Synthesis of Titanium dioxide nanoparticles by sol-gel method for water remediation application

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Abstract: *Titanium dioxide is one of the effective photocatalysts used to degrade the harmful constituent of industrial pollutants in water. Thus, the primary goal of this study is to synthesize and characterize TiO_2 nanoparticles for water remediation applications. The TiO_2 nanoparticle (TNPs) is synthesized by the sol-gel method without surfactant. The physicochemical properties of the synthesized TNPs are analyzed by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and dynamic light scattering (DLS). The photocatalytic response of the TNP for methyl orange (MO) dye degradation is studied. Also, the antibacterial property of TNPs against E. coli and S. Aureus is investigated. The DLS result demonstrated that synthesized TNPs have a particle size of 121 nm. The XRD graph reveals the nanocrystalline anatase form of the TNPs. The characteristics peak of Ti-O-Ti bonds is observed between 400 to 850 cm^{-1} in the FTIR spectrum. The photocatalytic activity of TNPs is found to be 81.04%. In addition, TNPs exhibit suitable antibacterial properties against bacteria. The synthesized TNPs via the sol-gel method demonstrated good photodegradation and antibacterial properties, which confirm their potential use in water remediation applications.*

Keywords: *Antibacterial properties, Dye degradation*

1. Introduction

Water pollution treatment drew considerable attention due to the urgency of water contamination. Photocatalytic degradation has emerged as a desirable and effective approach for water and wastewater treatment (Shimi et al., 2022). Although a significant problem, creating effective catalysts for the breakdown of organic pollutants is essential for remediating the current harsh water environment. A metal oxide is one of the promising photocatalysts used in the water remediation process. TNPs are frequently used in water treatment due to their superior photoreactivity, nontoxicity, and affordability (Fiordaliso et al., 2022). Different techniques to synthesize TiO_2 nanoparticles include sol-gel, reverse-micelle, and hydrothermal methods.

The anatase phase of TiO_2 nanoparticles' electron transfers from the valance band to the conduction band better than the rutile phase, increasing the electron and hole pair. Electron and hole pairings enable several oxidative and reductive reactions. The purpose of this technique was to extract hydrogen energy from water by converting photo energy. The TiO_2 photocatalytic method's primary rationale is the oxidation of contaminants using hydroxyl radicals ($HO^{\cdot}$). The highly oxidative h (hole) oxidizes water, forming HO radicals that are incredibly aggressive and nonselective in their attack on the substrates in an aqueous solution. Electrons need to be absorbed by the electron acceptor. As a result, the photogenerated electron and hole pairs are split apart, transforming pollutants. Instead, the photogenerated electron and hole pairs will fuse, releasing unintentional thermal energy. The photogenerated electron and hole pairs should be separated as far as possible to increase the efficiency of photocatalysis. The TNP is the best photocatalytic material for better results under UV radiation. TNP generates electron-hole pairs, then effective redox performance and pollutant dye degradation (Zhang et al., 2021).

The present study analyzethe photocatalytic response of the TiO_2 for methyl orange dye degradation. Titanium oxide nanoparticle is synthesized at room temperature without surfactant by the sol-gel method. The morphological and optical characterization of the synthesized materials is performed using XRD, Raman spectra, FTIR, and DLS. Also, the antibacterial property of TiO_2 nanoparticles was investigated against the *E.coli* and *S.Aurus* bacterium.

2. Materials and methods

Titanium butoxide (97%) was acquired from Sigma-Aldrich. Ethanol, acetic acid, and methanol were obtained from Hi-Media. Milli-Q water (0.69 MΩ cm at 25˚ C) was employed throughout the synthesis and reaction steps.

2.1. Synthesis of TiO_2 nanoparticles

First, 1.7 ml of acetic acid and 20 ml of methanol were combined, and after 10 min, titanium butoxide precursor was enumerated drowsily and stirred for 300 rpm at 40˚ C for 90 min. The transparent solution was kept in a hot oven for the vaporization process at 60˚ C for 24 h. After that, dry material is grind using a mortar pester and then calcined for 1 h at 500˚ C.

2.2. Photocatalytic Degradation

First, 100 mL of MO dye aqueous solution was prepared with 0.1 g of MO dissolved in 80 mL of water. Then 20 mL ethanol (95%) was added to it. The 100 mL of MO dye aqueous solution and 10 mg of TiO_2 were dispersed inside a dark closed chamber. After that, the prepared solution was constantly stirred for 30 min at 40 ˚C to establish MO's absorption and desorption equilibrium (Song et al., 2022) and then kept inside TFM-20V high-performance UV transilluminator at room temperature. After 30 minutes, regularly collected 1 mL sample and centrifuged. The supernatant was poured into a quartz cuvette without dilution, and the concentration of MO was then measured at 464 nm using a UV-Vis spectrophotometer.

