Original Article

Photocatalytic Efficiency of Silver Doped TiO₂-PC500 for Dyes Removal from Water under UV and Solar Radiations: Comparative Study

Samira Mezbour, Mohammed Fouzi Ghorab

Laboratory of Water Treatment and Valorization of Industrial Wastes, Chemistry Department, Faculty of Sciences, University Badji Mokhtar Annaba, Annaba, Algeria

ABSTRACT

Silver doped TiO₂-Millenium-PC500 (Ag/TiO₂-PC500) was prepared by wet chemical reduction method and characterized by X-ray diffraction, scanning electron microscopy, X-ray fluorescence, fourier transformed infrared and Brunauer-Emmett-Teller techniques. Ultraviolet (UV) and solar photocatalytic efficiency of Ag/TiO₂-PC500 for the removal of congo red (CR) and crystal violet (CV) from water was investigated. The influence of several operational parameters (photocatalyst, dye concentrations, pH, H₂O₂) was studied. Ag/TiO₂-PC500 exhibits better performance under UV and solar irradiations for the discoloration of CR as compared to TiO₂-PC500. In the presence of Ag/TiO₂-PC500, at free pH, CR was completely discolored within 15 min under UV ($k = 0.064 \text{ min}^{-1}$) and solar irradiation ($k = 0.207 \text{ min}^{-1}$). The discoloration rates of CV markedly improved under UV and solar irradiation, with Ag/TiO₂-PC500 as compared to TiO₂-PC500 albeit not complete ($R \leq 63.9\%$). Addition of H₂O₂ (0.01 mol L⁻¹) improved significantly the discoloration of CV ($R \leq 99.3\%$) with both photocatalysts whatever the light source. The better performance of Ag/TiO₂-PC500 (84.87 m² g⁻¹) as compared to TiO₂-PC500 (287.09 m² g⁻¹) confirms the positive contribution of silver during the photocatalytic process through its ability to absorb UV and solar light and slow the electron-hole (e⁻/h⁺) recombination. The COD measurements show moderate mineralization rates for both dyes independently of the irradiation source.

Keywords: silver-doped-TiO₂-Millenium-PC500, solar photocatalysis, congo red, crystal violet

INTRODUCTION

It is firmly established that wastewaters produced by the ever increasing industrialization pose serious environmental and health problems to humans. Consequently, and in view of the growth of world population coupled with the scarcity of soft water, the decontamination of these wastewaters has become a necessity as well as a major challenge [1]. Several viable processes for wastewaters treatment have been developed. These include physical processes such as adsorption [2], electrochemical processes [3], coagulation, reverse osmosis and membrane processes [4] and chemical processes such as ozonation, ultraviolet (UV) ozonation, Fenton, photo-Fenton etc. [5]. Among these processes, the advanced oxidation processes (AOPs) have proven to be efficient for water

remediation [6–10]. Heterogeneous photocatalysis is which is one of these AOPs using semiconductors is most effective and attractive. Amongst the various semi-conductors used in heterogeneous photocatalysis titanium dioxide (TiO₂) is the most widely studied as it presents several advantageous properties such as chemical stability in wide pH range, low toxicity, low cost and activation by solar radiations [11–13]. Heterogeneous photocatalysis is often used to degrade recalcitrant organic pollutants and is based on the use of light to activate semiconductors and trigger photoreactions. The product of this photoreaction is the powerful oxidizing hydroxyl radical species (HO[•]) generated in aqueous solutions as shown in equations (1), (2) and (3) [14].

Corresponding author: Mohammed Fouzi Ghorab, E-mail:fouzi.ghorab@univ-annaba.dz

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This generally results, under optimized conditions, in a complete mineralization of organic pollutants. The activity of TiO_2 is strongly related to the light sources and the inherent recombination of the photo-induced electrons and holes. One drawback of the use of TiO_2 is its large band gap (~ 3.2 eV) which restricts its use in the UV region even though its photoactivity is attracting considerable attention when used under solar light as it can be activated by the 5% of UV light reaching the earth surface [15]. In order to extend titanium dioxide's photo-response capacity towards solar radiation, several artifices have been adopted [16,17].

Over the past few years, solar-driven photocatalysts using doped TiO_2 have been prepared using metal or non-metal in order to extend the photoresponse towards lower energy excitation [18,19]. These preparations include doping or photo-doping with transition metals, non-metals or/and the combination between them [20]. Solar driven photocatalysis is attracting more attention from researchers as solar irradiation is a low-cost source of energy, abundant, renewable and pollution-free. Because of its high stability, excellent electrical and thermal conductivity, biocompatibility and relatively lower cost [21,22] several researchers have used silver doped TiO_2 to study the photocatalytic degradation, under natural solar irradiation, of numerous organic contaminants [23] and in the antibacterial activities [24].

To the best of our knowledge, among the various types of commercial TiO_2 used for doping and degradation studies, TiO_2 -Millenium-PC500 has not been reported despite its high surface area ($>250 \text{ m}^2 \text{ g}^{-1}$) and 100%-anatase structure. In this study, Ag-doped TiO_2 -PC500 was prepared by wet chemical reduction method, characterized and used for the photocatalytic degradation of two dyes, an anionic dye congo red (CR) and a cationic dye crystal violet (CV) in aqueous suspensions under UV and solar light irradiations. The activity of the as-prepared photocatalyst was then compared to that of untreated TiO_2 -PC500.

MATERIALS AND METHODS

Materials

Titanium dioxide 'PC500' was from Millenium Inorganic Chemicals (Lyon, France); sodium carbonate, sodium nitrate and silver nitrate were from Fluka (Munchen, Germany).

The two dyes used, CR and CV, were from Biochem (Cosne-Cours-sur-Loire, France). HCl, HNO_3 and NaOH of analytical grade were from Fluka. Double distilled water was used through the experiments.

