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# Fabrication of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/silver orthophosphate Heterojunction Catalyst for the Visible Light Mediated Remediation of Refractory Pollutants



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ARTICLE INFO	A B S T R A C T		
<i>Keywords:</i> Silver orthophosphate Ternary composite Photodegradation Organic pollutants	The development of silver orthophosphate based ternary composite catalyst for the augmented visible light assisted photocatalytic abatement of toxic refractory pollutants was accepted. It was confounded that the synthesized catalyst effectively degrade toxic organic dyes including methylene blue (MB), methyl orange (MO), rhodamine B (RhB) and acid red 18 (AR 18) with complete decolourisation and above 90 % mineralization. The hazardous pesticides such as 2, 4-dichlorophenoxyacetic acid (2,4-D), highly toxic insecticide acephate and the pharmaceutical antibiotic tetracycline were succesfully degraded. Here, it is the first time reporting La <sub>2</sub> O <sub>3</sub> /Bi <sub>2</sub> O <sub>3</sub> doped silver orthophosphate ternary catalyst for the removal of toxic organic pollutants in a short time with excellent mineralization. The better reproducibility and accountable stability of the composite catalyst paved the way for making it a promising catalyst for future applications.		

#### 1. Introduction

The excess use of hazardous pesticide and toxic organic dyes are a severe threat to human health and the environment. Most of the commonly used dyes such as methylene blue, methyl orange, acid red 18 and rhodamine B (RhB) contaminate aqueous solutions and causes heavy water pollution. The use of organochlorine (OC) compounds such as 2,4-dichlorophenoxyacetic acid (2,4-D) [1], organophosphorus (OP) compounds such as acephate [2] and the antibiotic tetracycline [3] will accumulate in the water sources which causes harm to the bioorganisms. 2,4-D is a highly toxic water-soluble herbicide that is a hormonally active agents and hence referred to as endocrine-disrupting agents causing chromosomal mutations. Acephate is an insecticide commonly used in fruits and vegetables that can harm the environment due to the accumulation of its residues [4]. Tetracycline is a low-cost antibiotic in which its uncontrolled use may harm the living organisms [5]. Hence it is inevitable to develop a suitable catalyst that can control all these toxic dyes and pesticides in less time with more efficiency. Even though various degradation techniques are available, photodegradation is green, cost-effective and low energy consumption. The development of semiconductor-based photocatalyst heterojunction shows excellent degradation efficiency with accountable mineralization. The main drawback of these catalyst heterojunctions is their rapid recombination tendency. So the main challenge for these degradation techniques was to

develop a new catalyst for reducing the recombination tendency and improving the catalytic efficiency. Several silver based photocatalyst such as AgBr [6], Ag<sub>2</sub>CO<sub>3</sub> [7], Ag<sub>3</sub>PO<sub>4</sub> [8], Ag<sub>2</sub>CrO<sub>4</sub> [9], etc shows better photocatalytic activity. Silver orthophosphate (Ag<sub>3</sub>PO<sub>4</sub>) having a narrow bandgap which shows high photocatalytic activity in the silver-based family. The noticeable peculiarity of Ag<sub>3</sub>PO<sub>4</sub> was its very low valence band level which promotes the generation of more active photogenerated holes and electrons [10-12]. However, the main drawback of Ag<sub>3</sub>PO<sub>4</sub> was its poor photostability and a high tendency for photoreduction of silver ions  $(Ag^+)$  from  $Ag_3PO_4$  into metallic silver. These challenges can be reduced by proper doping of Ag<sub>3</sub>PO<sub>4</sub> with highly active photocatalyst composite [13]. Recently reported Ag<sub>3</sub>PO<sub>4</sub> based binary composite such as Ag<sub>3</sub>PO<sub>4</sub>/WO<sub>3</sub> [14], Ag<sub>3</sub>PO<sub>4</sub>/NaTaO<sub>3</sub> [15], Ag<sub>3</sub>PO<sub>4</sub>/NiFe<sub>2</sub>O<sub>4</sub> [16], Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> [17], etc. and ternary composite including Ag<sub>3</sub>PO<sub>4</sub>/ZnO/Fe<sub>3</sub>O<sub>4</sub> [18], BiVO<sub>4</sub>/RGO/Ag<sub>3</sub>PO<sub>4</sub> [19], gC<sub>3</sub>N<sub>4</sub>/MoS<sub>2</sub>/Ag<sub>3</sub>PO<sub>4</sub> [20], etc. shows good degradation property. Lanthanum based oxides are the nontoxic catalyst which possesses excellent stability and enhanced catalytic efficiency. Lanthanum oxide (La<sub>2</sub>O<sub>3</sub>) is one of the active rare-earth metal oxides for the effective degradation of dyes and pesticides. Several reported La2O3 based composite such as La<sub>2</sub>O<sub>3</sub>@TiO<sub>2</sub> [21], ZrO<sub>2</sub>@La<sub>2</sub>O<sub>3</sub> [22], ZnO@La<sub>2</sub>O<sub>3</sub> [23], etc shows pronounced catalytic activity. The role of La2O3 in the composite is the proper transfer and rapid separation of photogenerated electrons and holes. The coupling of La2O3 with a bismuth-based

