

# Removal of EDTA From Photovoltaic Industry Wastewater By Ag-TiO<sub>2</sub> Photocatalyst

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The presence of EDTA in wastewaters originating from photovoltaic (PV) process may cause significant environmental impacts. The aim of this work was the treatment of the effluents, resulting from the baths of the PV process, by a photocatalytic process based on TiO<sub>2</sub> silver doped (Ag-TiO<sub>2</sub>) and using synthetic solutions containing EDTA. The influence of the various parameters such as the quality and quantity of the photocatalyst, initial concentration of the pollutant, the initial pH was studied. XRD characterizations were also done. Results mainly showed that with doping TiO<sub>2</sub> with Ag, it possible to obtain higher yields in the photocatalytic degradation of EDTA than in absence of dopant. The optimal Ag-TiO<sub>2</sub> catalyst dose was found to be 1.5 g/L, whereas, the optimal initial pH value was found to be 2.5.

Keywords : Photovoltaic wastewater, EDTA, Doped Ag-TiO<sub>2</sub> photocatalyst

## 1. Introduction

The fabrication of photovoltaic (PV) cells includes the use of more than 200 organic and inorganic compounds (Doble and Kumar, 2005). Consequently, effluents from PV industry may contain harmful agents, such as acids, nanoparticles, organics, etc. Among organic contaminants, complexing agents such as EDTA may consist a threat for environment (Kunz et al. 2002). Biologic degradation of EDTA is very slow and only occurs in abiotic medium in presence of sun light. In order to reduce negative effects of complexing agents, many treatment processes were studied including chemical oxidation (with oxidants such as ozone and chlorine, etc), physico-chemical (adsorption on activated carbon, etc). Electrochemical methods were also used in EDTA degradation (Khelifa et al., 2009). Recently, advanced oxidation processes (AOP's) such as photocatalysis, had known remarkable success in organic pollutants removal (Hoffmann et al., 1995, Aoudj et al., 2018). Photocatalysis was used in removal of phenol, dyes, pharmaceuticals, etc (Chatterjee et al. 1994). In photocatalysis, TiO<sub>2</sub> is undoubtedly the most used semiconductor. Besides, catalyst modification such as doping may result in increasing the photoactivity. Several works reported that doping sensitively improves the TiO<sub>2</sub> photocatalytic efficiency (Hoffmann et al., 1995). Most recently, some research teams focused their studies on silver based photocatalysts owing to their interesting properties (Harikisbor et al., 2014, Asai et al., 2002). In this work, a silver doped photocatalyst Ag-TiO<sub>2</sub> was synthesized and then used in the degradation of EDTA which is an ubiquitous pollutant in PV industry wastewater. The effect of some influencing parameters such as initial pH, initial pollutant concentration and Ag-TiO<sub>2</sub> dose were studied.

## 2. Experimental

### 2.1 Experimental setup

The experimental setup comprises a photoreactor which is a glass thermostated cell which is irradiated by a UV lamp (PHILIPS, UVA, 20 W).

## 2.2 Ag-TiO<sub>2</sub> synthesis

The preparation of photocatalysts is based on the sol-gel impregnation method as reported in the study of Giannakas et al. (2016). In this technique, 3.4 ml of n-butoxyde de titane (IV) precursor is added dropwise to a 50 ml aqueous solution containing well determined amounts of the dopant AgNO<sub>3</sub>. The obtained suspension is left to rest during 24 h at ambient temperature. It is, then, dried at 110 °C for at least 48 h. The obtained xerogels undertake a heating treatment at 500 °C of 1 h with a heating rate of 5 °C/min. The calcinated powders are then dispersed in water under a ultra-sound treatment in order to remove impurities. Finally, the materials are dried again at 110 °C during 24 h and then ground with an agate mortar.

