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EVALUATION OF PURE AND AG-DOPED TiO_2 FILMS IN THE PHOTOCATALYTIC ACTIVITY OF PHENOL

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Evaluation of Pure and Ag-Doped TiO₂ Films in the Photocatalytic Activity of Phenol

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Abstract- Pure TiO₂ films, modified by the addition of Degussa P25 powder and Ag-doped were synthesized using sol-gel route and immobilized in borosilicate support at different withdrawing rates and dipping time. They were characterized by X-ray diffractometry, scanning electronic microscopy and high-resolution field-emission gun scanning electronic microscopy. Their photocatalytic activities under UV irradiation were examined using phenol. The higher activities were achieved through the Ag-doped films deposited with 0.4 mm s⁻¹ and two dipping. Approximately 90% of the organic contaminant was photodegraded after 24 h of irradiation.

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1. INTRODUCTION

Heterogeneous photocatalysis has received a great deal of attention as an advanced oxidation process (AOP) for degrading persistent organic compounds, reducing chemical oxygen demand (COD) and eliminating microorganisms in water bodies to allow for its reuse [1-5]. The advantage of this process is that it leads to the total mineralization of the organic contaminants, whether they are simple or complex molecules. The photocatalysis mechanism is based on the activation of a semiconductor, by sunlight or artificial light (Ultraviolet visible radiation). The interaction of light with the semiconductor excites electrons in the valence band toward the conduction band. This excitation produces holes (h⁺) in the valence band that will act as oxidizing sites, while the photogenerated electrons (e⁻) combine with the dissolved oxygen, preventing the recombination of the electron-hole pair. In addition, the oxygen reacts with reduction sites, the electrons of the conduction band, initially forming superoxide ion-radical (O₂⁻) and later, peroxides. The latter can react with the photogenerated electron (or superoxide ion-radical) forming OH radicals. By this mechanism, both molecular and dissociated water (OH⁻ groups bound at the TiO₂ surface) react with the photogenerated h⁺ holes to form highly oxidizing hydroxyl radicals [6]. The

organic pollutant can thus be degraded directly at the surface of the semiconductor through the photogenerated hole, or through the hydroxyl radical, resulting in complete mineralization or in the formation of persistent intermediaries for subsequent oxidation.

Different semiconductors have been tested for photodegradation of several organic pollutants. Of all, titania has proved to be the best material because of its many desirable properties. It possesses photostability, is biologically inert, inexpensive, and displays chemical stability within a wide range of pH [7]. Although this method is quite efficient, its disadvantage is that the catalyst is suspended in the solution in the form of powder, which of course makes the separation process difficult and expensive, rendering the method unfeasible on a large scale. In order to resolve this problem, more recent studies propose the use of TiO₂ in the form of films obtained via sol-gel immobilized in inert substrate [8,9].

Although the use of films is an advance for enabling of large-scale photocatalysis, the physically adhered film can be leached during the photocatalytic process. To overcome this difficulty it is necessary to prepare films with suitable physical and chemical properties for photocatalysis and firmly adhered to the substrate.

Another important factor is the greater efficiency of the photocatalytic process. It makes the recombination of the electron-hole pair difficult, extending the occurrence time for reactions that lead to the formation of oxidizing species. This can be achieved through modifications on the semiconductor's surface and/or structure or by the addition of sensitizers that improve the system's quantum yield [10-12].

The addition of noble metals on the surface of the semiconductor can improve its photocatalytic activity [13-17]. This deposition can produce traps to withdraw photoinduced electrons or holes leading to a decrease of the electron-hole recombination in photocatalytic process and an increase in the ability of visible light absorption by TiO₂ [13]. Some noble metals such as Pt, Pd, Rh and Au are very expensive to be used in industrial scale, leading to the search for less valuable metals but which have similar performance as sensitizers. According to the literature, among the metal dopants such as Fe, Cr, Zn, Ag, etc, Ag is the most

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promising as a modifier of TiO₂ for organic pollutants photodegradation [17].

Thus, this study describes the synthesis and characterization of thin titania films prepared by the sol-gel route and modified with silver ions. These films were immobilized in borosilicate support and their photocatalytic activities under UV irradiation were analyzed using phenol as a model organic contaminant.

