

Ag₃PO₄ Enhanced TiO₂ for Visible Light Photocatalysis of 2-Chlorophenol in Wastewater

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Abstract— Facile in-situ synthesis and characterization of stable Ag₃PO₄/TiO₂ nanoparticles and their effectiveness for visible light photocatalysis has been reported. The surface morphology, crystal structure and chemical properties of the photocatalyst were characterized by using UV-vis-NIR spectroscopy, FSEM, XRD, XPS, TEM and nitrogen physisorption. The synthesized nanoparticles were polycrystalline with calculated energy band gap in the range of 2.3-2.5 eV. Deposition of Ag₃PO₄ over the surface of TiO₂ resulted in stability increase and a significant shift in the UV absorption spectrum towards visible region. The photocatalytic experiments were performed under 112 W visible light irradiation ($\lambda > 400$ nm). The catalyst showed complete degradation of 15 mg/L 2-CP within 120 minutes while 92.5 % degradation of 25 mg/L 2-CP was achieved under optimized conditions. The study confirmed that Ag₃PO₄ /TiO₂ has high potential for degradation of 2-CP from wastewater under visible-light irradiation.

Keywords— Ag₃PO₄/TiO₂ nanoparticles, 2-chlorophenol, visible light photocatalysis, wastewater.

I. INTRODUCTION

Recently, application of heterogeneous photocatalysis as an advance oxidation process for eradication of toxic organics has been seen as a potent solution to wastewater contamination problems [1], [2]. TiO₂ has become the most extensively studied photocatalyst. However the large energy band gap (3.2 eV) limits its use only to ultraviolet (UV) light driven photocatalysis which comprises only about 4% of solar spectrum incident on earth. Such dependence makes TiO₂ unsuitable for use in visible light activated photocatalytic applications [3]-[8]. Current research focuses on development of modified photocatalysts able to harness the visible spectrum of light which comprises the larger portion (~46%) of sunlight [9]-[11]. The strategies adopted to achieve such goal for instance may include creation of low energy impurity states within the TiO₂ band gap through noble metal doping or co-deposition that may promote formation of electron hole pairs [12]-[15]. Ag₃PO₄ has been reported to effectively utilize visible light for water splitting and organic contaminants degradation [16]-[19]. A few studies suggest that Ag₃PO₄ shows up to twelve times faster degradation of certain dyes compared to commercially available TiO₂-xNx and BiVO₄

with up to 90 % quantum efficiency upon exposure to light with wavelength over 420 nm [19],[20]. However the instability and photo-corrosion of Ag₃PO₄ in aqueous medium

has been associated with the loss in photocatalytic efficiency over time making catalyst recycling and reuse difficult [21],

[22]. Therefore, it is highly desirable to synthesize modified and stable photocatalysts that can effectively utilize the visible light harnessing power of Ag₃PO₄ nanoparticles with minimal consumption of expensive Ag precursors. Recently a facile in-situ preparation route for Ag₃PO₄ nanoparticles deposition onto the TiO₂ (Degussa P25) surface has been reported to increase both the stability and photocatalytic activity of TiO₂ based photocatalysts [23]. This study reports in-situ precipitation method for the synthesis of Ag₃PO₄/TiO₂ nanoparticles and evaluates the effectiveness of synthesized nanomaterials for visible light photocatalysis of 2-CP as a model pollutant in water. The degradation pathways as a linear function of the concentrations of chlorophenol and catalyst have been considered for the interpretation of the kinetic data in this work. The choice of 2-CP was made due to the fact that phenol and its derivatives are commonly encountered organic pollutants in petrochemical, pharmaceutical and chemical industry wastewater causing severe environmental problems if not properly removed before discharge [24]. 2-CP among eleven phenolic compounds has been included in the priority pollutants list of United States Environmental Protection Agency (US EPA) and the European Union Water Framework Directive list of priority substances [25], [26]. Also the biological, physical, and physicochemical water treatments are often ineffective or environmentally incompatible for degradation of such organic contaminants [27].