## 2.3 Experimental procedure

Acide effluents from PV process often contain dissolved organic pollutants such as EDTA. In order to simulate these effluents, the used synthetic solutions in the different experiments are prepared by dilution of stock solution (1000 mg/L of EDTA) to well determined concentrations. The pH adjustment was done by adding solutions of H<sub>2</sub>SO<sub>4</sub> (1N) and NaOH (1N). The synthetic solutions to be treated are introduced in the photoreactor. They are, first, kept in the dark for 30 minutes in order to reach the adsorption equilibrium between pollutant and photocatalyst. Once the reactor is illuminated by the UV lamp, the timer is switched on, and samples are periodically withdrawn in order to monitor EDTA concentration over time. Samples were filtered with nylon seringue filters of 0.22µm. All runs were done at ambient temperature and under constant stirring rate. Results are given either as normalized concentration (C/C<sub>0</sub>) or removal efficiency R(%) which is given by the following equation :

$$R(\%) = \frac{(C_0 - C)}{C_0} \times 100$$

Where, C<sub>0</sub> is the initial concentration and C is the concentration at time t.

## 2.4 Analytical methods

The solution pH was measured using a pH-meter HANNA HI4222. The concentration of EDTA was determined by colorimetry using xylenol zirconium-orange complex (Rodier ,1996), with a HACH DR 2500 spectrophotometer. DRX spectra of photocatalysts TiO<sub>2</sub> and Ag-TiO<sub>2</sub> were obtained by a D2 PHASER.BRUKER diffractometer.

## 3. Results and discussion

### 3.1 Effect of doping

In order to improve the photocatalytic activity of TiO<sub>2</sub>, many techniques are used. The improvement strategies involves structural modifications such as doping by incorporating impurities (metals or non-metals) in TiO<sub>2</sub> surface (Daghrir et al, 2013, Byrne et al.,2018). In this study, silver was chosen as dopant. In order to examine its effect, a comparison was done between 0.1g/l of TiO<sub>2</sub> and 0.1 g/l Ag-TiO<sub>2</sub>.

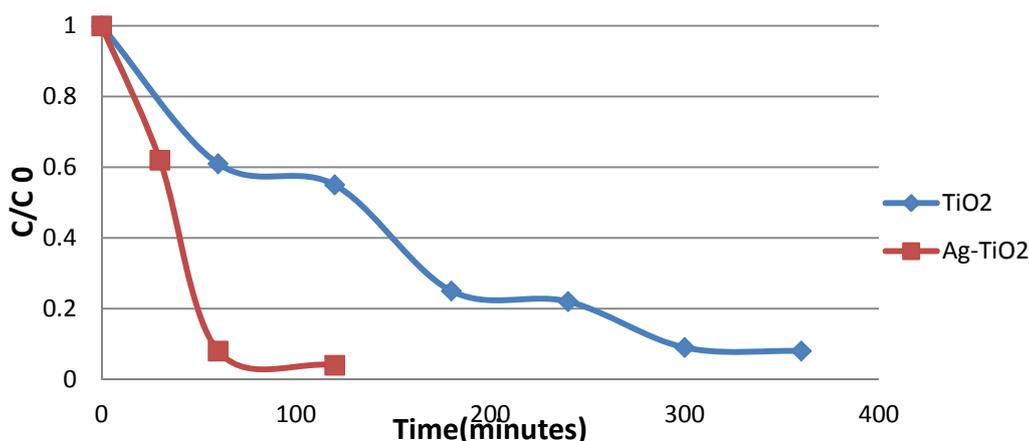


Figure 1 Effect of doping by TiO<sub>2</sub> and Ag-TiO<sub>2</sub> on EDTA degradation under UV irradiation. Initial pH,2.5 ;[Ag-TiO<sub>2</sub>],0.1 g/l ; [EDTA],10<sup>-3</sup> M.

In Figure 1, results show the effect of TiO<sub>2</sub> doping on the removal of EDTA. It can be observed that a better efficiency of 96 % was obtained by using Ag-TiO<sub>2</sub> after 120 min treatment time, while only 44 % degradation

efficiency was obtained by  $\text{TiO}_2$ . This result demonstrates that the doping of  $\text{TiO}_2$  by silver sensitively improves its photocatalytic activity.

