

Photoactivity Performance of TiO₂/cellulose and ZnO/polystyrene; Intensified Effect of Oxidants on Degradation Efficiency of Acetaminophen

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The photoactivity of TiO₂ nanoparticles and ZnO nanofibers deposited on cellulose and polystyrene was investigated. The synthesized catalysts were characterized by SEM, XRD and FT-IR. The X-rays diffraction pattern showed that the TiO₂ materials are mainly composed of anatase phase with a small amount of rutile phase. Peaks found for ZnO are assigned to well crystallized ZnO oxides. The SEM images confirmed the dispersion of TiO₂ nanoparticles and ZnO nanofibers on cellulose and polystyrene, respectively. The photoactivity of the two catalysts was tested for the degradation of acetaminophen. Results showed that for an initial drug concentration of 10 mg l⁻¹, the removal of the pollutant under UV light in the presence of TiO₂/cellulose reached 80%. Under the same conditions, ZnO/polystyrene was inactive under UV, visible and solar radiations. The study of the effect of H₂O₂ and K₂S₂O₈ as oxidants showed an intensified effect of peroxydisulfate (S₂O₈²⁻) on degradation efficiency of the pollutant; in fact, in the presence of TiO₂/cellulose and ZnO/polystyrene, 85.4 and 93.1% of acetaminophen were respectively removed from the contaminated solutions after adding 1 mM of S₂O₈²⁻. The present findings reveal that under UV light the photocatalytic systems TiO₂-K₂S₂O₈/cellulose and ZnO-K₂S₂O₈/polystyrene show promising results for treating effluents charged with acetaminophen.

Keywords: Drug residue, Photocatalytic activity, Phytotoxicity, Supported photocatalyst, Degradation reaction

INTRODUCTION

Some semiconductors are considered as effective photocatalysts in several treatment processes of pollutants and undesirable compounds present in liquid or gas effluents [1,2]. Moreover, semiconductor-based photocatalysis has been used in the field of microorganism inactivation due to its outstanding performance and mild reaction conditions and in energy generation [3-5]. The photonic activation of these semiconductors led to absorption of radiation wavelengths and generation of [•]OH groups and electron-hole pairs that are able to react with organic molecules *via* degradation and/or oxidation-

reduction reactions.

The catalysts TiO₂ and ZnO are cost-efficient, environmentally friendly materials possessing excellent chemical stability under various conditions. They have been shown to be prominent photocatalyst candidates to be used in photodegradation processes [6-9] and therefore, they are promising for applications in environmental problems at large scale. Photocatalysts are implemented into reactor apparatus either in suspension or in supported form. This last configuration is preferred since they can be separated from a liquid medium without the need for filtration and allowed avoiding the addition of reactants during the process, as it is the case during the usual photo-Fenton process. Moreover, the high aggregation tendency of the semiconductor led to a loss of active sites as well as

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catalytic efficiency [10]. On the other side, when the semiconductor particles are attached to a support, the photoexcited groups of the semiconductor could be transferred to the surface of the support layers which could restrain the recombination of the photoexcited electron-hole pairs and could therefore improve the photocatalytic efficiency [11]. Thus, immobilizing the catalyst on a large surface support has become one of the most preferred approaches since adopting the photocatalytic processes.

A great deal of research has been focused on the development of supported catalysts using different systems [5]. Among these materials, glass fibers, zeolites, silica, activated carbon, minerals, metallic supports, polyester, chitosan, polystyrene and cellulose have proved to be highly active photocatalytic media [12-15]. Cellulose, a biopolymer extracted from cell walls, is a carbon material with a large surface area and high porosity. It contains hydroxyl groups facilitating the interactions with the photocatalyst *via* hydrogen and electrostatic interaction [16]. For its part, polystyrene, a transparent thermoplastic polymer, offers many perspectives for supporting catalytic materials which can modify their optical and other properties avoiding the inherent problems of colloidal particle deposition on low thermal resistant substrates [13]. In some cases, it is essential to intensify the photocatalysis operation in order to increase the photoactivity of the catalysts. In this context, several studies suggested adding oxidants with high oxidizing power to increase the effect of catalysts in the degradation of organic molecules [17,18]. Particularly, peroxydisulfate anion ($S_2O_8^{2-}$) is a strong two-electron oxidizing agent with a redox potential of 2.01 V. The sulfate radicals ($SO_4^{\cdot-}$) could be produced from this oxidant *via* thermal, photochemical or redox decomposition [19]. The radical $SO_4^{\cdot-}$ which is stable in water is considered as a strong oxidant leading to a higher rate of oxidation of organic contaminants.