2.3. Investigation of antibacterial activities of the synthesized nanocomposite material

The antibacterial activity of TNPs was determined by the disc diffusion method against E. coli and S. Aureus. Initially, the Muller Hinton agar was autoclaved at 121˚ C, poured into the sterile petri dish, and seeded with 100 µL of bacterial growth media. With the help of a sterile L-rod, the sample was uniformly spread on the agar plates, and the 6 mm biopsy punch was made using a biopsy punch. The TiO_2 sample with different concentrations (mg/mL) was loaded into the well plates, and antibiotics were used as a positive control. Following a 24-hour incubation period at 37 degrees Celsius, the agar plates were scaled to measure the inhibition zone.

3. Result and discussion

The XRD graph for the synthesized TNP are shown in Figure 1 (a). The diffraction peak for synthesized TNPs shown at 2θ = 25.36˚, 37.99˚, 48.12˚, 54.19˚, 55.19˚ due to the planes (011), (004), (020), (015), and (121) respectively. These confirm the tetragonal anatase phase formation of TiO_2, according to JCPDS card ref No. 98-010-6857. The highest peak was found in orientation (011). The average crystallite size obtained is 121 nm, and crystallinity is 68.22%. Figure 1. (b) depicts the TNPs Raman spectra, with the peaks at 146 cm^{-1}, 399 cm^{-1}, 517 cm^{-1}, and 639 cm^{-1}, associated with Eg, Eg, B_1g, A_1g, and Eg, respectively, revealing the anatase form of TNPs (Ilie et al., 2017). The peaks originate due to the vibration of O-Ti-O bonds. The Eg peaks are due to symmetric stretching, B_1g due to symmetric bending, and A_1g due to antisymmetric bending (Kang et al., 2020). FTIR of the TNP was recorded from 4000 to 400 cm^{-1}. FTIR (Figure 2. a)) shows -OH stretching causes the peak at 2925 cm^{-1}; the peak at 2362 cm^{-1} denotes hydrogen bonding matching the oxygen groups. The peak identified at 1103 cm^{-1} was related to Ti-O-OC bonding (Manzoor et al., 2018). Figure 2. b) shows the particle size distribution measured by DLS. According to the size measuring investigation, the particle size was 121 nm.

