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Synthesis of TiO_2-Ag Nanocomposites via Green Route for Dye Degradation and Antimicrobial Studies

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Abstract: ***Synthesis of nanocomposites through green synthesis offers a few advantages over the chemical and physical procedures as it an easy, fast and eco-friendly alternative that does not involve hazardous chemicals. In this work, we report the green synthesis of TiO_2-Ag nanocomposites using titanium tetra isopropoxide (TTIP) and silver nitrate ($AgNO_3$) as precursors, Aloe veraplant extract as reducing agent. The characterization of nanocomposites is done by X-ray powder diffraction (XRD), UV-Visible spectroscopy, Scanning electronic microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Electrocatalytic activity of these nanocomposites was examined by degradation of crystal violet dye using potentiostat. The antimicrobial activity was tested against both gram positive and gram negative bacteria viz. Bacillus subtitles and Escherichia coli respectively. Green synthesized TiO_2-Ag nanocomposites were of anatase phase of TiO_2 and average crystallite size was 7.06±3.2 nm. Complete decolourization of crystal violet dye was achieved in 8 h of electrolysis using TiO_2-Ag nanocomposites. Further antimicrobial activity of TiO_2-Ag nanocomposites is studied. The diameter of inhibition zone for gram positive Bacillus subtilis and gram negative Escherichia coli is 13 mm and 21 mm respectively. The nanocomposites exhibited greater antimicrobial activity against the gram negative bacteria Escherichia coli. The green TiO_2-Ag nanocomposites showed effective electro-catalytic and antimicrobial activity by degrading the dye and inhibiting the bacterial growth respectively.***
Key words: TiO_2-Ag, nanocomposites, green synthesis, dye degradation, antimicrobial, gram positive, gram negative

I. INTRODUCTION

The textile industries have a high environmental impact, due to the release of large volumes of wastewater that contain high organic content and strong color adding agents. To avoid the dangerous accumulation of dyes in the aquatic environment, present research efforts to develop nanoparticles for their removal in industrial wastewaters [1]. Generally titanium dioxide nanoparticles are used for dye degradation. Titanium dioxide nanoparticles have hydrophobicity, non-toxic, catalyst and large band gap properties [2]. Since ancient times silver has been known for improving immunity in human beings. Silver nanoparticles have attracted great attention due to their unusual optical, chemical, magnetic, electronic, catalyst and antibacterial properties [3]. The noble metal nanoparticles have good dispersity on the particles of the TiO_2 support, resulting in excellent catalytic activities [4]. Further TiO_2 support enhances the antibacterial effect of silver nanoparticles. In the present study plant extract is used for synthesizing TiO_2-Ag nanocomposites to enhance both catalytic properties (principally for dye degradation) and anti microbial properties. Green synthesis is eco friendly; the product has fewer side effects when used for biomedical uses, low cost and can be used for various applications.

II. EXPERIMENT

A. Materials

Fresh and healthy Aloe Vera (Aloe barbadensis mill) plants were collected from the garden in Department of Chemical Engineering, JNTUA College ofEngineering, Ananthapuramu, Andhra Pradesh. Titanium tetra isopropoxide (TTIP), Silver nitrate ($AgNO_3$), Sodiumsulphate (Na_2SO_4),and Crystal violet dyewere purchased from Sigma Aldrich Chemicals (India) Ltd and are AR grade. Agar-Agar and Peptone were purchased from S D Fine- Chem Limited (India), Sodium chloride (NaCl, 99% pure) and Beef extract were purchased from Molychem (India).Nafion (10%) liquid solution is purchased from Dupont Chemicals, USA. Double distilled water was used throughout the experiments. All chemicals were used without any further purification.

B. Characterizations

X-ray diffraction (XRD) analysis of TiO_2-Ag powder was carried out by a WRD PANalytical "XPERT 3 PRO", employing Cu-Kα radiation of wavelength 0.154 Å. Scanning electron microscopy (SEM) was performed at 15 kV. A Systronics PC-based double

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beam UV-Vis spectrophotometer (type: 2201)was used to generate the spectrum for the scan range 190-1000 nm. Fourier Transform Infrared Spectroscopy (FTIR) was conducted to identify the functional groups.