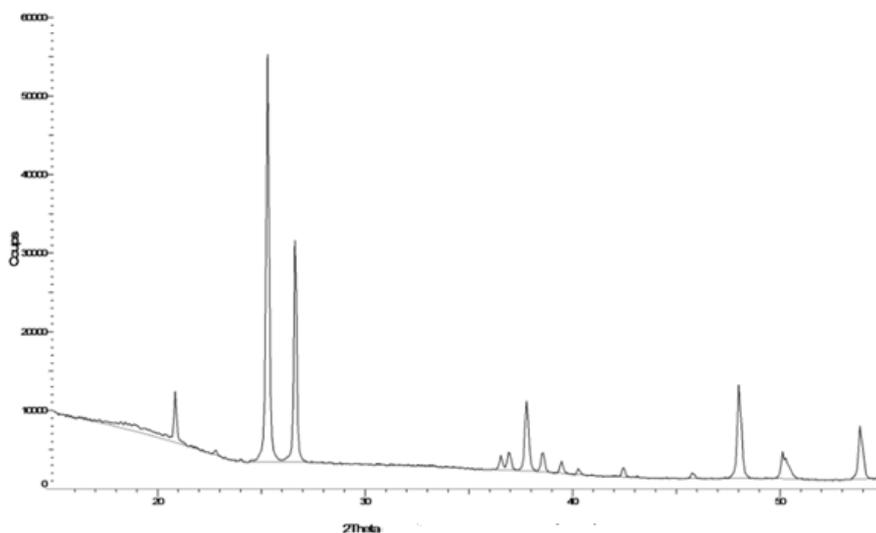


Figure 2. DRX spectra of  $\text{TiO}_2$

The Figure 2 shows DRX spectrum of pure (commercial)  $\text{TiO}_2$ . It can be noted the presence of peaks at  $2\theta = 25.3$ ;  $37.8$ ;  $48$  et  $53.91$ , which may be attributed to anatase phase of  $\text{TiO}_2$ . This is in good agreement with standard JCPDS (PDF=21-1272) of anatase.

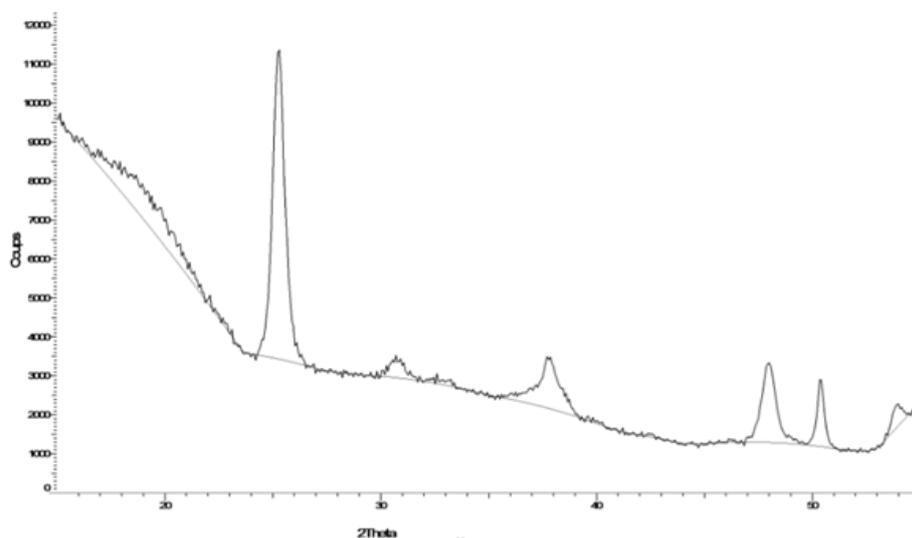


Figure 3. DRX spectra of  $\text{Ag-TiO}_2$

Figure 3 shows DRX spectrum of synthesised  $\text{Ag-TiO}_2$ . It can be noted the presence of peaks at  $2\theta = 25.3$ ;  $37.8$ ;  $47.9$  and  $53.16$ . The presence of anatase phase without phases of impurities such as Ag or AgO confirms the complete doping of Ag in  $\text{TiO}_2$  matrix (Harikisbor et al., 2014). This result demonstrates that the synthesized  $\text{Ag-TiO}_2$  is of anatase phase and not rutile or brookite types. Due to the higher production rate of electron-hole pairs and the lower recombination rate electron-hole with anatase in comparison with rutile, the mobility of electrons is superior in anatase. The positive effect of doping on photocatalytic activity may be explained by the fact that presence of silver reduces the recombination phenomenon which results in increasing the activity in photocatalytic reactions (Asai et al., 2002).

