

ORIGINAL RESEARCH PAPER

Silver Doped TiO₂ Nanoparticles: Preparation, Characterization and Efficient Degradation of 2,4-dichlorophenol Under Visible Light

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ABSTRACT

Hydrothermally synthesized TiO₂ nanoparticles containing different amounts of silver were characterized by X-Ray diffraction (XRD), Fourier transform infrared (FT-IR) and scanning electron microscopy equipped with energy dispersive X-ray microanalysis (SEM/EDX) techniques. XRD results showed prepared samples include 100% anatase phase. The presence of silver in TiO₂ nanoparticle network was established by XRD, SEM/EDX and FT-IR techniques. The photocatalytic performance of the prepared catalysts was tested for the degradation of 2,4-dichlorophenol (2,4-DCP) under visible light. The experiments demonstrated that 2,4-DCP was effectively degraded in the presence of Ag/TiO₂ samples. It was confirmed that the presence of Ag on TiO₂ catalysts could enhance the photocatalytic degradation of 2,4-DCP in aqueous suspension. It was found that an optimal dosage of 1.68 wt% Ag in TiO₂ achieved the fastest 2,4-DCP degradation (95% after 180 min irradiation) under the experimental conditions. On the basis of various characterizations of the photocatalysts, the reactions involved to explain the photocatalytic activity enhancement due to Ag doping include a better separation of photogenerated charge carriers. GC-MS analysis showed the major intermediates of 2,4-DCP degradation are simple acids like oxalic acid, acetic acid, etc. as the final products.

KEYWORDS: 2,4-dichlorophenol; Degradation; Silver; TiO₂

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INTRODUCTION

Recently the research based on advanced oxidation methods for water and wastewater purification are expanding progressively. Photochemical and photocatalytic methods are used for treating wastewater containing chloroaromatic compounds [1,2]. There has been a growing distress related to the environmental, health impacts and environmental damage due to chloroaromatic compounds during the last two decades [3]. The presence of chloroaromatic compounds in the aqueous environment is a result

of the extensive use of chlorinated compounds in a range of industrial processes. These compounds are resistance to degradation and accumulate in the environment [4]. Recently adverse effects of chloroaromatic compounds on the human nervous system have been reported and have been linked to many health disorders [5]. Therefore, it is important to find novel and cost-effective methods for the safe and complete degradation of chloroaromatic compounds such as chlorophenols (CPs).

Heterogeneous photocatalysis technology based

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on semiconductors is one of the advanced oxidation processes used for degradation of organic pollutants [6]. In this process the semiconductor absorbs irradiation and generates active species such as hydroxyl radicals which leads to complete oxidation of organic components present in wastewater. Titanium dioxide (TiO₂) is a semiconductor with wide band gap (3.2eV), used as photocatalyst for destruction and removal of highly toxic and non-biodegradable pollutants. TiO₂ has its advantages over the other semiconductor photocatalysts such as ZnO, SnO₂ and etc. TiO₂ is chemically stable, environmentally friendly, non-toxic and cheaper [7]. TiO₂ is synthesized using various methods such as chemical vapor deposition (CVD), plasma, hydrothermal and sol-gel [8]. Despite the many known advantages of using TiO₂, it suffers from the shortcoming of having a large band gap (~3.2 eV) which restricts its use to the ultraviolet (UV) region. Such radiation is not very abundant in the solar radiation that reaches the Earth, which limits the use of TiO₂ in solar energy utilization [9].

During two last decades, there has been a great deal of interest in the preparation of nanostructured titania [10–13] to increase the efficiency of these photochemical processes. In addition, a variety of attempts has been made to incorporate various metal species into the TiO₂ network to enhance the photocatalytic activity and/or broaden the absorption of the solar spectrum by the doped TiO₂. Methods that have been used include ion exchange, impregnation and co-precipitation [14,15]. Some interesting effects have been observed from these implantation studies. Metal-doped TiO₂ has been widely studied for improving photocatalytic performance on the degradation of various organic pollutants under visible-light [16–18]. The intrinsic properties of TiO₂, such as charge carrier recombination rates, the particle size and interfacial electron transfer rates and extending photoresponse of TiO₂ into the visible range influence directly by silver doping [19–21]. The metal acts as a sink for photoinduced charge carriers and promotes interfacial charge-transfer processes.

