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Study on Photo-Catalytic and Antimicrobial Activity of Green Synthesized TiO_2 Nanoparticles Coated Vitrified Tiles

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ABSTRACT

In the current study, a facile and eco-friendly method has been developed for the synthesis of titanium dioxide nanoparticles from titanium isopropoxide solution using *Datura metel* (Vellai Umathai) leaves and orange peel extract. Silver nanoparticles (60 nm) and silver nanoplates (130 nm) have been synthesized and characterized using UV-visible spectroscopy, X-ray diffractometer (XRD), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The silver nanoparticles are doped with TiO_2 nanoparticles. The photocatalytic activity of Ag nanoparticles and nanoplates doped TiO_2 nanoparticles coated on vitrified tiles was investigated, wherein, degradation of methylene blue, rapidly on exposure to sunlight was observed. Analysis of the antimicrobial activity measured using colony forming units showed a 4-log reduction in the growth of the Gram-negative bacteria and a 5-log reduction in the growth of the Gram-positive bacteria.

1. Introduction

Biological synthesis of nanoparticles by plant extracts are at present gaining importance towards development of ecofriendly nanoparticle synthesis particularly for biomedical applications. Several plants including *Alfalfa*, *Aloe Vera*, *Cinnamum camphorra*, *Emblica officianalis*, *Carica papaya*, *Parthenium hysterophorus*, *Diopyros kaki*, Eucalyptus hybrid, *Hibiscus rosasinensis*, *Capsicum annum*, *Cissus quadrangularis*, *Pelargonium graveolens*, *Medicago sativa*, Lemongrass, *Capsicum annuum*, *Ocimum sanctum* and tamarind have been used in the efficient and rapid synthesis of silver and gold nanoparticles. The three chief parameters towards synthesis of ecofriendly and green chemistry nanoparticle synthesis, are the choice of solvent medium, the reducing agent and the Non-toxic material used for the stabilization of nanoparticles [1,2]. Among the various biosynthetic approaches, the use of plant extracts has numerous advantages including easy availability, safety of handling and the presence of various metabolites. Titanium dioxide nanoparticles (TiO_2 NPs), are amongst the most important material for cosmetic, pharmaceutical [3], skin care products, essentially towards protection of skin from UV rays, providing opacity to products such as paints, plastics, papers, inks, food colorants and toothpastes [4]. The titania nanoparticles also possess interesting optical, dielectric, antimicrobial, chemical stability and catalytic properties leading to its industrial applications as pigments, fillers, catalyst supports and as photocatalysts [5]. A growing concern recently is the development of increased microbial resistance to antibiotics and the development of resistant strains for which these nanoparticles can be investigated.

Among the major applications of the TiO_2 nanoparticles, are the degradation of chlorinated compounds like 2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol which are used as intermediates in the making of insecticides, herbicides, preservatives etc., which cause severe environmental pollution due to their mutagenicity and carcinogenicity [6,7]. Nanoparticulate TiO_2 as antibacterial coatings and wastewater disinfectants have been reported [8]. When silver is doped onto titania, it is deposited on the surface of the titania nanoparticles and not into the lattice structure of the photocatalyst. In this study, the green synthesized TiO_2 coated on vitrified tiles were evaluated for its photocatalytic and antimicrobial activity. The photocatalytic activity of TiO_2 coated surfaces was evaluated by measuring the degradation rate of methylene blue (MB) under UV and sunlight. The antibacterial activity was evaluated using the Gram-Negative *Escherichia coli* (*E. coli*) and Gram-Positive *Lactobacillus plantarum* bacterial strains. The obtained results indicate that TiO_2-coated surfaces show strong antibacterial activity suitable for industrial applications.

2. Experimental Methods

2.1 Materials

Leaves of *Datura metel* were collected from Taramani, Chennai. Fruit extracts were collected without any impurities. Titanium tetra-isopropoxide was purchased from Avra Synthesis Pvt. Ltd, Chennai, India.

