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Biogenic synthesis of Ag-doped TiO_2 photocatalyst using citrus paradisi extract for solar trigged degradation of methylene blue

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K E Y W O R D S

Photocatalytic Degradation

Ag Doped Tio_2

Citrus Paradisi

Photocatalysis

Methylene Blue

Water Purification

A B S T R A C T

The world has witnessed substantial deterioration of water resources by different effluents. The most reported among effluents that have caused damage to the water resources are azo dyes that need to be expelled by most efficient techniques such as photocatalysis. This specific study has focused on the synthesis and augmentation of TiO_2 for the degradation of methylene blue (MB). In this work TiO_2 was synthesized by biogenic route using the extract of Citrus paradisi and the synthesized metal oxide (TiO_2) was doped with Ag to escalate the photocatalytic degradation of MB. The synthesized biogenic photocatalyst was characterized by employing XRD and FTIR techniques, which confirms the purity of TiO_2. The stability of Ag-doped TiO_2 photocatalyst was investigated by performing Zeta-potential and the surface morphology was studied thorough FE- SEM. The photocatalytic efficiency of the photocatalysts were evaluated using UV-vis-Spectroscopy. The XRD analysis confirmed the phase purity of synthesized TiO_2 and Ag-doped TiO_2. The presence of functional groups associated with the TiO_2 and Ag-doped TiO_2 were also observed through FTIR. The developed photocatalysts via biogenic route were tested for the degradation of MB that exhibited 56.38% for TiO_2 and 85.55% Ag-TiO_2 in 120mins respectively.

1. Introduction

The deterioration of water resources around the globe is a worldwide concern that needs to be addressed swiftly. According to a report published by the World Bank, around 17-20% of industrial water is the primary source of water pollution. Environmental awareness has compelled the scientific community to develop sustainable strategies for removing dyes and other effluents produced by multiple industries over time. [1-5]. Several approaches like membrane filtration [6], ozonation [7], ion exchange [8], adsorption [9] [10], catalytic reduction [11] and photocatalytic degradation [12] are employed, to remove dyes and different grades of pollutants. Since absorption techniques are only recommended for pre-release elimination of effluents because of easy operation and cost effectiveness [13]. However, due to certain demerits like low absorption efficiency, deprived mechanical stability of adsorbents results in ineffective removal of effluents making them less preferred [14, 15].

Photocatalysis involves heterogeneous catalysis where a metal oxide semi-conductor photocatalyst

absorbs certain spectra of visible light that results in redox reaction that in turn produces ROS species those expel environmental effluents from aquatic and atmospheric organic pollutants. Photodegradation is inherited with several advantages over available conventional water treatment techniques, such as complete degradation is obtained within few hours using renewable energy source at ambient temperature [16, 17]. Another feature that makes photocatalysts superior is non-formation of secondary toxic residues as all the organic effluents are mineralized by H_2O and CO_2 that are non-hazardous in nature [18, 19]. Oxides of transition metals are employed in the process of photodegradation due to their superior chemical and physical attributes like high surface area, better stability, catalytic efficiency, suitable morphology, non-toxic nature and appropriate bandgap. Though metal oxide photocatalysts hold reasonable light harvesting characteristics yet various studies conclude that some factors like high charge recombination rate of photo-generated electron-hole pairs and wide band gap confine practical applications [20, 21].

For the enhancement of the photocatalytic performance of most of the metal oxides, it has been proposed that the development of heterojunction by introducing noble metals in the crystal lattice of metal oxide produce surface plasmon effect, that results in the oscillation of surface electron primarily produced on the surface of noble metals is moved to the conduction band of the semi-conductor metal oxide due Schottky barrier, that keeps photogenerated charges disintegrated [22]. As a result, metal oxide photocatalyst doping improves Photocatalysis caused by electron-hole separation expands light absorption, improves surface electron excitation due to plasmon resonance caused by UV irradiation, and aids in the modification of surface properties of metal oxide photocatalysts. [23]. Many metal oxides like TiO_2[24] CuO [25], CeO_2 [26], MgO[27], and doped photocatalyst [28] were developed, but had inadequate efficacy for the photodegradation of azo dyes. This could be due to the swift charge recombination rate during the photodegradation, in this regard doping is one of the viable methods to prevent such phenomenon to achieve extended and enhanced photodegradation. This work reports the synthesis of TiO_2, through biogenic route that shall help in reducing toxic by-products [29], and augmentation by Ag doping TiO_2 for efficient photocatalytic degradation of MB.