To the best of knowledge, the application of TiO₂ nanoparticles containing different amounts

of silver for heterogeneous photocatalytic degradation of 2,4-dichlorophenol (2,4-DCP) has not been reported so far. The aim of this work is,

the silver doped to TiO₂ nanoparticles (Ag/TiO₂) with photocatalytic activity were synthesized by hydrothermal method. The as-prepared sample was characterized by X-ray diffraction (XRD), fourier infrared spectroscopy (FTIR), scanning electron microscopy/energy dispersive X-ray (SEM/EDX). Moreover, the photocatalytic performance of the prepared samples in degrading 2,4-DCP was estimated using UV-Vis spectrophotometry

EXPERIMENTAL

Materials and Reagents

Silver nitrate (AgNO₃), 99.9%, was supplied by (Merck, No.101510). Tetraisopropylorthotitanat, for synthesis, 99.9%, (Merck No. 8.21895), ethanol, 96%, (Merck, No.159010), acetylacetone, 99% , (Merck No. 800023) and deionized water were used for photocatalyst synthesis. High-purity 2,4-DCP, 98%, (Merck No. 803774) was used as a probe molecule for photocatalytic tests.

Photocatalyst Preparation

Pure TiO₂ and TiO₂-based photocatalyst containing different amounts of silver were synthesized with little modification in the described procedure in ref. [22]. In a typical reaction, a mixture of 20 mL Ti(OC₃H₇)₄, 20 mL ethanol and 1.62 mL acetylacetone was prepared and stirred for 30 min at room temperature. Then, a new mixture containing X mg AgNO₃ (this amount calculated for 0.5-3 wt% Ag in final solid), 80 mL ethanol and 2 mL H₂O was added into the first solution, which led to clear solution. This solution was transferred into an autoclave, and then heated to 240 °C at a heating rate of about 2 °C min⁻¹. Finally, the temperature was kept at 240 °C for 6 h. After cooling, the obtained solid washed with ethanol and water and dried at 100 °C for 2 h in air. These photocatalysts are labelled as Ag/TiO₂ (a), where (a) is the weight percentage of Ag in the final solid that obtained by EDX analysis. A solution without AgNO₃ was also prepared for pure TiO₂ synthesis.

Characterization

Fourier transform infrared (FTIR) analysis was applied to determine the surface functional groups, using FTIR spectroscopy (FTIR-2000, Bruker), where the spectra were recorded from 4000 to 400 cm⁻¹. The XRD patterns were recorded on a Siemens, D5000 (Germany). X-ray diffractometer

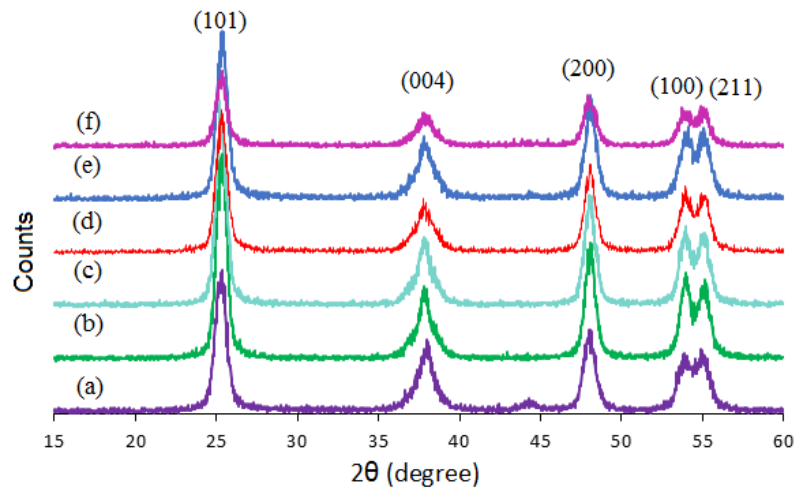


Fig. 1. XRD patterns of a) TiO₂, b) Ag/TiO₂ (0.17), c) Ag/TiO₂ (0.73), d) Ag/TiO₂ (1.68), e) Ag/TiO₂ (1.62) and f) Ag/TiO₂ (1.98)