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catalyst shows excellent photocatalytic activity [24–26]. Hence it was planned to develop a binary composite with La<sub>2</sub>O<sub>3</sub> and bismuth-based catalyst. We aimed to develop an efficient photocatalyst for the removal of toxic dyes and pesticides in a short time. In this paper, La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> binary catalyst doped silver orthophosphate ternary composite was developed for the successful treatment of refractory pollutants with excellent mineralization and pronounced catalytic efficiency.

## 2. Experimental

## 2.1. Materials

Lanthanum nitrate  $(La(NO_3)_3.6H_2O, Bi(NO_3)_3.5H_2O, sodium hydrogen phosphate (Na_2HPO_4), silver nitrate (AgNO_3) and tetracycline <math>(C_{22}H_{24}N_2O_8)$  of analytical grade were supplied from Merck, India and are used as such. Distilled water was used throughout the experiment.

#### 2.2. Synthesis of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> composite

 $La(NO_3)_3.6H_2O$  (0.01 g) was dissolved in 15 mL deionized water and Bi(NO\_3)\_3.5H\_2O (0.015 g) was dissolved in 15 mL ethylene glycol. The two solutions are mixed and kept for 1 h continue stirring. Then the solution is allowed for 10 min microwave irradiation and the resultant dark yellow solution is calcined for 3 h at 600 °C in a muffle furnace and the obtained powder was used for further characterizations.

## 2.3. Synthesis of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> composite

Add  $La_2O_3/Bi_2O_3$  (0.01 g) composite into 15 mL deionized water and sonicated for 10 min. The solution was allowed for continuous stirring and add an equimolar amount of  $Na_2HPO_4$  into the above solution and after 10 min add AgNO<sub>3</sub> solution into it with vigorous stirring. Ag<sub>3</sub>PO<sub>4</sub> was formed in the binary composite results in the formation of  $La_2O_3/Bi_2O_3/Ag_3PO_4$ .

#### 2.4. Characterization techniques

Fourier transform infrared (FT-IR) spectroscopy was done for understanding the bonding interaction between the composites using Perkin Elmer 400 spectrometer. The structural characterization of the composite was determined using X-ray diffraction (XRD) analysis using Bruker AXS D8 Advance X-ray diffractometer of wavelength ( $\lambda = 1.5406$ A°) with Cu Kα radiation. The surface morphology of the catalyst composite was examined using field emission scanning electron microscope (FESEM) with VEGA 3 TESCAN. The inner structure of the composite was done with a high-resolution transmission electron microscope (HRTEM) with a specification of the JOEL-JEM-2100 microscope. The quantification of elemental states was analyzed with X-ray photoelectron spectroscopy (XPS) using a VG Multi-Lab 2000 system containing Mg Ka radiation at 20 kV. The diffused reflectance spectroscopy (DRS) is analyzed with Shimadzu-UV-3600 Plus of Japan for measuring the band gap using the Tauc plot. The surface area of the composite catalyst was determined using the Brunauer-Emmet-Teller (BET) of Thermo Fischer Scientific. The chromatographic separation of the pesticides and antibiotics was done using high-performance liquid chromatography (HPLC) using SPD-20A, Schimadzu Corporation, Japan. The organic and mobile phase was acetonitrile and 0.02 M ammonium acetate with 0.1 % formic acid respectively with an injection volume of 5  $\mu$ L with a flow rate of 1 mL/min. The total organic carbon (TOC) analysis was done with TOVCPH total organic carbon analyser, Shimadzu Corporation, Japan. The path of the photodegradation was examined using ultraperformance liquid chromatography coupled to quadrupole time-offlight mass spectrometry (Waters Xevo G2 Q TOF) in positive and negative electrospray ionization.