C. Synthesis of TiO_2-Ag Nanocomposites

Precursor solution was prepared by continuous stirring of 5 ml of TTIP and 50 ml of ethanol for 1 hr. To this 1 mM $AgNO_3$ solution with 30 ml of *Aloe vera* extract was added dropwise under continuous stirring for 1 h. The solution obtained was drayed initially at 110 ºC for 1 h and later at 200 ºC for the same time period, followed by calcination at 500 ºC for 1 h. Finally, particles obtained were ground to fine powder by using a mortar and pestle [5].

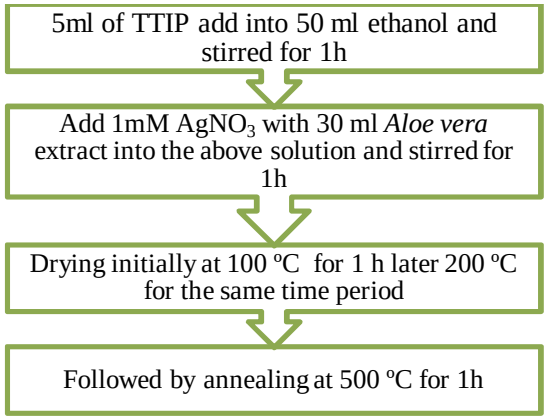


Fig 1: Flow chat of TiO_2-Ag nanocomposites synthesis

D. Electrochemical Analysis

Cyclic voltammetry (CV) experiments were carried out at room temperature using Potentiostat (K-lyte 1.0). The cell used for voltammetric experiments was the three-electrode type (fig 2) Ag/AgCl as a reference electrode, Pt mesh as a counter electrode, and bare Ti and Ti/TiO_2-Ag as working electrodes. 55mg/L of crystal violet dye is chosen as electrolyte solution along with 1M Na_2SO_4 as supporting electrolyte. Chronoamperometric studies were performed at different fixed voltagesat a scan rate of 0.05 V/s. The fixed voltages were obtained from initial CV graph, where the first oxidation peak rises duringthe forward scan at 0.6 V and at 1.1 V for bare Ti and Ti/TiO_2-Ag respectively. UV-Vis spectrophotometer was used to measure the decolorization efficiency at different time intervals and is calculated by the using the formula.% decolorisation = $(A_0 - A) / A_0 \times 100$, where A_0 and A are the absorbances(at the maximum wavelength, λ_{max}) of dye solution before/initial (at $t = 0$) and after electrochemical treatment (at $t > 0$) [6].