Preparation of Ag/ TiO_2 -PC500

Silver doped TiO_2 -PC500 was prepared by a wet chemical reduction method similar to that reported in the literature [25]. The method adopted here corresponds to a loading ≤ 1 wt.% which, according to several studies, gives the best photocatalytic performance [26,27]. Firstly, 5 g of TiO_2 -PC500 powder was thoroughly mixed with 4.6 mL of a 0.1 M-solution of AgNO_3 and 5 mL of a 1%-solution of Na_2CO_3 as reducing agent then the suspension was dried at 100°C and finally heated at 400°C for 6 h.

Characterization methods

X-ray diffraction (XRD) powder profiles of TiO_2 -PC500 and Ag/ TiO_2 -PC500 were obtained using a D8 Advance A 25 BRUKER X-ray diffractometer; Bruker, Karlsruhe, Germany) with Cu $K\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) operated at 40 kV and 25 mA. The crystallite sizes of the photocatalysts were calculated using Scherrer's equation (4) [28].

$$D = \frac{k\lambda}{B\cos\theta} \quad (4)$$

where D is the crystallite size; k is a constant (0.89); B is the full width at half-maximum height (FWHM) of anatase (101) diffraction peak and θ is the diffraction angle.

The (101) reflections of anatase and the Scherrer's equation were used for the estimation of average crystallite size. The analysis was carried out in the $5\text{--}80^\circ$ (2θ) range. Scanning electron microscopy (SEM) images were taken using a Jeol JSM6360LV with Maximum resolution of 50 nm and maximum voltage of 30 kV. The chemical compositions of the photocatalysts were determined by X-ray fluorescence (XRF) (XEPOS/XEP01; Spectro Co., Kleve, Germany). Fourier transformed infrared (FT-IR) spectra of the two photocatalysts were recorded in the region $4000\text{--}400 \text{ cm}^{-1}$ (Shimadzu Co., Japan). The Brunauer-Emmett-Teller surface areas (SBET) of the samples were determined from a N_2 adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using a Quantachrome Instruments V11.0. Before analysis, the samples were degassed under vacuum at 200°C for 14 h to evacuate the physisorbed moisture.

Photocatalytic experiments

The photocatalytic experiments were carried out using two types of irradiations: artificial UV and natural solar light. The photocatalytic experiments under UV irradiation were carried out using an experimental set up as described in our previous work [29]: a Pyrex double jacket reactor kept under a metal enclosure of cylindrical shape (35 cm diameter and 50 cm in height), it presents two openings one to introduce the UV lamp (Phillips TLD15W) with $\lambda_{\max}$ at 350 nm. The second opening allows the introduction of the reactor (150 mL) and sampling. The experiments under solar irradiation were carried out using 250 mL-Pyrex beakers open to the atmosphere in front of the chemistry department during the period June and July 2018. The intensities of solar radiation were measured at 365 nm with a radiometer VLX-3W (Vilber Loumart, Marne-la-Vallée, France) equipped with a 1-cm-diameter cell. During the period of experiments these were in the range 1.6 to 1.9 mW cm⁻². Water evaporation during the solar experiments was estimated at 6% after 4 h of exposure. Due to the inherent non-reproducibility of solar radiations and in order to minimize experimental errors, the study of each parameter was performed simultaneously on a set of experiments. This is considered to be within experimental errors. In a separate trial, experiments were performed in triplicate under the same experimental conditions in order to evaluate the errors. All the results were reproducible within $\pm 10\%$ variation.

PZC determination

The point of zero charge (PZC) was determined for both photocatalysts using the salt addition method [30] where 0.200 g of the photocatalyst was added to 40.0 mL of 0.1 mol L⁻¹ NaNO₃ in ten 50-mL beakers. The pH was adjusted using a pH-meter to 2, 3, 4, 5, 6, 8, 9 and 10 (± 0.1 pH units) with 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH as required in each beaker. These were shaken for 24 h in a revolving shaker to reach equilibrium. After this period of time the resulting pH was measured and the initial pH (pH₀) vs. the difference between initial and final pH values (Δ pH) was plotted. The PZC was taken as the point where Δ pH = 0.

Method of analysis

The discoloration of CR and CV were monitored using respectively a UV/Vis spectrophotometer (JENWAY 7315 series) at $\lambda_{\max} = 499$ nm and $\lambda_{\max} = 591$ nm. Prior to their analysis samples were filtered through a Millipore membrane (0.45 μ m). Calibration curves for dyes' concentrations measurements gave determination coefficients $R^2 \geq 0.998$.

Solutions pHs were monitored using a JENWAY pH-meter. The dark adsorption of dyes on photocatalysts, referred to as percentage removal, was calculated using equation (5):

$$\text{Removal}(\%) = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (5)$$

where C_0 and C_f are respectively the initial and final dyes concentrations.

The photodiscoloration of dyes after dark stirring, referred to as percentage discoloration, was calculated using equation (6):

$$\text{Discoloration}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (6)$$

where C_0 is the dye concentration at the end of the dark stirring and C_t the dye concentration at a given time. The mineralization of the dyes was measured by COD at regular intervals using closed reflux titrimetric method and calculated using equation (7):

$$\text{Mineralization}(\%) = \frac{\text{COD}_0 - \text{COD}_f}{\text{COD}_0} \times 100 \quad (7)$$

where COD_0 and COD_f are respectively the initial and final substrate mineralization.