2. Materials and Methods

2.1 Materials

All the materials were of analytical grade. Titanium tetra isopropoxide (TTIP, 98% purity) was purchased from Sigma Aldrich and used as precursor to synthesize titania. Ethanol 99.5% pure was procured from Fisher Scientific. Sweden. Silver nitrate (AgNO3, of ≥ 99.0% purity) was used as dopant and acquired from Honeywell Fluka. Sodium hydroxide (NaOH, ≥98.0% purity) and methylene blue were bought from Dae-Jung chemicals Republic of South Korea.

2.2 Preparation of reducing agent from citrus paradisi extract

Farm fresh grapefruits (citrus paradisi) were procured from an indigenous orchard located at Kandiaro city of district Nausheroferoze, in the province of Sindh Pakistan. Before extraction of the extract from the pulp, grapefruits were washed and peeled. Lately 500ml of the fruit extract was poured in a glass beaker. The extract obtained from citrus paradisi was placed under cover with aluminum foil under dark for 20days for fermentation process. After completion of the fermentation cycle a clear white acetic acid was produced with a pH range in 2-3 after filtration.

2.3 Synthesis of TiO_2 Using Citrus paradisi extract

The nanoparticles of biogenic TiO_2 photocatalyst were synthesized by employing sol-gel process. For the first step of this typical synthesis 40ml of de-ionized water was stirred, during this constant stirring titanium isopropoxide was added in the beaker containing de-ionized water. After adding the precursor (titanium isopropoxide), the solution was left under stirring for 30mins till the mixture was completely homogenized. After the solution was entirely homogenized, 9ml of reducing agent prepared through fermentation of citrus paradisi extract was added dropwise using burette under gentle stirring for 90mins. During this interval 0.1M of NaOH was supplemented to homogenized solution containing the precursor with reducing agent under stirring at room temperature for further 90mins more to complete the precipitation process. After the precipitation process ended the solution was centrifuged till pH of 7 was achieved. Later on, the solution was left to settle down the white precipitates and the leftover water was decanted to start the drying at 80℃ for overnight. After the powder was completely dried, calcination process was performed at 350 ℃ for 120 mins in an automated muffle furnace.

2.4 Preparation of Ag doped TiO_2

Ethanol was mixed with de-ionized water with ratio of 30:70 (100mL). 500mg of TiO_2 nanoparticles synthesized via biogenic route were dispersed in the solution and sonicated for 2 hours. The obtained solution after Sonication was homogenized at 350 rpm under constant stirring. After adequate homogenization, 50mL of 0.4M of AgNO3 was added dropwise under gentle agitation and was aged for 24hrs. in dark.

3. Characterization

Composition of the phase and size of the crystallite was done using XRD Diffractometer (XRD). Patterns of XRD were recorded using BRUKER D8 ADVANCE (40Kv/30mA) consisting of Cu K radiation at a scanning rate of 2θ/min and Scherrer equation was employed to compute the crystalline dimension of the crystal. Surface topography was examined using Field Emission Scanning Electron Microscopy (FESEM) JEOL-JSM -6380LV. Fourier Transform infrared spectroscopy (FTIR) was employed to identify the functional groups absorbed on the surface of TiO_2 with transmission mode ranging from 400-4000cm-1. UV-vis-Spectroscopy was performed using Perkin Elmer Lambda 365 consisting closed quartz cell to investigate optical absorptions (optical path length :1cm). Particle size distribution was calculated using Malvern Zeta Sizer nano ZS.