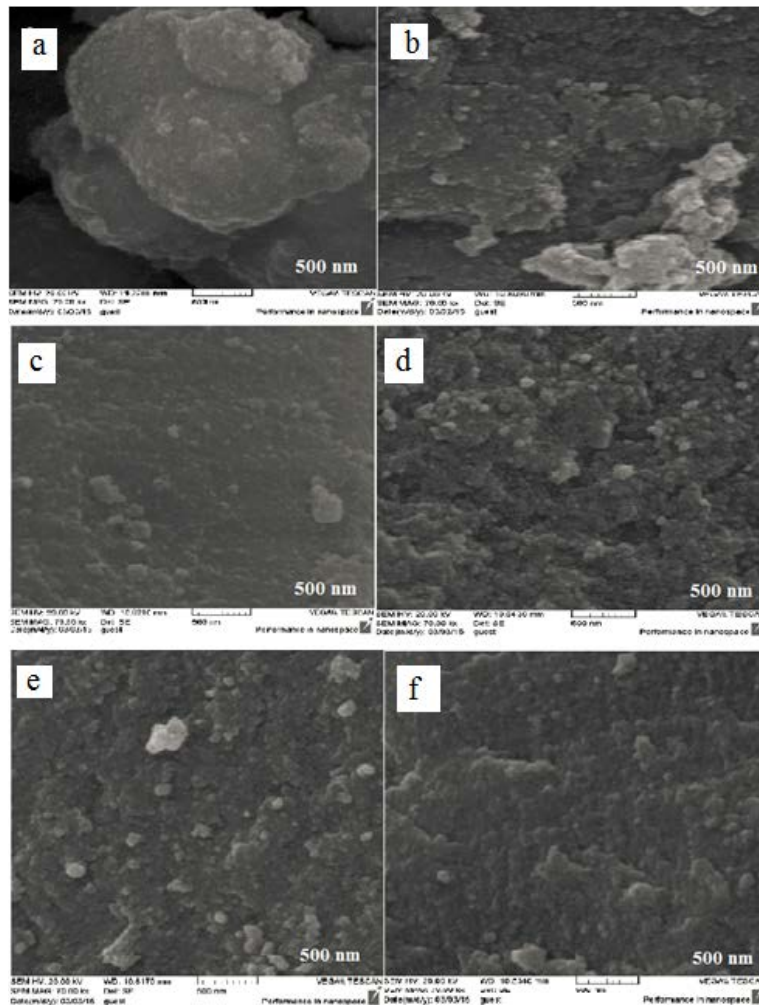


Fig. 2. SEM micrographs of a) TiO₂, b) Ag/TiO₂ (0.17), c) Ag/TiO₂ (0.73), d) Ag/TiO₂ (1.68), e) Ag/TiO₂ (1.62) and f) Ag/TiO₂ (1.98)

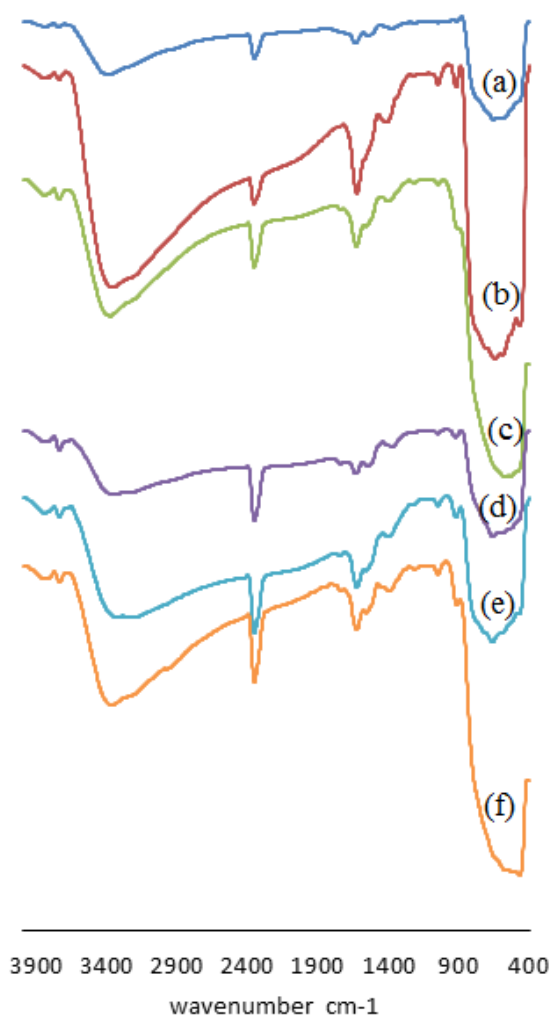


Fig. 3. FTIR spectra of a) TiO₂, b) Ag/TiO₂ (0.17), c) Ag/TiO₂ (0.73), d) Ag/TiO₂ (1.68), e) Ag/TiO₂ (1.62) and f) Ag/TiO₂ (1.98)