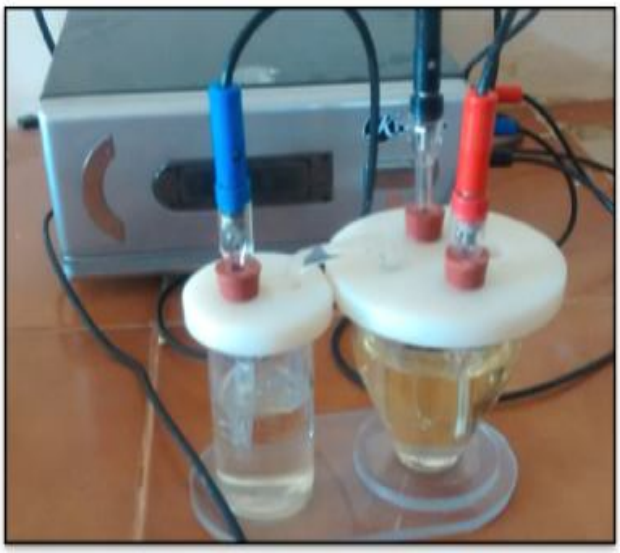


Fig 2: Potentiostat

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E. Antimicrobial Studies

Escherichia coli (E.coli) and *Bacillus subtilis (B. subtilis)* bacteria were cultivated in Luria Bertani (LB) medium. First LB medium was prepared by using three compounds that are 5 g L^{-1}NaCl, 5 g L^{-1} peptone, and 1.5 g L^{-1} beef extract (fig 3). For 100 ml of LB medium, 0.5g of NaCl, 0.5 g of peptone, and 0.15 g of beef extract were dissolved in 100 ml distilled water then the solution was autoclaved at 121 ºC for 20 min. After cooling the solution was inoculated. To cultivate the bacteria, solution was put into the orbital shaker at 38 ºC (room temperature) for 8 h. After orbital shaking solution density increased, this indicated the bacterial growth in the LB medium. This LB medium was stored in refrigerator at 4 ºC for further use. Nutrient medium was prepared using 5 g L^{-1}NaCl, 5 g L^{-1} peptone, 50 g L^{-1} agar-agar, and 1.5 g L^{-1} beef extract. For 200 ml of nutrient medium 10 g agar-agar, 1 g NaCl, 1 g peptone, 0.3 g beef extract were dissolved in 200 ml double distilled water. The solution was autoclaved at 121ºC for 20 min. Before reaching 45 ºC, the solution was poured into petri dishes and left for solidification in a UV laminar chamber. After solidification, the nutrient media was inoculated with bacterial culture and incubated for 48 h for bacterial growth. These petri dishes containing bacterial colonies were subjected to antimicrobial test studies (fig 4). 2 mg of Penicillin was dissolved in 5 ml of water; in this solution two 6 mm What man paper discs were immersed. Similarly two more discs were immersed in TiO_2-Ag nanocomposites dissolved in 5 ml of ethanol. After some time (around 7 min) the discs were dried naturally, and then placed in petri dishes containing bacterial colonies. These petri dishes were incubated at 38ºC for 48 h. The antimicrobial activity was assessed by observing and measuring inhibition zones formed around the discs after incubation period.

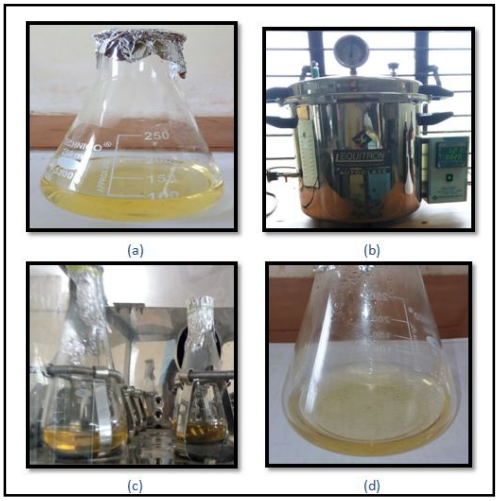


Fig 3: (a) LB medium before autoclaving, (b) Autoclaving of LB medium, (c) After bacterial inoculation placed in an orbital shaker for 8h (d) After orbital shaker LB medium showing bacterial growth.

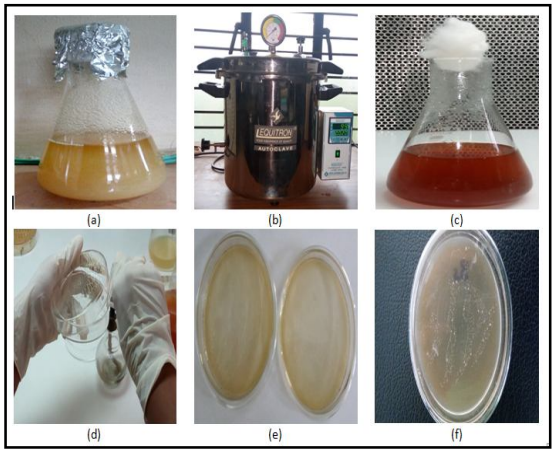


Fig 4: (a) Nutrient medium before autoclaving, (b) Autoclaving of nutrient medium, (c) Nutrient medium after autoclaving, (d) Nutrient medium poured into Petri dishes, (e) Solidification of the nutrient medium after pouring, and (f) Bacterial colonies after 48 h of inoculation.

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III. RESULTS & DISCUSSIONS

A. XRD Analysis

The crystalline nature of synthesized nanocomposites was identified using X-ray diffractogram (XRD) pattern (fig. 5).The diffractogram pattern was indexed properly for all crystalline peaks and compared with JCPDS data file. Figure (5) shows the major peaks at 2θ values of 25.36°, 38.01°, 47.98°, 54.76° which corresponds to the planes of (101), (004), (200), and (211) of tetragonal anatase TiO_2 (JCPDS Card No. 21-1272) [7],[8]. The peaks at 2θ values of 37.26°, 44.76°, 64.85° correspond to the planes of (111), (200), and (220) of face-centered cubic Ag (JCPDS card no. 04-0783) [9],[10]. The averagecrystallite size of TiO_2-Ag nanocomposites was estimated to be 7.06±3.2 nm from Debye-Scherer formula. The composite showed crystalline phase peaks of both TiO_2 & Ag and hence confirms the composite formation.