II. EXPERIMENTAL

a) Chemicals

All chemicals used in this study were of analytical grade without further purification. Titania, supplied by Degussa (P25), was predried at 150°C under vacuum for 10 h and then used immediately.

b) Preparation of the TiO₂ films

Titanium dioxide suspensions were prepared by the sol-gel method, according to the following procedure: titanium(IV) isopropoxide (Ti(i-OPr)₄, Aldrich Chemical, 97%) was mixed quickly with glacial acetic acid under constant stirring (molar ratio H⁺/Ti = 4). Next, this solution was diluted with isopropyl alcohol in 1:1 Ti/alcohol ratio and the resulting solution (solution A) kept under agitation for ~1 h. Alcohol and a nitric acid solution (solution B) were then added to the mixture, still under continual stirring, keeping the molar ratios at alcohol/Ti = 7.6 and H⁺/Ti = 0.5 [18]. Solution A and Solution B were mixed and the resulting solution (Solution C) was kept under stirring for ~2 h. The immobilized films prepared immediately after the obtainment of this sol were called pure 0 h TiO₂. When these films were kept under refrigeration for 24 h before to be immobilized they were denominated pure 24 h. It was also prepared a sol following the same procedure above described, being the Solution A the same. However, to the solution B was added TiO₂ P25 in a proportion of 1.0 g of titania per liter of ethanol and this solution was sonicated for ~20 min before to be mixed with Solution A. These films immobilized immediately after sol formation were named mixed 0 h TiO₂ and those immobilized after to be kept under refrigeration for 24 h were called mixed 24 h TiO₂. Titania films modified by silver were also prepared. For this, beyond TiO₂ P25 in a proportion above mentioned, it was added AgNO₃ to the Solution B to get Ag/TiO₂ films at different Ag loadings from 0.15 to 5 weight%.

The TiO₂ solution prepared (Solution C) were immobilized, by the dip-coating deposition method, in a tubular borosilicate support, whose area available for the formation of the thin film was ~ 132 cm². The withdrawing rate was varied as well as the dipping time. The films were dried at room temperature and then calcined at 250°C for 15 min and at 450°C for 4 h.

c) Characterization

The thin films were characterized by several techniques. X-ray diffractometry (XRD) was performed with a Rigaku diffractometer model D/Max-2100/PC automatic, equipped with a nickel monochromator using Cu K_α (λ = 1.5405 Å) radiation at 40 kV and 20 mA. The method employed was the small angle, using a scanning velocity of 2° min⁻¹ and scans between 15° and 80°. Scanning electronic microscopy (SEM) and high-resolution field-emission gun scanning electronic microscopy (FEG-SEM) were done on a Zeiss, model DSM 94A and on a Leo, model Supra 35 microscopes, respectively.

d) Photocatalytic experiments

The photocatalytic activity, using a solution containing 15.0 mg L⁻¹ of phenol, was investigated. The photodegradation experiments were conducted in a cylindrical reactor in which the sample was kept at a temperature of 25°C, under stirring, saturated with oxygen, and irradiated with light at predominant wavelength of 365 nm, produced by four 15 W light bulbs. The incident irradiation, measured with a model PMA2100 version 1.16 Solar Light Company Inc. photometer/radiometer, was 5.11 mW cm⁻². Aliquots of 7 mL of the solution were removed at various times during the photocatalytic process and the photodegraded phenol content was evaluated by UV-VIS spectro photometry by using a spectrophotometer Thermo Spectronic model Genesys 6.

III. RESULTS AND DISCUSSION

a) The pure 0 h TiO₂ and pure 24 h TiO₂ films

The photocatalytic activity of the pure 0 h TiO₂ and pure 24 h TiO₂ films immobilized in a support of borosilicate utilizing 0.4 mm s⁻¹ withdrawing rate and two dipping was evaluated towards phenol. Under these circumstances, approximately 55% and 65% of phenol degradation after 24 h of illumination was achieved using the pure 0 h TiO₂ and pure 24 h TiO₂ films, respectively. These results may be considered satisfactory since the covered surface area of the substrate was equal to 0.0132 m². Without the catalyst, only 5% of the standard phenol solution was found to have become photo degraded after 24 h of illumination.