RESULTS AND DISCUSSION

Catalyst characterization

X-ray diffraction

Figure 1 shows the XRD patterns of TiO₂-PC500 and Ag/TiO₂-PC500. The relevant peaks of TiO₂anatase phase are at 2θ equal to 25° (101), 37° (110), 48° (200), 54° (211), and 62° (204) [31]. No TiO₂ as rutile phase was observed in all samples. The absence of characteristic peaks corresponding to Ag can be due to the low proportion of deposited metal and to its more homogeneous dispersion onto TiO₂-PC500 surface [32,33]. Although the presence of Ag does not seem to alter the crystalline structure of TiO₂ the XRD peaks of Ag/TiO₂-PC500 present a small shift as compared to untreated TiO₂-PC500. This is illustrated by the shift of the (101) peak from $2\theta = 25.356^\circ$ in the case of TiO₂-PC500 to $2\theta = 25.363^\circ$ for Ag/TiO₂-PC500. This shift describes the expansion of the lattice by Ag doping [34]. The crystallite sizes of the two catalysts are reported in **Table 1**. It is found that pure TiO₂-PC500 has an average size of 5.94 nm which

Fig. 1 XRD patterns of TiO₂ PC500 and Ag/TiO₂ PC500 (A = anatase).

increases to 18.85 nm for Ag/TiO₂-PC500 (**Table 1**). The increase in particle size may be explained by the fact that Ag radius (1.44 Å) is greater than that of Ti⁴⁺ (0.60 Å) [35]. Furthermore, the calcination temperature may also contribute to this increase [36].

SEM analysis

The SEM micrographs taken at 3000 times magnification are shown in **Fig. 2**. A comparison of micrographs reveals that the spherical shape of particles is conserved with the presence of relatively greater agglomerates on Ag/TiO₂-PC500 as compared to TiO₂-PC500. This is further confirmed by the increase in the particle size as shown in the XRD analysis (section *X-ray diffraction*).

XRF analysis

The elemental compositions of TiO₂ and Ag doped TiO₂ were determined by XRF. The results of XRF analysis of TiO₂-PC500 and Ag/TiO₂-PC500 are reported as numerical values in **Table 2**. The results of the chemical analysis of Ag/TiO₂-PC500 show the presence of Ag in the as-synthesized photocatalyst at 0.762 weight percent.

Surface area

The results of the surface area of TiO₂-PC500 and the as-prepared Ag/TiO₂-PC500 are presented in **Table 1** along with their crystallite sizes. The surface area of TiO₂-PC500 is found to be 287.09 m² g⁻¹, in good agreement with that specified by Liu *et al.* [37]. However, the surface area of Ag/TiO₂-PC500 has decreased to 84.87 m² g⁻¹. This sig-

Fig. 2 SEM images of (a) TiO₂-PC500 and (b) Ag/TiO₂-PC500.

nificant decrease may be accounted for by the aggregation of nanoparticles as observed in SEM images and increase in the TiO₂ particle size. This trend is frequently found when doping TiO₂ with metals as reported by Thu *et al.* [38] for the Cu-doped TiO₂.

FT-IR analysis

Figure 3 shows the relevant regions to this study of FT-IR spectra of TiO₂-PC500 (a) and Ag/TiO₂-PC500 (b). The band at 1627 cm⁻¹ is assigned to the OH bending vibration of the chemisorbed and/or physisorbed water molecules on the surface of the catalysts. Of particular interest to the present study is the new band at ~1385 cm⁻¹ which is tentatively assigned to the interaction between Ag and TiO₂ particles [39]. Furthermore, there are bands at ~3430, 3390 and 3380 cm⁻¹ (**Fig. S1**) are assigned to Ti-OH stretching vibration [40] and

Table 1 Elemental composition of TiO₂-PC500 and Ag/TiO₂-PC500.

Element (wt%)	Si	P	S	Ca	Ti	Zr	Nb	Ag
TiO ₂ -PC500	0.416	0.0501	0.172	0.037	58.9	0.0137	0.221	-
Ag/TiO ₂ -PC500	0.377	0.0576	0.173	0.0343	58.4	0.0138	0.186	0.762

Table 2 Surface area and Crystallite size of TiO₂-PC500 and Ag/TiO₂PC500.

Photocatalyst	Metalloading (wt.% Ag)	Surface area (m ² g ⁻¹)	Crystallite size (nm)
TiO ₂ -PC500	0	287.09	5.94
Ag/TiO ₂ -PC500	0.762	84.87	18.85

Fig. 3 FT-IR spectra of (a) TiO₂-PC500 and (b) Ag/TiO₂-PC500.

a strong band between 750 and 400 cm⁻¹ (**Fig. S1**) assigned to the stretching vibration of the Ti-O-Ti bond [41].

Determination of Point of Zero Charge (PZC or pH_{PZC})

PZC values are known to be very sensitive to experimental conditions (sample mass, ionic strength, temperature etc.) [42]. Under our experimental conditions the PZC value for TiO₂-PC500 was found to be equal to 6.2 (**Fig. 4**). This is in good agreement with that reported by Aguedach *et al.* [43]. The PZC value of Ag/TiO₂-PC500 was found to be equal to 7.5 (**Fig. 4**) indicating a higher degree of hydration [42].

Adsorption and direct photolysis

Prior to the study of photocatalytic activities of both photocatalysts it was necessary to determine their dark adsorption behavior towards the two substrates. The results of adsorption expressed as % removal 'equation (5)' for CR (50 mg L⁻¹) and CV (25 mg L⁻¹) solutions with TiO₂-PC500 (1 g L⁻¹) and Ag/TiO₂-PC500 (1 g L⁻¹) respectively are shown in **Fig. 5**.

Fig. 4 PZC determination for TiO₂-PC500 and Ag/TiO₂-PC500.

Two distinct adsorption behaviors between the photocatalysts towards the dyes are observed. With TiO₂-PC500 the removal rate is significantly higher for both dyes (32.9% for CR and 29.7% for CV) as compared with Ag/TiO₂-PC500 (10.6% for CR and 16.50% for CV). The decrease of adsorption between TiO₂-PC500 and Ag/TiO₂-PC500 for both substrates can be accounted for by the decrease in the surface area of Ag/TiO₂-PC500 and increase in particle sizes as compared to TiO₂-PC500. As result of these changes, the number of adsorption sites available for the same amount of substrate used decreases which lead ultimately to a decrease in the removal rates with Ag/TiO₂-PC500. For the subsequent studies a 30-minute period of dark stirring was adopted for all manipulations in order to reach equilibrium between the dyes' solutions and photocatalysts' surface. Furthermore, the results of photolysis (absence of the photocatalysts) of dyes solutions both under UV and solar irradiations gave negligible discoloration rates (<3% after 120 min).

