Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2026, т. 24, № 1, сс. 241–247
https://doi.org/10.15407/nnn.24.01.0241

PACS numbers: 61.05.cp, 78.20.Ci, 78.30.Hv, 78.40.Ha, 78.67.Bf, 81.16.Fg

Degradation of Methylene Blue Using ZnO Nanoparticles Prepared by Biochemical Synthesis

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In this paper, ZnO nanoparticles are synthesized by biosynthesis method using aloe vera gel/leaf aqueous extract. The obtained nanoparticles are characterized using IR and XRD. The IR results show the absorption band of Zn–O at 498 cm^{-1}, while the powder XRD pattern confirms the hexagonal wurtzite-type structure with particles' size of 35.01 nm. ZnO nanoparticles are used as catalysts for degradation of methylene blue using hydrogen peroxide as an oxidant. The catalytic activity is calculated.

У цій роботі наночастинки ZnO було синтезовано методом біосинтези з використанням водного екстракту ґелю/листя алое вера. Одержані наночастинки було охарактеризовано за допомогою ІЧ- і рентґенівської дифракційної спектроскопії. Результати ІЧ-спектроскопії показують смугу вбирання Zn–O при 498 $см^{-1}$, тоді як порошкова рентґенівська дифрактограма підтверджує гексагональну структуру типу вюртциту з розміром частинок у 35,01 нм. Наночастинки ZnO було використано як каталізатори для деґрадації метиленового синього із застосуванням перекису водню як окиснювача. Було розраховано каталітичну активність.

Key words: ZnO nanoparticles, plant extract, aloe vera gel, methylene blue degradation.

Ключові слова: наночастинки ZnO, рослинний екстракт, ґель алое вера, деґрадація метиленового синього.

(Received 27 August, 2024)

1. INTRODUCTION

Metal oxides, mainly ZnO, have attracted attention for environmen-

tal remediation [1–3]. Residual dye contents in textile wastewater have complex aromatic structures that are difficult to degrade by a biological treatment. Therefore, over the last few decades, considerable attention has been paid to decomposing these textile waste dyes by improving the properties of metal oxides, mainly ZnO, by preparing nanoparticles (NPs). Several methods have been developed for their synthesis including physical, chemical and biological methods [4–7].

The use of plant extracts in the synthesis techniques make the use of moderately pollutant free chemicals to synthesize nanomaterials and increase the use of eco-friendly solvents such as water. Green chemistry seeks reducing pollution at the source [8]. Green chemistry encompasses all aspects and types of chemical processes that reduce negative impacts to human health and the environment. This principle focuses on choosing reagents that encounters the least risk and generate only benevolent by products. Though physical and chemical methods are trendier for the synthesis of NPs, the biogenic fabrication is a better choice due to eco-friendliness. Because of the need of environmental friendly NPs, researchers are using green methods for the synthesis of various NPs for pharmaceutical applications [9–12].

The biological approaches of using microorganisms and plants or plant extracts for the synthesis of NPs have been suggested as valuable alternatives to chemical methods. Several biological systems including bacteria, fungi and yeast have been used in synthesis of nanoparticles. Nanoparticles, due to their smaller size and large surface, exhibit remarkable novel properties and methodical applications in the field of biotechnology, sensors, medical, catalysis, optical devices, DNA labelling, drug delivery, and they are rewardingly treated as a bridge between bulk material and atomic and molecular structures.

It is well known that ZnO is an important metal oxide semiconductor. ZnO NPs have found fabulous applications in biomolecular detection, diagnostics, and microelectronics [13–16].

The aim of this study is to prepare ZnO NPs using a green chemical method and examine the catalytic properties of the ZnO nanocomposites for methylene blue (MB) oxidation.

2. MATERIALS AND METHODS

2.1. Materials

($Zn(CH_3COO)_2$ 99%), (NaOH 99.5%) were supplied from Riedel de Haen. These chemicals were utilized in the synthesis of the samples using distilled water.

2.2. Preparation of ZnO Nanoparticles

Aqueous zinc acetate solution 50 mL of 0.02 M was prepared and added to the aqueous leaf extract of aloe vera 100 mL of 50% because of better size distribution of ZnO NPs at room temperature. The resulting mixture was stirred for 20 min. Then, sodium hydroxide solution 8 mL of 3.0 M NaOH was added drop wise to increase the pH to 12. The resulting pale creamy mixture was then stirred (2 h). The white precipitate was collected by filtration; it was washed with distilled water and with ethanol (96%) to remove the impurities. The resulting white powder of ZnO NPs was dried in a vacuum oven (at 80°C during 2 h). Then, the product was calcinated at 700°C during 3 h. The yield of the ZnO NPs was of 99%.