2.2 Synthesis of TiO_2 Nanoparticles

Freshly collected leaves of *Datura metel* (10 g) were used to prepare the aqueous leaf extract, 50 g orange peel were boiled with 150 mL distilled water for 1 hour to prepare the orange peel extract, and both were stored for nanoparticle synthesis. 15 mL of solution containing 5 mL of titanium tetra-isopropoxide (TTIP) and 15 mL isopropanol were made to react with 100 mL water. To this reaction mixture 2 mL aqueous leaf extract of *Datura metel* (Vellai Umathai) was added and the pH was adjusted to 4.5 using orange peel extract. The reaction mixture was subjected to continuous stirring at 60 °C for 4 hours. There was a colour change to yellowish brown. The precipitate was collected by centrifugation and washed with distilled water, and then heated at 90 °C on a hot plate to collect the dried powder which was brown in colour.

2.2.1 Synthesis of Silver Nanoparticles (Ag-NPs)

Briefly, 2 g glucose and 1 g PVP were dissolved in 40 g water and heated to 90 °C. Then 0.5 g $AgNO_3$ dissolved in 1 mL water was added. The dispersion was kept at 90 °C for 1 h and then let to cool to room temperature. The particles were collected by ultracentrifugation (29.400 g; 30 min), redispersed in pure water and collected again by ultracentrifugation leading to the removal of NO^{3-}, excess glucose and its oxidation products, excess PVP, and excess Ag^{+}.

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2.2.2 Synthesis of Silver Nanoplates (Ag-NPLs)

The procedure for the synthesis of silver seed hydrosol is as follows: 0.5 mL of 1.0 M $AgNO_3$ solution and 2 mL of 4 M PVP solution were added to 17.5 mL distilled water under ice cold condition for 15 min. Then 0.3 mL of ice cold aqueous $NaBH_4$ solution was added all at once with vigorous stirring and the stirring was continued for 45 sec. The resulting mixture was heated at 75–80 °C for 10 min to decompose excess $NaBH_4$ present in the solution. The growth solution containing aqueous solution of 0.5 mL $AgNO_3$, 10 mL PVP and 0.2 mL of trisodium citrate solution were prepared in a 25 mL conical flask. Next, different volumes of seed solution were added to this growth solution under stirring for 10 min for good mixing. These solutions were then stored in the darkroom at Room temperature for 24 h.

2.2.3 Coating of Doped TiO_2 Nanoparticles on Tiles

The as-synthesized TiO_2 nanoparticles were mixed with 2 mL of solution containing silver nanoparticle and nanoplates. The coating technique was adapted from the experimental guidance of Zan et al. [9]. Briefly, 2 wt.% TiO_2 was mixed with aqueous solution of polyvinyl alcohol, and sonicated using ultrasound to form a poly-disperse suspension. Vitrified tiles were cut in 30 cm x 22 cm (for measurement of photocatalytic activity) and 2 cm × 2 cm (for antimicrobial activity) dimensions and were sterilized by autoclaving, wiping with alcohol and were subjected to UV exposure for 30 minutes. This was followed by a single Dip-coating procedure and the coated tiles were air-dried for 24 hours, followed by calcination at 800 °C for 1 hour. Thus, the coated tiles were used for further studies.

E. coli (Gram negative) and *Lactobacillus plantarum* (Gram positive) were used to assess the antibacterial potential of the green synthesized TiO_2 nanoparticles. Towards this the TiO_2 nanoparticle coated vitrified tiles and the uncoated tiles were covered with sterile aluminium foil and parafilm on all other sides except the smooth surface, and were sterilized under UV light for 30 minutes. The bacterial cell viability assay was performed by suspending 100 µL per mL of 0.5 Mc Farland constant bacterial culture on 1 mL nutrient broth which was layered on the Tiles and kept under sunlight for 4 hours, and then incubated at 37 °C for 12 hours which was followed by plating on to agar plates.

3. Results and Discussion

3.1 UV-Visible Spectroscopy

The green synthesized TiO_2 nanoparticles were analyzed using UV-visible optical spectroscopy. The absorption spectrum shows the characteristic peak of TiO_2 at 371 nm (Fig. 1). The band gap was calculated by fitting the data using the equation $\alpha h\nu = E_d(h\nu - E_g)$, where, hν= photon energy, α = energy the absorption coefficient, E_d = absorption edge width parameter, E_g = band gap and it was found to be 3.34 eV.