4. Results and Discussion

4.1 Physiochemical Attributes

The average particle size distribution of TiO_2 and Ag-TiO_2 synthesized using Citrus paradisi extract was recorded as shown in Fig. 1. The physico-chemical properties such as agglomeration and surface charges are critical factors that influence the photocatalytic degradation. TiO_2 and Ag-doped exhibit negative values that are in good agreement with previous research investigations. In our study TiO_2 was doped with Ag for augmentation of photocatalytic behavior. The reduction of surface charges is evident in the Ag-TiO_2, due to pronounced effect of Ag+ ion that holds Ti++[30]. Furthermore, this phenomenon creates surface active sites for the separation of water molecules and helps to retain h+, that in return reduce charge recombination of e-/h+ pairs by curtailing -OH groups on the surface of Ag/TiO_2 photocatalyst and increased ROS species are formed that promote photodegradation of effluents specifically azo dyes.[31]. Studies have established a fact that if substantial positive and negative zeta potential is induced on the particles, such phenomenon will lead to repulsion of the particles hence no agglomeration of particles will occur [32].

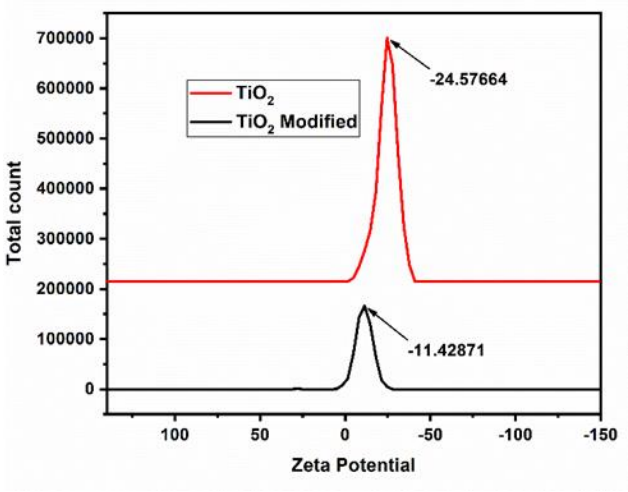


Fig. 1. Zetapotential of TiO_2 and Ag doped TiO_2

4.2 Identification of Phase, crystallinity, and IR-spectroscopy

The phase identification of biogenic TiO_2, and Ag-doped TiO_2 (Biogenic) was performed in 2θ= 20-80° range, as illustrated in Fig.2. The XRD patterns of pristine biogenic TiO_2 can be seen at 25°, 36°, 47°, 53°, 62.6° and 78° respectively that correspond to (101), (103), (112), (200), (105), (204), (206) crystal planes of anatase tetragonal phase of TiO_2. This diffraction pattern is indexed with JCPDS card no. 01-075-1537. Similarly, the XRD pattern for Ag-TiO_2 exhibits no change in the diffraction pattern and exists only in anatase phase, since no other peaks corresponding to rutile and brookite phase are present, this further validates that the nps of biogenic synthesized TiO_2 are highly refined. This corresponding phenomenon suggests that the dopant is only attached at the surface interface of the crystal lattice of the biogenic TiO_2 nanoparticles, and the dopant did not have substantial influence on the crystal lattice of Ag- biogenic TiO_2. It is observed from this diffraction pattern anatase phase remains stable even after doping the biogenic TiO_2, such phenomenon exists in all Ag doped TiO_2 photocatalysts. Several research groups have established this fact that metal dopants only lay on the interface of the crystal lattice without developing a covalent bond with crystal lattice of metal oxides [33]. Another reason that is important to elaborate

here is that this retention of anatase phase in Ag-TiO_2 does not rely on the concentration of Ag but doping certainly plays pivotal role in the formation of anatase phase in comparison to rutile or any morphological phase of TiO_2 [34, 35].

