SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITIES OF POLYMER CAPPED TITANIUM DIOXIDE NANOPARTICLES

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Abstract:

Scientific research has demonstrated a growing interest in the topic of nanotechnology in recent years, leading to the development of many ways for producing nanoparticles, including chemical synthesis approaches. In this study, the synthesis, characterization and antibacterial activities of polymer capped titanium dioxide nanoparticles. Polyvinyl alcohol serves as a polymer capping agent. The synthesized polymer capped titanium dioxide nanoparticles were characterized by X-ray diffraction (XRD), Scanning electron microscopy SEM with EDAX, Atomic force microscopy (AFM), Transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR) analysis. The antibacterial activity of nanoparticles was determined by gram-positive and gram-negative bacteria.

Keywords: Polyvinyl alcohol, Antibacterial, Titanium dioxide, Nanotechnology, Capping agent.

1. Introduction:

According to the definition given in the context of chemistry, nanoscale materials are structures with a size between 1 and 100 nm. In recent years, these materials have helped to accelerate the development of nanoscience and nanotechnology. Despite sharing a same chemical composition, nanomaterials frequently differ significantly from their macro scale counterparts in terms of their physico-chemical and biological properties [1]. Nanomaterials are materials with specific properties and geometric dimensions at the nanoscale. Among nanomaterials, nano oxide has been connected to remarkable significance. Nano-structured materials are gaining a lot of attention, particularly in organic and pharmaceutical applications, because nanomaterials can be utilized selectively and to achieve specific aims [2]. Over the past few years or so, there has been a significant increase in the risk of bacterial and biological attacks, particularly in the food, water, and packaging industries that are consumed by humans. Scientists are motivated to create novel inorganic antibacterial nanoparticle materials with minimal side effects and easy to implement. Certain materials, like metal oxide semiconductors, could become completely new materials with optical and/or electrical properties distinct from those of their bulk counterparts if their dimensions are reduced to the nanoscale. This makes it possible for researchers to investigate the advantages of nanomaterials in a variety of scientific domains, including biology, optoelectronics, and the environment [3–8].In biological and environmental remediation applications, titanium dioxide nanoparticles—along with other metal oxide semiconductors like ZnO, MgO, CuO, and $Fe_2O_3$are thought to be the best material because of their abundance, affordability, high surface area-to-volume ratio, non-toxicity, and special physiochemical properties. In addition, it exhibits good thermal stability, biocompatibility with chemicals, and a distinct photocatalytic activity. It is commonly recognized that the size, shape, and surface chemistry of titanium dioxide nanoparticles including the quantity of surface defects have a major impact on their antibacterial activity and photocatalytic activity [9–13]. Titanium's special properties have found many applications, including the production of dyes [14], cosmetics [15], sunscreen formulations [16–17], photocatalysts and catalysts [18–19], photostability and oxidative power [20], and more. According to reports, there is no health hazards associated with titanium dioxide nanoparticles used in cosmetic sunscreen products [21]. It's interesting to note that titanium can interact with human blood in circulation to improve wound healing and promote skin tissue regeneration [22]. These days, biomolecules have a greater role in the creation of nanoparticles than other components like chemicals and green extracts. Several capping agents, such as adenine with tricarboxylic acid [23], ethylene glycol [24], acid molecules [25], hydroxyl appetite [26], and pyridine [27], have been demonstrated in earlier papers to be used in the synthesis of nanoparticles. The production, characterisation, and antibacterial properties of polyvinyl alcohol-capped titanium dioxide nanoparticles were thus the main topics of the current investigation. Polyvinyl alcohol is used as a capping agent.

2. Materials and Method:

2.1. Synthesis of polymer capped Titanium dioxide nanoparticles:

The polymer-capped TiO_2nanoparticles were prepared by simple chemical method. Three milliliters of titanium butoxide was mixed with 6 g of polymer (PVA) under magnetic stirring at 80°C to form a titanium alkoxide complex. Then, 0.7 mL of HCl was added to the titanium alkoxide complex. The formed solution was transferred to a stainless (Teflon) lined autoclave (50 mL) and heated in an oven at 180 °C for 5 h. After that, the reaction products were collected by high-speed centrifugation (8000 rpm) and thoroughly washed with hot ethanol under magnetic stirring for 2~3 times. Then, the products were dried in the oven at 50 °C for 24 h.