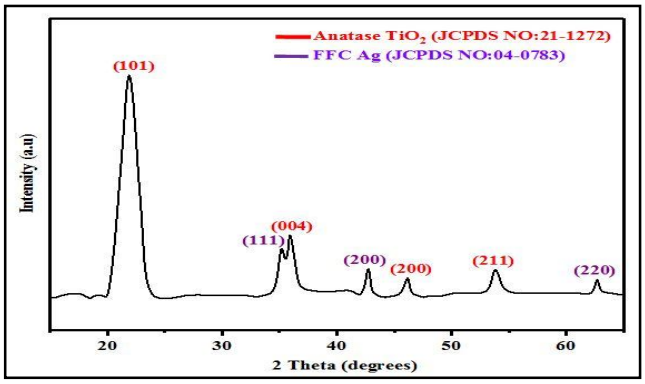


Fig 5: XRD analyses of TiO_2-Ag nanocomposites

B. FTIR Spectroscopy

FTIR analysis was performed to identify functional groups on surface of nanomaterials (fig6). The broad peak at 500-900 cm^{-1} corresponds to the Ti-O-Ti stretching vibrations, whereas the peak at 1384 cm^{-1} indicates vibrations of the Ti Ligands, peak at 1633 cm^{-1} O-H bonds in water, peak at 3450 cm^{-1} stretching vibrations of hydroxyl groups of Ti-OH on the surface. Further, the peak at 3884 cm^{-1} attributes to the –OH stretching vibrations of alcohol [11], [12].

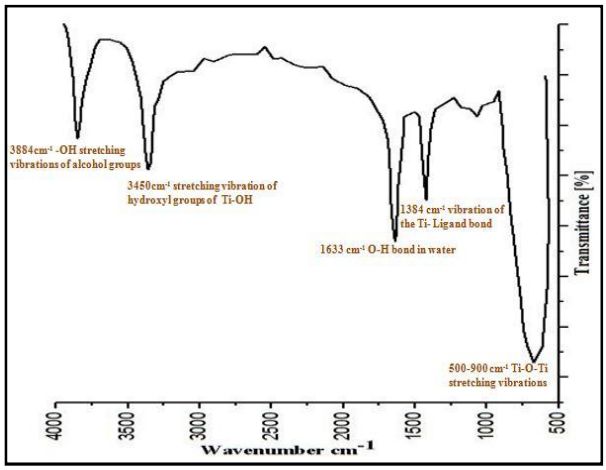


Fig 6: FTIR analyses of TiO_2-Ag nanocomposite

C. SEM Analysis

The particle size, shape and surface morphology characteristics of synthesized samples can be obtained from scanning electron microscopy (SEM). Figure (7) shows the image of TiO_2-Ag nanocomposites within the magnification of 1 µm. The TiO_2-Ag nanocomposites contain irregularly shaped particles which may be due to the aggregation of tiny crystals [5]. The particle size ranged from 47.7 to 101 nm.

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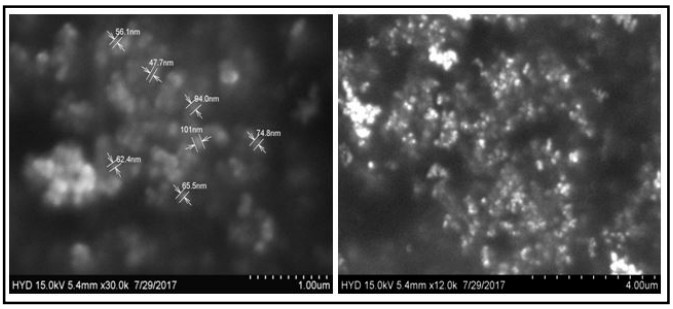


Fig 7: SEM analyses of TiO_2-Ag nanocomposites

D. UV-Vis Spectroscopy

UV-Vis spectrometer was used to measure the optical properties of nanoparticles. Figure (8) shows the UV-Visible spectrum of TiO_2-Ag nanocomposites. Because of surface plasmon resonance TiO_2 nanoparticles have an absorbance at 380 nm and Ag nanoparticles at 603 nm. Both nanoparticles exhibit absorbancein the visible region. Hence this nanocomposite works in the visible region for antimicrobial studies [11].