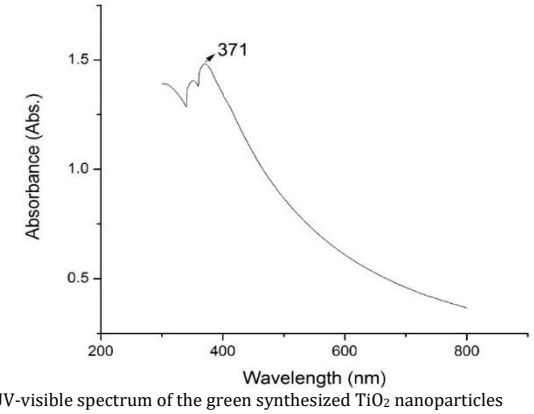

Fig. 1 UV-visible spectrum of the green synthesized TiO_2 nanoparticles

3.2 X-Ray Diffraction Analysis

The XRD pattern reflects the shape of the wave functions of the electronic states of the Ti-O-Ti-O chain on the TiO_2/H_2O interface. XRD analysis showed three distinct diffraction peaks at, 53.2°, 61.8°, 66.5° which is indexed for the planes (101), (004), (200), respectively of the cubic face centered titanium dioxide. There was a change in the crystalline structure of the nanoparticles changing from rutile before heating (Fig. 2a) to anatase after heating (Fig. 2b) [10]. The absence of identified peaks after heating confirms the crystallinity and higher purity of the synthesized nanoparticles. The average crystallite size of the nanoparticles was calculated using the Scherrer's formula, $D = k\lambda / \beta Cos\theta$, where D (nm) is the average crystallite size perpendicular to the reflecting planes, k is the constant which equals to 0.91, λ is the X-ray wavelength; β is the full-width at half maximum (FWHM) and θ is the diffraction angle. The average crystallite sizes of the synthesized nanoparticles were calculated to be 80 nm before heating (Fig. 2a) and 20 nm after heating (Fig. 2b).

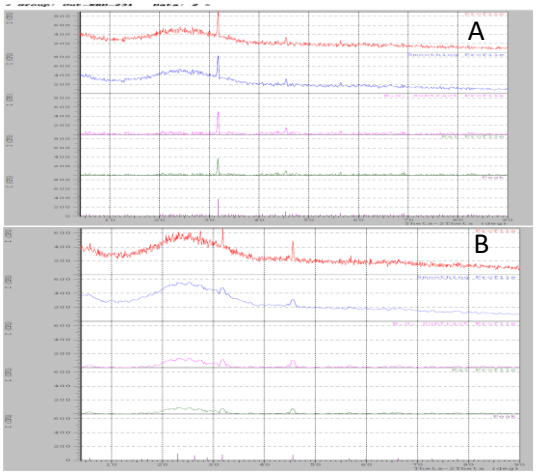

Fig. 2 XRD for synthesized TiO_2 nanoparticles a) Before heating and b) After heating)

3.3 FESEM Analysis of Green Synthesized TiO_2 Coated Vitrified Tiles

FESEM images of the synthesized nanoparticles were measured and topographically analyzed. They were observed to be morphologically smooth and spherical with a size of 40 nm (Fig. 3).

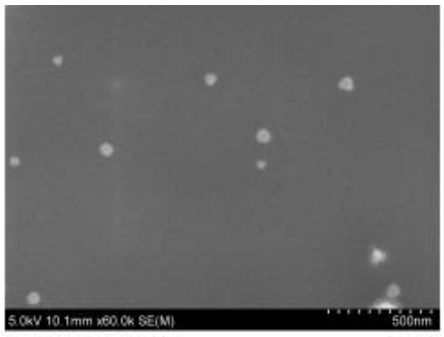

Fig. 3 FESEM image of the synthesized TiO_2 nanoparticles

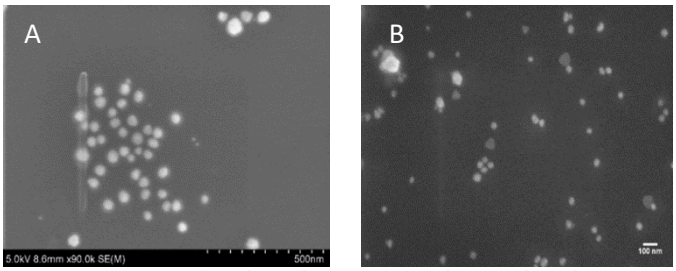

Fig. 4 FESEM images of synthesized TiO_2 nanoparticles coated in tile a) Before calcination and b) after calcination

The FESEM images of the synthesized TiO_2 nanoparticles coated on vitrified tiles before and after calcination are shown in Fig. 4. The green synthesized TiO_2 nanoparticles coated on vitrified tiles show that the synthesized nanoparticles are highly mono dispersed particles and spherical shaped with particle size of 80-100 nm before calcination which reduced to around 15-20 nm after calcination in comparison to the size of the nanoparticle of 40 nm, which is in line with the results from XRD, confirming the role of *Datura metel* extract to change the size and morphology of the synthesized TiO_2 nanoparticles.