3. Result and Discussion:

3.1. XRD Analysis:

As-prepared polymer-capped TiO_2 NPs' crystal structures were studied by XRD, and the results are shown in Fig. 1. When the observed XRD pattern was compared to the accepted JCPDS card [88-1172], it was found that rutile-phased TiO_2 nanoparticles with a tetragonal primitive structure with lattice parameters of a = 4.566 Å and c=2.948 Å had formed. The peaks at 2θ = 27°, 36°, 41°, 44°, 54°, 56°, 64° and 69°correspondto (110), (101), (111), (210), (211), (220), (310) and (301), respectively [28]. The result indicates that all the prepared

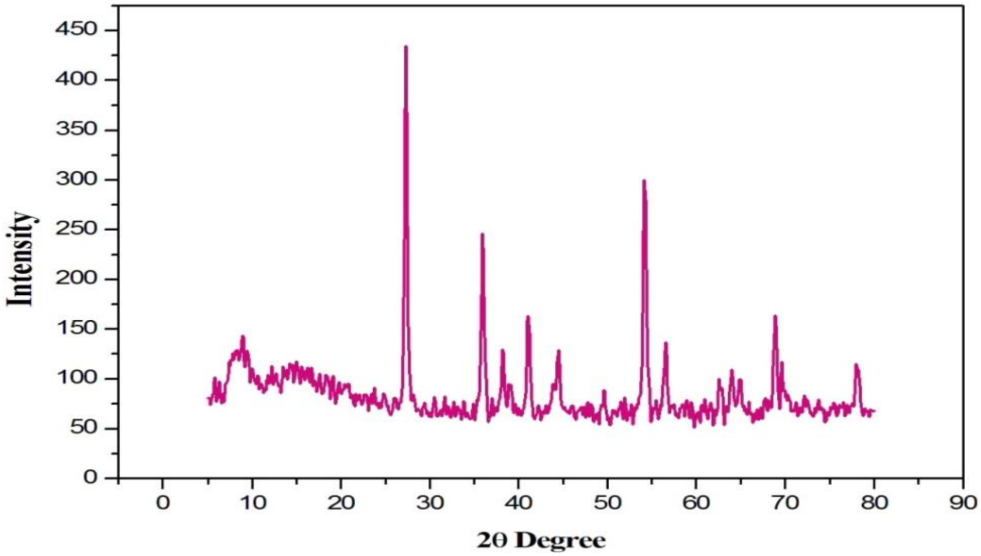

Fig.1. XRD pattern of PVA capped Titanium dioxide nanoparticles

polymer-capped TiO_2 nanoparticles are rutile phase. The capped polymers have no influence on the crystal structures of TiO_2 nano particles. This result was well matched with Ravichandran Rekha et al., 2019 [29]. Furthermore, the average crystalline sizes of all the polymer-capped TiO_2nanoparticles were estimated with the XRD data according to the Scherrer formula,$D = K\lambda/(\beta\cos\theta)$, where K is the scherrer constant, λ the X-ray wavelength, β the peak width of half maximum, and θ is the Bragg diffraction angle. It can be seen that the crystalline size D of the PVA capped TiO_2 nanoparticles. The size of the polymer capped titanium dioxide nanoparticle is 23.6 nm.