using Cu K_α radiation as the X-ray source. The diffractograms were recorded in the 2θ range of 15-60°. The morphology of nanoparticles were characterized using scanning electron microscope (SEM) (Vegall-Tescan Company) equipped with an energy dispersive X-ray (EDX).

Photocatalytic Degradation Monitoring

In a typical run, the suspension containing catalyst and 50 mL aqueous solution of 2,4-DCP (40 mg/L) was stirred first in the dark for 30 min to establish adsorption/desorption equilibrium. Irradiation experiments were carried out in a self-built reactor. A visible (Halogen, ECO OSRAM, 500W) lamp was used as irradiation source (its emitting wavelength ranges from 350 nm to 800

nm with the predominant peak at 575 nm). At certain intervals, small aliquots (2 mL) were withdrawn and filtered to remove the catalyst particles. These aliquots were used for monitoring the degradation progress, with Rayleigh UV-2601 UV/VIS spectrophotometer.

Statistical Analysis

All experiments were performed in triplicate and the average values were presented. The data were analyzed by one-way analysis of variance (ANOVA) using SPSS 11.5 for Windows. The data was considered statistically different from control at $P < 0.05$.

Identification of Intermediates

The reaction intermediates were identified by GC-MS in an Agilent 190915-433 instrument equipped with a HP-5MS capillary column (30 m × 0.25 mm). The column temperature was programmed at 50 °C for 2 min, and from 50 to 250 °C at a rate of 10 °C min⁻¹. The samples used for GC-MS analysis were prepared according to the following procedure: The obtained degradation product was acidified to pH 1 and subsequently extracted with dichloro-methane. After dichloromethane was evaporated to dryness under vacuum, 10 mL methanol was added to dissolve the residue. Then, 1 mL concentrated sulfuric acid was added and the combined solution was refluxed for about 3 h. The solution was further extracted with dichloromethane followed by concentrating to about 1 mL under reduced pressure. The released chloride ions originating from the degradation of 2,4-DCP were identified and determined by the AgNO₃ method.

RESULT AND DISCUSSION

X-ray Diffraction Analysis

The x-ray diffraction patterns of the pure TiO₂ and silver doped TiO₂ nanoparticles are shown in Fig. 1. The nanocrystalline anatase structure was confirmed by (101), (004), (20 0), (105) and (211) diffraction peaks [23]. The XRD patterns of anatase have a main diffractions at $2\theta = 25.2^\circ$ corresponding to the 101 plane (JCPDS 21-1272) while the main diffractions of rutile and brookite phases are at $2\theta = 27.4^\circ$ (110 plane) and $2\theta = 30.8^\circ$ (121 plane), respectively. Therefore, rutile and brookite phases have not been detected [24,25].