Pharmaceuticals, as the hazardous pollutants, enter the environment, mainly *via* wastewaters and can reach surface waters and groundwaters. They are released through wastes from pharmaceutical industries and hospitals in addition to their presence in bathing, sewers and trash [20]. Particularly, acetaminophen has been detected in water samples from rivers and WWTPs (wastewater treatment plants) in concentrations (150 to 250 $\mu\text{g l}^{-1}$) greater than the

limit of detection [20-22]. The pharmaceutical products and their metabolites can also be found in soils, and in surface water by runoff and in groundwater by leaching. Several studies have been published on the removal of hazardous pharmaceutical products from water and wastewater using conventional and modern wastewater treatments. Among these techniques, photocatalysis could be a proper technique for eliminating these products from wastewaters. Indeed, several research studies have demonstrated the capability of TiO_2 and other semiconductors (ZnO, CuO, ...) to oxidize drugs dissolved in water [23].

This experimental work was investigated in order to study the performance of supported TiO_2 and ZnO on cellulosic tissue and polystyrene, respectively. This performance was tested *via* the photocatalytic degradation under UV, visible and solar irradiations of acetaminophen as a representative compound of drug residues. To increase the photoactive efficiency of the two photocatalysts, H_2O_2 and $K_2S_2O_8$ were added as oxidants. In addition to the photocatalyst activity, the impact of the phytotoxicity of the obtained effluents after two treatments, photocatalysis and biological treatments, was explored since the degradation of contaminants can generate metabolites, sometimes even more toxic than the original compound.

EXPERIMENTAL

Chemicals and Materials

Acetaminophen ((N-(4-hydroxyphenyl) acetamide)) was supplied by SAIDAL company (Annaba, Algeria) and used as received (Fig. 1). The aqueous solutions were prepared using distilled water with a resistance of 15.0 M Ω cm and then stored at 4 °C in order to minimize drug degradation.

The first photocatalytic medium was composed of cellulosic fibers coated with a catalyst mixture (TiO_2 /P25, zeolite and silica). P25-Degussa TiO_2 nanoparticles were supplied by Ahlstrom Company and titanium tetraisopropoxide was purchased from Sigma Aldrich. The second catalyst was composed of ZnO impregnated on polystyrene petri dish. The other analytical grade chemicals (hydrogen peroxide 32%, potassium peroxydisulfate 99%, hydrochloric acid 36%, sodium hydroxide) were purchased from Merck, Germany and used without further purification.

The preparation methodology of TiO_2 supported on

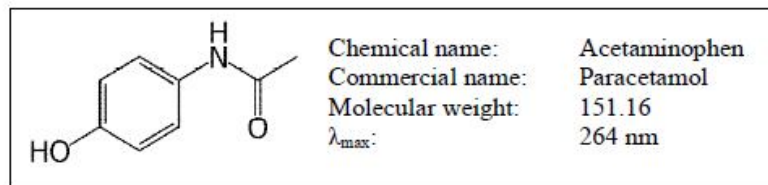


Fig. 1. Chemical structure of acetaminophen molecule.

cellulose tissue catalyst was well previously described by Rouibah *et al.* [24]. Briefly, cellulosic fibers were impregnated with a suspension composed of 40% dry powder and 60% pure water; the obtained catalyst was dried in an oven at 105 °C and stored until use. To prepare ZnO/polystyrene catalyst, thin ZnO films were sputtered on polystyrene petri dish by direct current magnetron sputtering at 300 mA and ~400 V in Ar atmosphere (at ~0.1 Pa) using ZnO-Al₂O₃ (98% ZnO-2% Al₂O₃) target obtained from K. Lesker, Hastings, UK [13,25]. This procedure led to a uniform transparent ZnO film.

Analytical Techniques

The two catalytic systems obtained were characterized by several techniques:

- XRD: The X-ray diffraction using Cu K α radiation ($\lambda_{\text{Cu}} = 0.154056$ nm) at a grazing incident angle of 4° was performed to determine the crystalline structure and crystallite size of the catalysts in an Ultima IV Rigaku instrument.

- Optical microscopy: The optical visualization, performed with Eclipse LV100ND type, magnification of 5×0.15 , was necessary to distinguish some details on the surface of the two catalytic systems. The optical microscope was accompanied by NIS Elements D software (4.10.00);

- SEM: The scanning electronic microscopy (QUANTA 250 with 300, 1200 and 2000 x magnification) was used to analyze the morphology and size of the catalysts deposited.