Photocatalytic activity

Effect of photocatalyst dose

The effect of photocatalysts doses was tested for TiO₂-PC500 and Ag/TiO₂-PC500 in the range 0.25 – 2 g L⁻¹ using dyes solutions of CR (50 mg L⁻¹) and CV (25 mg L⁻¹) under UV and solar irradiations for 240 min. **Figure 6** shows the percent discoloration obtained for both dyes using Ag/TiO₂-PC500. In all cases, the percentage removal increases with increase in photocatalysts doses. However, it can be noticed

Fig. 5 Adsorption of CR and CV $\text{TiO}_2\text{-PC500}$ and $\text{Ag/TiO}_2\text{-PC500}$. Experimental conditions: $[\text{CR}] = 50 \text{ mg L}^{-1}$, $[\text{CV}] = 25 \text{ mg L}^{-1}$, free pH, photocatalyst dosage 1 g L^{-1} .

Fig. 6 Effect of photocatalyst ($\text{Ag/TiO}_2\text{-PC500}$) dosage. Solar irradiation: CR (a), CV (b); UV irradiation: CR (c), CV (d). Experimental conditions: $[\text{CR}] = 50 \text{ mg L}^{-1}$, $[\text{CV}] = 25 \text{ mg L}^{-1}$, free pH, irradiation time: 240 min.

from **Fig. 6 (b)** that a small difference in the removal rate of CV exists between 1 g L^{-1} and 2 g L^{-1} . Similar results were obtained using $\text{TiO}_2\text{-PC500}$ under UV and solar irradiations

(**Fig. S2**). Since it is a comparative study of the performance of the photocatalysts under investigation, the same dose of 1 g L^{-1} was used for both catalysts for subsequent studies

Fig. 7 Effect of initial dyes concentrations (CR, CV): (a) CR (Ag/TiO₂-PC500 /solar light), (b) CV (Ag/TiO₂-PC500 /solar light). Experimental conditions: photocatalyst dosage 1 g L⁻¹, free pH, irradiation time: 240 min.

under UV and solar irradiations.

Effect of initial dye concentration

The effect of initial dye concentration was tested for both dyes in the range 25–100 mg L⁻¹ under UV and solar irradiations. **Figure 7** shows the percent discoloration at various initial dye concentrations under solar irradiation. The discoloration efficiency decreases with increase in dyes initial concentration, then decreases for higher concentrations. This decrease may be accounted for by the screen effect: at higher initial substrate concentrations the number of photons reaching the photocatalyst surface is hindered by the greater number of substrate molecules present in solution and those adsorbed on the surface. As result, a smaller number of hydroxyl radicals (HO[•]) are produced and a decrease of discoloration efficiencies are observed [22]. In the present study, the optimal concentrations of 50 mg L⁻¹ and 25 mg L⁻¹ were used for CR and CV respectively for subsequent investigations.

Effect of pH

The solution pH is an important parameter for the photo-reaction taking place on the photocatalyst [14]. The surface charge properties of the latter and size of aggregates present depend strongly on this parameter. The effect of pH on the discoloration under UV and solar irradiations of CR and CV was studied in the pH range 1.5–11. The results presented in **Fig. 8 (a-h)** together with the kinetic rates constants calculated on the basis of a pseudo-first order mechanism ‘equa-

tion (8)’, show two distinct behaviors amongst the substrates.

$$\ln \frac{C_0}{C_t} = k_{app} t \quad (8)$$

where C_0 and C_t (mol L⁻¹) are the dyes initial and at a given time, t is the reaction time (min) concentrations and k_{app} the apparent rate constant (min⁻¹).

The removal rate of CR (anionic dye) increases with acidification of the solution in the presence of the two photocatalysts under UV and solar irradiations. However, the removal rate of CV (cationic dye) increases with increase in pH values. Indeed, for CR, under UV irradiation, removal rates reach a maximum value of 62.7% ($k_{app} = 0.042$ min⁻¹) in the presence TiO₂-PC500 and 100% ($k_{app} = 0.086$ min⁻¹) with Ag/TiO₂-PC500. Under solar irradiation at the same pH (1.5), the removal rate of CR markedly increases through a more rapid process with Ag/TiO₂-PC500 ($R = 100\%$; $k_{app} = 0.230$ min⁻¹) as compared to TiO₂-PC500 ($R = 72.7\%$; $k_{app} = 0.012$ min⁻¹). Conversely, in the case of CV, under UV irradiation and pH = 11, removal rates reach, after 240 min, maximum values of 86.2% ($k_{app} = 0.260$ min⁻¹) and 94.6% ($k_{app} = 0.300$ min⁻¹) with TiO₂-PC500 and Ag/TiO₂-PC500, respectively. Similar rates of discoloration are observed at pH = 11 for CV under solar irradiation ($R = 86.2\%$; $k_{app} = 0.064$ min⁻¹) and solar irradiation ($R = 96.6\%$; $k_{app} = 0.153$ min⁻¹) with TiO₂-PC500 and Ag/TiO₂-PC500 respectively. The difference in behavior between CR and CV dyes is accounted for by the amphoteric character of TiO₂ surface. At pH smaller than pH_{PZC} the photocatalyst surface acquires positive charges ‘equation (9)’

Fig. 8 Effect of pH on the photodiscoloration of the dyes: (a) CR (TiO₂-PC500/UV light), (b) CR (Ag/TiO₂-PC500/UV light), (c) CV (TiO₂-PC500, UV light), (d) CV (Ag/TiO₂-PC500/UV light), (e) CR (TiO₂-PC500/Solar), (f) CR (Ag/TiO₂-PC500/Solar), (g) CV (TiO₂-PC500/Solar), (h) CV (Ag/TiO₂-PC500/Solar). Experimental conditions: photocatalysts dosage 1 g L⁻¹, [CR] = 50 mg L⁻¹, [CV] = 25 mg L⁻¹, irradiation time: 240 min.

which favors more electrostatic attractions with the negatively charged CR. Conversely, at pH greater than pH_{PZC} , the catalyst surface is negatively charged due to the significant fraction of surface sites present as TiO^- 'equation (10)'.