#### 3. Results and Discussion

#### 3.1. Structure and morphology

The bonding interactions of the synthesized composite was developed by Fourier transform infrared (FT-IR) spectroscopy. Fig. 1a shows the sharp peak at 644 and 578  $\text{cm}^{-1}$  are due to the formation of La<sub>2</sub>O<sub>3</sub> nanoparticle. The peak at 505.57  $\text{cm}^{-1}$  corresponds to the vibrations of Bi-O bond of Bi<sub>2</sub>O<sub>3</sub> nanoparticle. Also the peaks at 860 and 660 cm<sup>-1</sup> show the interatomic vibration modes of Bi-O bond. The sharp peak at 542.36 and 942.67 cm<sup>-1</sup> determines the vibration modes of phosphate molecules. The structural determination of the composite was done with the X-ray diffraction (XRD) technique. The planes (011), (012), (003), (111), (112) and (005) represent the angle 28.54, 39.43, 44.67, 54.56 and 77.46°, respectively of hexagonal La<sub>2</sub>O<sub>3</sub> with the primitive crystal lattice (JCPDS No: 83-1344). Bi<sub>2</sub>O<sub>3</sub> formation is manifested with the diffraction planes of (120), (-211), (130), (131) and (231) at the angle of 27.43, 32.54, 37.21, 41.45 and 45.67°, respectively of monoclinic Bi<sub>2</sub>O<sub>3</sub> system with primitive crystal lattice (JCPDS No: 41-1449). The formation of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> binary composite was confirmed by the peaks at 32.12, 36.34, 43.54, 47.52 and 62.18° for the planes of (-211), (130), (003), (111) and (241), respectively. The structural confirmation of 10 wt. % La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> was mainly assigned with the presence of a phosphate group in the composite. The sharp peaks at 21.32, 30.32, 33.45, 36.67, 48.31, 52.75 and 57.35° for the planes of (110), (200), (210), (310), (222), (320) and (321), respectively show the planes of Ag<sub>3</sub>PO<sub>4</sub>. The peaks at 62.34 and 77.43° determine the peak of Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>, respectively. All these diffraction studies confirm the formation of the ternary nanocomposite (JCPDS No: 06-0505) (Fig. 1b). The diffused reflectance spectra (DRS) of the various modified composite shows the wavelength shifting to redshift in the visible region shows the improvement in the photocatalytic activity of the composite (Fig. 1c). The calculation of the bandgap reveals the reason for the high activity of the composite. The bandgap of the binary composite can be found using the Tauc plot. The ternary composite shows less binding energy (1.81 eV) on comparing with the binary composite (2.62 eV). The measurement of the bandgap of the synthesized composite can be done with the Kubelka- Munk equation,

$$\alpha h\vartheta = A(h\vartheta - Eg)^{1/n} \tag{1}$$

Where  $\propto$  represents absorption coefficient,  $h\vartheta$  is the incident photon energy, A is a constant and n depends on the type of optical transition. Here the combination of the composite results n = 2, describes indirect transition [27]. The optical band gap calculated using the Tauc plot is used to find the valence band and conduction band potentials of the particle which results in the mechanism of photodegradation. The following equations are used to found the valence band and conduction band potential,

$$E_{VB} = \chi - E_e + 0.5 \text{ Eg}$$
<sup>(2)</sup>

$$E_{CB} = E_{VB} - E_g \tag{3}$$

## 3.2. Structure and morphology

The activity of the catalyst depends on its surface morphology. Hence, field emission scanning electron microscopy (FESEM) analysis is carried out. Fig. 2(a & b) shows the non-uniform irregular shaped La<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> nanoparticles, respectively. The fabrication of the binary composite La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> morphology was depicted in Fig. 2c. The development of spherical shaped silver orthophosphate was successfully depicted in Fig. 2d. The binary composite La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> was anchored to the Ag<sub>3</sub>PO<sub>4</sub> nanoparticle was successfully observed here. To confirm the elemental composition and the arrangement of various elements in the