### 3.2 Effect of EDTA initial concentration

The effect of varying initial concentration on the kinetics of EDTA degradation was studied in presence of doped  $\text{TiO}_2$ . Figure 4 illustrates EDTA degradation at different initial concentrations :  $2.5 \cdot 10^{-4}$ ,  $2.5 \cdot 10^{-5}$  and  $0.5 \cdot 10^{-3}$  M. The maximal EDTA removal efficiency of 100 % was recorded with the concentration of  $2.5 \cdot 10^{-5}$  M in only few minutes. An efficiency of 99 % was obtained with initial concentration of  $0.5 \cdot 10^{-3}$  M after 2 hours. With the concentration of  $2.5 \cdot 10^{-4}$  M, a degradation efficiency was 97 % after 5 hours. It is clear that decreasing EDTA initial concentration results in faster degradation rates. This behaviour may be explained either by (i) the decreasing in the holes  $h^+$  and/or  $\text{OH}^\cdot$  radicals photo-generation on the catalyst surface due to the coverage of active sites by the pollutant molecules or (ii) the absorption of a significant amount of light UV energy by adsorbed pollutant molecules rather than  $\text{Ag-TiO}_2$  surface, which reduces the radiation intensity absorbed by the photocatalyst and hence decreased the treatment efficiency. It may be concluded that when the initial concentration increases, the reaction rate decreases and consequently, the catalyst surface required for the degradation increases too.

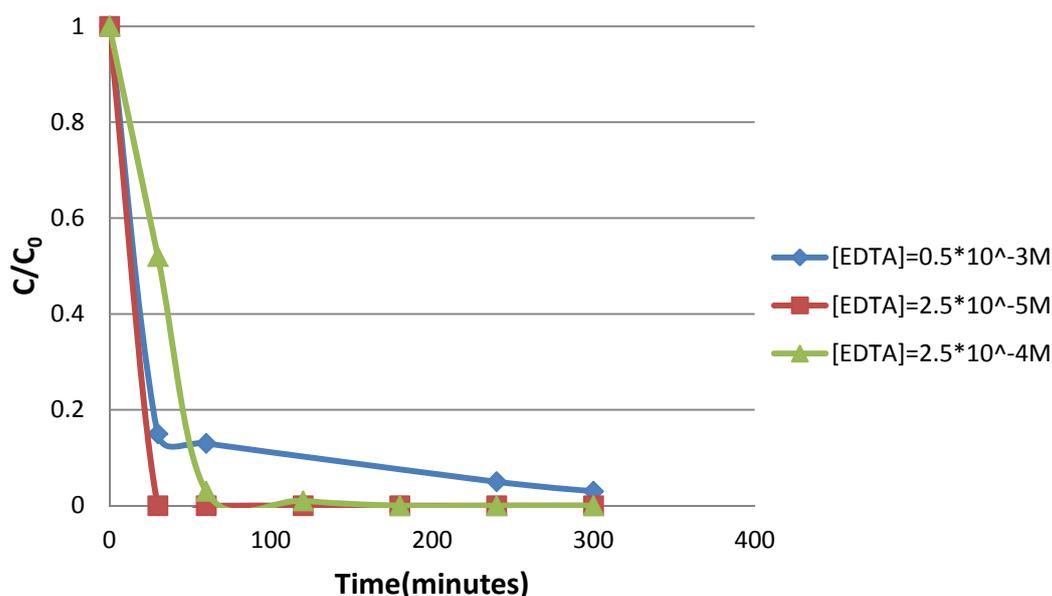


Figure 4. Effect of initial concentration on EDTA degradation by  $\text{Ag-TiO}_2$  under UV irradiation. Initial pH, 2.5 ;  $[\text{Ag-TiO}_2]$ , 0.1 g/L

### 3.3 Effect of $\text{Ag-TiO}_2$ concentration

In order to optimize the quantity of  $\text{Ag-TiO}_2$  necessary for EDTA degradation, three photocatalyst doses are used 0.5 ; 1.5 and 2 g/L. The results are given in figure 5.