FTIR spectroscopy technique was employed to identify the functional groups present in pristine TiO_2 and Ag doped TiO_2 as shown in Fig 3. The peaks present in the 500-876 cm^{-1} zone are linked to bending vibrations of Ti-O-Ti, the peaks in this zone are common for all the metal oxides. Similarly, the corresponding region present in the fig below confirms the presence of pristine TiO_2. In a similar fashion the bands at 3455 and 2929 cm^{-1} are attributed to OH group. In the spectra of doped TiO_2 there is no major difference seen, except a distinct peak at 1385cm^{-1} related to Ag-O-Ti group, which is not present in the spectra of pristine TiO_2, this peak is present due to interactions between TiO_2 and Ag molecules. Additionally, the peak appearing at 1639 cm^{-1} in both the spectra relates to bending of OH bonds. Prior research additionally indicates that Ag does not change or influence the molecular structure in the powders since Ag is doped on the surface of the metal oxide, however it does not mean that it has no effect on the photocatalytic behavior [36]. Moreover, presence of OH groups is considered pivotal such that they enhance the photocatalysis and make the photocatalyst capable of apprehending charges for producing ROS species that further accelerate photocatalysis.

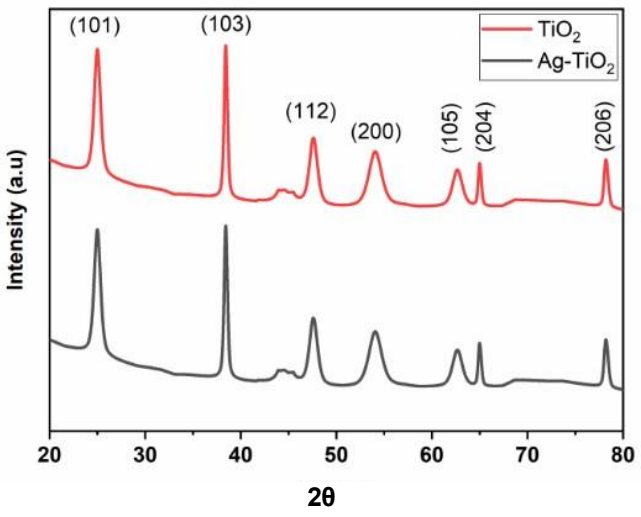


Fig.2. XRD Spectra of TiO_2 and Ag doped TiO_2

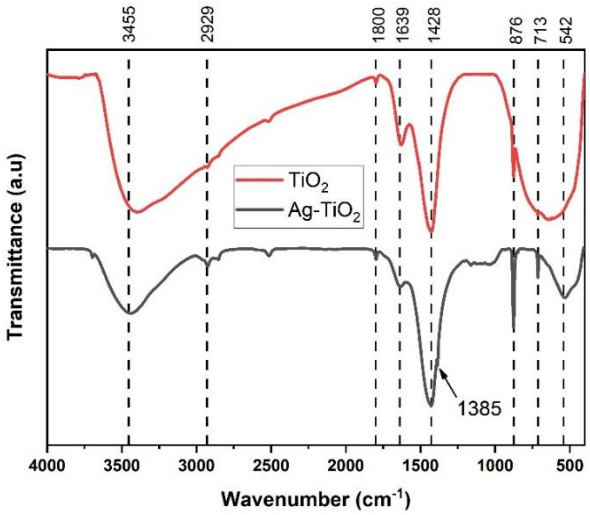
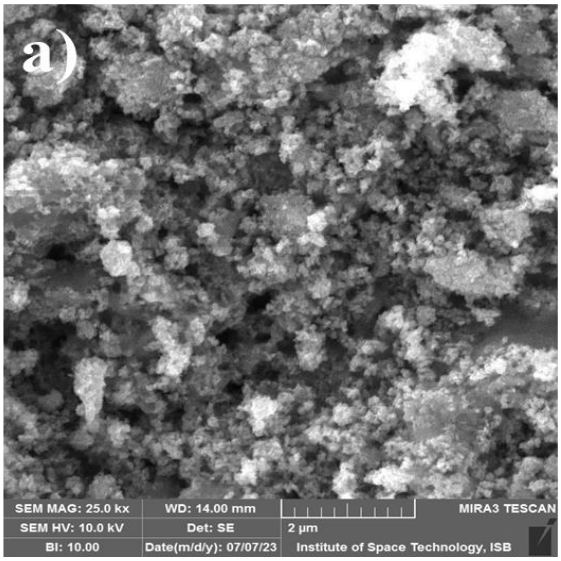