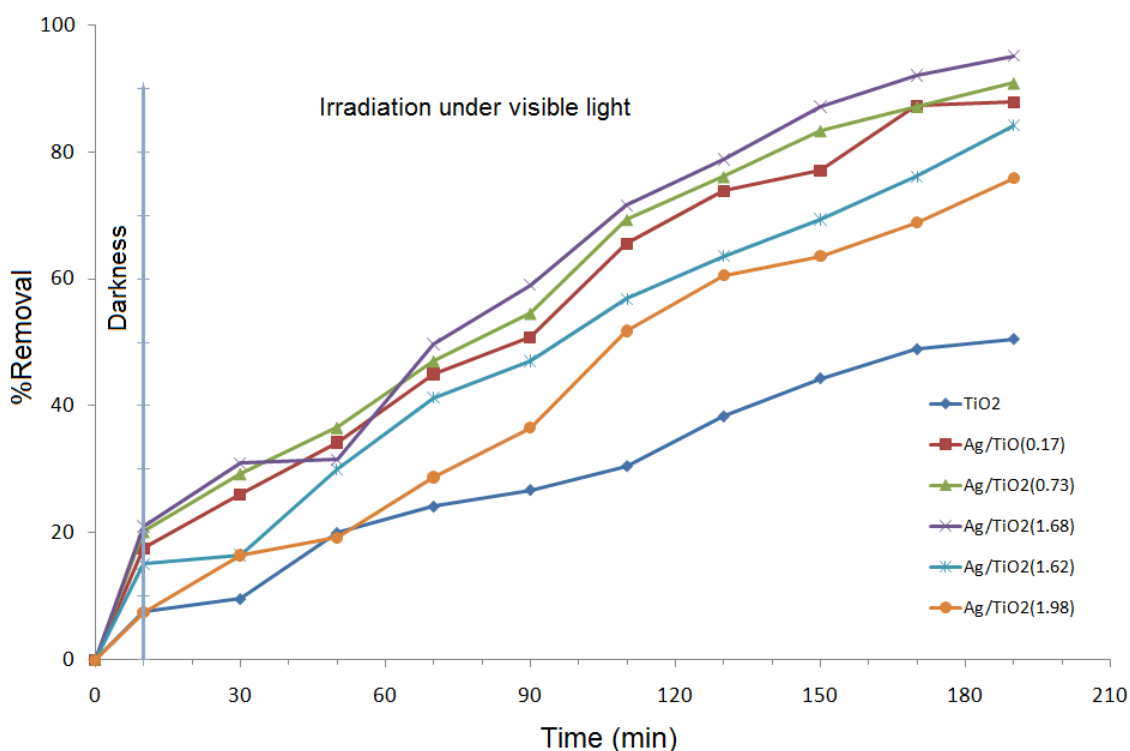


Fig. 4. Photocatalytic degradation of 2,4-DCP in the presence of prepared samples under visible light. (Initial concentration of 2,4-DCP, 40 mg/L; volume, 100 mL; catalyst dosage, 50 mg)

The x-ray diffraction patterns of the silver doped TiO₂ nanoparticles (Fig. 1b to f) coincides with the of pure TiO₂ and show no diffraction due to the silver species, thus suggesting that silver particles are well dispersed on the TiO₂ surface. Doping with silver does not disturb the crystal structure of anatase TiO₂ indicating that the silver dopants are merely placed on the surface on crystal without being covalently anchored into the crystal lattice. There are no diffraction pattern characteristics of the silver in the XRD patterns. Hence these metal sites are expected to be below the visibility limit of x-ray analysis. The diffraction patterns of pure TiO₂ and Ag/TiO₂ samples showed considerable line width, indicating small particles. The crystal size of each sample is calculated from the full width at half maximum (FWHM) of the (101) diffraction peak using Scherrer's equation [26].

$$D = K\lambda / \beta \cos\theta \quad (1)$$

Where D is the average crystal size of the sample, λ the X-ray wavelength (1.54056 Å), β the fullwidth at half maximum (FWHM) of the diffraction peak (radian), K is a coefficient (0.89) and θ is the

diffraction angle at the peak maximum. The results are demonstrated in Table 1. All prepared samples are in nano-size range, from 9.80 to 11.00 nm, and all Ag/TiO₂ samples show equal or larger crystal size compared to pure TiO₂. The increased particle size may be explained by the fact that the ionic radius of Ag⁺ (1.15 Å) is greater than that of Ti⁴⁺ (0.60 Å).

SEM/EDX Analysis

In order to investigate the surface morphology of the synthesized Ag doped TiO₂ nanoparticles, SEM studies were performed. The SEM images of TiO₂ and Ag/TiO₂ samples are shown in Fig. 2. The SEM images of Ag/TiO₂ samples show that the distribution of silver on the surface of titanium dioxide is not uniform and the Ag/TiO₂ catalyst contains irregular shaped particles which may be due to the aggregation of tiny crystals. However, it can not be ruled out that some silver particles are too small to be observed at the resolution of the used microscope. The SEM images also reveal that the doping of silver metal does not leave any change in the topology of the catalyst surface.