3.2. SEM with EDX Analysis:

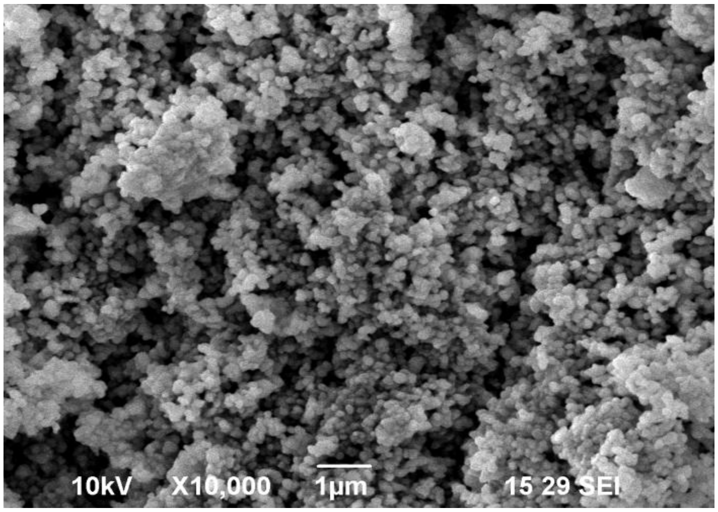

Fig.2. SEM image of PVA capped Titanium dioxide nanoparticles

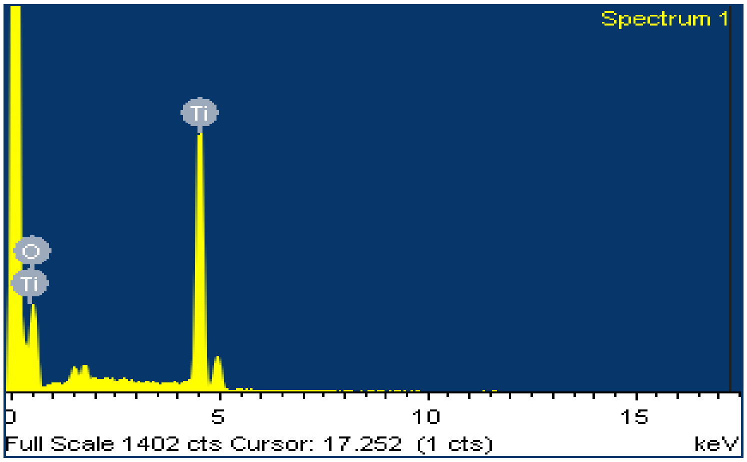

Fig.3. EDX spectrum of PVA capped Titanium dioxide nanoparticles

SEM was used to investigate the surface morphology of PVA capped titanium dioxide nanoparticles. The SEM image of the nanoparticles is shown in Fig. 2. The PVA cappedtitanium dioxide nanoparticles are spherical in shape and have a particle size of 25 to 50 nm, proving the importance of polymer capping in the size and morphology of titanium dioxide nanoparticles, which is consistent with the results from XRD. The synthesized particles have a spherical shape with good dispersion. Less agglomeration of nanoparticles also appeared, this may be due to aggregation of primary TiO_2 particles at high calcination temperature which is necessary to accelerate the crystal growth of titanium dioxide was reported by Al-Taweel et al., 2016 [30].The chemical element composition of the as grown PVA capped titanium dioxide nanoparticles was researched by X-ray energy dispersive spectroscope, and its spectrum is shown in Fig.3. It shows that the samples primarily contain Ti, O. The result of EDAX also indicates that the presence of polymer capped titanium dioxide nanoparticles.