Fig. 3. FTIR Spectra of TiO_2 and Ag doped TiO_2

4.3 Surface Morphology of the Synthesized Ag-TiO_2

FE-SEM was employed to assess the surface topography of biogenic Ag/TiO_2 nano photocatalyst. The surface morphology was analyzed at 25X and 50X magnifications. The SEM images of the examined biogenic doped photocatalyst illustrate a non-homogenous distribution of silver on the surface of TiO_2. The Ag- doped titania also possesses irregular geometry along with formation of clusters/agglomerates. Such agglomeration of the photocatalyst nanoparticles could be beneficial during the separation from the aqueous media containing the azo dye after treatment. Furthermore, rough, porous and sponge like morphology can be seen in micrographs. Such morphology has been proved in escalating the photocatalytic degradation [4].



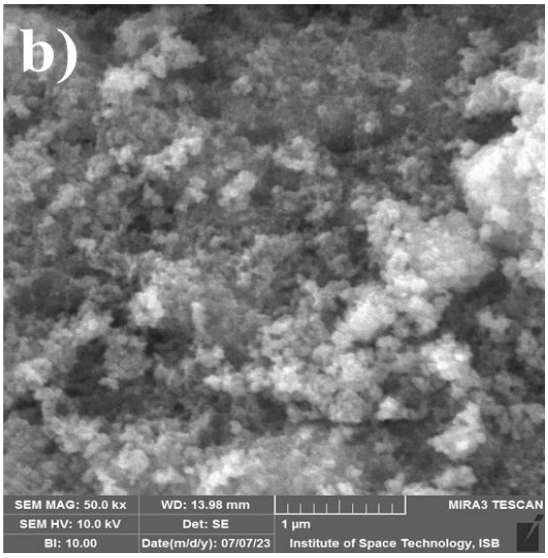


Fig. 4. FE-SEM images of Ag-TiO_2 Nano Photocatalyst

4.4 Assessment of Photocatalytic Degradation and Mechanism

For the assessment of photocatalytic performance methylene blue (MB) was degraded using biogenic TiO_2 and Ag-TiO_2. Diminutive changes are visible in the concentration of MB in absence of photocatalyst and similar phenomenon was also observed when the azo-dye was kept under dark. The above-mentioned phenomenon concludes that for photocatalytic degradation presence of light is mandatory for substantial and swift degradation of effluent. Extensive depletion in the concentration of MB is apparent in both pristine and Ag doped titania after the exposure of sunlight. The outcomes of photocatalytic degradation of MB under sunlight and in presence of photocatalyst are exhibited in Fig 4. The photo triggered reaction in presence of pristine TiO_2 and Ag-doped titania resulted in ~ 56% and 85% of effluent degradation respectively after 120 minutes of exposure in daylight Perpetual reduction of the absorbance values with respect to time shows the photodegradation of MB. These degradation values further validate the doping of TiO_2 with Ag and possess excellent degradation ability in 120mins. The substantial degradation of the model effluent is due to the synergistic influence of Ag and TiO_2 nanoparticles. Ag-TiO_2 exhibits the strongest photodegradation because of the doping's ability to delay charge recombination, which opens up more of the solar spectrum for absorption. The obtained efficiency of Ag-TiO_2 is due to several factors like crystallinity, surface characteristics, morphology, and optical attributes and effectiveness of charge separation. The mechanism that led to high degradation by Ag-TiO_2 is because when the doped photocatalyst was irradiated to sunlight that caused to separate the charge i.e., an electron from the valence band. The photoinduced electrons present in the conduction band (CB) of the TiO_2 got transferred to the Ag particles due to Schottky heterojunction present at Ag/TiO_2 interface. Moreover, these reacted with the dissolved oxygen to produce superoxide radical O^{-2}. Simultaneously, the photogenerated h+ reacted and formed OH radical. These ROS species are highly strong oxidizing agents that accelerate swift degradation of azo-dyes during photocatalytic reactions. The resulting high photocatalytic efficiency for Ag-TiO_2 photocatalyst could be due to delayed photoinduced e-/h+ recombination by improved photoinduced charge carrying separation due to interfacial process of charge transfer. [37].

