

PACSnumbers: 61.05.cp, 78.30.Fs, 81.16.Be, 81.20.Ka, 82.33.Ln, 82.65.+r, 89.60.Ec

Catalytic Activity of TiO₂ Nanoparticles Prepared by Green Synthesis

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In this paper, TiO₂ nanoparticles (NPs) are synthesized by biosynthesis method using *Aloe vera* gel/leaf aqueous extract. The obtained NPs are characterized using IR spectroscopy and XRD methods. The IR results show the absorption bands of Ti–O at 724 cm^{–1} and Ti–O–Ti at 662 cm^{–1}, while the powder XRD pattern confirms the tetragonal anatase-type structure with NPs' size of 29.34 nm. TiO₂ NPs are used as catalyst for degradation of methylene blue, using hydrogen peroxide as oxidant. The catalytic activity is estimated.

У цій роботі наночастинки (НЧ) TiO₂ було синтезовано методом біосинтези з використанням водного екстракту гелю/листя алое вера. Одержані НЧ було охарактеризовано за допомогою ІЧ-спектроскопії та рентгенівської дифрактометрії. Результати ІЧ-спектроскопії показують смуги вбирання Ti–O при 724 см^{–1} та Ti–O–Ti при 662 см^{–1}, тоді як порошкова рентгенівська дифрактограма підтверджує тетрагональну структуру типу анатазу з розміром НЧ у 29,34 нм. НЧ TiO₂ було використано як каталізатор для деградації метиленового синього з застосуванням перекису Гідрогену як окиснювача. Було оцінено каталітичну активність.

Key words: TiO₂ nanoparticles, plant extract, *Aloe vera* gel, methylene blue degradation.

Ключові слова: наночастинки TiO₂, рослинний екстракт, гель алое вера, деградація метиленового синього.

(Received 16 September, 2024)

1. INTRODUCTION

Metal oxides, mainly, TiO₂, have attracted attention for environ-

mental 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, 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 sizes 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.

Researchers have demonstrated that plant-mediated synthesis can yield TiO_2 nanoparticles with unique properties that enhance their photocatalytic efficiency and biocompatibility. For instance, use of green tea extract produced TiO_2 nanoparticles with improved photocatalytic activity compared to those synthesized through conventional methods.

Similarly, studies have reported the successful synthesis of TiO_2 nanoparticles using extracts from various medicinal plants, leading to novel applications in both environmental and biomedical fields [13, 14].

The aim of this study is to prepare TiO_2 NPs, using a green chemical method, and examine the catalytic properties of the TiO_2 nanocomposites for methylene blue (MB) oxidation.

2. MATERIALS AND METHODS

2.1. Materials

(TiOSO₄ 99%), (NaOH 99.5%) were supplied from Riedel deHaen. These chemicals were utilized in the synthesis of the samples using distilled water.

2.2. Preparation of TiO₂ Nanoparticles

Titanium oxy sulphate 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 TiO₂ 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 dropwise to increase the pH to 10. The resulting pale creamy mixture was then stirred (2 h). The white precipitate was then collected by filtration; it was washed with distilled water and then with ethanol (96%) to remove the impurities. The resulting white powder of TiO₂ NPs was dried in a vacuum oven (at 80°C 2 h). After that, the product was calcinated (at 700°C, 3 h). The yield of the TiO₂ NPs was of 89%.

2.3. Characterization

The crystallite structure and sizes of the synthesized nanoparticle 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 transform infrared (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 H₂O₂ solution (30% v/v) was added.

The ultraviolet–visible (UV–Vis) absorbance was determined at wavelength of 665 nm (for MB). The catalytic activity (*Ca*, %) of MB was calculated as

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

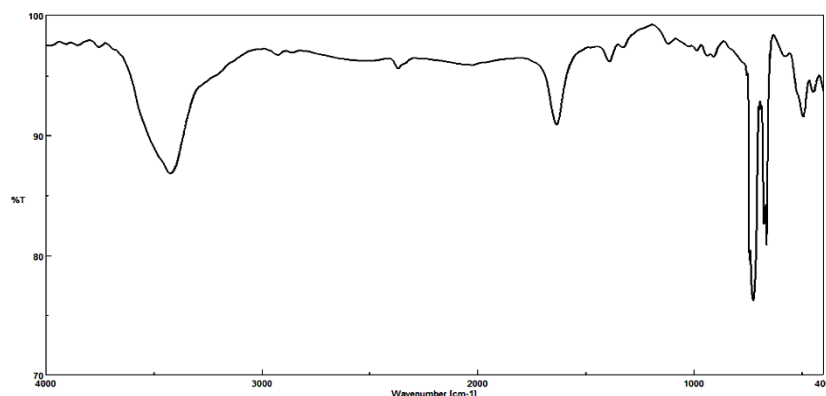


Fig. 1. FT-IR spectra of synthesized TiO₂ NPs.