The difference in the photocatalysts behavior can be further argued upon by the difference of their respective pH_{PZC} values and the dyes free pHs. In the case of CR, its free pH (6.6) being closer to pH_{PZC} of TiO_2 -PC500 ($\text{PZC} = 6.2$), the number of positive sites (TiOH_2^+) generated at the surface is not sufficient to attract enough CR molecules due to the formation of clusters [41]. Consequently, a small discoloration rate and a slower process are observed under UV ($R = 45.3\%$; $k = 0.055 \text{ min}^{-1}$) and solar irradiations ($R = 52.1\%$; $k = 0.010 \text{ min}^{-1}$). On the other hand, the PZC of Ag/TiO_2 -PC500 (7.5) is significantly higher than CR free pH (6.6). This difference enables the generation of enough positive sites which achieve a complete discoloration under UV ($R = 100\%$; $k = 0.064 \text{ min}^{-1}$) which is faster under solar irradiation ($R = 100\%$; $k = 0.207 \text{ min}^{-1}$). In the case of CV, its free pH (6.5) being also closer to that of TiO_2 -PC500 the number of positive sites (TiOH_2^+) generated at the surface is sufficient to restrain its discoloration. A partial discoloration is also observed with Ag/TiO_2 -PC500 ($\text{pH}_{\text{PZC}} = 7.5$) both under UV and solar irradiation ($R = 63.9\%$). The improvement in the rates of dyes discoloration with Ag/TiO_2 -PC500 under solar light is reasonably explained by the difference in the Fermi level position of TiO_2 -PC500 which is higher than that of metallic Ag [44]. As result, a Schottky barrier is formed at the metal-titania junction [45] which improves the charge separation and hence a slowing of the e^-/h^+ recombination [27].

It is worth noting that in the case of CV no complete discoloration is observed, at $\text{pH} \geq 6.5$, after 240 minutes, neither with Ag/TiO_2 -PC500 ($R_{\text{UV}} = 94.6\%$; $R_{\text{sol}} = 96.6\%$) nor with TiO_2 -PC500 ($R_{\text{UV}} = R_{\text{sol}} = 86.2\%$). This incomplete discoloration is probably due to the functional groups of CV (triarylmethane dye) which, under the present experimental conditions, seem to be more recalcitrant than those of CR (azo dye). The latter are known to be more readily discolored compared to molecules containing methyl groups [46]. These results may have repercussions when choosing photocatalysts for the treatment of industrial effluents depending

of the nature of dyes present. Under solar irradiation and natural pH, Ag/TiO_2 -PC500 is more efficient for effluents charged with anionic dyes.

Effect of H_2O_2

To possibly further improve the discoloration rate of the chosen dyes it was interesting to investigate the effect of addition of an electron acceptor, namely H_2O_2 . Its effect on the discoloration rate of dyes under UV and solar irradiations was studied in the concentration range 10^{-3} to $10^{-1} \text{ mol L}^{-1}$ under the following experimental conditions: free pH; photocatalysts dosage: 1 g L^{-1} ; dye concentrations $\text{CR} = 50 \text{ mg L}^{-1}$, $\text{CV} = 25 \text{ mg L}^{-1}$. **Table 3** presents the results of discoloration rates where it can be noticed that for CR, with TiO_2 -PC500 under UV irradiation, the discoloration rate increases proportionally to H_2O_2 concentrations to reach a maximum value of $R = 96.0\%$. In the presence of Ag/TiO_2 -PC500, under UV irradiation a total discoloration is achieved. This process is even more efficient under solar irradiation in the presence of Ag/TiO_2 -PC500 ($R = 100\%$ for all H_2O_2 concentrations) as compared to TiO_2 -PC500 ($R = 53.0\%$ for H_2O_2 $10^{-3} \text{ mol L}^{-1}$ and $R = 100\%$ for H_2O_2 $10^{-2} \text{ mol L}^{-1}$). The enhancement of the discoloration rate can be explained by the reaction of adsorbed H_2O_2 with the e^- of the conduction band (CB) or with O_2^- according to equations (11) and (12) [46] to produce $\text{HO}^\bullet$ radicals which are known to be the main species responsible for the photocatalytic degradation processes of organic dyes in the presence of TiO_2 [47]:

The higher rates and rapid discoloration obtained under solar irradiation can be accounted for by a further possible source of $\text{HO}^\bullet$ generated by the photolysis of H_2O_2 . This reaction takes place only at irradiations $\lambda < 300 \text{ nm}$ which may be present in the solar irradiation used [47].

In the case of CV it can be noticed, from the same table, that in the presence of TiO_2 -PC500 under UV, the discoloration rates increase to reach a maximum value ($R = 98.0\%$) with H_2O_2 concentration of $10^{-2} \text{ mol L}^{-1}$. Beyond this concentration, no improvement of discoloration rate is observed ($R = 98.0\%$). Similarly, no significant improvement is observed with Ag/TiO_2 -PC500 under UV irradiation ($R = 99.1\%$). Under solar irradiation in the presence of TiO_2 -PC500 a maxi-

Table 3 Effect of H₂O₂ concentration on the discoloration of CR and CV in the presence of Ag/TiO₂-PC500 and TiO₂-PC500. Experimental conditions: photocatalyst dosage 1 g L⁻¹, free pH, irradiation sources: UV and solar; irradiation time: 240 min.