2.3. Characterization

The crystallite structure and size of the synthesized nanoparticles' samples were calculated using an x-ray powder diffractometer (XRD) (Philips-PW-1840) with a CuK_α radiation of 1.5418 Å in a 2θ range of 20–80°, while the analysis of the chemical composition was carried out using Fourier transformation infrared red (FT–IR) model: Jasco Spectrum 4100 FT–IR spectroscopy.

2.4. Catalytic Degradation Experiments

The degradation experiments were performed in the glass bottle 250 mL containing 100 mL of MB solution. In details, a certain amount of catalyst 0.1 gr was added to the MB solution 64 mg/L under stirring for 1 h in the dark. 10 mL of H_2O_2 solution 30% v/v was added.

The ultraviolet–visible (UV–Vis) absorbance of supernatant was determined at wavelength of 665 nm (for MB).

The catalytic activity (Ca, %) of MB was calculated by Eq. (1):

$$Ca = \left[(A_0 - A_e)/A_0\right] \cdot 100\%, \quad (1)$$

where A_0 and A_e are the initial and equilibrium absorptions of MB, respectively.

3. RESULTS AND DISCUSSION

3.1. FT–IR Spectroscopy

The FT–IR spectra of ZnO nanoparticles are presented in Fig. 1. All FT–IR spectra results, which were observed in the range of 400–

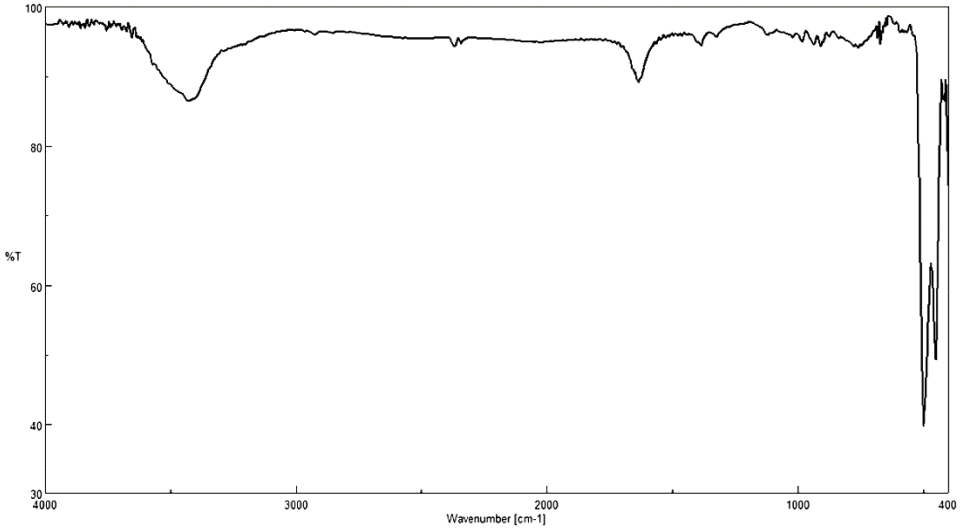

Fig. 1. FT–IR spectra of synthesized ZnO NPs.

TABLE. The absorption bands wave number of the FT–IR spectra of ZnO NPs.

Wave number, cm^{-1}	Bond type
3425	O–H (stretching)
1634	H–O–H (bending)
498	Zn–O (stretching)
450	Zn–O–Zn (stretching)

4000 cm^{-1} at room temperature, are arranged in Table. The most important absorption bands in the spectra are at 450 cm^{-1}, 498 cm^{-1} and belong to Zn–O, Zn–O–Zn, respectively.

3.2. XRD Analysis

The XRD pattern for the prepared ZnO nanoparticles *via* biochemical method was shown in Fig. 2. The phase of the samples has a hexagonal structure. The calculated unit cell parameters ($a = b = 3.242$ Å, $c = 5.188$ Å) with a good agreement with the values reported in the JCPDS file # 96-210-7060.

Figure 3 shows the lattice cells of prepared metal ferrite.