TABLE. The absorption-bands' wave number of the FT-IR spectra of TiO₂ NPs.

Wave number, cm ⁻¹	Bond type
3424	O-H (stretching)
1633	H-O-H (bending)
724	Ti-O (stretching)
662	Ti-O-Ti (stretching)

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 TiO₂ nanoparticles are presented in Fig. 1. All FT-IR spectra results were observed in the range of 400–4000 cm⁻¹ at room temperature and are arranged in Table. The most important absorption bands in the spectra are at 724 cm⁻¹, 662 cm⁻¹, which belong to Ti-O, Ti-O-Ti, respectively.

3.2. XRD Analysis

The XRD pattern for the prepared TiO₂ nanoparticles *via* biochemical method was shown in Fig. 2. The phase of the samples was tetragonal structure. The calculated unit cell parameters ($a = b = 3.781$ Å, $c = 9.435$ Å) in a good agreement with the values reported in the JCPDS file # 96-152-6932.

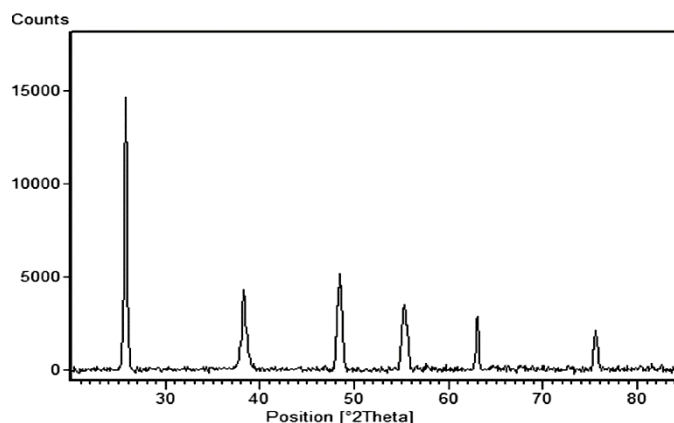


Fig. 2. XRD patterns of TiO₂ NPs.

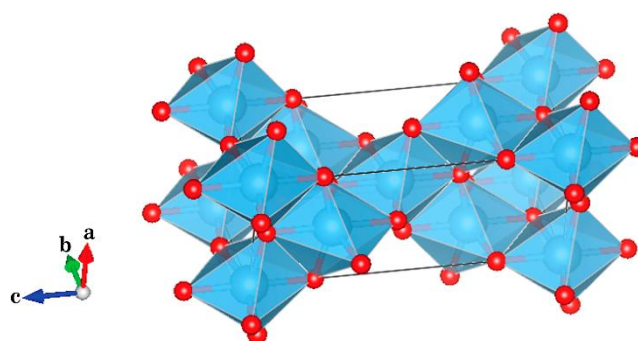


Fig. 3. Lattice cell of TiO₂ NPs.

Figure 3 shows the lattice unit cell of prepared TiO₂ NPs.

The average crystallite size was calculated using Scherrer's equation, which is expressed as follows [15]:

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (2)$$

where K is Scherrer's constant ($K = 0.89$, if assuming spherical particles), λ is the x-ray wavelength, β is the peak full-width at half maximum ($FWHM$), and θ is the Bragg's diffraction angle. The average crystallite size was of 29.34 nm.

3.3. The Catalytic Activity

The catalytic activity of TiO₂ NPs prepared by the biochemical

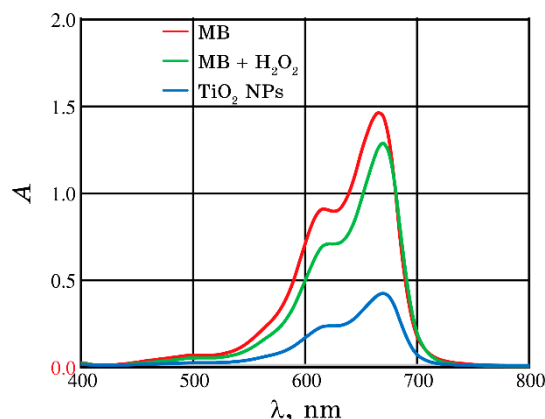


Fig. 4. UV-Vis spectra of MB with and without TiO_2 NPs.

method was studied through the methylene blue oxidation reaction using hydrogen peroxide.

Figure 4 shows the absorption spectra of methylene blue with and without TiO_2 NPs after 90 min of reaction time. The catalytic activity was calculated through Eq. (1).

As can be seen from the previous results, the catalytic activity reached to 67.72%.

4. CONCLUSION

TiO_2 NPs was successfully synthesized using biochemical method. The resulting compounds were characterized using XRD technique, which confirmed the size of nanoparticles, and IR spectroscopy. The catalytic activity was studied, and it was found that the TiO_2 NPs has a high catalytic activity.

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