Fig. 1. (a) FT-IR, (b) XRD, (c) DRS and (d) Tauc plot of La<sub>2</sub>O<sub>3</sub> (LaO), Bi<sub>2</sub>O<sub>3</sub>(BiO), 47 wt % La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> (LaO/BiO) and 10 wt % La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>.



Fig. 2. FESEM of (a)  $La_2O_3$ , (b)  $Bi_2O_3$ , (c) 47 wt %  $La_2O_3/Bi_2O_3$  and (d) 10 wt %  $La_2O_3/Bi_2O_3/Ag_3PO_4$ .

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whole composite, elemental mapping was done. Fig. 3a represents the elemental mapping of all the elements present in the catalyst composite. Each element are represented by different colours and the mapping image of each of the elements are separately shown (Fig. 3(b–f)).

The internal structural aspects of the synthesized catalyst composite were depicted with transmission electron microscope (TEM) analysis, which was manifested in 100 nm scale. As analysed by FESEM, the inner nonuniform particles of La<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> are revealed in Fig. 4a & b. The blending of the irregular La<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> was shown in Fig. 4c. The doping of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> on the pristine spherical shaped Ag<sub>3</sub>PO<sub>4</sub> was confirmed in Fig. 4d. The adjunction of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> binary composite on the spherical shaped Ag<sub>3</sub>PO<sub>4</sub> accounts for its enhanced photocatalytic activity. The high resolution TEM shows the fringe width of the composite and was found that the fringe width of the bulk Ag<sub>3</sub>PO<sub>4</sub> in the composite was 0.135 nm. The bright spots in the selected area electron diffraction (SAED) confirm the crystalline nature of the developed ternary composite (Fig. 4e & f).

## 3.3. Surface area and elemental quantification of the composite

The activity of the catalyst composite was determined with their

available surface area and the pore diameter. The surface area of the composite was analyzed with Brunauer-Emmet-Teller (BET) and the pore diameter with the Barret-Joyner-Halenda (BJH) plot. The surface area possessed by silver orthophosphate is only 0.68 m<sup>2</sup>/g and the pore diameter was 5.26 nm. On coupling with more surface area possessed composite (La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>), the surface area of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> becomes 12 times higher than the pristine Ag<sub>3</sub>PO<sub>4</sub> nanoparticle (Fig. S1). Table 1 shows the surface area and pore diameter possessed by various modified composites.

The chemical states of the elemental composition in the composites are illustrated with X-ray photoelectron spectroscopy (XPS). Fig. 5a represents the La 3d spectrum of La<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/ Ag<sub>3</sub>PO<sub>4</sub> composites. All the spectra reveal the characteristic satellite splitting of La in the range of 834.58 and 851.31 eV, which is the splitting due to La 3d 5/2 and La 3d 3/2, respectively. These peaks show the presence of La<sup>3+</sup> state of the element in the composite. Also, the energy gap between the two satellite peak is at about 16.73 eV, which reveals the formation of La<sub>2</sub>O<sub>3</sub> phase. The figure reveals the slight shifting of the two satellite peaks in La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/ Ag<sub>3</sub>PO<sub>4</sub> which manifested the formation of binary and ternary composites. Fig. 5b shows the elemental state of bismuth in the fabricated



Fig. 3. Elemental mapping of all the elements in 10 wt % La2O3/Bi2O3/Ag3PO4.



Fig. 4. TEM image of (a)  $La_2O_3$ , (b)  $Bi_2O_3$ , (c) 47 wt %  $La_2O_3/Bi_2O_3$ , and (d) 10 wt %  $La_2O_3/Bi_2O_3/Ag_3PO_4$ , HRTEM (e) and (f) SAED pattern of 10 wt %  $La_2O_3/Bi_2O_3/Ag_3PO_4$ .

Table 1	
BET surface area and BJH pore diameter of various modified composites.	