H ₂ O ₂ (mol L ⁻¹)	Ag/TiO ₂ -PC500				TiO ₂ -PC500			
	CR		CV		CR		CV	
	Discoloration (%)		Discoloration (%)		Discoloration (%)		Discoloration (%)	
	UV	Solar	UV	Solar	UV	Solar	UV	Solar
0	100	100	63.91	63.92	45.26	52.05	43.91	39.90
10 ⁻³	100	100	74.80	79.81	53.08	53.08	53.31	56.01
10 ⁻²	100	100	99.11	99.30	96.04	96.04	98.02	99.01
10 ⁻¹	100	100	99.10	98.53	96.04	96.04	98.03	97.22

imum discoloration rate (R = 99.0%) is reached with H₂O₂ concentration of 10⁻² mol L⁻¹ followed by a slight decrease (R = 97.2%) at 10⁻¹ mol L⁻¹. The same trend is observed in the presence of Ag/TiO₂-PC500 where a maximum discoloration rate (R = 99.3%) is reached with H₂O₂ concentration of 10⁻² mol L⁻¹ followed by a slight decrease (R = 99.5%) at 10⁻¹ mol L⁻¹. The slight decrease of the discoloration rate of CV at higher H₂O₂ concentrations can be accounted for by the consumption of hydroxyl radicals (HO[•]) by excess H₂O₂ 'equations (13) and (14)' [48] and the scavenging of the photoproducted positive holes (h⁺) 'equation (15)' [23].

COD Measurements

To investigate the extent of mineralization of the chosen dyes, COD measurements were carried out for both catalysts. The histograms in **Fig. 9** depict the COD removals of CR and CV with both photocatalysts under UV and solar irradiations. In all cases the results clearly indicate a better mineralization efficiency of Ag/TiO₂-PC500 as compared to TiO₂-PC500. However, despite the total discoloration of CR its mineralization is partial but improves, in the presence of Ag/TiO₂-PC500, from 29.4% under UV to 42.0% under solar irradiation. This is the same order in the discoloration process observed under similar conditions. The COD of CV decreases, in the presence of Ag/TiO₂-PC500, from 50.3% under UV to 22.5% under solar light despite the fact that no

noticeable change in its discoloration rate is observed under similar conditions. The difference in the dyes mineralization reiterates the effect of their specific functional groups (section *Effect of pH*).

CONCLUSIONS

Silver doped TiO₂-PC500 was prepared by wet chemical reduction (0.76 wt.%) and characterized. It showed markedly better performances as compared to untreated TiO₂-PC500 despite its small surface area as compared to that of untreated TiO₂-PC500. At free pH, CR was completely discolored within 15 min in the presence of Ag/TiO₂-PC500 both under UV and solar lights. However, CV was partially discolored under similar conditions. Dyes discoloration fitted well with a pseudo-first order mechanism with respect to their concentrations. The difference in discoloration rates of dyes can be ascribed to their specific functional groups. The dyes discoloration was further improved by addition of H₂O₂ (10⁻² mol L⁻¹). Moreover, even if the COD removal of both dyes was incomplete, Ag/TiO₂-PC500 showed a better performance as compared to TiO₂-PC500. The enhanced photoactivity of Ag/TiO₂-PC500 can be explained by a significant inhibition of e⁻/h⁺ recombination.

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Fig. 9 COD for CR and CV with Ag/TiO₂-PC500, TiO₂-PC500 under UV (a) and solar irradiation (b). Experimental conditions: Dyes [CR] = 50 mg L⁻¹, [CV] = 25 mg L⁻¹, free pH, photocatalysts dosage 1 g L⁻¹, irradiation time = 240 min. Each point is an average of triplicates.

SUPPLEMENTARY MATERIALS

Supplementary Materials for this article are available on the journal website in a separate file.

https://www.jstage.jst.go.jp/article/jwet/17/4/17_18-099/_supplement/_download/17_18-099_1.pdf

REFERENCES

- [1] International Water Association: Global Trends & Challenges in Water Science, Research and Management: A compendium of hot topics and features from IWA Special Groups, 2nd ed., IWA, London, United Kingdom, 2016.
- [2] Gupta VK, Suhas K: Application of low-cost adsorbents for dye removal – A review. *J. Environ. Manage.*, **90**(8), 2313–2342, 2009. PMID:19264388 doi:10.1016/j.jenvman.2008.11.017
- [3] Cong VH, Sakakibara Y, Komori M, Kishimoto N, Watanabe T, Mishima I, Ihara I, Tanaka T, Yoshida Y, Ozaki H: Recent developments in electrochemical technology for water and wastewater treatments. *J. Water Environ. Technol.*, **14**(2), 25–36, 2016. doi:10.2965/jwet.15-029
- [4] Hai FI, Yamamoto K, Nakajima F, Fukushi K: Removal of structurally different dyes in submerged membrane fungi reactor—Biosorption/PAC-adsorption, membrane retention and biodegradation. *J. Membr. Sci.*, **325**(1), 395–403, 2008. doi:10.1016/j.memsci.2008.08.006
- [5] Kazmi AA, Thul R: Colour and COD removal from pulp and paper mill effluent by q Fenton's oxidation. *J. Environ. Sci. Eng.*, **49**(3), 189–194, 2007. PMID:18476442
- [6] Amita S, Amita R: Advanced Oxidation Processes for Wastewater Treatment: Emerging Green Chemical Technology, 1st ed., Academic Press, London, United Kingdom, 2018.
- [7] Ameta R, Solanki MS, Benjamin S, Ameta SC: Chapter 6: Photocatalysis. In: Ameta SC, Ameta R (eds.): Advanced Oxidation Processes for Waste Water Treatment: Emerging Green Chemical Technology. Academic Press, London, United Kingdom, pp. 135–175, 2018.
- [8] Stefan MI: Advanced Oxidation Processes for Water Treatment: Fundamentals and Applications. IWA Publishing, London, United Kingdom, 2018.
- [9] Chong MN, Jin B, Chow CWK, Saint C: Recent developments in photocatalytic water treatment technology: A review. *Water Res.*, **44**(10), 2997–3027, 2010. PMID:20378145 doi:10.1016/j.watres.2010.02.039
- [10] Prihod'ko RV, Soboleva NM: Photocatalysis: Oxidative processes in water treatment. *J. Chem.*, **2013**, Article ID 168701, 2013. doi:10.1155/2013/168701
- [11] Demeestere K, Dewulf J, Van Langenhove H: Heterogeneous Photocatalysis as an advanced oxidation process for the abatement of chlorinated, monocyclic aromatic and sulfurous volatile organic compounds in air: State of the art. *Crit. Rev. Environ. Sci. Technol.*, **37**(6), 489–538, 2007. doi:10.1080/10643380600966467