Micrographs were obtained by SEM and FEG-SEM for pure 24 h TiO₂ film with different withdrawing rates and dipping time. It was observed a decrease of particles` size, roughness and porosity of film as well as an increase of micro cracks on the surface film when the withdrawing rate increased. The photo catalytic activity of this film towards phenol also decreases with the increase of withdrawing rate in agreement with the results of film`s characterization. The increase of this parameter promotes the increase of micro cracks leading to the decrease of the amount of available catalyst for degradation of the organic contaminant [19-

21]. A decrease in the photo catalytic activity was also observed when the dipping time increased. This is probable due to higher recovering of actives sites by successive layers of titania hindering the contact of UV radiation. Another fact to be considered under this condition is the increase of rutile phase. Several studies have shown that pure anatase TiO₂ has a higher activity than pure rutile under oxidizing conditions and a discussion about this was taken by Balasubramanian *et al.* [19]. The higher photo catalytic activity was confirmed for the pure 24 h TiO₂ film deposited with 0.4 mm s⁻¹ and two dipping, and its thickness, using SEM micrograph, was estimated at 140 nm.

b) *The mixed 0 h TiO₂ and mixed 24 h TiO₂ films*

The photo catalytic activity of the mixed 0 h TiO₂ and mixed 24 h TiO₂ films was also evaluated for the

degradation of phenol and the results are presented in Figure 1. In the same Figure are shown the activities for the pure 0 h TiO₂ and pure 24 h TiO₂ films. As may be observed it was similar for pure 0 h TiO₂ and mixed 0 h TiO₂ films. On the other hand, the higher activity was found for the mixed 24 h TiO₂ film. This behavior may be attributed to the higher viscosity of the sol after aging process for 24 h. According Balasubramanian *et al.* [21], the addition of TiO₂ P25 to the sol also increase the viscosity since it leads to the particle growth during the drying step and serve as nucleation sites. Thus the particle growth occurs on the surface of the P25 particles.

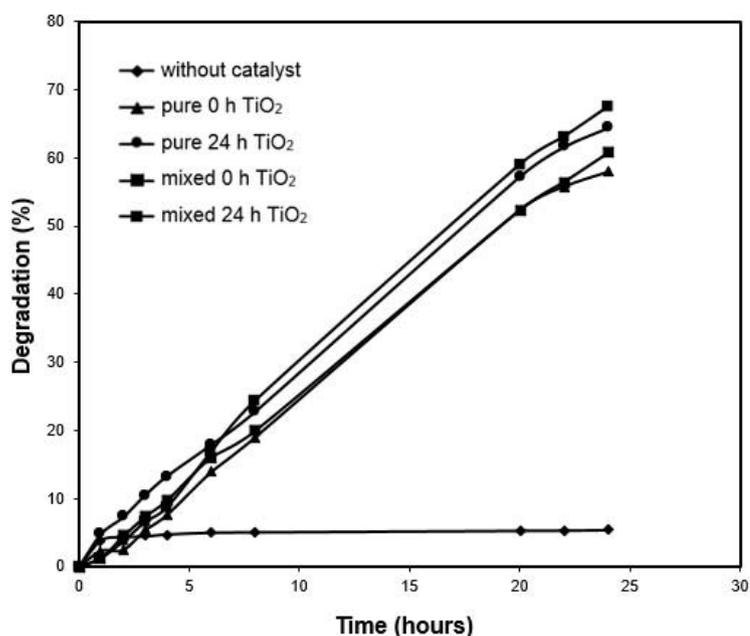


Figure 1 : Photo degradation of phenol as a function of irradiation time in the absence and presence of catalysts: pure 0 h TiO₂, pure 24 h TiO₂, mixed 0 h TiO₂ and mixed 24 h TiO₂ films under UV illumination, oxygen atmosphere and stirring (pH 5).

The thickness of the mixed 24 h TiO₂ film, estimated using SEM micrograph was 188 nm, being higher than that obtained for the pure 24 h titania film (140 nm). This result corroborates the increase in viscosity of mixed film and is consistent with published studies which show that the film thickness increases with increasing viscosity within a certain range [21,22]. Furthermore, Figure 1 shows that the phenol degradation percentage in the first 8 h of irradiation is around 25%, which increases to 68% after 24 h of irradiation. This difference is probable due to the presence of intermediates hindering the process of photo degradation at the beginning of irradiation.