The degradation of EDTA with a photocatalyst concentration of 0.5 g/L, after 4 hours treatment, is only 83 %. When a concentration of 1.5 g/l of  $\text{Ag-TiO}_2$ , it can be observed that the removal of EDTA is faster. After 2 h the degradation efficiency of EDTA was 98 %. This improvement may be explained by the increase in specific surface with increasing the catalyst dose which enhances electronic exchange between the pollutant and the catalyst. When a concentration of 2 g/L of  $\text{Ag-TiO}_2$  is considered, the degradation efficiency of EDTA was 97 % after 5 h UV illumination. At this concentration, the solution is rendered cloudy and the particles are less active. Thus, the concentration of 1.5 g/L may be considered as optimal value in the studied conditions.

For high  $\text{Ag-TiO}_2$  concentrations, two concomitant effects may be distinguished ; one positive effect which is the increase of specific surface with better adsorption of pollutants on active sites and higher electron/hole generation, and a negative effect which is the screen effect that prevents UV light penetration resulting in reducing removal efficiency. Herrmann and Guillard (2000) reported that the initial degradation rate of a variety of organic pollutants, using static or dynamic photoreactor, is directly dependent on the concentration of  $\text{TiO}_2$ . An optimum is reached corresponding to a maximal absorption of photons by  $\text{TiO}_2$ . For higher concentrations of catalyst, the solution turns turbid which hinders the light penetration in the bulk of the reactor and consequently, it affects the photocatalytic efficiency (Harikisbor et al., 2014).

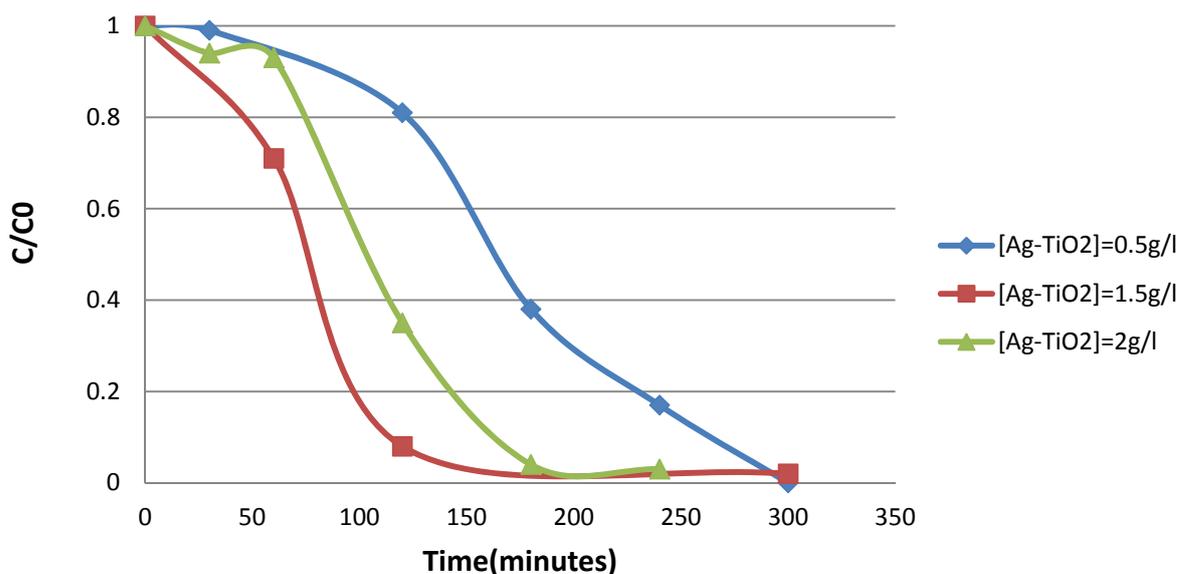


Figure .5 Effect of Ag-TiO<sub>2</sub> concentration on the EDTA degradation. Initial [EDTA], 10<sup>-3</sup> M ; initial pH, 2.5.