3.3. AFM Analysis:

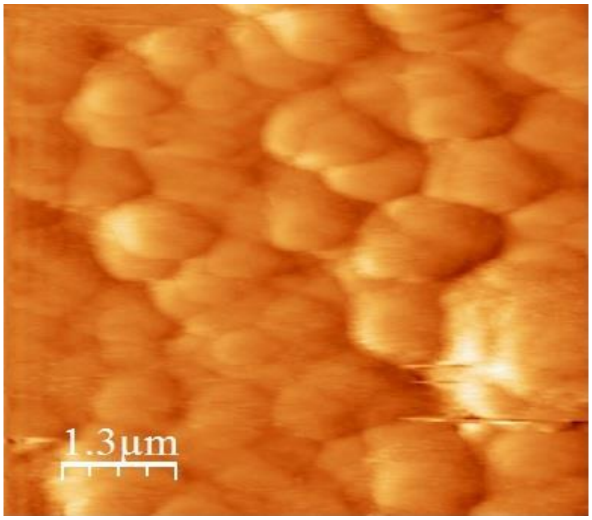

Fig.4. AFM image of PVA capped Titanium dioxide nanoparticles

AFM is a basic technique and inevitable for all nanoscopic researcher. The AFM image of PVA capped titanium dioxide nanoparticles synthesized by chemical method and the resulting image is given in the figure.4. The micrograph exhibit an uniform distribution with spherical covering the nanoparticles surface can be seen for this sample. It is observed that the particle is of nanometer size with uniform distribution. The surface roughness, RMS average value and heights have been determined by AFM analysis. The PVA capped metal oxide nanoparticle is in good agreement with XRD result.

3.4. TEM Analysis:

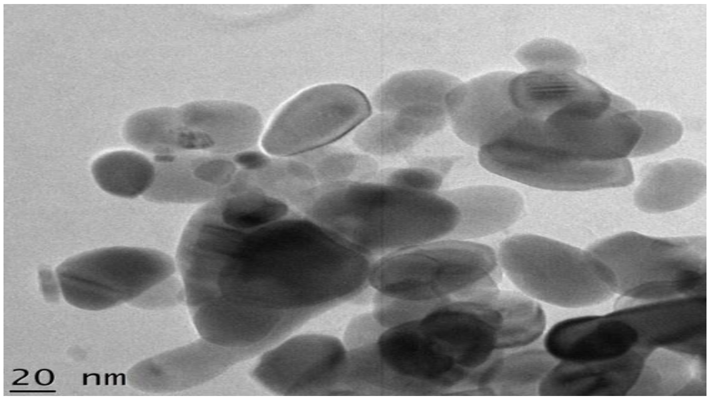

Fig.5. TEM image of PVA capped Titanium dioxide nanoparticles

The morphology and structure of the prepared product were further investigated with TEM analysis. TEM image of PVA capped titanium dioxide nanoparticles is shown in figure.5. The above figure shows the physical separation of the particles was preserved during processing, preventing the formation of agglomerates, as shown in the TEM image of PVA-capped TiO_2 nanoparticles. Additionally, it can be seen that there are some shadows encircling the TiO_2 nanospheres, suggesting the presence of capped PVA. This is because PVA can create a shell around the particles to stop them from aggregating and growing huge in size.