- [12] Lazar MA, Varghese S, Nair SS: Photocatalytic water treatment by titanium dioxide: recent updates. *J. Catal.*, **2**(4), 572–601, 2012.
- [13] Han F, Kambala VSR, Srinivasan M, Rajarathnam D, Naidu R: Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: A review. *Appl. Catal. A Gen.*, **359**(1-2), 25–40, 2009. doi:10.1016/j.apcata.2009.02.043
- [14] Herrmann JM: Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catal. Today*, **53**(1), 115–129, 1999. doi:10.1016/S0920-5861(99)00107-8
- [15] Fujishima A, Rao TN, Tryk DA: Titanium dioxide photocatalysis. *J. Photochem. Photobiol. Photochem. Rev.*, **1**(1), 1–21, 2000. doi:10.1016/S1389-5567(00)00002-2
- [16] Gutierrez-Mata AG, Velazquez-Martínez S, Álvarez-Gallegos A, Ahmadi M, Hernández-Pérez JA, Ghanbari F, Silva-Martínez S: Recent overview of solar photocatalysis and solar photo-Fenton processes for wastewater treatment. *Int. J. Photoenergy*, **2017**, Article ID 8528063, 2017. doi:10.1155/2017/8528063
- [17] Pelaez M, Nolan NT, Pillai SC, Seery MK, Falaras P, Kontos AG, Dunlop PSM, Hamilton JWJ, Byrne JA, O'Shea K, Entezari MH, Dionysiou DD: A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal. B*, **125**, 331–349, 2012. doi:10.1016/j.apcatb.2012.05.036
- [18] Wen J, Li X, Liu W, Fang Y, Xie J, Xu Y: Photocatalysis fundamentals and surface modification of TiO₂ nanomaterials. *Chinese J. Catal.*, **36**(12), 2049–2070, 2015.
- [19] Zhang J, Tian B, Wang L: Chapter 7: Modifications of photocatalysts by doping methods. In: Zhang J, Tian B, Wang L, Xing M, Lei J (Eds.): *Photocatalysis: Fundamentals, Materials and Applications*, Springer, Singapore, pp. 197–221, 2018.
- [20] Kumar SG, Devi LG: Review on modified TiO₂ photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics. *J. Phys. Chem. A*, **115**(46), 13211–13241, 2011. PMID:21919459 doi:10.1021/jp204364a
- [21] Chen Q, Shi W, Xu Y, Wu D, Sun Y: Visible-light-responsive Ag–Si codoped anatase TiO₂ photocatalyst with enhanced thermal stability. *Mater. Chem. Phys.*, **125**(3), 825–832, 2011. doi:10.1016/j.matchemphys.2010.09.049
- [22] Krejčíková S, Matějová L, Kočí K, Obalová L, Matěj Z, Čapek L, Šolcová O: Preparation and characterization of Ag-doped crystalline titania for photocatalysis applications. *Appl. Catal. B*, **111–112**, 119–125, 2012. doi:10.1016/j.apcatb.2011.09.024
- [23] Malato S, Fernández-Ibáñez P, Maldonado MI, Blanco J, Gernjak W: Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catal. Today*, **147**(1), 1–59, 2009. doi:10.1016/j.cattod.2009.06.018
- [24] Nigussie GY, Tesfamariam GM, Tegegne BM, Weldemichel YA, Gebreab TW, Gebrehiwot DG, Gebremichel GE: Antibacterial activity of Ag-doped TiO₂ and Ag-doped ZnO nanoparticles. *Int. J. Photoenergy*, **2018**, Article ID 5927485, 2018. doi:10.1155/2018/5927485
- [25] Sökmen M, Değerli S, Aslan A: Photocatalytic disinfection of *Giardia intestinalis* and *Acanthamoeba castellanii* cysts in water. *Exp. Parasitol.*, **119**(1), 44–48, 2008. PMID:18255065 doi:10.1016/j.expara.2007.12.014
- [26] Behnajad MA, Modirshahla N, Shokri M, Rad B: Enhancement of photocatalytic activity of TiO₂ nanoparticles by silver doping: photodeposition versus liquid impregnation methods. *Global NEST J.*, **10**(1), 1–7, 2008.
- [27] Seery MK, George R, Floris P, Pillai SC: Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis. *J. Photochem. Photobiol. Chem.*, **189**(2-3), 258–263, 2007. doi:10.1016/j.jphotochem.2007.02.010
- [28] Zak AK, Abd. Majid WH, Abrishami ME, Yousefi R: X-ray analysis of ZnO nanoparticles by Williamson-Hall and size-strain plot methods. *Solid State Sci.*, **13**, 251–256, 2011. doi:10.1016/j.solidstatesciences.2010.11.024
- [29] Djellabi R, Ghorab MF: Solar photocatalytic decolorization of Crystal violet using supported TiO₂: effect of some parameters and comparative efficiency. *Desalination Water Treat.*, **53**(13), 1–7, 2013.
- [30] Cardenas-Peña AM, Ibanez JG, Vasques-Medrano R: Determination of point zero charge for electrocoagulation precipitates from an iron anode. *Int. J. Electrochem.*, **7**, 6142–6153, 2012.