### 3.4 Effect of initial pH

Solution pH is a very important parameter in photocatalysis, because it determines surface charges of the photocatalyst. In order to assess the influence of the initial pH on EDTA photocatalytic degradation, the following initial pH values : 2 ; 2.5 ; 7 ; 9 were studied. Figure 6 illustrates the variation of the removal efficiency of EDTA in function of initial pH. The degradation is obviously better in acidic media. The degradation efficiency reached the maximal value at initial pH of 2.5 with 98 % after 3h irradiation, the removal was about 94 % at initial pH of 2. For pH= 7, the elimination was 37 %, while at initial pH of 9 it was only 9.30 %. This is a major advantage of the Ag-TiO<sub>2</sub> based photocatalysis process because PV wastewaters are acidic by nature (Aoudj et al.2015). For acid pH values, TiO<sub>2</sub> surface is positively charged (TiOH<sub>2</sub><sup>+</sup>), which enhances the adsorption of anions by electrostatic attraction (in acid medium EDTA species is predominantly in the form EDTA<sup>2-</sup>). While in basic medium, surface is negatively charged (TiO<sup>-</sup>) and attracts cations. When the pH is close to pHPZC, TiO<sub>2</sub> posses as much positive charges as negative ones and the phenomenon of TiO<sub>2</sub> agregation and formation of clusters is then enhanced (Harikisbor et al., 2014, Asai et al., 2002).

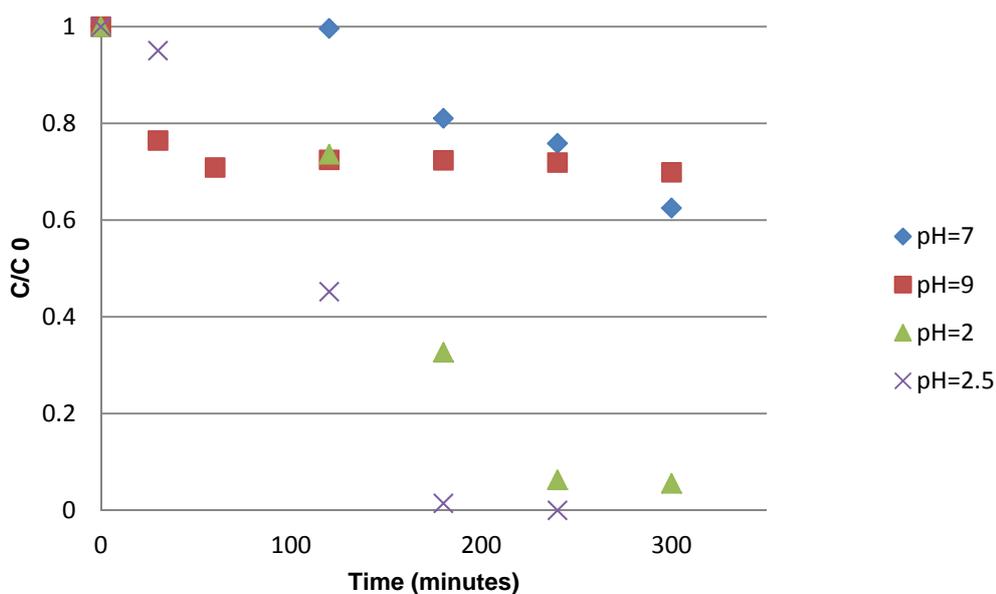


Figure 6. Effect of initial pH on the EDTA degradation. Initial [EDTA], 10<sup>-3</sup> M ; [Ag-TiO<sub>2</sub>], 0.1 g/l

#### 4. Conclusion

In this study, a silver doped TiO<sub>2</sub> photocatalyst (Ag-TiO<sub>2</sub>) was synthesized and characterized. The results illustrate that Ag-TiO<sub>2</sub>, under UV irradiation, shows to be efficient in EDTA degradation. A complete removal may be obtained. From the study of the influence of different parameters, the following conclusions may be drawn Doping sensitively improves photocatalytic activity. In similar conditions, the use of Ag-TiO<sub>2</sub> gives 96 % degradation with 44 % for TiO<sub>2</sub>.