-		-
Sample	Surface Area (m <sup>2</sup> /g)	Pore Diameter (nm)
La <sub>2</sub> O <sub>3</sub>	12.35	14.21
Bi <sub>2</sub> O <sub>3</sub>	15.51	18.24
47 wt % La <sub>2</sub> O <sub>3</sub> /Bi <sub>2</sub> O <sub>3</sub>	13.17	15.15
Ag <sub>3</sub> PO <sub>4</sub>	0.68	5.26
10 wt % La <sub>2</sub> O <sub>3</sub> /Bi <sub>2</sub> O <sub>3</sub> /Ag <sub>3</sub> PO <sub>4</sub>	8.602	3.24

composites. The two prominent peaks at 159.02 and 164.37 eV reveals the formation of Bi-O bond, which occurs due to the splitting of Bi 4f 2/7 and Bi 4f 2/5, respectively. The energy separation between the two symmetric peaks are at about 5.4 eV which is attributed to the formation of  $Bi^{3+}$  oxidation state of  $Bi_2O_3$ . The slight shift observed for the Bi 4f symmetric peaks for  $La_2O_3/Bi_2O_3$  and  $La_2O_3/Bi_2O_3/Ag_3PO_4$  shows the formation of composite materials. Moreover, the O 1s spectra at a peak

range of 532.05 and 532.53 eV reveal the formation of O-La in La<sub>2</sub>O<sub>3</sub>. Also, the prominent peak at 528.91 and 531.07 eV attributed to O-Bi bond formation. The minor shifting observed for these two peaks in La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub> confounded the composite formation (Fig. 5c). The sharp peaks at 366.81 and 372.76 eV of Ag corresponds to 3d 5/2 and 3/2 supports the formation of Ag<sub>3</sub>PO<sub>4</sub>. The formation of phosphate molecule was examined with the prominent peak at 131.42 (2p 3/2) and 132.37 (2p 1/2) eV corresponds to the formation of phosphate molecule. All the results are in well agreement with binary and ternary composite formation (Fig. 5d & e).

## 3.4. Photocatalytic degradation

The photocatalytic activity of the synthesized catalyst was analyzed with various toxic acidic and basic dyes such as methylene blue (MB), methyl orange (MO), rhodamine B (RhB) and acid red 18 (AR 18). The low bandgap energy possessed by the catalyst composite shift to longer



**Fig. 5.** XPS of (**a**) La 3d of La<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>, (**b**) Bi 4f of Bi<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>, (**c**) O 1s of La<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>/ Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>, (**d**) Ag 3d, and (**e**) P 2p of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>.

wavelength which results in the absorption of solar radiation in the visible region. Moreover, the synthesized binary composite can able to form an Z-scheme pathway in the presence of visible light which will be easier for the generation of photogenerated electrons and hole pairs and are responsible for the abatement of refractory pollutants. The optimization of the photocatalytic abatement was done with MB and observed an accountable degradation efficiency. Fig. 6a shows the UV–vis. spectra of the photocatalytic degradation of MB with and without the catalyst. It was shown that the presence of catalyst shows an enhanced degradation of 97.42 % degradation efficiency within 5 min. Fig. 6b shows the degradation efficiency in the C/C<sub>o</sub> vs. time graph. The % of degradation is calculated with the following equation,

Here C<sub>0</sub> represents the analyte initial concentration and C<sub>t</sub> represents the concentration at time t. The photodegradation efficiency of the modified composite is compared with the bar diagram and confirmed the very high degradation efficiency for 10 wt % La2O3/Bi2O3/Ag3PO4 ternary composite (Fig. 6c). The kinetics of the photocatalytic study was analyzed by plotting  $-\ln C/C_0$  vs time graph. Fig. 6d shows the kinetic study and reveals that the experiment follows pseudo-first-order kinetics with a high rate constant of the order  $k = 0.6111 \text{ min}^{-1}$ . To extend the application of the developed catalyst composite, a photodegradation study was also done for MO, RhB and AR 18. It was observed that the complete decolorisation and mineralization occur for MO at a wavelength of 463 nm within 5 min with 97.33 % degradation efficiency. At the same time, the degradation study for RhB and AR 18 realized accountable degradation efficiency with excellent decolorisation and mineralization. The RhB degraded within 2 min at the wavelength of 553.5 nm with 96.26 % efficiency whereas AR 18 degraded within 10 min at the wavelength of 536 nm with an efficiency of 95.79 %. All these

dyes are in better agreement with the pseudo-first-order kinetics during the process of photodegradation (Fig. S2, S3 & S4). These high efficiency and very low time interval make the catalyst a promising one for future industrial applications.