Experimental Materials

Silver phosphate (Sigma-Aldrich); Degussa Titania (P25) (Sigma-Aldrich); Sodium phosphate; 2-Chlorophenol (2-CP) (Merck) standard grade was utilized as pollutant. De-ionized water was used for solution preparation. All other chemicals were of analytical grade.

Synthesis of Ag₃PO₄/TiO₂ photocatalyst

Synthesis of 0.3-molar ratio of silver phosphate doped onto Degussa Titania (P25) (Aldrich procured) was carried out using the in-situ precipitation method reported in literature [23]. Degussa P25 (0.02 mol) was dispersed in 50 ml distilled water and the solution was sonicated for 5 min. Silver nitrate (0.018 mol, Sigma-Aldrich) was then added to the sonicated P25 solution and the resulting solution magnetically stirred for 10 min at 250 rpm. Sodium phosphate (0.006 mole) was dispersed in 50 ml distilled water and was then added dropwise to the previously prepared solution. The final solution

was then magnetically stirred at 250 rpm for 5 h. A color change was observed from white to yellow. The resulting solution was then filtered, washed and dried in air overnight.

Material Characterization

Characterization of the synthesized $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ was performed by powder X-ray diffraction (XRD) measured with a Philips PANalytical Xpert PRO X-ray diffractometer using $\text{CuK}\alpha$ radiation (45 kV accelerating voltage and 20 mA applied current). The surface area was determined by the Brunauer-Emmett-Teller (BET) method using a Quantachrome Autosorb IQ. X-ray photoelectron spectroscopy (XPS); (PHI 5000 VersaProbe II). Transmission electron microscopy (TEM) was performed on a Morgagni Transmission Electron Microscope and the images were obtained at an accelerating voltage of 60 kV. Field emission scanning electron microscopy (FESEM) (JSM-7500 F; JEOL–Japan) using parallel beam geometry and a multi-purpose thin film attachment. Optical reflectance of the synthesized powder material was recorded by UV–vis–NIR spectrophotometer (PerkinElmer UV/Vis/NIR; Lambda 750) equipped with integrating sphere was used to record the diffuse reflectance spectra of the synthesized powder nanocomposite in the wavelength range of 200–900 nm. Kubelka–Munk (K–M) transformation was applied on the % R values to calculate the band gap of the synthesized $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ nanoparticles by plotting $(F(R) \times hv)^2$ and $(F(R) \times hv)^{1/2}$ versus hv (eV).

Photocatalytic Experiments

Luzchem photochemical reactor (LZC4) system was used for evaluation of the visible light photocatalytic performance of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ in terms of 2-CP degradation. In a typical experiment fixed amount (0.5 to 1.5 g/L) of the photocatalyst was mixed with the 2-CP solution in a cylindrical reactor cell (250 ml capacity) provided with air circulation to ensure aerobic conditions required for photocatalysis. Magnetic stirring was provided to ensure thorough mixing. The reaction contents were irradiated with visible light lamps from top and sides with spectral range from 400 to 700 nm and spectral irradiance of 17.45 mW/cm^2 monitored by Luzchem power monitor at a distance of 12 cm from the light source and a maximum of 180 min irradiation time. For analysis 2.5 ml samples were drawn after every 30 minutes and analyzed by using UV-visible spectrophotometer (HACH LANGE DR6000) at 274 nm. The 2-CP degradation efficiency was calculated, after analysis, using the following relation:

$$\text{Degradation \%} = \left[\frac{C_0 - C_t}{C_0} \right] \times 100 \quad (1)$$

where C_0 and C_t denote initial and residual concentration of 2-CP (mg/L) respectively and t denotes the irradiation time (min).

Results and Discussion

Morphology, structural and optical properties of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$

The X-ray diffraction (XRD) peaks corresponding to the body-centered cubic (bcc) phase of Ag_3PO_4 are presented in **Fig. 1** for $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composite. The diffraction peaks for Ag_3PO_4 nanoparticles are represented in black font color at 2θ values 21.8° , 29.6° , 33.5° , 36.7° , 48.2° , 55.0° , 57.5° , 60.9°

and 72.1° corresponding to the diffractions from the (110), (200), (210), (211), (310), (222), (320), (321), and (332) crystal planes. Results shown exhibit crystalline integrity as reported in literature [23] , [28] and the XRD peaks for Degussa P25 are easily distinguishable from the XRD patterns with representative (101), (004), (200), (211) and (002) crystalline planes represented in red font color.