- [31] Mogal SI, Gandhi VG, Mishra M, Tripathi S, Shripa-
thi T, Joshi PA, Shah DO: Single-step synthesis of
silver-doped titanium dioxide: influence of silver on
structural, textural, and photocatalytic properties. *Ind.
Eng. Chem. Res.*, **53**(14), 5749–5758, 2014. doi:10.1021/
ie404230q
- [32] Girginov C, Stefchev P, Vitanov P, Dikov H: Silver
doped TiO₂ photocatalyst for methyl orange degrada-
tion. *J. Eng. Sci. Technol. Rev.*, **5**(4), 14–17, 2012.
doi:10.25103/jestr.054.03
- [33] Nainani R, Thakur P, Chaskar M: Synthesis of silver
doped TiO₂ nanoparticles for the improved photcata-
lytic degradation of methyl orange. *Mater. Sci. Eng. B*,
2(1), 52–58, 2012.
- [34] Khan M, Gul SR, Li J, Cao W, Mamalis AG: Pre-
paration, characterization and visible light pho-
tocatalytic activity of silver, nitrogen co-doped TiO₂
photocatalyst. *Mater. Res. Express*, **2**(6), 066201, 2015.
doi:10.1088/2053-1591/2/6/066201
- [35] Sarteeep Z, Pirbazari AE, Aroon MA: Silver doped
TiO₂ nanoparticles: preparation, characterization and
efficient degradation of 2,4-dichlorophenol under
visible light. *J. Water Environ. Nanotechnol.*, **1**(2),
135–144, 2016.
- [36] Chen YF, Lee CY, Yeng MY, Chiu HT: The effect of
calcination temperature on the crystallinity of TiO₂
nanopowders. *J. Cryst. Growth*, **247**(3-4), 363–370,
2003. doi:10.1016/S0022-0248(02)01938-3
- [37] Liu I, Lawton LA, Bahnemann DW, Liu L, Proft B, Rob-
ertson PKJ: The photocatalytic decomposition of mi-
crocystin-LR using selected titanium dioxide materials.
Chemosphere, **76**(4), 549–553, 2009. PMID:19375779
doi:10.1016/j.chemosphere.2009.02.067
- [38] Thu TN, Thi NN, Quang VT, Hong KN, Minh TN,
Hoai NL: Synthesis, characterisation, and effect of pH
on degradation of dyes of copper-doped TiO₂. *J. Exp.
Nanosci.*, **11**(3), 226–238, 2016. doi:10.1080/17458080.
2015.1053541
- [39] García-Serrano J, Gómez-Hernández E, Ocampo-
Fernández M, Pal U: Effect of Ag doping on the crys-
tallization and phase transition of TiO₂ nanoparticles.
Curr. Appl. Phys., **9**(5), 1097–1105, 2009. doi:10.1016/j.
cap.2008.12.008
- [40] Wang Y, Huang Y, Ho W, Zhang L, Zou Z, Lee S:
Biomolecule-controlled hydrothermal synthesis of C–
N–S-tridoped TiO₂ nanocrystalline photocatalysts for
NO removal under simulated solar light irradiation. *J.
Hazard. Mater.*, **169**(1-3), 77–87, 2009. PMID:19398265
doi:10.1016/j.jhazmat.2009.03.071
- [41] Arbuj SS, Hawaldar RR, Mulik UP, Wani BN, Amal-
nerkar DP, Waghmode SB: Preparation, characteriza-
tion and photocatalytic activity of TiO₂ towards methy-
lene blue degradation. *Mater. Sci. Eng. B*, **168**(1-3),
90–94, 2010. doi:10.1016/j.mseb.2009.11.010
- [42] Bertus LM, Carcel RA: Prediction of TiO₂ and WO₃
nanopowders surface charge by the evaluation of point
zero charge (PZC). *Environ. Eng. Manag. J.*, **10**(8),
1021–1026, 2011. doi:10.30638/eemj.2011.148
- [43] Aguedach A, Brosillon S, Morvan J, Lhadi EK: Influe-
nce of ionic strength in the adsorption and during pho-
tocatalysis of reactive black 5 azo dye on TiO₂ coated
on non woven paper with SiO₂ as a binder. *J. Hazard.
Mater.*, **150**(2), 250–256, 2008. PMID:17543449
doi:10.1016/j.jhazmat.2007.04.086
- [44] Sclafani A, Herrmann JM: Influence of metallic sil-
ver and of platinum-silver bimetallic deposits on the
photocatalytic activity of titania (anatase and rutile)
in organic and aqueous media. *J. Photochem. Photo-
biol. Chem.*, **113**(2), 181–188, 1998. doi:10.1016/S1010-
6030(97)00319-5
- [45] Shan Z, Wu J, Xu F, Huang FQ, Ding H: Highly ef-
fective silver/semiconductor photocatalytic composites
prepared by a silver mirror reaction. *J. Phys. Chem. C*,
112(39), 15423–15428, 2008. doi:10.1021/jp804482k
- [46] Khataee AR, Kasiri MB: Photocatalytic degradation of
organic dyes in the presence of nanostructured titanium
dioxide: Influence of the chemical structure of dyes. *J.
Mol. Catal. Chem.*, **328**(1-2), 8–26, 2010. doi:10.1016/j.
molcata.2010.05.023
- [47] Liao CH, Kang SF, Wu FA: Hydroxyl radical scaveng-
ing role of chloride and bicarbonate ions in the H₂O₂/UV
process. *Chemosphere*, **44**(5), 1193–1200, 2001.
PMID:11513408 doi:10.1016/S0045-6535(00)00278-2
- [48] Li X, Li J, Bai J, Dong Y, Li L, Zhou B: The inhibi-
tion effect of tert-butyl alcohol on the TiO₂ nano assays
photoelectrocatalytic degradation of different organics
and its mechanism. *Nano-Micro Lett.*, **8**(3), 221–231,
2016. PMID:30474033 doi:10.1007/s40820-015-0080-2