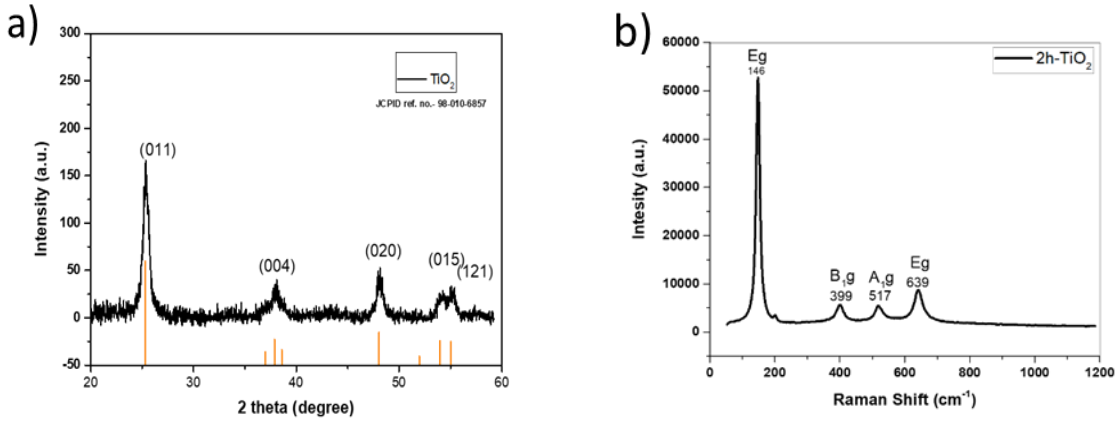

Figure 1. a) XRD of synthesized TNP b) Raman spectra of synthesized TNP

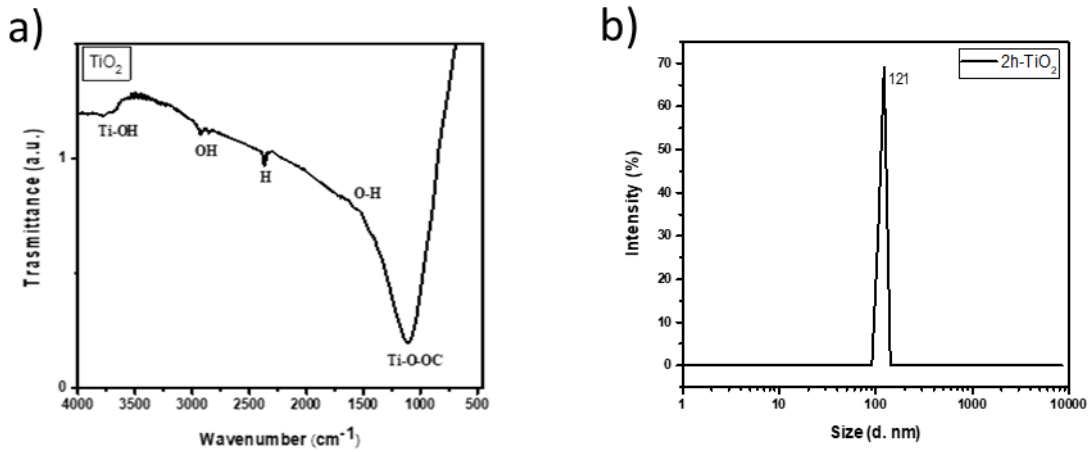

Figure 2. a) FTIR and b) DLS of TNP

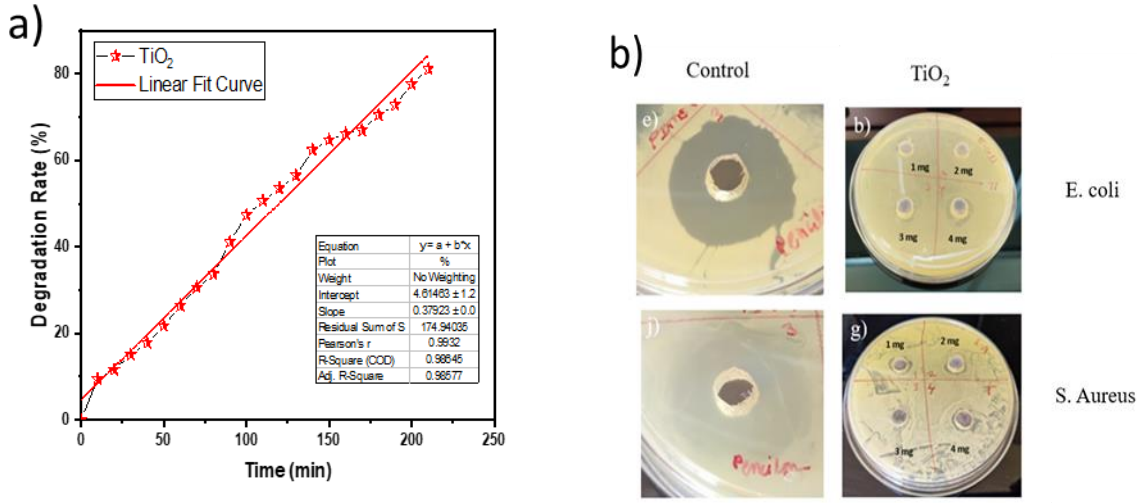

Figure 3. a) Photocatalytic activity of TNPs under UV radiation b) The inhibition zone captured for *E. coli bacteria* and *S. Aureus* bacteria of TNPs and positive control

Figure 3. a) represents the degradation rate of MO using TNP as a photocatalyst. The reaction proceeded up to 210 min, and the photocatalytic rate of MO was 81.04 %, calculated using the following formula,

$$\text{Photodegradation rate} = \frac{(C_0 - C)}{C_0} \times 100 \qquad (1)$$

where C is the initial concentration and C_0 is the current concentration of the MO solution (Naikwade et al., 2020). Without TNPs under UV radiation, the MO solution exhibited no degrading properties. The law of mass action illustrates that the photocatalytic process is a pseudo-first-order reaction given as,

$$r = -\frac{dC}{dt} = kC \qquad (2)$$

Where C represents the amount of MO present on the surface of TNPs, and k is a constant during the absorption process at time t. The linear fitting with $\ln\frac{C_t}{C_0}$ and time t gives the following expression from the graph, y = 3.7263x + 5.5595, R^2 = 0.986. The good regression coefficient R^2 = 0.986 indicated the photocatalytic degradation of MO by TNPs satisfied the pseudo-first-order reaction. Figure 3. b) illustrates the zone of inhibition for various concentrations of synthesized materials captured by a camera, with the corresponding measurement in Table 1. The results reveal that as the amount of material used rises, the antibacterial property of the material increases.

Table 1: Zone of inhibition of synthesized materials measured by the scale

Materials	Concentration (mg/mL)	E. coli (cm)	S. Aureus (cm)

TiO_2	1	1	1.3
	2	1.1	1.2
	3	1.2	1
	4	1.5	1.3
Control [(Penicillin-500 unit Streptomycin-5 mg Neomycin-10 mg)/ml]	200 µL	3	2.6

4. Conclusion

The XRD and Raman spectrum result confirms the synthesized TNPs were anatase phase and crystalline in nature. The anatase phase of TiO_2 is more stable and chemically active than other phases of TiO_2. Therefore, it is more suitable for catalyst application. The synthesis material evaluates the antibacterial activity. The result shows that synthesized materials are antibacterial against *E. coli* and *S. Aureus* bacterium. The photocatalytic activity of synthesized TNPs is found to be 81.04%.

5. NO OBJECTION FROM CO-AUTHORS

The authors have no conflicts of interest to declare.

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