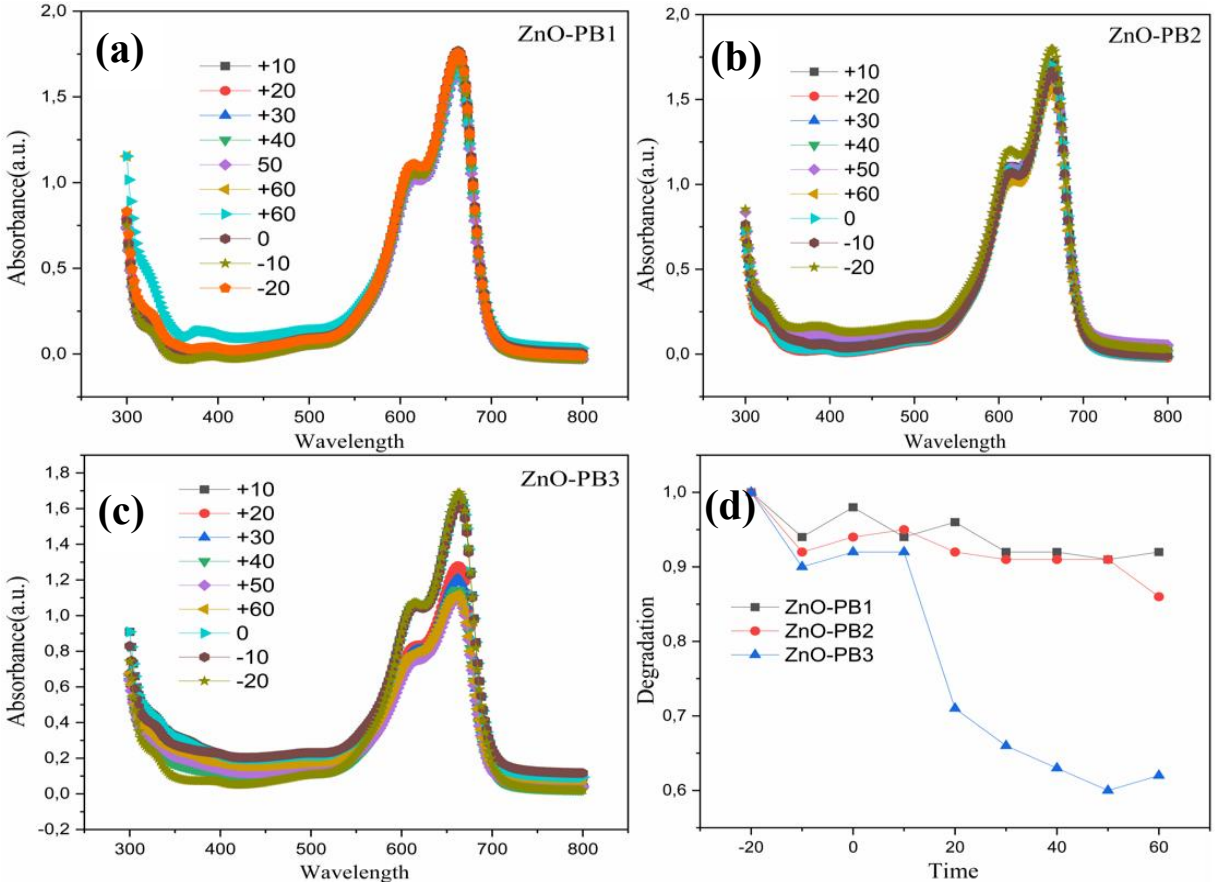


Figure 5(a-c). The absorbance spectra of methylene blue as a function of wavelength of radiation for ZnO-PB1, ZnO-PB2 and ZnO-PB3, respectively. (d) The degradation percentage of methylene blue as a function of time for ZnO-PB1, ZnO-PB2 and ZnO-PB3 samples.

4. Conclusions

This work explores the green synthesis of ZnO nanoparticles using pine bark extract. The amount of extract used during synthesis influenced the crystallite size of ZnO nanoparticles. The morphology of the samples has formed in a spherical shape. Additionally, the characteristic diffraction peaks were successfully obtained in the XRD results, and it confirms our green synthesis ZnO nanoparticles fit with the other synthesis processes. Furthermore, the ZnO materials demonstrated good photocatalytic activity, achieving 34% degradation of methylene blue within 80 minutes. It is promising that the ZnO nanoparticles obtained by green-synthesizing process using pine bark extract for the first time show photocatalytic activity at a level comparable to the literature.

Table 2. Comparative chart of ZnO nanoparticles synthesized using different plants.

Number	Biological entity	Pollutant	Degradation Efficiency	Time of Degradation	Reference
1	Pithecellobium dulce peel	MB	63%	120 min	[12]
2	Pyrus pyrifolia	MB	80.30%	210 min	[13]
3	Suaeda japónica Makino	MB	54%	60 min	[14]
4	*Camellia sinensis* powder	MO	80%	180 min	[15]
5	Corriandrum sativum	-	81.90%	240 min	[16]
6	*Phoenix dactylifera* waste	EY	90.6%	180 min	[17]
7	*Salvadora persica* leaf	MB	95%	150 min	[18]
8	*Syzygium cumini* leaf	MB	91.4%	180 min	[19]
9	*Tabernaemontana divaricate* leaf	MB	100%	90 min	[20]
10	*Buchanania lanzan* leaf	MG	95%	150 min	[21]
11	*Garcinia cambogia* fruit	MB	81.5%	90 min	[22]
12	Hibiscus sabdariffa	MB	97%	150 min	[23]
13	Scutellariabaicalensis	MB	98.6%	210 min	[24]
14	Corymbia citriodora	MB	83.45%	90 min	[8]

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Authors' Contributions
FA: Conceptualization**,** Methodology, Writing - Original Draft, Software. **AE:** Writing - Review & Editing, Validation, Supervision.

Declaration of Ethical Standards
The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Conflict of Interest

There is no conflict of interest in this study.

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