Table 1. Average crystal size of the synthesized nanoparticles calculated by Scherrer equation

Sample	TiO ₂	Ag/TiO ₂ (0.17)	Ag/TiO ₂ (0.73)	Ag/TiO ₂ (1.68)	Ag/TiO ₂ (1.62)	Ag/TiO ₂ (1.98)
Crystal size (nm)	9.80	9.80	9.90	10.80	10.70	11.00

Table 2. Elemental analysis of synthesized nanoparticles obtained by EDX analysis

Sample	Nominal Ag (wt%)	Ag (wt%)	Ti (wt%)	O (wt%)
TiO ₂	0.00	0.00	40.44	47.27
Ag/TiO ₂ (0.17)	0.50	0.17	30.33	56.03
Ag/TiO ₂ (0.73)	1.00	0.73	40.19	46.03
Ag/TiO ₂ (1.68)	2.00	1.68	36.19	50.52
Ag/TiO ₂ (1.62)	2.50	1.62	43.19	42.79
Ag/TiO ₂ (1.98)	3.00	1.98	42.85	44.54

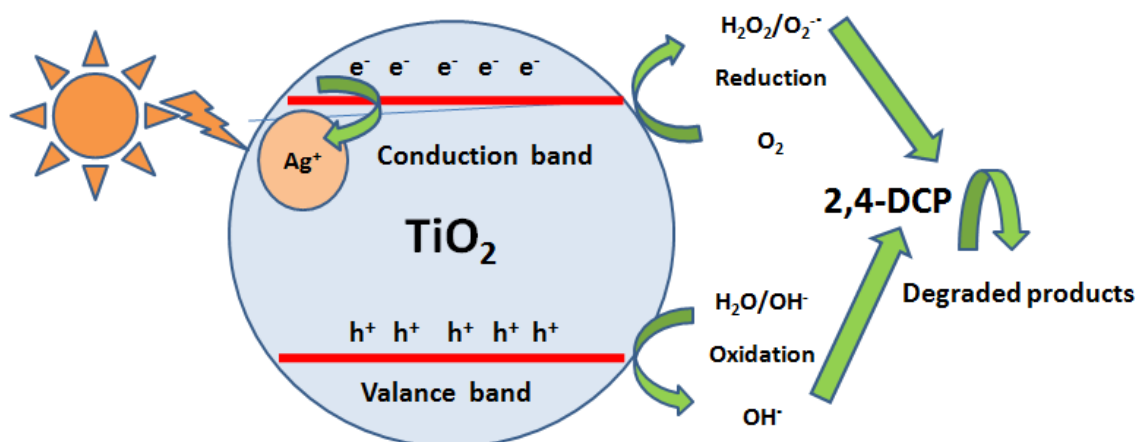


Fig. 5. Our proposed mechanism for photocatalytic degradation of 2,4-DCP

Also Fig. 2 show the hardness and density of nanoparticles increase as silver content increase in TiO₂ lattice [27]. Spongy and porous structure causes more surface area at high hardness; that surely would be more efficient for absorption and photocatalytic applications [28]. Table 2 is the result of elemental determination for the synthesized samples that obtained by EDX analysis. According to Table 2, doped silver amounts are lower than nominal amounts; it can be explained by the loss of silver nitrate during the hydrothermal synthesis or possibly TiO₂ network does not have the more capacity to dope higher amounts of silver.

FTIR Analysis

The FTIR spectra of the synthesized samples are shown in Fig. 3. The peaks observed at ~3400, 2930 and 2850 cm⁻¹ are attributed to the Ti – OH bond [29]. The spectra shows relatively strong band at ~1630 cm⁻¹ observed for all the photocatalysts which is due to the OH bending vibration of chemisorbed

and/or physisorbed water molecule on the surface of the catalysts. The strong band in the range of 700 –500 cm⁻¹ is attributed to stretching vibrations of Ti –O–Ti bond [30]. The FTIR spectra of Ag/TiO₂ samples revealed a peak at about 1385 cm⁻¹, which was not observed for the undoped TiO₂. The intensity of this peak increased with the increase of silver precursor (AgNO₃) in the composite samples. The peak at 1385 cm⁻¹ was assigned tentatively to the interaction between Ag and TiO₂ particles [31].