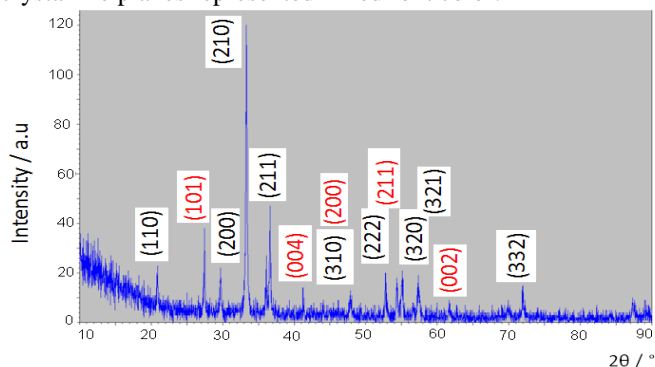


Fig. 1: XRD patterns of the prepared $\text{Ag}_3\text{PO}_4/\text{TiO}_2$; Ag_3PO_4 (black font) and Degussa P25 (red font)

The porosity and surface area of the photocatalyst were analyzed by N_2 physisorption using Quantachrome Autosorb IQ. After degassing the sample at a temperature of 200°C for 180 min, nitrogen porosimetry was performed at a temperature of 77 K over the 0 to 1 pressure ratio. Results reported in Table I relate to the values available in literature [29].

TABLE I
 POROSIMETRIC DETERMINATIONS OF $\text{Ag}_3\text{PO}_4/\text{TiO}_2$

Catalyst	BET SSA (m^2/g)	Pore Volume(cm^3/g)
Degussa P25	50	0.1
$\text{Ag}_3\text{PO}_4/\text{TiO}_2$	15	0.0358
Ag_3PO_4 ^[30]	1.6	0.002

The FSEM and TEM images of synthesized $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ nanoparticles are shown in **Fig. 2** (a) and (b) respectively. From the TEM image of the $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ composite, two distinct particles are identified. Larger particles with average particles size of 28-78 nm diameters represent TiO_2 Degussa P25 while the finer particles mainly deposited on the surface of TiO_2 in the range of 10-17 nm belong to Ag_3PO_4 . The smaller size range of Ag_3PO_4 nanoparticles can be attributed to the adsorption of silver ions onto the negatively charged surface of TiO_2 thus limiting the growth of Ag_3PO_4 nanoparticles. Therefore the size of Ag_3PO_4 in the composite structure can be controlled by using appropriate amount of AgNO_3 Precursor.

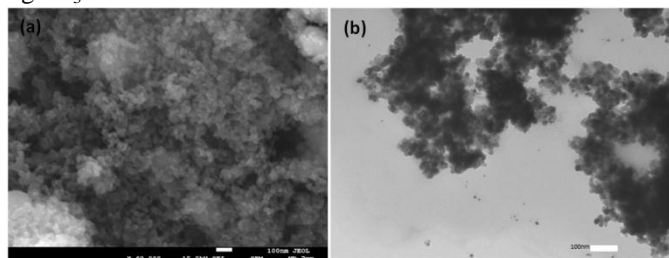


Fig. 2: (a) FSEM and (b) TEM images of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$

shown in **Fig. 6**, an initial increase in catalyst dose from 0.5 to 1 g/L showed increase in degradation efficiency from 56% to 70.3% attributed to increased number of catalyst active sites with catalyst dose. However further increase in catalyst dose to 1.5 g/L showed decrease in degradation efficiency up to 41.4%. At high catalyst dose agglomeration and decreased penetration of light become significant thus responsible for the decreased photodegradation [38].