Even though photodegradation of these toxic dyes occurs with complete decolourisation, the extend of mineralization of the degraded dyes has to be analyzed. For that, total organic carbon (TOC) analysis was done for all the dyes before and after degradation. Fig. 7 shows the TOC analysis data which reveals the TOC removal percentage of MB, MO, AR 18 and RhB as 91.36, 95.18, 94.55 and 93.44 %, respectively. The data confirms the complete decolourisation and mineralization of these dyes with the developed composite catalyst within a short time [28]. Table 2 represents the previously reported catalyst for the photodegradation of various dyes. The data helps to compare the efficiency of the synthesized catalyst with other early reported catalysts which reveals the excellent efficiency and accountable time for the complete decolourisation and mineralization of the toxic organic dyes.

The activity of the synthesized catalyst can be verified with various pesticides and antibiotics. The organochlorine pesticide 2,4-dichlorophenoxyacetic acid (2,4-D), organophosphorus insecticide acephate and antibiotic tetracycline were used for this. All the pesticides and antibiotics were treated with the synthesized catalyst and undergo visible light-mediated photodegradation. The determination of the degradation tendency of the catalyst was observed with the highperformance liquid chromatography (HPLC). The standard of 2,4-D, acephate and tetracycline were optimized in the retention time of 8.10, 17.06 and 2.88 min, respectively. The effect of the photodegradation study was done by comparing the intensity of the standard solution with the degraded solution after several hours. The intensity of the peak of 2,4-D, acephate and tetracycline were almost decreased after 180, 60 and 120 min, respectively. These suggest the accountable



Fig. 6. (a) UV-vis. spectra of MB, (b) C/C<sub>0</sub> vs time graph, (c) bar diagram for comparison of degradation efficiency, and (d) kinetic study of the composite.



Fig. 7. TOC removal (%) of MB, MO, AR 18 and RhB with 10 wt %  $\rm La_2O_3/Bi_2O_3/Ag_3PO_4.$ 

activity of the developed photocatalyst (Fig. 8)

The mineralization of the composite catalyst with these pesticides and antibiotics can be determined with the total organic carbon (TOC) analysis. Fig. 9 shows the TOC removal % of 2,4-D, acephate and tetracycline in different periods. About 65.98 % TOC removal occurs for 2,4-D after 180 min whereas acephate shows a TOC removal of 89.56 %. Tetracycline shows an effective TOC removal of about 92.93 %. These results manifested the enhanced mineralization of toxic organic pesticides and antibiotics.

Even though these toxic pesticides and antibiotics show better

Table 2				
Comparison	with	previously	reported	works.

No	Catalyst	Irradiation Light	Pollutants Degraded	Time (min)	Reference
1	Fe <sub>3</sub> O <sub>4</sub> /ZnO/ Ag <sub>3</sub> PO <sub>4</sub>	Visible Light	RhB	100	[29]
2	PANI/Ag <sub>3</sub> PO <sub>4</sub> /	Visible Light	RhB	40	[30]
	NiFe <sub>2</sub> O <sub>4</sub>	-	MO	25	
3	Ag <sub>3</sub> PO <sub>4</sub> / nanocellulose	Visible Light	МО	80	[ <mark>31</mark> ]
4	Ag <sub>3</sub> PO <sub>4</sub> /PAN	200 W mercury lamp	MB	60	[32]
5	Ag <sub>3</sub> PO <sub>4</sub> / bentonite	Visible Light	RhB	21	[33]
6	Ag <sub>3</sub> PO <sub>4</sub> /HHSS <sup>a</sup>	Visible Light	MO	12	[34]
7	La2O3/Bi2O3/	Visible Light	MB	5	This work
	Ag <sub>3</sub> PO <sub>4</sub>		MO	5	
			RhB	2	
			AR 18	10	

