

Photocatalytic Degradation of Quinoline Yellow over Ag3PO4

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1	Photocatalytic degradation of Quinoline Yellow over Ag ₃ PO ₄
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19	
20	Abstract
21	In this study, the ability of Ag_3PO_4 to achieve the photocatalytic degradation of quinoline
22	yellow (QY) a hazardous and recalcitrant dye, under UVA and visible light was investigated.
23	The photocatalyst Ag ₃ PO ₄ was synthesized through a precipitation method, and characterized
24	by X-ray diffraction (XRD), scanning electron microscope (SEM), BET Brunauer-Emmett-
25	Teller (BET) analysis, UV- Differential Reflectance Spectroscopy (DRS) and Fourier
26	transform infrared spectroscopy (FTIR). Ag_3PO_4 could successfully induce the photocatalytic
27	degradation of QY under UVA and visible light. Optimal parameters were 0.5 $g.L^{-1}$ of the
28	catalyst, 20 ppm of QY and pH~7. Ag ₃ PO ₄ was 1.6-times more efficient than TiO ₂ Degussa
29	P25 under UV_A light in degrading QY. Total organic carbon (TOC) analyses confirmed the
30	almost complete QY mineralization. At least 8 intermediate degradation products were

31 identified by liquid chromatography coupled to high resolution mass spectrometry. The 32 stability of Ag_3PO_4 was satisfactory as less than 5% Ag metal appeared in XRD analyses after 33 3 reuse cycles. These results show that under optimized conditions Ag_3PO_4 can efficiently 34 achieve quinolone yellow mineralization.

35 Keywords: Ag₃PO₄, visible light, dye, Photocatalysis, Photoproducts

36

37 **1. Introduction**

Advanced Oxidation Processes (AOPs), especially heterogeneous photocatalysis, is an 38 environmentally friendly technique [1] that is used for pollutants elimination in water and air 39 [2], bacterial inactivation [3], reduction of heavy metals to less harmful species and water 40 splitting [4]. Photocatalysis initiates oxidation reactions through the generation of holes (h^+) 41 and electrons (e) pairs. The resulting radicals act as oxidants of organic pollutants and 42 43 convert them into CO₂, H₂O and inorganic salts [5]. For this reason, extensive investigation was directed toward semiconducting materials which have positive points like the 44 45 environmental safety and facile preparation. On the other hand, popular photocatalysts such as ZnO [6], TiO₂ [7,8], and SnO₂ are attractive because of their low cost, environmental 46 friendliness [4], thermal stability and bio safe property [9,10]. However, because they possess 47 a wide gap (Eg > 3 eV), their efficacy and sensitivity only occur under UV-light making 48 solar-light application not enough efficient [11, 12]. In this respect, active research is directed 49 to the elaboration of catalysts active under visible light for the wastewaters treatment [13-15]. 50

Recently, Ag₃PO₄ has gained great attention as a photocatalyst [16]. It exhibits a high photocatalytic activity upon visible-light irradiation for organic pollutants decomposition [17-20] and selective oxidation of alcohols [18]. Its photocatalytic properties depend on morphology, and active surface area [21-23]. The photocatalytic degradation of anionic dyes by Ag₃PO₄ was reported to involve the photogenerated holes that show a high oxidation capability in the valence band [24]. In addition, the existence of PO_4^{3-} makes easy the separation of electrons and holes (e⁻/h⁺) pairs through the interfacial junction electric field which generates a dipolar moment. Ag₃PO₄ synthesized by a one step process has shown that both the free radicals and the photo holes generated contribute to the dyes mineralization [22]. For application of photocatalysis process in the environmental protection, it is important to use cheap, easily synthesized or readily available photocatalyst.