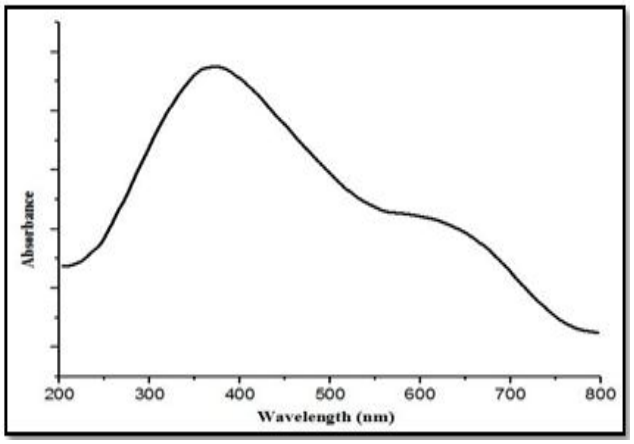


Fig 8: UV-Vis spectrum analyses of TiO_2-Ag nanocomposites

E. Dye Degradation

1)Cyclic Voltammetric Studies: Cyclic Voltammetry (CV) studies are used to determine the rate of dye degradation before and after electrochemical treatment. During forward scan of the cyclic voltammetry, anodic (Oxidation) peaks were observed at positive currents; in reverse scan cathodic (Reduction) peaks were observed at negative currents. Oxidation peak indicates the presence of complex/reactive groups in dye molecules. The high peak current in initial CV indicates the presence of more number of reactive groups in dye molecules that leads to the higher oxidation of groups. To degrade these complex/reactive groups in crystal violet dye, potential (V) is applied on electrode that was chosen based on cyclic voltammetry (CV) curves.

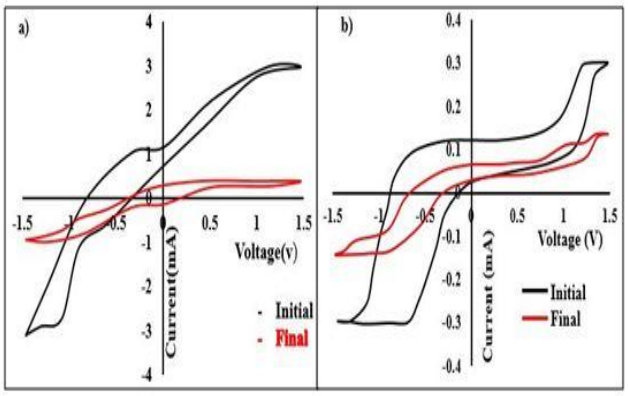


Fig 9: Voltammetric plots of crystal violet for dye degradation using (a) Bare Ti and (b) TiO_2-Ag@Ti.

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Cyclic voltammetry plots correspond to working electrode of bare Ti and modified electrode of Ti/TiO_2-Ag are shown in fig9(a and b). Dye degradation experiments were performed using Potentiostat. Potentiostat consists of three electrodes namely; the working electrode (anode) is fabricated electrodes, reference electrode is Ag/AgCl, and counter electrode (cathode) is Platinum mesh. Crystal violet dye (55 mg/L) dissolved in 1M Na_2SO_4 solution is the electrolyte. The extent of dye degradation was explained with CV plots before (at t=0) and after electrolysis treatment (at t>0) of crystal violet dye. The cathodic and anodic peak currents originated are observed to have reduced with the time of electrolysis. The decrease in peak currents of crystal violet certified to the oxidation of dye. Moreover, this information is very much important to assess the achievability of the electrochemical process for the degradation of crystal violet dye. The oxidation current in CV curve represents the oxidation of dye molecules. The best performance of prepared electrodes was shown by the Ti/TiO_2-Ag nanocomposites compared to bare TiO_2. The TiO_2-Ag nanocomposites contribute a free path to electrons in enhancing the conductivity leading to quick oxygen evolution [13].

2) UV-Vis Spectroscopy Analysis: During the electrochemical decolourization process, the change in absorbance characteristics of the crystal violet dye was observed at different intervals of time using UV-Vis absorption spectra analysis. The spectrum of crystal violet dye shows a maximum absorbance at 576 nm in the visible region representing the presence of methyl groups which is accountable for strong color of crystal violet dye. The absorption spectra were generated for various samples collected at different times during electrochemical treatment [14]. Decolourization curve of bare Ti is shown in figure (10 a), and that of TiO_2-Ag@Ti shown in figure (10b). Complete decolorization was achieved within 14 hours for Ti, and 8 hours for TiO_2-Ag. TiO_2-Ag nanocomposites showed a faster rate of decolorization as Ag nanoparticles have dispersity on the particles of the TiO_2 support which reduces the band gap of TiO_2 nanoparticles and hence facilitates free electron path [15]. Further, the large surface area of the nanocomposites accommodates a number of dye molecules to interact with oxidants. Therefore, TiO_2-Ag nanocomposites increase the catalytic performance and increase the rate of crystal violet dye degradation.

