Synthesis of TiO2NPs with agricultural waste for photocatalytic and antibacterial applications

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Abstract. Titanium dioxide (TiO2) nanostructures with palm trunk mince were deposited via hydrothermal technique. The crystalline structure of TiO2 has two phases anatase and rutile, which analyzed by X-ray diffraction (XRD). TiO2 NPs morphology were examined by field-emission scanning electron microscopy, which revealed that product has hexagonal nanobelts, nanorods, and nanowires. Photocatalyst activates of TiO2 were studied on degradation of methylene blue dye (MB) under UV irradiation, MB absorption decrease with increasing the irradiation time, which optimum degradation showed with nanowires shape comparable with nanorod and nanobelts shapes. The antibacterial study clearly indicates that the palm trunk extract mediated of TiO2 NPs exhibit the excellent antimicrobial activity.

Keywords. Green synthesis, palm trunk extract, Hydrothermal method, TiO2 NPs, Antimicrobial Activity

1. Introduction

The rapid development of nanotechnology has gained much alertness, especially in the field of nanoscaled fibers, wires, rods, tubes and particles. Research in areas related to the molecular compounds for nanomaterial is needed to develop manufacturing techniques. The main objective of nanoparticles technology is to produce products with special physical and chemical functions, which are mainly related to their nanometer scale. Metal oxide nanoparticles have attracted high alertness by their glory potential application in different fields, such as catalysis, magnetic recording media, microelectronics, medicine, antibacterial activity, removing the environmental pollution, sterilization and restraining virus [1]. TiO2 have gotten much interest due to its physical and chemical properties in different applications [2], especially in the form of nanoparticles for both high catalytic surface area and activity [3]. It is well known that TiO2 occurs in nature in three crystalline structures, namely, rutile, anatase and brookite forms [4]. In particular, the most stable phase is rutile whereas brookite and anatase are metastable, anatase was investigated for its important in many applications like lithium-ion batteries, filters [5]. However, the challenge in maintaining this stability remains stable from easy conversion to rutile when heat treated [6-8]. The almost ideal photocatalyst is TiO2 which should have some properties like, chemically and biologically inert, stable in photocatalytic reactions, easy to produce and use, cheap, not dangerous and efficient under sun irradiation.
Thus, titanium dioxide is suitable for photocatalytic applications [9]. The hydrothermal method is a combination of single crystals based on the solubility of minerals in hot water under high pressure, the term "hydrothermal" is of geological origin [10]. The aim of this work is to prepare TiO2 NPs for antibacterial and photoelectric applications.

2. Experimental Procedures

The simple and easy hydrothermal method was successfully synthesized titanium dioxide (TiO2) nanostructure, the films were deposited on glass substrate using (100 ml) of distilled water and 2 g of the dried palm trunk mince. The solution was stirred for half an hour. The plant extract solution was filtered with a filter paper to get rid of impurities, and then put in the centrifuge for a quarter-hour to throw out the remainder of impurities. The next step, 1g of titanium isopropoxide was added in 10 ml of distilled water and stirred for half an hour. Then, mix with 20 ml of the plant extract solution with titanium isopropoxide solution to become an aqueous solution. The preparation processes repeated several times to study the physical properties of the films. Photocatalytic activity of TiO2 nanostructures was characterized by measuring the degradation of MB dye solution. 80mg of powder sample was ultrasonically dispersed in 200ml of MB solution with a concentration of 20mg/L. Absorption spectra were recorded via UV-Vis spectrophotometer (UV Optima SP-3000+). Percentage of dye degradation was calculated utilizing the following:

\[
\text{Degradation} = \left(\frac{C_0 - C}{C_0}\right) \times 100\%
\]

Where, \(C_0\) and \(C\) is initial dye concentration and dye concentration at time (t) respectively.

The deposited thick films were characterized by X-Ray diffraction (miniflex II Rigaku, Japan). Peak positions and relative intensities of XRD and the standard cart (JCPDS 036-1451). The optical studies were performed in the wavelength between 250nm to 900 nm by a Hitachi U-2000 Japan double beam spectrophotometer. FE-SEM is examine the surface morphology and to estimate structure uniformity. Surface morphology of the deposited films was obtained by FESEM (Hitachi S-4160). Antimicrobial activity of TiO2 NPs using dried palm trunk versus pathogenic microorganisms was obtained by a highly effective method of diffusion under aerobic condition. The inhibitory activity against all pathogenic microorganisms was tested on Mueller-Hinton agar. Agar plates were inoculated with 250 μL (1.5×10^8 (CFU)/ ml for bacteria and 1.5 ×10^6 (CFU)/ ml for mold and yeast, comparison with 0.5 McFarland standards tube) with each indicator microorganisms (Escherichia coli, Staphylococcus aureus, proteus spp, candida Albicans and Trichophyton rubrum) after growing them in a nutrient broth. Wells (6mm) were cut in Mueller-Hinton agar plate and 150 μL of TiO2 NPs using dried palm trunk was added into each well. Plates were incubated at 37 °C within 24 hrs-48hrs for bacteria and 30 °C within 72 hrs for yeast and mold.

3. Results and Discussions

3.1. UV-VIS Spectrum Analysis

Figure 2 shows UV–visible spectrophotometer for TiO2 prepared by hydrothermal technique with palm trunk extraction. The highest value of absorption at 350 nm with sharp peaks in the UV region. The peaks are also intense which shows that the particles are tiny in size with suitable spread out the whole surface. Therefore, this property of metal oxide nanoparticles could effectively be used as a novel solution strategy. The unique properties of TiO2 NPs with plant extract and their mechanism of action as antibacterial agents in UV-light induce to use on drug-resistant bacteria [11].