62 Dyes are widely used in food and cosmetic products as well as in the textile industries for their variety of colors and their chemical stability. The production of synthetic dyes 63 exceeds 700 000 tons per year among which 140000 tons are released in the effluents in a 64 65 non-controlled way [25]. Given their toxicity [26], these dyes represent an important source of pollution and a serious threat for the aquatic environment [27]. Many dyes show a high 66 stability against temperature, light and biodegradation [28] making their elimination a major 67 68 challenge in the water treatment processes. Physico-chemical treatments (coagulation/filtration, coagulation/flocculation, adsorption, etc.) are currently used for the 69 70 elimination of industrial effluents [26]. However, such techniques do not degrade 71 contaminants but only transfer them from a liquid phase to the solid phase, and additional treatments are thus required [30]. 72

73 Quinoline Yellow (QY) is a synthetic dye and one of the most employed food additives, even though it has also applications in cosmetic and pharmaceuticals preparations 74 [31]. This dye may cause some diseases like dermatitis and allergic reactions, and has been 75 banned by the standards of the food industry in countries like USA, Australia, Norway and 76 Iran [32,33]. Many N-containing dyes like QY undergo natural anaerobic reductive 77 degradation, which can generate aromatic amines suspected to be carcinogenic [26]. For these 78 79 reasons, it is necessary to undertake investigations aiming to eliminate it from water resources. Several studies concerning QY heterogeneous photocatalysis were investigated 80

using ZnO [34], TiO₂ [34,35] and TiO₂/polyaniline composite [36]. However, to our
knowledge, product studies are scarce.

Here, we investigated the photocatalytic degradation of QY using Ag₃PO₄ as a 83 photocatalyst. Ag₃PO₄ was elaborated by a facile method at room temperature, namely the 84 precipitation. The first part of this paper concerns the physical characterization of the material 85 using XRD, SEM, DRS, BET method, and FTIR spectroscopy. It is complementary to the 86 electrochemical properties previously reported [20]. The second part of this paper is focused 87 on the optimization of operating parameters such as pH, catalyst dose and QY initial 88 concentration. Then, photoproducts were characterized by means of ultrafast high-pressure 89 liquid chromatography (UHPLC) coupled to electrospray ionization high-resolution mass 90 spectrometry (ESI-HRMS), while mineralization and the photocatalyst stability were also 91 carried out. 92

93

94 **2. Experimental**

95 2.1. Chemicals

Quinoline Yellow was a mixture of the mono- and disulfonic acids (acid yellow 3, Sigma-96 Aldrich, Fig. 1). The other chemicals were: titanium dioxide Degussa P25 (TiO₂ P25,99.5%, 97 Evonik), disodium phosphate (Na₂HPO₄,99%, Merck), silver nitrate (AgNO₃, 99.9%, Alfa 98 Aeser), sodium hydroxide (NaOH, 99.99%, Sigma-Aldrich), perchloric acid (HClO₄, 99.99%, 99 Sigma-Aldrich), sodium acetate for HPLC LiChropur ($C_2H_3NaO_2$, $\geq 99\%$, Supelco), potassium 100 bromide FT-IR grade (KBr, 99%, Merck), formic acid for LC-MS LiChropur (CO₂H₂, 98% -101 100%, Supelco), acetonitrile LiChrosolv hyper grade for LC-MS (CH₃CN, Merck) and 102 acetonitrile gradient grade for HPLC ACS (≥ 99.9 %, Carlo Erba). All reagents were used 103 104 without any purification process. Water was purified using a RIOS 5 reverse osmosis and synergy (Millipore) device (resistivity 18 M Ω .cm, DOC < 0.1 mg.L⁻¹). 105

106 **2.2. Synthesis of Ag₃PO₄**

107 Ag₃PO₄ was prepared by precipitation as previously described [20]. Briefly, 15 mL of a 108 Na₂HPO₄ solution (3 mM) was mixed dropwise to 30 mL of AgNO₃ solution (3 mM) under 109 magnetic stirring during 3 h at room temperature. The precipitate with a yellow color 110 characteristic of Ag₃PO₄, was collected and washed with deionized water and ethanol. The 111 yellow powder was recovered after drying at 70 °C under static vacuum overnight.