Photocatalytic Degradation of 2,4-DCP

To evaluate the photocatalytic activity of the synthesized samples and find out the optimum content of Ag doping, a set of experiments for 2,4-DCP degradation with an initial concentration of 40 mg L⁻¹ under visible light was carried out in aqueous suspension using TiO₂ or Ag/TiO₂ catalysts with a Ag content between 0.17 wt% and 1.98 wt%, and the experimental results are shown in Fig. 4. The experimental results demonstrated

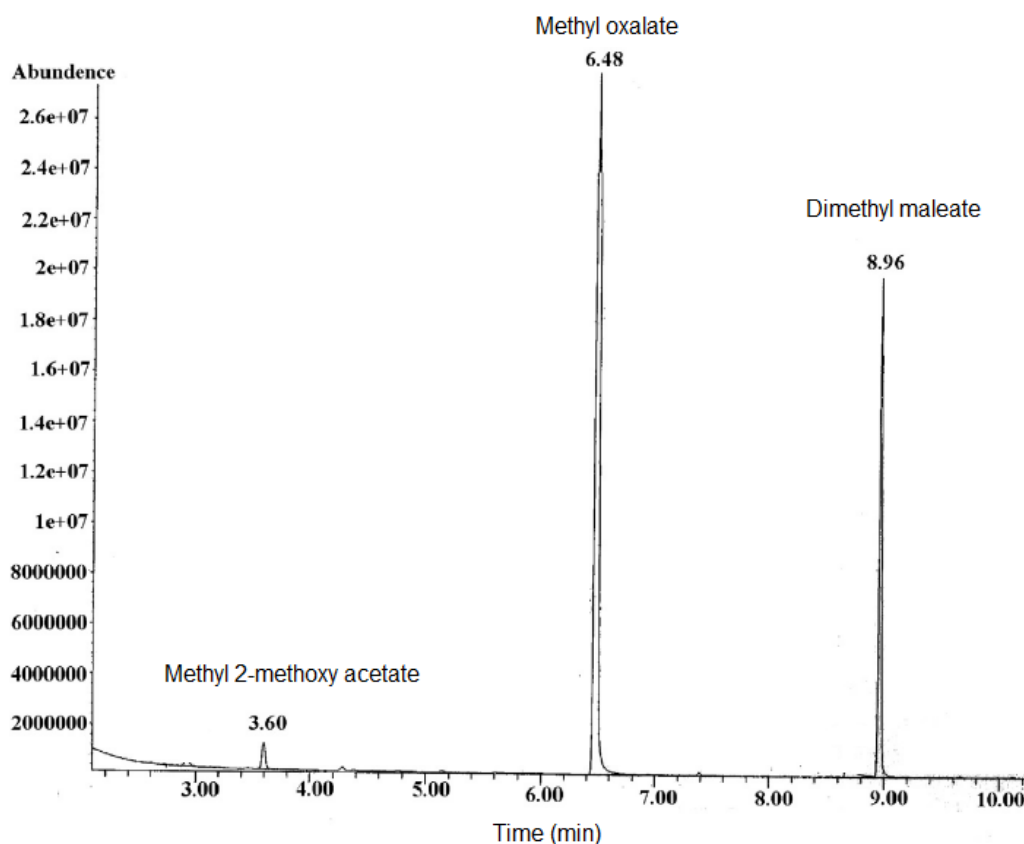


Fig. 6. GC-Chromatogram of the final products of the photocatalytic degradation of 2,4-DCP by Ag/TiO₂(1.68)

that among the prepared samples, the Ag/TiO₂ (1.68) catalyst achieved the highest efficiency of the 2,4-DCP degradation (95% degradation obtained after 180 min irradiation). A further more Ag content on TiO₂ seems to be detrimental to the 2,4-DCP photodegradation efficiency. From the Fig. 4, the results show that the photocatalytic activity of pure TiO₂ is lower than that of Ag/TiO₂ samples. It implies that the Ag dopant promotes the charge pair separation efficiency for TiO₂ catalysts. It may be explained that at the Ag content below its optimum level (1.68 wt%), the Ag particles deposited on the TiO₂ surface can act as electron-hole separation centers [32]. The electron transfer from the TiO₂ conduction band to Ag particles at the interface is thermodynamically possible because the Fermi level of TiO₂ is higher than that of Ag metal [33]. This results in the formation of a Schottky barrier at metal semiconductor contact region and improves the photocatalytic activity of TiO₂. On the contrary, at the Ag content beyond its optimum value, the Ag particles can also act as recombination centers,

thereby decreasing the photocatalytic activity of TiO₂. It has been reported that the probability for the hole capture is increased by the large number of negatively charged Ag particles on TiO₂ at high Ag content, which reduces the efficiency of charge separation [34,35]. In this study, the Ag/TiO₂ samples under visible light demonstrated a considerable degradation of 2,4-DCP in aqueous solution. We will discuss about the mechanism of photocatalytic degradation in next section.