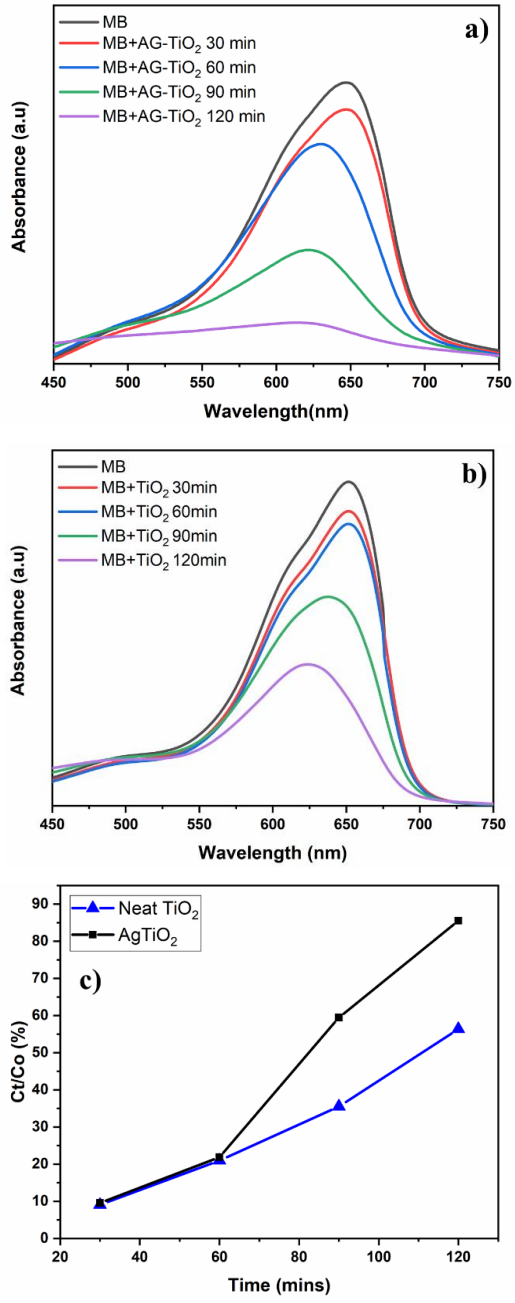


Fig. 5. (a) Photocatalytic degradation of MB with Ag doped TiO_2, (b) Photocatalytic degradation of MB with pristine TiO_2 (c) Degradation efficiency of pristine and Ag Doped TiO_2

5. Conclusion

In this study TiO_2 was synthesized via biogenic route for the degradation of MB. Since metal oxides are prone to high charge recombination in this regard the synthesized titania was later doped with Ag to escalate the photocatalytic degradation of the model effluent. The synthesized photocatalyst were tested under sunlight for the photodegradation. The Ag-doped Titania had the highest efficacy with 85.55% Degradation in 120mins, that suggests that doping can have substantial influence on the degradation of azo dyes and other metal oxides may also be used to for the photodegradation of various azo dyes.

6. Acknowledgement

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