112

113 **Fig. 1** Quinoline Yellow structure using ChemSketch software

114 **2.3. Characterization of Ag₃PO₄**

The synthesized phase was confirmed by X-ray diffraction using Co K α line (λ = 1.790300 Å) 115 at a 2θ scan rate of 2 per min. The micrograph of the sample was examined by SEM analysis 116 using a JEOL microscope (Model JSM 6360- LV). The BET surface area and pore volume 117 118 were calculated from the N₂ adsorption/desorption isotherm at 77K using an ASAP 2010 Micrometrics equipment. The external surface area, micropore area and micropore volume 119 120 were computed by the t-plot technique. The total pore volume was determined from the liquid N_2 volume at high relative pressure (0.99). The subtraction of the micropore volume from the 121 total volume gave the volume of mesopore. The DRS was measured using a 122 123 spectrophotometer (Specord 200 Plus). The concentration of Ag before and after recycling in hydrolyzed samples was determined using Atomic Absorption Spectrophotometry (AAS) 124

125 (Perkin-Elmer A700). A calibration curve was created by analyzing Ag (1, 2, 3, 4 μ g.mL⁻¹) 126 standard solutions, and the instrument was adjusted to 328.1 nm.

127 **2.4. Photocatalytic experiments**

Irradiations were conducted in two devices; one was equipped with fluorescent tubes (Philips 128 HPK 15 W) emitting in the near UV region (maximum at 365 nm) while the other with LED 129 (Delleled 5W) emitting within the wavelength range 400-800 nm. Pyrex reactors were 130 connected to a thermostatically controlled water bath. For irradiation under visible 50 mL of 131 suspensions containing Ag₃PO₄ and QY were added to the reactor of 100 mL of capacity 132 while for UVA irradiation 15 mL of suspensions were placed in the reactor of 30 mL 133 capacity. Solution pH was adjusted using NaOH or HClO₄. In both systems, the suspensions 134 were kept at 25 °C under constant agitation (600 rpm). Aliquots of 0.5 mL were regularly 135 withdrawn, vigorously centrifuged and filtered through a 0.45 µm filter (Waters, Millipore) 136 137 before analyses. The degradation yield (%) was evaluated from the relationship:

138 Degradation in
$$\% = \frac{C_0 - C_t}{C_0} \times 100$$

139 (1)

140 C_0 being the initial QY concentration and C_t the concentration at time (t).

141 **2.5 Analytical Analyses**

A UV-vis spectrophotometer (Model Specord 200 plus) was used to monitor the degradation of QY ($\lambda_{max} = 434$ nm). QY and its photoproducts were separated using a Shimadzu 8040 HPLC system, equipped with a SPD-M30A DAD detector, and a Nucleodur 100-3 C₁₈ endcapped column (125 mm×4.0 mm, 3 µm particle size). The mobile phase was a mixture of (A) 30 mmol.L⁻¹ sodium acetate and (B) acetonitrile in the proportions of 80% A and 20% B, at a constant flow rate of 0.75 mL.min⁻¹. The detection wavelength was set at 290 nm and the temperature oven at 30 °C.

UHPLC-ESI-HRMS was performed on an Orbitrap Q-Exactive (Thermo Scientific) mass 149 spectrometer coupled to a Ultimate 3000 RSLC (Thermo Scientific) apparatus. The mass 150 spectrometer with heated electrospray ionization was operated in both positive and negative 151 ESI modes with a spray voltage of 3 kV for both modes. The column was a Waters analytical 152 column (2.1 mm×100 mm, 1.7 µm particle size) and the column oven temperature was 153 regulated at 30 °C. The aqueous solvent (A) was a mixture of formic acid (0.1%) and 154 acetonitrile as organic phase (B). The separation was achieved using a gradient program 155 156 consisting of 0-7.5 min 5%, 7.5-8.5 min 99% of the mobile phase B. The injection volume was taken at 10 μ L while the flow rate was fixed at 0.450 mL.min⁻¹. 157

A Shimadzu 5050 TOC analyzer was used to monitor the mineralization of QY. Thepercentage of mineralization was calculated using the following equation:

160 Mineralization =
$$\frac{(OC_0 - OC_t)}{OC_0} \times 100$$

161 (2)

where OC_0 is the organic carbon present in the solution at time 0 and OC_t at time t. OC is obtained by subtracting the inorganic carbon from total carbon.