The average crystallite size was calculated using Scherrer's equation, which is expressed as follows [17]:

$$D = K\lambda/(\beta \cos\theta) , \qquad (2)$$

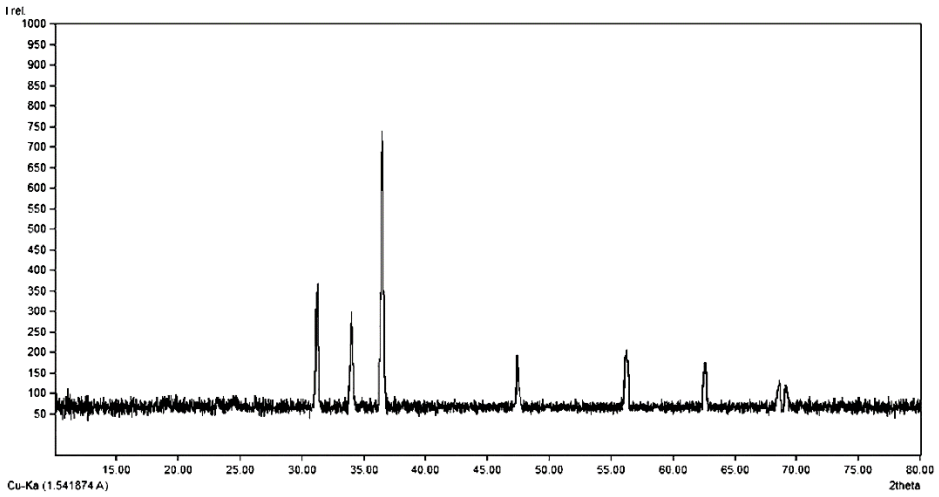

Fig. 2. XRD patterns of ZnO NPs.

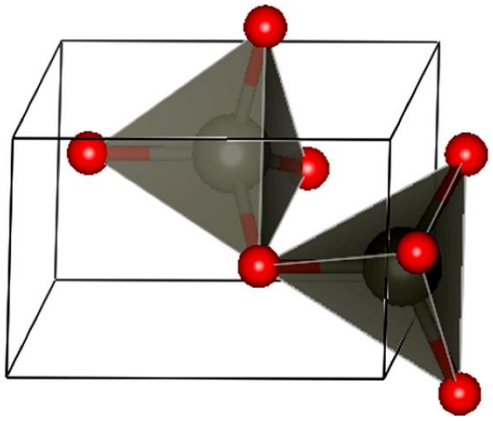

Fig. 3. Lattice cells of ZnO NPs.

where K is Scherrer's constant ($K = 0.89$ assuming spherical particles), λ is the x-ray wavelength, β is the peak width at half maximum (FWHM), and θ is the Bragg's diffraction angle. The average crystal size was of 35.01 nm.

3.3. The Catalytic Activity

The catalytic activity of ZnO NPs prepared by the biochemical method was studied through the methylene blue oxidation reaction using hydrogen peroxide. Figure 4 shows the absorption spectra of

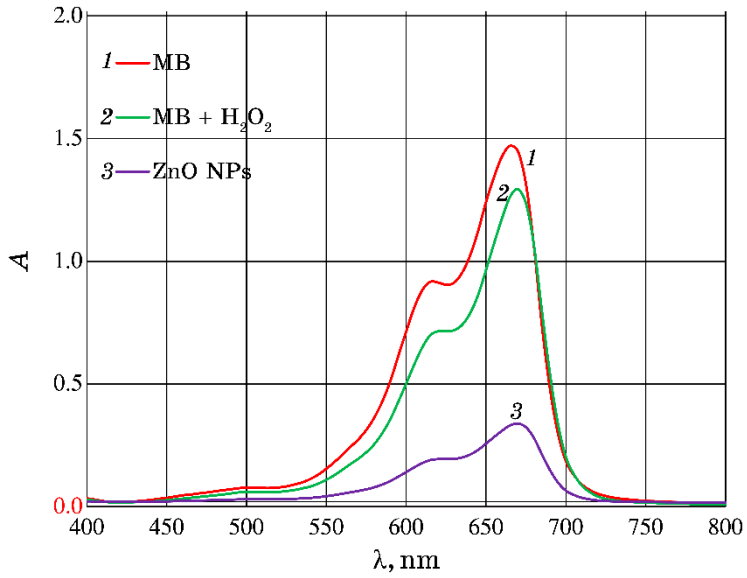

Fig. 4. UV–Vis spectra of MB with and without ZnO NPs.

methylene blue with and without ZnO after 30 min of reaction time. The catalytic activity was calculated by means of Eq. (1).

As can be seen from the previous results, the catalytic activity reached to 88.7%.

4. CONCLUSION

ZnO NPs was successfully synthesized using biochemical method. The resulting compounds were characterized using XRD techniques, which confirmed the size of nanoparticles, and IR spectroscopy. The catalytic activity was studied, and it was found that the ZnO NPs have a high catalytic activity.

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