<sup>a</sup> HHSS – hierarchial hollow silica spheres.

mineralization, the nature of the degraded product should be mentioned. Thus high-resolution mass spectra (HRMS) are analyzed for comparing the standard and degraded product of 2,4-D, acephate and tetracycline. The HRMS results confirm that all the degraded products obtained were less toxic than the standard solution. The 2,4-D (m/z = 219.96) get converted in to 2,4-dichloro anisole (m/z = 175.97) and acephate (m/z = 183) degraded to form a small compound (m/z = 111.04) and the heavier tetracycline antibiotic (m/z = 445) degraded in to bicyclic compound with an m/z of 210 (Figs. S5 &S6). The degradation route of 2,4-D, acephate and tetracycline are described below (Fig. 10).



Fig. 8. HPLC and C/C<sub>0</sub> of (a & b) 2,4-D, (c &d) acephate, and (e &f) tetracycline, respectively.



Fig. 9. TOC analysis of 2,4-D, acephate, and tetracycline 10 wt %  $\rm La_2O_3/Bi_2O_3/Ag_3PO_4.$ 

The essential criteria needed for an effective catalyst was its

recyclability which was analysed by doing photodegradation studies of about four different cycles. It was observed that an enhanced photodegradation efficiency occurs in all the different cycle runs suggesting the excellent recyclability of the catalyst. To use a catalyst for industrial purposes, the stability of the catalyst needs to be evaluated. The structural properties of the composite were identified by comparing XRD, FT-IR and XPS survey spectrum of the fresh and used samples. The results reveal that there occurs only a slight variation of the peaks which is attributed to the high stability of the developed composite (Fig. 11a–d).

The photodegradation mechanism of the catalyst composite needs to be explained. Several experiments are analyzed for the enhanced activity of the catalyst. Fig. 12a shows the fluorescence spectra of the various modified composite. The intensity of the fluorescence spectra of the optimized ternary catalyst composite decreases as compared with the unmodified system. This reveals the less recombination tendency possessed by the developed catalyst which allows the rapid movement of electron-hole pairs in the composite. To account for the active species of degradation steps, a radical scavenger experiment was carried out. The experiment was done with ethylenediamminetetraacetic acid (EDTA) for holes, benzoquinone (BQ) for superoxide radical and isopropyl alcohol for hydroxyl radical. Fig. 12b reveals the order of active species for photodegradation was  $h^+ > O_2^- > OH^-$ . Thus holes ( $h^+$ ) were



Fig. 10. Degradation route of 2,4-D, acephate, and tetracycline with 10 wt % La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>.



Fig. 11. (a) Recycling runs of the composite for the degradation of MB, (b) XRD, (c) FT-IR, and (d) XPS survey spectra of fresh and used catalyst.

considered as the main active species for photodegradation [35]. The effect of photocurrent was analyzed using an amperometric experiment done in  $0.1 \text{ M} \text{ Na}_2\text{SO}_4$  solution. The experiment was done with a proper switch on and off method with the various modified composite. It was found that the modified ternary composite shows an enhanced current

which is twice as possessed by the bare GCE suggesting the better catalytic activity of the composite (Fig. 12c). The electrochemical activity of the synthesized composite was analyzed with the potentio electrochemical impedance spectroscopy. The impedance analysis was done in the solution of 0.1 M KCl and 5 mM ferric ferrocyanide solution with a



Fig. 12. (a) Fluorescence spectra, (b) scavenger study, (c) amperometric experiment and (d) Nyquist plot of the various modified composite.

frequency ranges from 5 Hz to 25 MHz. The radius of the obtained Nyquist plot describes the resistance possessed by the composite. Fig. 12d shows a very low radius of the developed composite than the other unmodified systems reveals the low resistance shown by the composite. This low resistance reveals the high transfer of electrons throughout the composite which corroborates the excellent electrochemical activity of the composite [36].