Photo degradation of phenol using the mixed 24 h TiO₂ film was also evaluated at different pH values as

shown in Figure 2. As may be seen, the photo catalytic activity increased with decreasing pH. This result may be attributed to the characteristic of the TiO₂ whose surface becomes positively charged with increasing acidity promoting electrostatic attraction with the phenolate anion. As a result, the adsorption of the substrate increases. Pecchi *et al.* have also observed that the percentage of pentachlorophenol adsorbed on TiO₂ P25 increases with decreasing pH [23].

c) *The Ag doped TiO₂ films*

The same sol utilized to prepare the mixed 24 h TiO₂ film was used to get Ag doped TiO₂ films. So, AgNO₃ was added to Solution B for obtaining films with the following silver content: 0.15, 0.5, 2 and 5 weight %, named as 0.15%Ag/TiO₂, 0.5%Ag/TiO₂, 2%Ag/TiO₂ and

5%Ag/TiO₂, respectively. By using all these films, the photo degradation of phenol was about 90% after 24 h of irradiation as may be observed in Figure 3. Accordingly, these results were better than those obtained with the mixed 24 h TiO₂ film.

As the photo catalytic activity was similar for all doped films, studies of characterization were carried out for the 0.15%Ag/TiO₂ film. FE-SEM micrographs showed little particles, porous structure and increased thickness when compared to those

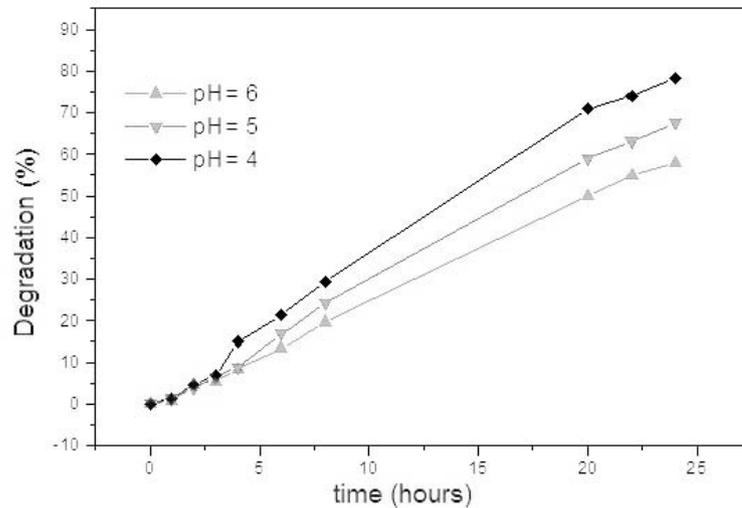


Figure 2 : Photo degradation of phenol as a function of irradiation time for mixed 24 h TiO₂ films at different pH values. (a) pH 4, (b) pH 5 and (c) pH 6.

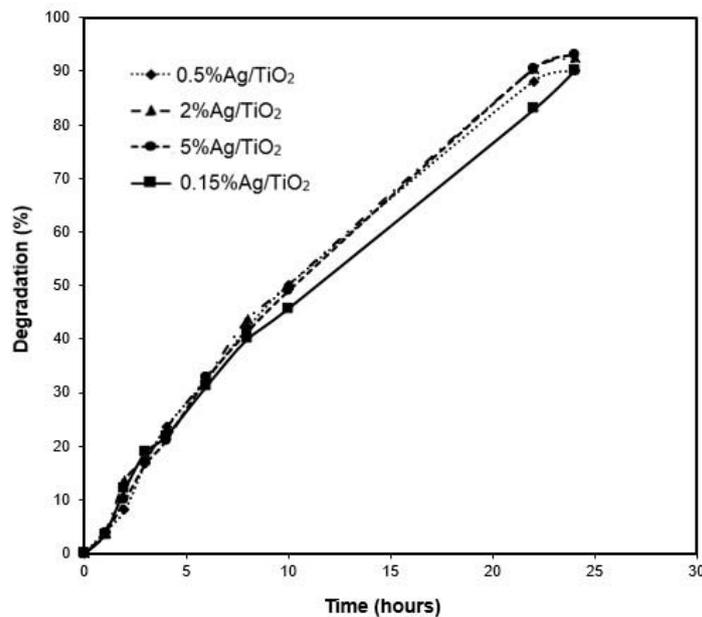


Figure 3 : Photo degradation of phenol as a function of irradiation time for Ag doped TiO₂ films at different Ag loadings

obtained for the mixed 24 h TiO₂ film (188 nm). The thickness of the 0.15%Ag/TiO₂ film was estimated at 210 nm.