3.5. FTIR Analysis:

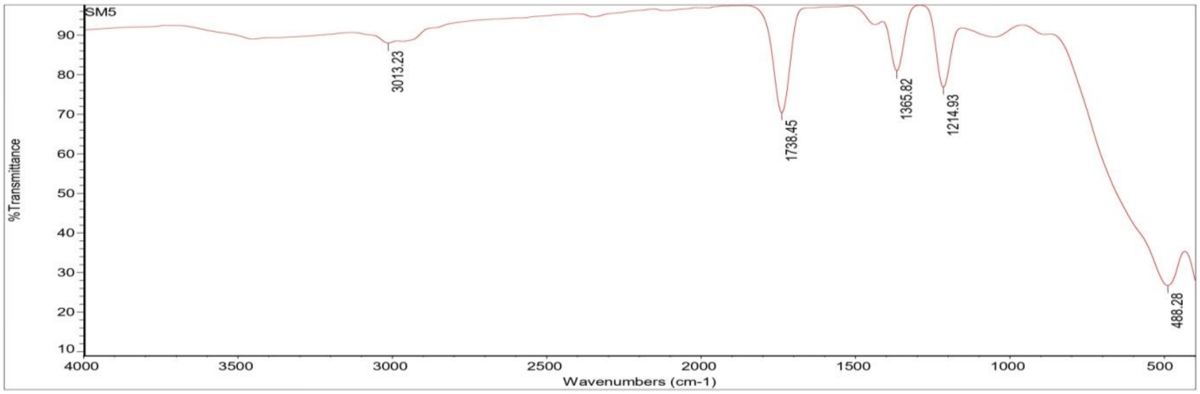

Fig.6. FTIR image of PVA capped Titanium dioxide nanoparticles

In FTIR (Fig. 6) analysis showed that synthesized PVA capped TiO$_2$ nanoparticles, with prominent peaks at 3451 cm^{-1}, 1738.45 cm^{-1}, 1365.82 cm^{-1}, 1214.93 cm^{-1}, and 488.28 cm^{-1}were obtained. The peak at 3451 cm^{-1} corresponds to the OH stretching vibrations. The peak at 3013.23 cm^{-1} may be associated with the stretching vibration of aromatic C-H bonds or possibly alkyne C-H bonds. The peak at 1738.45 cm^{-1} is often associated with the stretching vibration of carbonyl (C=O) groups, such as those found in aldehydes, ketones, esters, or carboxylic acids. The peak at 1365.82 cm^{-1} could correspond to the bending vibration of methyl (CH$_3$) or methylene (CH$_2$) groups, or it may be associated with the symmetric stretching vibration of COO- groups. The peak at 1214.93 cm^{-1} may be related to the stretching vibration of C-O bonds in alcohols, ethers, or esters. A broad absorption band at 488.28 cm^{-1} can be found in the FT-IR spectra of PVA capped TiO$_2$ nanoparticles, which can be ascribed to the vibration of Ti–O–Ti groups.

3.6. Antibacterial studies of PVA-capped Titanium oxide nanoparticles

Figure 8 shows the PVA capped Titanium oxide nanoparticles exhibit good antimicrobial activity against Pseudomonas aeruginosa, Bacillus subtilis, Staphylococcus aureus and Enterobacter spp. (Table 1). The maximum zone of inhibition was observed in 100 µL of PVA capped Titanium oxide nanoparticles against Pseudomonas aeruginosa (10mm), Bacillus subtilis(11.2mm), Staphylococcus aureus (13mm) and Enterobacter spp. (13.4mM) (Fig.7). Among the various nanoparticles, TiO$_2$ NPs are the most often studied for their photocatalytic antibacterial action, according to Colth up et al., 1950 [31]. Potential mechanisms involving interactions between nanoparticles and biological molecules have been proposed by Wiley et al., 2001 [32]. The electromagnetic response between the treated material surface and the microorganisms is caused by the negative charge of the microbes and the positive charge of the metal oxide nanoparticles. Once the electromagnetic reaction has been formed, the microbe is oxidized, which ultimately results in cell death. By inhibiting DNA replication and inactivating proteins, the interaction of nanoparticles with phosphorus- or sulfur-containing substances, such as DNA and thiol groups of proteins, might harm microbes [33]. They are the cause of the pits that develop in the walls of bacterial cells, which enhance cell permeability and cause cell death [34]. As a result, TiO$_2$ NPs' antibacterial effect has good potential for use as an antibacterial agent against microorganisms.

Table 1: Antibacterial studies of PVA-capped Titanium oxide nanoparticles

Microorganisms	Zone of inhibition (mm) crude extract				STD
	25µL	50µL	75µL	100µL	25µL
Pseudomonas aeruginosa	8.27±0.57	8.967±0.56	9.0±1.0	10.00±1.0	13.33±0.57
Bacillus subtilis	9.33±0.57	10±0.577	11±1.154	11.2±0.154	14±1.0
Enterobacter spp.	10.3±0.527	10.3±0.577	12.7±0.577	13.4±0.0.54	16.33±0.577
Staphylococcus aureus	9.0±1.00	10.6±0.57	11.0±0.10	13.00±0.5	14±1.0