Mechanism of Photocatalytic Degradation

Fig. 5 shows our proposed mechanism for photocatalytic degradation of 2,4-DCP. It is acknowledged that the radius of the Ag⁺ and Ag atom is much larger than the Ti⁴⁺, so very unlikely for Ag⁺ and Ag atom to enter the TiO₂ lattice [36]. In fact, the Ag atoms were in direct contact with the TiO₂ nanoparticles. Because the work function of the metal Ag is higher than that of TiO₂, electrons are removed from the TiO₂ particles to the vicinity of the Ag particles. This results in the

formation of Schottky barriers at the Ag–TiO₂ contact region and results in charge separation [37] i.e. the electronic interaction occurring at the contact region between the metal deposits and the semiconductor surface [38]. The Ag deposits act as electron traps immobilizing the photogenerated electrons in the traps and shortly transferring them to oxygen to form highly oxidative species such as O₂^{•-}. This type of electron scavenging by Ag metal is reported to be a faster process compared to the electron transfer to oxygen (or) recombination with holes [38] since, the trapping of electron by Ag metal from TiO₂ occurs at a faster rate when compared to the electron transfer from TiO₂ to O₂ [39,40].

More specifically, Schottky barriers facilitate the electron transfer from TiO₂ nanoparticles (with high Fermi level) to Ag (with low Fermi level), resulting in higher transferring efficiency of electrons [41]. The effect of Schottky barriers in our particular case was evidenced by the fact that all the Ag-loaded TiO₂ had higher photocatalytic efficiencies than Ag free TiO₂. Firstly, the Schottky barriers facilitate the photoelectron movement to a certain direction, from the semiconductor TiO₂ nanoparticles to adjacent Ag atom or cluster. Sample Ag/TiO₂(1.68) (Fig. 4) has the highest photocatalytic activity and can be attributed to the fact that Ag was distributed at surface of the TiO₂. For this sample, the Schottky barriers attract the electrons and the holes will be left on the surface layer of the TiO₂. This attraction greatly inhibits the recombination of electron–hole pairs. The enriched holes in the surface layer can directly degrade 2,4-DCP, at the same time, it can oxidize H₂O adsorbed on the surface and produce hydroxyl radicals (OH[•]) that can degrade organic matters effectively.

Identification of Intermediate Products

The intermediate species formed during degradation of 2,4- DCP, were identified by GC–MS. The major reaction intermediates identified in an aliquot withdrawn after 200 min following a degradation condition specified as in Fig. 4. Presence of these intermediates (Fig. 6) supports our proposed mechanism which is based on OH radicals (Fig. 5). The hydroxyl radicals attack 2,4-DCP converting it to chlorocatechol and then to chlorobenzoquinone. Subsequently, hydroxyl groups would break the aromatic rings

of chlorobenzo-quinone transferring them into simple acids like oxalic acid, acetic acid, etc. as the final products [42,43]. In addition to identifying the organic intermediates, chloride ions were also detected and identified as one of the final products of the photocatalytic degradation. The amount of Cl⁻ in the reaction media at the end of the photocatalytic experiment almost equals the amount of chlorine present in 2,4-DCP indicating essentially complete degradation.

CONCLUSION

TiO₂-based photocatalysts containing different amounts of silver were synthesized and characterized by several techniques successfully. XRD analysis confirmed all the prepared samples consist of pure anatase phase. The XRD and SEM/EDX data showed that the incorporation of silver in TiO₂ network increases the crystal size. Among the Ag/TiO₂ samples, the Ag/TiO₂ (1.68) photocatalyst exhibited the highest photocatalytic activity under visible light. GC-MS analysis showed, the hydroxyl radicals attack 2,4-DCP converting it to chlorocatechol and then to chlorobenzoquinone. Subsequently, hydroxyl groups would break the aromatic rings of chlorobenzo-quinone transferring them into simple acids like oxalic acid, acetic acid, etc. as the final products

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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