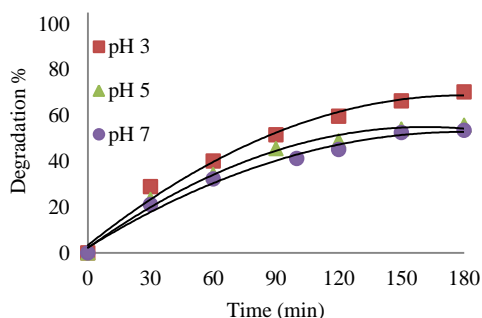


Fig. 5: Effect of pH change on photocatalytic degradation of 2-CP (Catalyst dose: 1g/L, 2CP conc. =50 mg/L, Vis. Irradiation 112W).

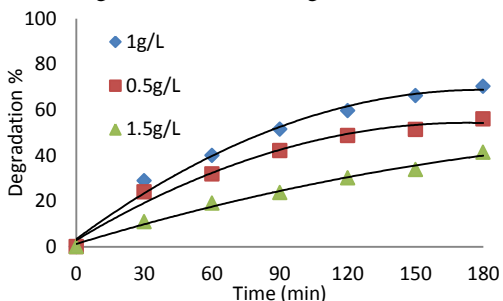


Fig. 6: Effect catalyst dose

(pH =3, 2CP conc. =50 mg/L, Vis. Irradiation 112W)

The photocatalytic performance of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ under optimized conditions was investigated over a wide initial pollutant concentration range from 15 to 50 mg/L (**Fig. 7**). Keeping the catalyst dose of 1g/L, 100 % degradation efficiency was observed when 15 mg/L of 2-Cp was exposed to visible light for 120 minutes. However further increase in 2-CP concentration to 25 and 50 mg/L resulted in decrease in degradation efficiency from 92.5% to 70.3% respectively for 180 min of irradiation time. This can be attributed to the decreased probability of 2-CP molecules to react with the active species on the surface of $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ with increase in initial concentration. To evaluate the structural stability, the photocatalyst was recovered after use from the solution by decanting and centrifugation followed by washing with distilled water, filtration, and drying at 40°C for 180 min. The recovered catalyst was subjected to reuse for 3 runs with fresh 2-CP solution and it showed 100% visible light degradation efficiency for 15 mg/L of 2-CP as shown in **Fig. 8**.

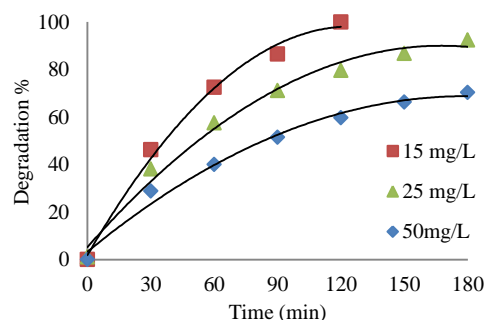


Fig. 7: Effect catalyst dose on photocatalytic degradation of 2-CP (pH =3, Catalyst dose = 1g/L, Vis. Irradiation 112W)

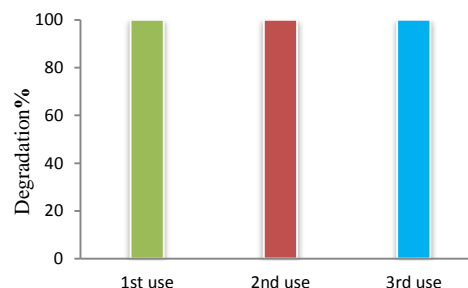


Fig. 8: Catalyst reuse (Catalyst dose = 1g/L, pH =3, 2-CP conc. 15mg/L, Vis. Irradiation 112W)

Conclusions

In-situ precipitation method was adopted to synthesize stable visible light active $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ nanoparticles photocatalyst. The photocatalytic activity of the synthesized catalyst was successfully tested for degradation of 2-CP under visible irradiation. The XRD and TEM studies confirmed the crystallinity and the nano size of the particles. The XPS analysis results confirmed the presence of Ag, P, O and Ti elements with their respective oxidation states corresponding to $\text{Ag}_3\text{PO}_4/\text{TiO}_2$. The synthesized catalysts showed high photoactivity with complete degradation of 15 mg/L 2-CP achieved at pH 3 within 120 minutes and 92.5 % degradation of 25 mg/L within 180 minutes of visible light irradiation.

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