3.4 Surface Analysis of The Green Synthesized TiO_2 Coated Tiles

Figs. 5a-d show the surface topography and roughness of the TiO_2 nanoparticle coated tiles before and after heat treatment. As can be seen from the AFM images, the surface roughness of the TiO2 coated tiles have drastically decreased after heat treatment. The Fig. 5a shows surface topography of the tiles coated with TiO_2 before heat treatment which shows high surface roughness, whereas the surface of the tiles is relatively smooth after heat treatment as can be seen from the Fig. 5b.

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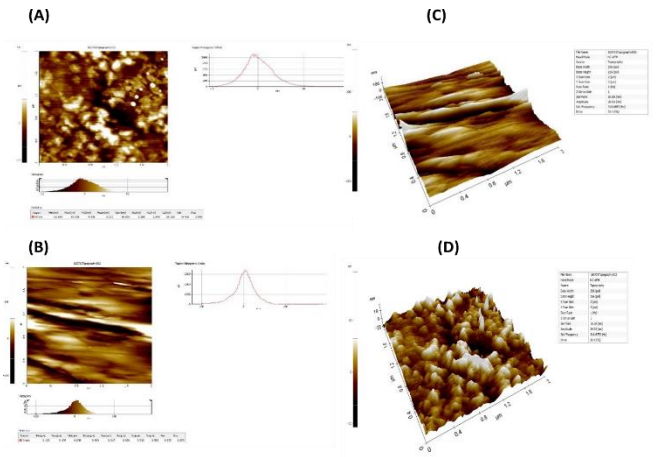

Fig. 5 Atomic force microscopy images of TiO_2 coated tiles a) roughness 2-D plot of TiO_2 coated tile before heating, b) roughness 2-D plot of TiO_2 coated tile after heating, c) 3-D plot of TiO_2 coated tile before heating and d) 3-D plot of TiO_2 coated tile after heating

3.5 Photocatalytic Degradation

3.5.1 Optimization of the Concentration of Ag-NPs and Ag-NPLs as Dopants of the Green Synthesized TiO_2 Nanoparticles

The optimization of the concentration of the Ag-NPs and Ag-NPLs to act as dopants of the green synthesized TiO_2 nanoparticles was performed by measuring the ratio of Co (Initial concentration of methylene blue at time = 0) and C (concentration of methylene blue at time = t) under UV light. Plotting of C/Co vs Time showed the optimum concentration of 1.5 mol.% for both the Ag-NPs (Fig. 6) and the Ag-NPLs (Fig. 7).

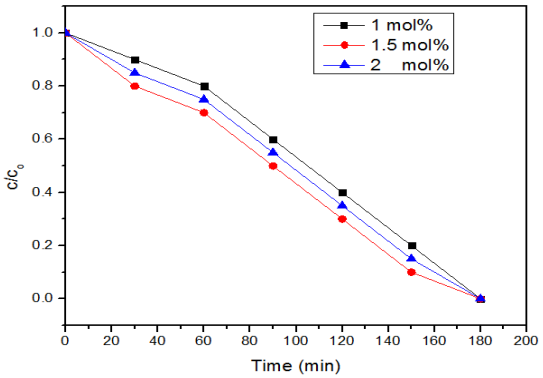

Fig. 6 Degradation of methylene blue at 1,1.5, 2 mol.% concentrations of Ag-NPs as dopant on the green synthesized TiO_2 NPs under ultraviolet rays