The influence of Ag doping on the microstructure of the film was analyzed through X-ray diffraction and the results are presented in Figure 4. The patterns for the mixed 24 h TiO₂ and the 0.15%Ag/TiO₂ films showed the predominance of the anatase phase with a pronounced (1 0 1) peak at $2\theta = 25.3^\circ$. Other

peaks of smaller intensity, at 37.7° , 38.5° , 48.1° , 55.1° , 59.3° , 62.4° were attributed to the same phase [9,20,24].

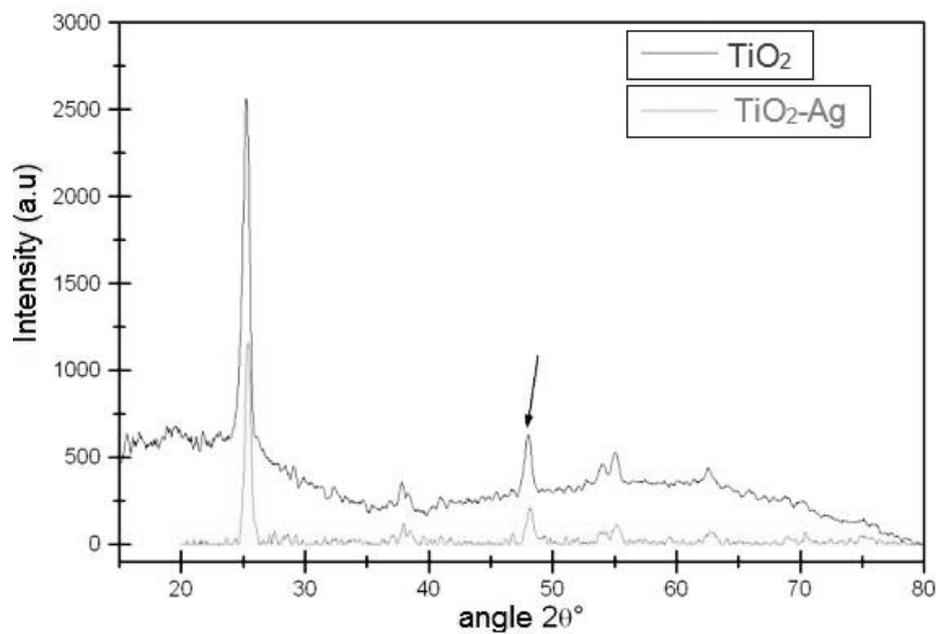


Figure 4 : XRD patterns for the mixed 24 h TiO₂ and 0.15%Ag/TiO₂ films

Crystallite size was calculated by using Scherrer's formula [25]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the crystallite size, λ the X-ray wavelength used, β the broadening of diffraction line measured as half its maximum intensity and θ the corresponding angle. Values of 14 nm and 12 nm were found for the mixed 24 h TiO₂ and 0.15% Ag/TiO₂ films, respectively. So, the grain size decreases with the Ag doping. Researchers [15,17] have explained this behavior as follows: the radius of Ag⁺ (ca. 126 pm) is bigger than that of Ti⁴⁺ (ca. 68 pm), then Ag⁺ ions introduced by the sol-gel process would not enter the lattice of the anatase phase to form a stable solid solution. During the calcination step these dispersed Ag⁺ ions would gradually migrate from the volume of TiO₂ grains to their surfaces and further to the surface of TiO₂ film. Those Ag⁺ ions then would compete with Ti⁴⁺ and O²⁻ ions for the diffuse and reorganization, and the anatase crystallization and grain growth is hindered. Furthermore, because the Ag⁺ ions gradually moves along with the anatase grain boundaries to the surface of TiO₂ film, the energy necessary for the movement of anatase grain boundary would increase and the driving force for the anatase grain boundary migration consequently decreases.