From the study of the effect of EDTA initial concentration, it is concluded that the higher is EDTA concentration the lower is degradation rate.

The study of the effect of the concentration of Ag-TiO<sub>2</sub> shows the presence of an optimal value estimated at 1.5 g/L in this work. Initial pH plays a crucial role in EDTA degradation. The higher efficiency was obtained for acid pH with 98 % removal, then neutral pH (37 %) and finally alkaline pH (9.3 %).

#### References

- Aoudj, S., Khelifa, A., Drouiche, N., Hecini, M., 2015. Development of an integrated electrocoagulation-flotation for semiconductor wastewater treatment. *Desalination and Water Treatment*, 55, 1422-1432
- Aoudj S., Khelifa A., Zemmouri H., Hamadas I., Yatoui S., Zabchi N., Drouiche N., 2018, Degradation of EDTA in H<sub>2</sub>O<sub>2</sub>-containing wastewater by photo-electrochemical peroxidation *Chemosphere* 208, 984-990
- Asai, T. Umabayashi, T. Yamaki, et H. Itoh, 2002, Analysis of electronic structures of 3d transition metal-doped TiO<sub>2</sub> based on band calculations, *Journal of Physics and Chemistry of Solids*, 63, 1909-1920
- Byrne C., Subramanian G., Pillai S. C., 2018, Recent Advances in Photocatalysis for Environmental Applications, *Journal of Environmental Chemical Engineering*, 6, 3531-3555
- Chatterjee S., Sarkar S., Bhattacharyya S.N., 1994, Photodegradation of phenol by visible light in the presence of colloidal Fe<sub>2</sub>O<sub>3</sub>, *Journal of Photochemistry and Photobiology A: Chemistry* 81, 199-203.
- Daghrir R., Drogui P., Robert D., 2013, Modified TiO<sub>2</sub> For Environmental Photocatalytic Applications : A Review, *Industrial and Engineering Chemistry Research*, 52, 3581-3599
- Doble M., Kumar A., (Ed), 2005, *Biotreatment of Industrial Effluents*, Elsevier Butterworth, Heinemann, Burlington, MA 01803, USA
- Giannakas A.E., Antonopoulou M., Daikopoulos C., Deligiannakis Y., Konstantinou I., 2016, Characterization and catalytic performance of B-doped, B-N co-doped and B-N-F tri-doped TiO<sub>2</sub> towards simultaneous Cr(VI) reduction and benzoic acid oxidation, *Applied Catalysis B : Environmental*, 184, 44-54
- Harikisbor M., Sandhyarani M., Venkateswarlu K., Nellaippan T.A., Rameshbabu N., 2014, Effect of Ag doping on antibacterial and photocatalytic activity of nanocrystalline TiO<sub>2</sub>, *Procedia Materials Science*, 6, 557-556
- Herrmann J.M., Guillard C., 2000, Photocatalytic degradation of pesticides in agricultural used waters, *Comptes Rendus de l'Académie des Sciences - Series IIC -Chemistry* 3, 417-422
- Hoffmann M.R., Martin S.T., Choi W., Bahnemann D.W., 1995, Environmental Applications of Semiconductor Photocatalysis, *Chemical Reviews* 95, 69-96.
- Khelifa A., Aoudj S., Moulay S., Hecini M., de Petris -Wery M., 2009, Degradation of EDTA by in-situ electro-generated active chlorine in a electroflotation cell, *Desalination and Water treatment*. 7, 119-123
- Kunz, A., Peralta-Zamora, P. and Durán, N., 2002, Hydrogen Peroxide Assisted Photochemical Degradation of Ethylenediaminetetraacetic Acid. *Advances in Environmental Research*, 7, 197-202.
- Rodier J., *Analyse de l'eau*, (Ed) 1996, Dunod, Paris, France, (in French)