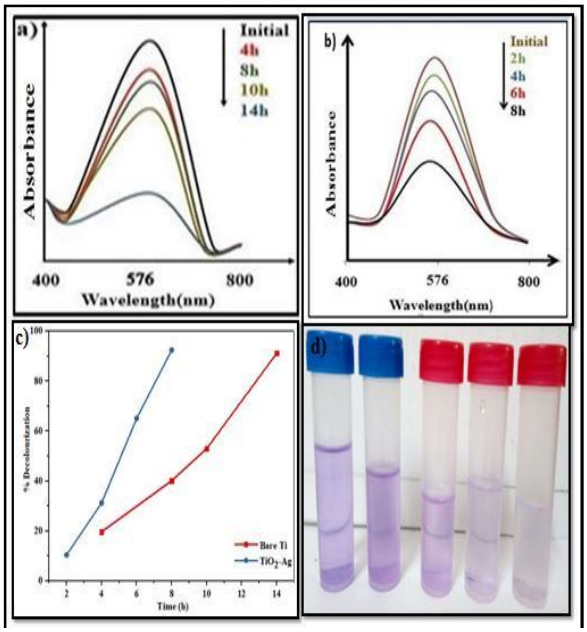


Fig 10: Absorbance V/s wavelength (nm) for (a) Bare Ti, and (b)TiO_2-Ag@Ti (c) % Decolourisation V/s time for Bare Ti and Ti/TiO_2-Ag (d) crystal violet dye at different intervals.

F. Antimicrobial Activity

The antimicrobial property of TiO_2-Ag nanocomposites was evaluated against gram-positive bacteria *Bacillus subtilis (B. subtilis)* and gram-negative bacteria *Escherichia coli (E. coli)* by using disc diffusion method. In this method inhibitory activity was measured based on the diameter of the clear inhibition zone. If there was no surrounding clear zone, it was assumed that there was no inhibitory zone [16]. The antimicrobial activity was assessed by observing and measuring inhibition zones formed around the discs after incubation period. The zone of inhibition around Penicillin and TiO_2-Ag nanocomposite discs are shown in fig (11) while numerical value of the diameter of inhibition zones was compiled in fig (12).

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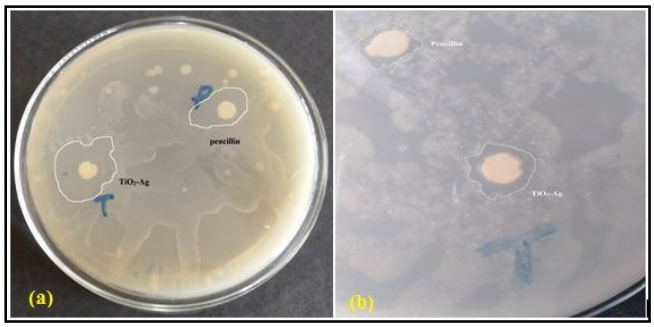


Fig 11: Antimicrobial activity assay of penicillin and TiO_2-Ag nanocomposites on (a) *B. subtilis* and (b) *E. coli*.

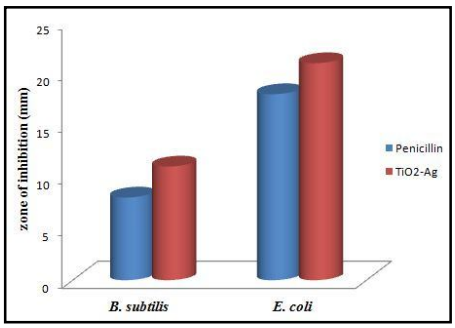


Fig 12: Graphical representation of antimicrobial activity

It is noticed from the results that the diameter of inhibition zone is higher for gram negative bacteria *Escherichia coli*(21 mm) than that of gram positive bacteria Bacillus subtilis (13 mm). This may be due to the difference in the compositions of thecell membranes [17].