164

165 **3. Results and discussion**

166 **3.1. Characterization of Ag₃PO₄**

167 The XRD pattern of Ag_3PO_4 had narrow peaks, characteristic of a high crystallization (Fig. 2 168 a). The simulated and the measured diffractograms showed a good fit of 1.6 with R_{wp} and R_{exp} 169 (%) less than 10% (Fig. 2b). The microstructural parameters obtained after the Rietveld 170 refinement were used to determine the dislocation density after elaboration. The coherent 171 domains of diffraction (Dv) had an average value of 178 nm and the corresponding 172 microstrain (ε) a percentage of 2.5×10⁻³. It is well known that the presence of crystallographic 173 defects, such as dislocations, has a strong influence on the properties of materials. The dislocation density (ρ) calculated from equations (3, 4, 5) was ρ = 2.6×10¹² in this work. This value is acceptable and confirm the crystal quality. During the elaboration, the dislocation assisted slip activities occured in the studied material. In addition, the processes used in this study had no effect on the lattice parameters (a= 6.0316 nm in this work), variation of which is only sensitive to the effects of electronic linkages of the chemical species.

179 $\rho = (\rho_D \rho_\epsilon)^{1/2}$

- 180 (3)
- 181 Where ρ_D and $\rho_{\epsilon are}$ calculated using eq 4 and 5:

$$182 \qquad \rho_{\rm D} = \frac{3}{{\rm D}{\rm v}^2}$$

183 (4)

184
$$\rho_{\varepsilon} = \frac{2K\varepsilon^2}{b^2}$$

185 (5)

b the Burger vector, and K is a constant equal to 10 for a Gaussian distribution of thedeformations.





189

Fig. 2. XRD spectrum: Identified atomic plane of the Ag₃PO₄ phase (a). Rietveld refinement of the Ag₃PO₄ phase (b)



Fig. 3. SEM images of Ag₃PO₄

The SEM micrographs of Ag_3PO_4 are illustrated in Fig. 3. It can be observed that the

Sample	Surface area (m ² .g ⁻¹)		Pore v	olume (ci	$m^{3}.g^{-1}$)	
	S _{BET}	S _{ext}	S _{mic}	V _T	V _{mes}	M _{mic}
Ag ₃ PO ₄	6	5.18	0.82	0.0192	0.0188	0.0004

morphology of the powder was uniform and agglomerated in spherical grains with regular size lying between 1 and 1.5 μ m. The particles surface was relatively smooth. The N₂ adsorption-desorption isotherm of Ag₃PO₄ is shown in Fig. 4. The isotherm belonged to the type IV according to IUPAC classification, which indicates a well-developed mesoporous nature. In addition, the desorption isotherm showed a H3-hysteresis, characteristic of a capillary condensation observed in mesoporous structures [36]. The detailed textual parameters of Ag₃PO₄ are gathered in Table 1. The specific surface area and total pore volume were equal to 6 $\text{m}^2.\text{g}^{-1}$ and 0.0192 $\text{cm}^3.\text{g}^{-1}$, respectively.

Table 1. Textural characteristics of Ag₃PO4

The formation of Ag_3PO_4 was further supported by the FTIR spectroscopy, using the 208 routine KBr technique in the 400 - 4500 cm⁻¹ region. The peaks centered at 545 and 1082 cm⁻¹ 209 ¹ (Fig. 5) were assigned to molecular vibrations of P-O of the phosphate (PO_4^{3-}) unit [18], and 210 the bands at 3401 and 1641 cm⁻¹ were attributed to the stretching vibration of O-H groups of 211 adsorbed water. The H₂O molecules and OH groups adsorbed on the surface of Ag₃PO₄ are 212 oxidized into free hydroxyl radicals that achieve the photodegradation of organic pollutants 213 [37]. The intense peak at 1383 cm⁻¹ corresponded to the nitrate impurity, AgNO₃ having been 214 used for the preparation of Ag₃PO₄ [38]. 215

The knowledge of the gap band (E_g) is of great utility in the solar energy conversion; it is evaluated from DRS by using the known relationship:

218
$$(\alpha_{\lambda}h\nu)^{k} = \text{Constant} \times (h\nu - E_{g})$$
 (6)

219 α_{λ} (cm⁻¹) is the optical adsorption coefficient and hv (eV) the energy of the incident photon. 220 The nature of the optical allowed transition is deduced from the exponent k (= 2, direct) or 221 (0.5, indirect). The gap E_g is deduced from the intersection of the plot $(\alpha hv)^2$ with the 222 abscissa-axis. The direct transition at 2.52 eV (Fig. 6) was in conformity with the yellow color 223 of Ag₃PO₄ that is a promising photocatalyst under visible light [20].



Fig. 4. BET of Ag₃PO₄ at 77 K



Fig. 5. FTIR spectrum of Ag₃PO₄



Fig. 6. Direct optical transition of Ag₃PO₄

225 **3.2. Photocatalytic degradation of QY**

Neither the irradiation of QY under UVA for 4 h in absence of Ag₃PO₄ nor the stirring 226 of QY solution pH 7 in presence of Ag₃PO₄ in the dark for 24 h led to a significant 227 concentration loss. These results demonstrated that direct photolysis and adsorption on the 228 photocatalyst were negligible in these conditions. The very poor adsorption of QY on Ag₃PO₄ 229 230 in neutral medium can be explained by electrostatic repulsion between the negatively charged surface of the photocatalyst and anionic QY as observed for methyl orange and orange G [39]. 231 In contrast, when the suspension containing Ag₃PO₄ and QY was exposed to UVA or visible 232 light, an almost complete degradation was achieved within 40 min and 70 min under visible 233 light and UVA, respectively (Fig. 7). Experiments were then undertaken to optimize 234 parameters. 235

236 **3.2.1. Parameters optimization**

In this set of experiments, Ag_3PO_4 suspensions were irradiated with visible light. The degradation profile of QY was monitored until 40 min. The QY decrease rate, r, obeyed an apparent pseudo-first order model (r = k × C), therefore the degradation rate constants, k, were obtained from the slope of the plots $ln(C/C_0)$ vs irradiation time.

The photocatalytic degradation of QY (20 ppm) by Ag_3PO_4 (0.5 g.L⁻¹) was studied by varying pH in the range of 4-11. As shown in Fig. 8, the degradation rate of QY was pH- dependent. The highest rate constant (0.094 min⁻¹) was observed at pH 7. The rate constant
drastically decreased below pH 7 by 65-90% while by 40-50% above (Fig. 8). This highest
efficiency at neutral pH, close to the natural environment, is a very positive point in terms of
application.

The reaction was also studied at QY concentrations in the range of 5 - 40 ppm, at a fixed dose of Ag_3PO_4 (0.5 g.L⁻¹) and at pH 7. Between 5 and 20 ppm, the rate constant laid between 0.065 and 0.072 min⁻¹, while at 30 and 40 ppm the value dropped to 0.02 and 0.011 min⁻¹, respectively. At 40 ppm, the absorbance of the QY solution was equal to 3.2 at 434 nm, QY had therefore a very strong filter effect and prevents Ag_3PO_4 to absorb light.

The Ag₃PO₄ photocatalyst dose was varied in the range of $0.25 - 1 \text{ g.L}^{-1}$ to avoid the photocatalyst excess and ensure a total absorption of efficient incident photons. Fig. 10 shows that the degradation rate increased with the catalyst dose and reached a maximum for 0.5 g.L⁻¹ . The rate constant k was equal to 8.6 min⁻¹. An increase of the catalyst dose up to 1.5 g. L⁻¹ led to a reduced photoactivity due to a lower availability of photoactive sites on the Ag₃PO₄ surface and a weak light utilization [40]. The optimal conditions (Ag₃PO₄ dose = 0.5 g.L⁻¹, [QY]=20 ppm and pH~7) were kept for experiments under UVA irradiation.



light (\bigcirc).([QY] ₀ = 20 ppm, Ag ₃ PO ₄	and Ag_3PO_4 dose = 0.5 g.L ⁻¹)
dose = 0.5 g.L^{-1} and pH ~ 7)	