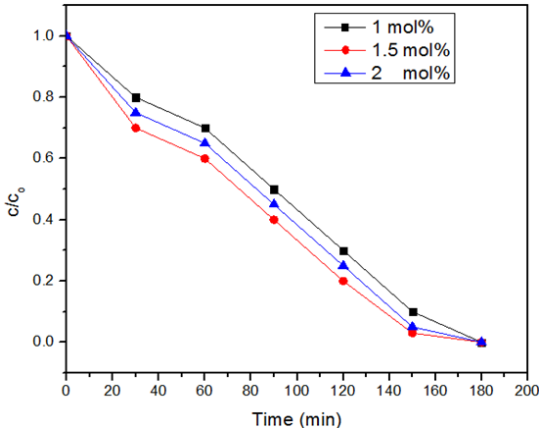

Fig. 7 Degradation of methylene blue at 1,1.5, 2 mol.% concentrations of Ag-NPLs as dopant on the green synthesized TiO_2 NPs under ultraviolet rays

3.6.2 Photocatalytic Degradation of Methylene Blue under UV and Sunlight

The photocatalytic degradation of methylene blue by the green synthesized TiO_2 doped with 1.5 mol.% of Ag-NPs and Ag-NPLs was studied under UV light and sunlight. Under UV radiation, an increased degradation of methylene blue was observed with the Ag-NPs and Ag-NPLs doped TiO_2 in comparison to the undoped TiO_2 (Fig. 8).

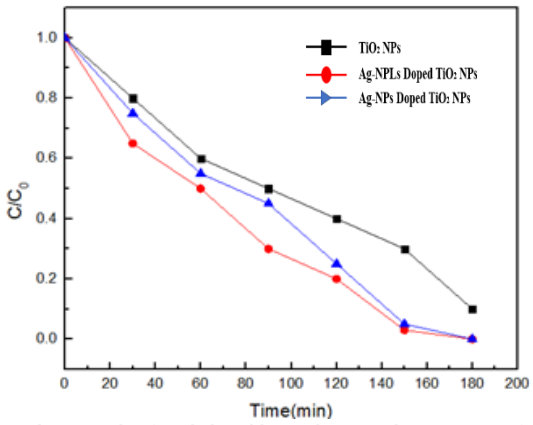

Fig. 8 Degradation study of Methylene blue under UV radiation using 1.5 mol.% of Ag-NPs and Ag-NPLs doped TiO_2 nanoparticles

A similar degradation of methylene blue by the Ag-NPs and Ag-NPLs doped green synthesized TiO_2 was observed under visible light. In contrast, the undoped TiO_2 showed very slight degradation of methylene blue (Fig. 9).

Interestingly, in both the studies the Ag-NPLs doped TiO_2 appeared to exhibit better photocatalytic activity compared to the Ag-NPs doped TiO_2. This could be due to the larger size and the related optical properties of Ag-NPLs.

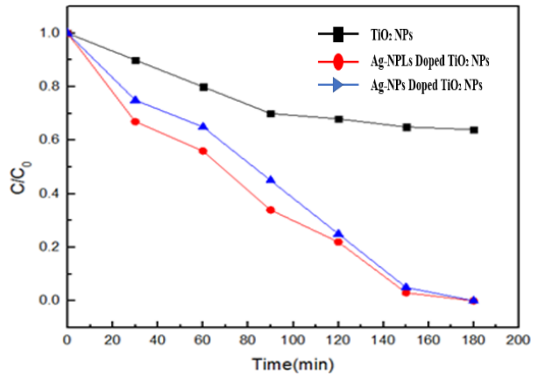

Fig. 9 Degradation study of methylene blue under sunlight using 1.5 mol.% of Ag-NPs and Ag-NPLs doped TiO_2 nanoparticles

These results confirm that the undoped and the Ag-NPs and Ag-NPLs doped TiO_2 act as a photocatalyst under UV irradiation. However, under the sunlight the Ag-NPs and Ag-NPLs doped green synthesized TiO_2 showed better degradation of methylene blue compared to the undoped TiO_2 [11,12].

3.6 Antibacterial Activity of Green Synthesized TiO_2 Nanoparticles

The antibacterial potential of the green synthesized TiO_2 nanoparticles coated on vitrified tiles were analyzed using the Gram negative *E.Coli* and the Gram positive organism *Lactobacillus plantarum* by comparing the number of colonies formed in the control tile and the green synthesized TiO_2 coated tile. The formation of colonies was studied by measuring the colony forming units (CFUs) [13,14]. For gram negative *E. coli, t*he TiO_2 coated tile showed 4-log reductions in the formation of the colonies in comparison to control (Figs. 10 and 11).