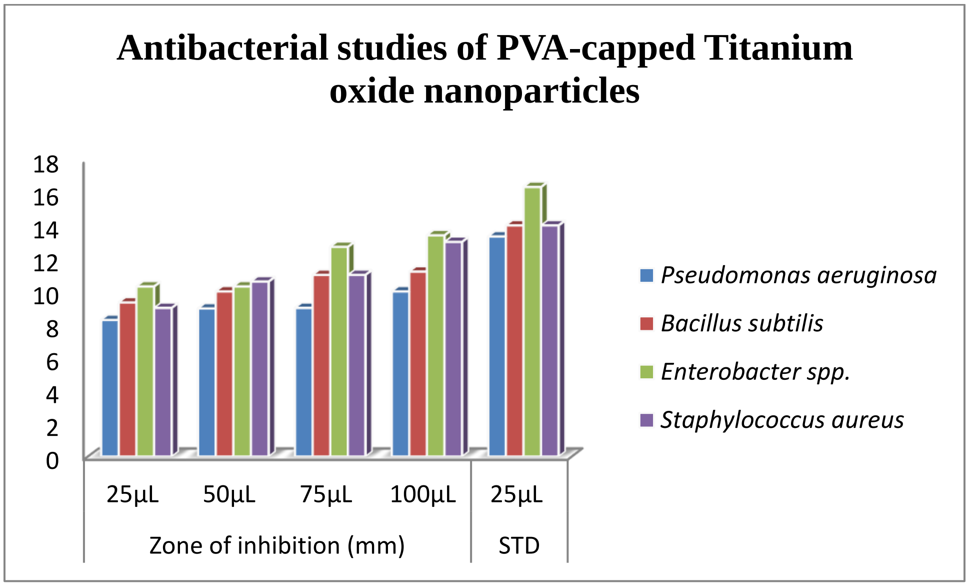

Fig.7. Antibacterial activity of PVA capped Titanium dioxide nanoparticles

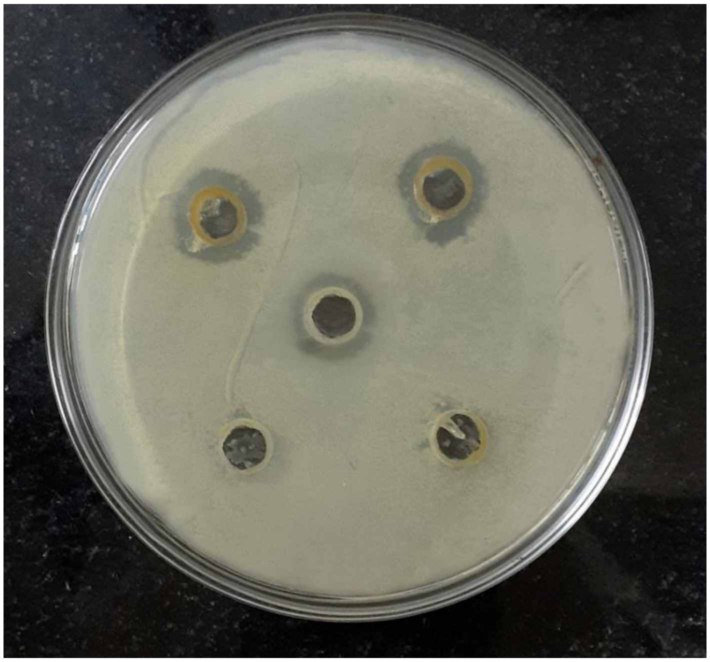

Fig.8. Antibacterial studies of PVA capped Titanium dioxide nanoparticles against Enterobacter spp.

4. Conclusion

In conclusion, we have demonstrated synthesis, characterization and antibacterial activities of polymer capped titanium dioxide nanoparticles. Polyvinyl alcohol is acted as surfactant. X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive

X (EDX), Atomic Force Microscopy (AFM), Fourier Transform Infrared (FTIR) and Transmission Electron Microscopy (TEM) were used to characterize the synthesized PVA capped titanium dioxide nanoparticles. The X-ray diffraction result revealed that the presence of rutile phase of TiO_2. SEM proved the spherical in shape and has a particle size of 25 to 50 nm, proving the importance of polymer capping in the size and morphology of titanium dioxide nanoparticles, which is consistent with the results from XRD.TEM analysis indicated that there are some shadows encircling the TiO_2 nanospheres, suggesting the presence of capped PVA. The PVA-capped titanium dioxide nanoparticles exhibit good accountability on the growth and destruction of infections, according to antibacterial investigations. In order to enable the use of TiO_2 nanoparticles in a range of industrial and medicinal applications, their antibacterial qualities are therefore frequently investigated in the future using different bacterial strains.

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