Conditions	$k(\min^{-1})$	\mathbf{R}^2	Reference



260 3.2.2. Compared photocatalytic activity Ag₃PO₄ /TiO₂ Degussa P25

The photocatalytic efficiency Ag_3PO_4 and TiO_2 Degussa P25 were compared at the dose of 0.5 g.L⁻¹. Under visible light Ag_3PO_4 was active while TiO_2 non active and under UVA, Ag_3PO_4 was 1.6-times more efficient that TiO_2 . This demonstrates the interest of Ag_3PO_4 as a photocatalyst.



- 267
- 268
- 269
- 270
- 271
- 272 **3.3 Product studies**

HPLC and UHPLC-ESI-HRMS analyses were conducted for products identification. 273 QY is sold by Sigma-Aldrich as a mixture of mono and disulfonic acids C₁₈H₁₂NO₅SNa -274 $C_{18}H_{11}NO_8S_2Na_2$. Yet, we only detected two peaks at m/z = 353.0352 in ES⁻. They 275 correspond to two isomeric forms of the monosulfonic acid (Fig. 11 a, Fig. 11 b). Three 276 samples were analyzed after 44, 70 and 175 min of irradiation under UVA. In the first two 277 samples the QY conversion extent was of 50% and 80% and in the third one QY was fully 278 279 degraded (Fig.11 c). A typical HPLC chromatogram is shown Fig. 11c and Table 3 gives the accurate and experimental m/z, the chemical formula in the limit of 5 ppm and the possible 280 structure of the 8 detected photoproducts (TPs) by UHPLC-ESI-HRMS. In general, TPs were 281 detected by negative electro spray ionization. 282

 TiO_2 Degussa P25 + QY + UVA

 $Ag_3PO_4 + QY + UVA$

 $Ag_3PO_4 + QY + Visible light$

 TiO_2 Degussa P25 + QY + Visible light

0.998

0.987

0.992

This work

This work

This work

This work

0.018

0.029

0.099

 $< 1.8 \times 10^{-4}$

TP1 showed m/z = 208.0074 corresponding to $C_9H_7O_3NS$ for the neutral molecule. This TP was likely quinoline sulfonic acid formed by C-C cleavage and its detection allowed us to locate the sulfonic group of QY on the quinoline ring. With m/z = 251.9977, TP2 had the molecular formula of $C_{10}H_7O_5N$ and corresponded to TP1+CO₂. It was therefore likely a carboxylated

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- 289
- 290 291 292

Table 3. UHPLC-HRMS data of QY-Ag₃PO₄ irradiated under UVA

Compound	Accurate	Exp.	Δppm	Chemical	Proposed chemical]
	m/z of	m/z of [M-		formula	structure	
	$[M-H]^{-}$	H^{-}				

Quinoline Yellow	353.0352	353.0287	1.84	C ₁₈ H ₁₁ O ₅ NS	SO ₃ H O N
TP1	208.0063	208.0074	-2.95	C ₉ H ₇ O ₃ NS	SO ₃ H
TP2	251.9961	251.9977	-4.96	C ₁₀ H ₇ O ₅ NS	SO ₃ H CO ₂ H
TP3	149.0233	149.0229	2.68	$C_8H_6O_3$	
TP4	165.0182	165.0187	-3.03	$C_8H_6O_4$	
TP5	121.0284	121.0286	-1.65	C ₇ H ₆ O ₂	
TP6	89.0233	89.0231	2.24	C ₃ H ₆ O ₃	0 O O O O H
TP7	87.0077	87.0074	3.45	C ₃ H ₄ O ₃	HO
TP8	61.9873	61.9868	-4.6	NO ₃ -	

294

quinoline sulfonic acid formed by cleavage of the 5-carbon ring. TP3 with m/z = 149.0229corresponded to a molecular formula of C₈H₆O₃. On the other hand, TP4 that showed m/z =165.018 corresponded to C₈H₆O₄ and most probably to phthalic acid. TP3 might be therefore the corresponding aldehyde. TP5 was identified to benzoic acid (m/z = 121.0286 and C₇H₆O₂). TP6 and TP7 with m/z = 89.0231 and 87.0074 were two aliphatic acids with 3 atoms of carbon produced by oxidation and opening of the rings. Nitrate ions (m/z = 62.0049) were also detected. TP1-TP5 were detected after 44 and 70 min of irradiation while TP6, TP7 and nitrate ions in the samples irradiated for 175 min. The degradation pathways aresummarized in Fig.12.