## 3.5. A plausible mechanism of photodegradation

All these experiments opened the platform to explain the photocatalytic mechanism of the developed catalyst. On irradiation of visible light, photogenerated holes and electrons are formed. The conduction band potential ( $E_{CB}$ ) of  $Bi_2O_3$  was about +0.11 V, which is not suitable for the production of super oxide radical ( $^{-}O_{2}$ ). The E° of  $O_{2}/^{-}O_{2}$  is -0.33 V vs NHE which tells the theoretical difficulty for the formation of <sup>-</sup>O<sub>2</sub> An interesting fact is that super oxide radicals can be developed in the gaseous phase reaction system when adequate amount of adsorbed O2 is present. Since high intensified solar radiation comprised of small percentages of ultraviolet radiations. Moreover, the configuration of  $\mathrm{La}^{2+}$ consist of a d electron which results in its intrinsic instability. Thus,  ${\rm La}^{2+}$ release the trapped electrons to the adsorbed O2 molecule and thus forming  $-O_2$  [37,38]. There occurs rapid transfer of electrons from the valence band of  $Bi_2O_3$  to its conduction band results in the accumulation of a large number of holes. The photogenerated holes from the valence band of Bi<sub>2</sub>O<sub>3</sub> get easily transferred to the valence band of Ag<sub>3</sub>PO<sub>4</sub> since the potential difference was only 0.40 V. The highly active electrons in the conduction band of Ag<sub>3</sub>PO<sub>4</sub> get easily move to the conduction band of Bi<sub>2</sub>O<sub>3</sub> which results in the generation of active holes in the valence band of Ag<sub>3</sub>PO<sub>4</sub>. These holes get combine with the toxic organic

pollutants result in the successful degradation of these refractory pollutants (Scheme 1). It was also confirmed with the scavenger study as the active species for photodegradation were holes ( $h^+$ ) and super oxide radicals ( $^{-}O_2$ ). The low fluorescence intensity for the modified composite reveals the less recombination property of the modified composite suggesting the accumulation of more holes in the valence band of Ag<sub>3</sub>PO<sub>4</sub>. On irradiation of visible radiation, La<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and Ag<sub>3</sub>PO<sub>4</sub> get excited and surrounded with photoactive holes and electrons (Eqs. 5, 6 & 7). The combination of Ag<sub>3</sub>PO<sub>4</sub> with electron and Bi<sub>2</sub>O<sub>3</sub> with holes get interconverted into Ag<sub>3</sub>PO<sub>4</sub> with holes and Bi<sub>2</sub>O<sub>3</sub> with electrons. The formation of superoxide radicals occurs from electrons surrounded by



Scheme 1. Plausible mechanism of photodegradation of La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub>/Ag<sub>3</sub>PO<sub>4</sub>.

 $La_2O_3 + h\upsilon \rightarrow La_2O_3 (h^+) + La_2O_3 (e^-)$  (5)

$$Bi_2O_3 + h\upsilon \rightarrow Bi_2O_3 (h^+) + Bi_2O_3 (e^-)$$
 (6)

$$Ag_{3}PO_{4} + h\upsilon \rightarrow Ag_{3}PO_{4} (h^{+}) + Ag_{3}PO_{4} (e^{-})$$
(7)

$$Ag_3PO_4 (e^-) + Bi_2O_3 (h^+) \rightarrow Ag_3PO_4 (h^+) + Bi_2O_3 (e^-)$$
 (8)

$$Bi_2O_3(e^-) \to O_2^- + La_2O_3(e^-) \text{ or } Bi_2O_3$$
 (9)

## 4. Conclusions

La<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> doped silver orthophosphate ternary catalyst composite for the efficient treatment of refractory pollutants was established. The successful removal of toxic dyes such as MB, MO, RhB and AR 18 with complete decolourisation and enhanced mineralization was done. Organochlorine herbicide 2,4-D, organophosphorus insecticide acephate and tetracycline were effectively degraded with the formation of small less toxic organic byproducts which demands the need for the developed catalyst for industrial applications.

#### CRediT authorship contribution statement

**Thomas Abraham:** Conceptualization, Methodology, Resources, Writing - original draft. **Ragam N. Priyanka:** Data curation, Visualization. **Subi Joseph:** Data curation, Visualization. **Anu Rose Chacko:** Data curation, Visualization. **Beena Mathew:** Conceptualization, Supervision, Project administration, Writing - review & editing.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.materresbull.20 21.111299.

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