The effect of Ag doping on the TiO₂ photo catalytic activity was also analyzed. The results, depicted in Figure 5, showed that the photo degradation of phenol using the 0.15%Ag/TiO₂ film was around 25% higher when compared to the mixed 24 h TiO₂ film.

Similar behavior has been observed by other investigators [17] and according to them the increase in the photo catalytic activity using the modified silver TiO₂ film can be related to the fact that the Fermi level of TiO₂ is higher than that of silver. By this reason, electrons would transfer from film to metallic silver particles resulting in a space charge layer at the boundaries between Ag and TiO₂. The electric field drives electrons to the interior and abstracts holes to the interfacial region of TiO₂ film, which enhances the photo generated electron-hole pair separation and inhibits their recombination. The charge separation efficiency and lifetime of photo generated charge carriers then increases. Relatively larger amount of generated hole can reach the interfacial region of TiO₂ film producing higher densities of reactive radicals such as HO₂, ·OH and H₂O₂,

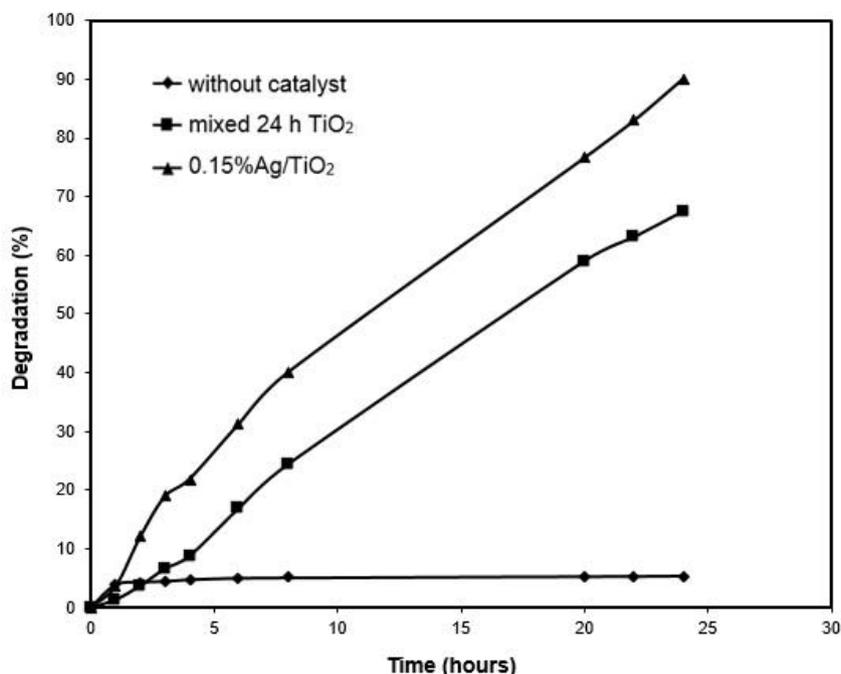


Figure 5 : Photodegradation of phenol as a function of irradiation time in the absence and presence of catalyst: mixed 24 h TiO₂ and 0.15%Ag/TiO₂ films under UV illumination, oxygen atmosphere and stirring (pH 5)

etc. For the TiO₂ photocatalytic oxidation proceeding mainly through the oxidization of photogenerated holes and its carriers, i.e. the reactive radicals, the photocatalysis is then facilitated. Besides, owing to the electrostatic interaction between the relatively positively charged TiO₂ film and negative ⁻OH and H₂O, absorption of hydroxyl groups and water on doped TiO₂ film would be improved. This also leads to the increase in the contents of surface hydroxyl groups on doped TiO₂ films, which facilitates the charge transfer and the TiO₂ photocatalysis.

IV. CONCLUSIONS

The photocatalytic activities of the following films: pure titania, modified by addition of TiO₂ P25 and doped with Ag at different loadings and immobilized in borosilicate substrate were investigated. The results, tested for phenol degradation, showed that the most promising were the Ag-doped films deposited at 0.4 mm s⁻¹ withdrawing rate and two dipping. Under these conditions, around 90% of the organic pollutant was photodegraded after 24 h of irradiation.

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