304



310

311 312

Fig. 12 Proposed degradation mechanism for QY in Ag₃PO₄ process

313 **3.4. Mineralization**

TOC evolution during the photocatalytic reaction was monitored to explore the percentage of QY mineralization under the optimal conditions (QY 20 ppm, Ag₃PO₄ dose

 $=0.5 \text{ g.L}^{-1}$ and pH 7) (Fig. 13). After 70 min of irradiation under UVA corresponding to the full degradation of QY, only 5% of OC were transformed into CO₂. Total OC removal was reached after 48 h of irradiation time. This long time to achieve complete mineralization indicates that intermediates were difficult to oxidize.





Fig. 13 Organic carbon evolution during QY photocatalytic degradation in presence of Ag₃PO₄ under UVA [QY] $_0 = 20$ ppm, Ag₃PO₄ dose = 0.5 g.L⁻¹ and pH ~ 7)

323

3.5. Catalyst stability and reusability

To assess the photostability and reusability of Ag₃PO₄ under visible irradiation for the 324 photodegradation of QY, three photodegradation experiments were successively performed. 325 326 After each cycle, the catalyst was centrifuged, filtered, thoroughly rinsed with water and ethanol and finally dried at 70°C. After three recycles, 87, 78 and 64% of QY were 327 photodegraded (Fig. 14 a) within 40 min. These results revealed some deactivation effects. 328 This reduction can be explained by the reduction of Ag^+ to metallic state Ag in the presence 329 of photogenerated electrons. To quantify the percentage of photoreduced Ag⁺ both XRD and 330 AAS analyses were carried out (Table 4). XRD results after the three cycles are shown in Fig. 331 14 b. Small peaks of Ag appeared (< 5%) [20,41]. On the other hand, results of the literature 332 showed that when dispersed in water and irradiated under visible light for a long time, 333 Ag₃PO₄ remained stable (dissolution <1 ppm). Our analyses in atomic absorption 334 spectroscopy confirmed this result (Table 4). 335



Fig. 14 Reusability of Ag_3PO_4 photocatalyst. XRD pattern after three cycles (a). Degradation yield after 40 min of irradiation under visible light for three runs (b). ([QY]₀ = 20 ppm, Ag_3PO_4 dose= 0.5 g.L⁻¹ and pH ~ 7)

Table 4. Solubility of Ag₃PO₄ in different conditions

342			
	$[Ag^+]^a$ (ppm)	After 75 min	After 24H of
343	conditions	of irradiation	irradiation
344	Ag_3PO_4 in the dark	0.018	0.019
245	Ag ₃ PO ₄ +Visible light	0.017	0.017
545	Ag ₃ PO ₄ +QY+Visible light	0.02	0.02

346

341

347 4. Conclusion

Ag₃PO₄ was synthesized by precipitation at ambient temperature. It was shown to 348 induce the photocatalytic oxidation of Quinoline Yellow under visible irradiation with an 349 efficiency much higher than that of TiO₂ Degussa P25 under UVA. The optimal parameters 350 351 such as initial pH, QY concentration and catalyst dose were determined. Photoproducts of QY were identified based on the UHPLC-ESI-HRMS analysis and were different than those 352 identified using TiO₂. The complete mineralization of QY could be achieved after 48 of 353 irradiation against 70 min for QY elimination. Some XRD peaks of Ag metal (~ 5%) were 354 355 noticeable after 3 reuses. It can be concluded that Ag₃PO₄ needs efficient hetero-junction to 356 avoid its photocorrosion. This is the subject of our future investigations.

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360						
361	Refe	rences				
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