IV. CONCLUSIONS

The TiO_2-Ag nanocomposites were successfully synthesized via green route from Aloe vera plant extract. The green synthesized nanocomposites have average particle size ranging from 47.4 to 101 nm. Average crystallite size was calculated as 7.06 ± 3.2 nm. Surface plasmonresonance of the TiO_2 and Ag nanoparticles was at 380 nm and 603 nm respectively. Ti functional groups were identified with the help of FTIR. In electrochemical dye degradation TiO_2-Ag nanocomposites enhanced the electrocatalytic performance compared to bare Ti.The antimicrobial studies showed that nanocomposites inhibited the gram-negative bacteria (Escherichia coli) more than that of gram-positivebacteria (Bacillus subtilis).

V. ACKNOWLEDGMENT

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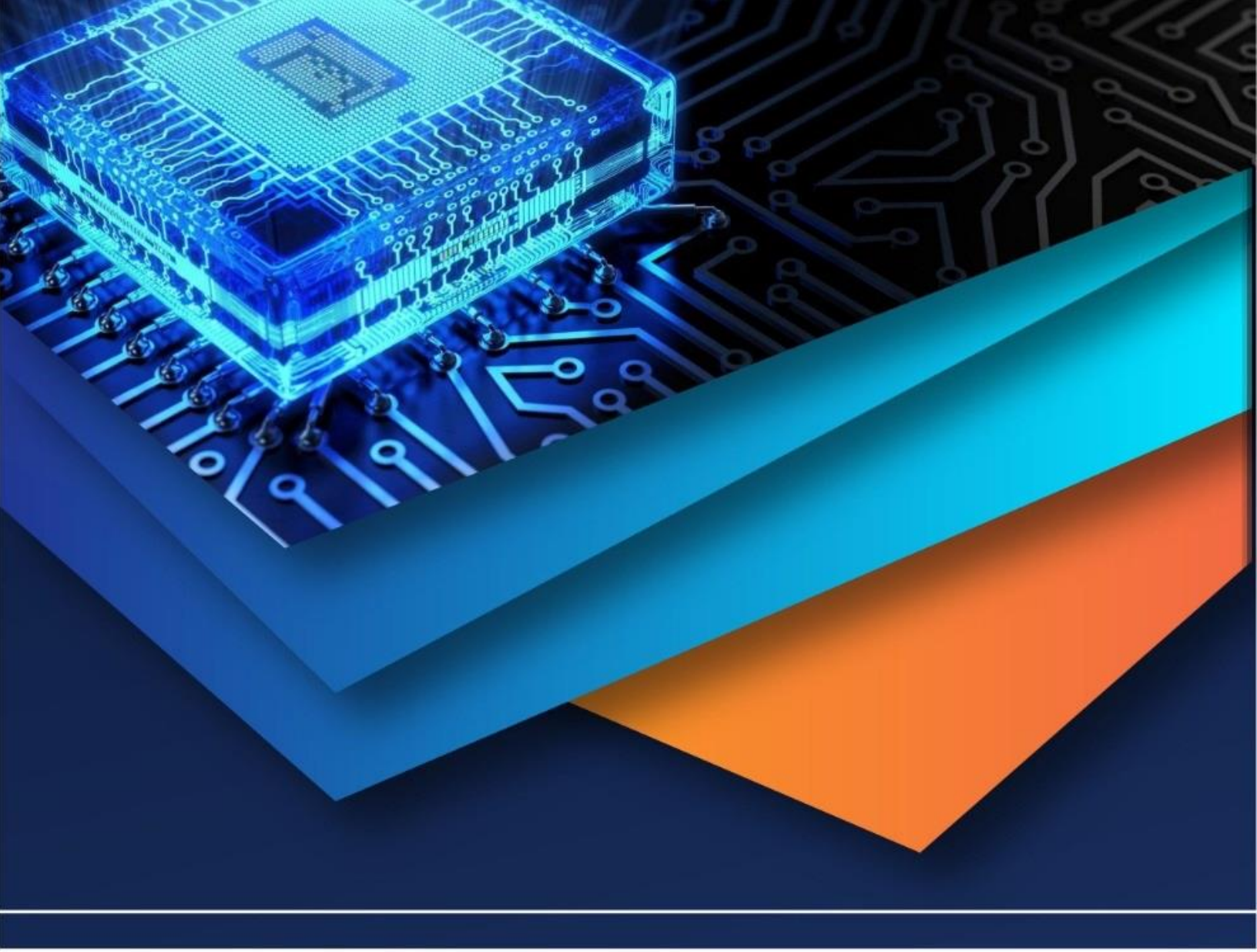
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