3.2. X-Ray diffraction

Figure 3 represents XRD patterns of TiO2 nanoparticles deposited by hydrothermal technique using palm trunk extract. The XRD pattern shows two phases anatase and rutile corresponding to (101), (103), (-114), (004), (217), (021), (105), (213), (116), and (301) respectively. The average crystallite size (D) was determined depending on (101) orientation utilizing Debye-Scherrer’s formula [12]:

\[
D = \frac{0.94 \lambda}{\beta \cos \theta}
\]
Where $\beta$: is the full width at half maximum (FWHM), $\lambda$: is x-ray wavelength =0.1546 nm and $\theta$: is Bragg’s angle. D, which has been obtained by this equation was very small and equal to (12 nm).

3.3. FE-SEM analysis
FE-SEM is a suitable technique for detecting the morphology of thin films. Figure 4 shows the SEM images of the TiO$_2$ NPs without plant extract and with plant extract which display the polycrystalline structure. The particles without plant extract have approximately cluster shape (see Fig. 4a), while in the case of with plant extract are agglomerated and have flower crystals. SEM images clearly show that particle sizes of TiO$_2$ in the first case (Fig 4b) are bigger than those in the second due to high density of palm trunk extract.

3.4. The Photocatalytic activity of TiO$_2$ NPs
The bioreduction of TiO$_2$ by hydrothermal method with palm trunk extraction. UV-visible spectroscopy analysis was carried out through the wavelength 250–950 nm of UV-vis (CARY 100 CONC plus UV-Vis-NIR, Split- beam Optics, Dual detectors) spectrophotometer measured at room temperature. The absorbance peak at near (340 to 410) nm. The absorbance band of nanoparticles perform a diversion in color site produced from the amount of available placement in specimen comparing to the CdO NPs. This optical phenomenon indicate that these NPs clarify quantum effects level.

Figure (5) shows the relationship between the absorption and irradiation time (0, 30, 60, 90, 120 min.) such the absorption of MB decreases with increasing the irradiation time. From this figure the effect of palm trunk extraction of TiO$_2$ NPs on MB degradation was appear.

3.5. Antibacterial application
The antimicrobial activity was specified by measuring diameter of inhibition zone around wells. The presence of a clearance zone on agar plates was used as an indicator of the bioactive potential of NOPS NP using dried palm trunk. Synthesis TiO$_2$ NPs using dried palm trunk extract as antimicrobial activity was examined using (vitro disc diffusion method), during the incubation zone of inhibition (ZOI). Diameter of inhibition zones of TiO$_2$ NPs on bacterial strains, of B. Subtilis is (28 mm) and Escherichia coli is (23 mm) at 200 $\mu$g/ml concentration as displayed in figure (6) and Table 1. Antibacterial studies elucidate that the B. subtilis is a more effective bacterial activity than the E. coli. The antibacterial effect of TiO$_2$ NPs is mainly due to attached to e bacterial cell wall due to electrostatic attraction. Furthermore, TiO$_2$ is interacting surface of a membrane and penetrate inside bacteria. This study indicates that palm trunk extract mediated of TiO$_2$NPS exhibit excellent antimicrobial activity is a high activity than TiO$_2$ nanoparticle effect after comparing the result with Haghi et al. [13].

4. Conclusions
Green synthesis of TiO$_2$ nanoparticles with green plants is a highly cost-effective, safe, non-toxic, eco-friendly way of synthesis which can be done on a big scale. The crystal size has been estimated from the most prominent (101) was found to be (12 nm). Formation of homogeneous and relatively spherical with cluster nanoparticles is shown in the image. Also, the size and the shape TiO2NPs were examined by (FE-SEM). The UV absorption peak at 350 nm clearly indicates by synthesis of TiO$_2$NPs. TiO$_2$ nanoparticles were synthesized using palm trunk extract which classified as eco-friendly by hydrothermal method (180 °C). The phytoconstituents present in the palm trunk extract was effective in the reduction and stabilization of TiO2 NPs. The pH was adjusted at 14 to get the optimum results. The Photocatalytic activity of TiO$_2$ NPs showed the absorption of MB decrease with increasing the irradiation time (0, 30, 60, 90, 120 min.) and the effect of palm trunk extraction on MB degradation was exhibited. The diameters of the inhibition zones of TiO$_2$ NPs were (28 mm) and (23 mm) on B. Subtilis and Escherichia coli Bectriaat 200 $\mu$g/mL concentration respectively. As a result, the bio-synthesized
(palm trunk extract) of TiO$_2$ NPs can use in future as Photocatalytic activity in photovoltaic devices and active antimicrobial agent in the biomedical field.

5. Acknowledgement

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Appendix

Figure 1. Hydrothermal cell parts (autoclave cell).

Figure 2. UV-vis spectrum analysis of TiO$_2$ synthesis by hydrothermal method with palm trunk extraction.

Figure 3. XRD patterns of TiO$_2$ synthesis by hydrothermal method with palm trunk extraction, (A represent anatases phase and R represent rutile phase).
Figure 4. FE-SEM images of biosynthesized TiO$_2$ NPs (A) without plant extract (B) with plant extract.

Figure 5. The relation between absorption of MB and wavelength of TiO$_2$ nanoparticles with palm trunk extraction.

Figure 6. Antimicrobial activity of TiO$_2$ nanoparticles with palm trunk extraction.

Table 1. Inhibition Zones of Bacillus subtilis and Escherichia coli Bectria.

| No. | Kind of Bectria     | Inhibition Zone (mm) at 200 μg/ml con. | Control (Dmso) |
|-----|---------------------|---------------------------------------|----------------|
| 1   | Bacillus subtilis   | 28                                    | -              |
| 2   | Escherichia coli    | 23                                    | -              |