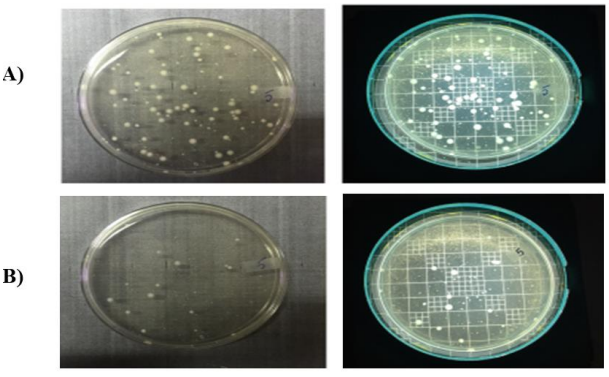

Fig. 10 The dark and light background picture of the colonies formed at a 10^{-5} dilution of both a) control and b) TiO_2 treated culture

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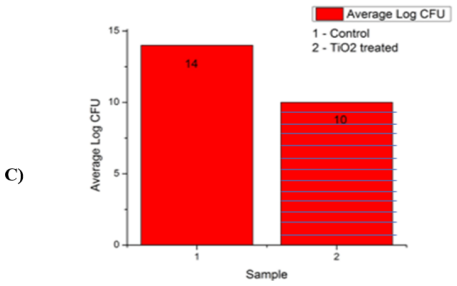

Fig. 11 Log CFU of control (*E.coli*) and TiO_2 treated *E.Coli*

3.6.2 Gram Positive- Lactobacillus plantarum

Analysis of the effect of the green synthesized TiO_2 coated tile on the formation of colonies was studied by measuring the CFUs. The TiO_2 coated tile showed 5-log reductions in the formation of the colonies in comparison to control (Figs. 12 and 13).

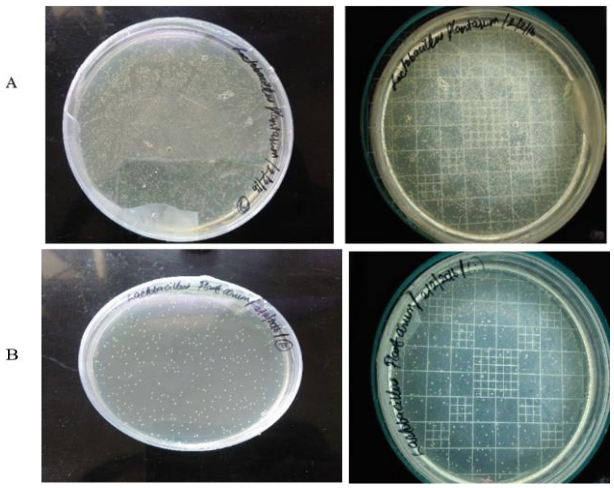

Fig. 12 The dark and light background picture of colony formed in 10^{-5} dilution of both a) control and b) TiO_2 treated culture, there is a fivefold reduction in the number of colonies formed

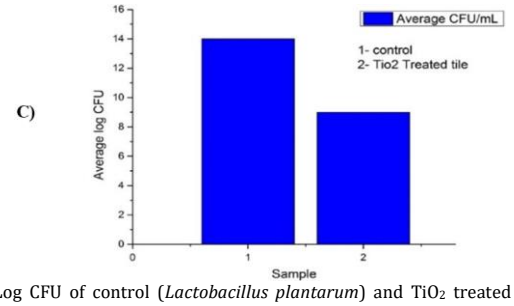

Fig. 13 Log CFU of control (*Lactobacillus plantarum*) and TiO_2 treated microbial cultures

4. Conclusion

The silver nanoparticles/nanoplates coated TiO_2 have been synthesized characterized for their morphology, structural and antibacterial activities. The nanoparticles were coated onto vitrified tiles and the photocatalytic activity and antibacterial effect evaluated. The photocatalytic dye degradation experiments showed a higher activity with Ag-NPs and Ag-NPLs doped TiO_2 nanoparticles coated tile samples. Moreover, the results obtained with TiO_2 coated vitrified tiles highlighted the antibacterial effect of TiO_2. The results obtained indicate that the TiO_2-coated surfaces show antibacterial activity highlighting that the titania could be used in the ceramic and building industry for the fabrication of coated surfaces to be placed in microbiologically sensitive environments, such as the hospital and food industry.

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