Other analytical techniques were used to analyze the aqueous phase:

- UV-Vis: A Secomam Prim UV-Vis spectrophotometer was used to monitor the photodegradation of acetaminophen at 264 nm;

- HPLC: A Shimadzu HPLC equipped with UV-Vis detector, model SPD-M10A (column Supelco;

250 mm \times 4.6 mm, particle size 5 μ m) operated at the wavelength of 243 nm, was applied to identify by-products after photodegradation operations. The mobile phase was a mixture of water and acetonitrile (50:50, v/v).

Activity of the Supported TiO₂ and ZnO; an Experimental Approach

The photocatalytic activity of the prepared catalysts (in duplicate) was performed in 1L-batch reactors equipped with a 9-Watt UV Philips bulb lamp ($\lambda = 365$ nm) and 40-Watt Vis bulb lamp ($\lambda = 400$ -800 nm). The two reactors were covered by an aluminum foil to avoid loss of UV light and entrance of visible light. The treated sample (initial volume = 500 ml) was stirred with the lamp off. All the experiments were elaborated at 20 ± 1 °C. After 30 min stirring (sufficient for establishing adsorption-desorption equilibrium), a first sample (3 ml) was collected ($t = 0$) and the light was turned on. Samples were then taken regularly (every 30 min) from the photoreactor for analysis in order to follow the abatement of the molecule from liquid phase. Acetaminophen concentration was evaluated by measuring the absorbance using a Secomam Prim UV-Vis spectrophotometer. Distilled water was used as blank. The calibration curve was obtained for the concentrations ranging between 0 and 10 mg l⁻¹.

Phytotoxicity Tests

To evaluate the toxicity of the photocatalytic treated samples, germination of Cresson seeds was used. The tests were carried out at room temperature with 10 seeds each by watering 5 ml of each sample. Seeds were irrigated with tap water providing a positive control. Germination index (GI%), shoot length, and number of seeds were recorded after 4 days; only GI values obtained according to the following relation are reported here:

$$GI (\%) = \frac{\text{Seed germination (\%)} \times \text{root length of treatment}}{\text{Seed germination (\%)} \times \text{root length of control}} \times 100$$

According to the Zucchini *et al.*'s [26] classification, there are three categories of toxicity 1) high phytotoxicity when GI is below 50%, 2) moderate phytotoxicity when $50\% < GI < 80\%$ and 3) absence of phytotoxicity when GI value is above 80%.

RESULTS AND DISCUSSION

Morphology and Crystal Structure

Structure and morphology of the synthesized catalysts play an important role in controlling the properties of the films to determine the performance for their applications in photodegradation processes. The XRD patterns of TiO₂/cellulose and ZnO/polystyrene, shown in Fig. 2, were recorded within the range of $2\theta = 10-80^\circ$. The diffraction peaks at 20.3° and 21.8° (Fig. 2a) correspond to the crystalline cellulose [27]. The most prominent peak for TiO₂ appeared at 25.2° which corresponds to the anatase face of titania. The other crystalline peak ($2\theta = 37.4^\circ$) which was less intense was attributed to the rutile form of TiO₂. According to some authors, the presence of silica prevented the transformation of TiO₂ from anatase to rutile phase [28,29]. In Fig. 2b, in addition to the peaks corresponding to the presence of silicone (SiO₂) and alumina (Al₂O₃), the several peaks found for ZnO at the position of $2\theta = 25, 28, 34$ and 56.50° were assigned to well crystallized ZnO oxides.

The optical microscope shows that the woven cellulose fibers are covered with whitish-colored TiO₂ particles/aggregates, as clearly seen in Fig. 3a. It also displays discontinuous clusters of ZnO randomly deposited on the surface of the petri dish (Fig. 3b). The SEM photos (Figs. 3c-d) show a greater resolution of the TiO₂ particles dispersion on cellulosic fibers separated by voids and ZnO nanoparticles uniformly dispersed in the polystyrene matrix. The ZnO thin films deposited on polystyrene have a nanofibrous morphology with smooth surfaces.

Activity of the Supported TiO₂ and ZnO

The photocatalytic activity of TiO₂/cellulose and ZnO/polystyrene was evaluated by treating 10 mg l⁻¹ of

acetaminophen as a function of UV, visible and solar irradiations time. As shown in Fig. 4, TiO₂/cellulose has the highest photocatalytic activity under UV light with 80.5% removal efficiency. Under visible light and sunlight, the catalyst was less active achieving only 23 and 7.3% of pollutant removal, respectively. In this case, the excited electrons have a little energy that makes difficult the exchange between semiconductor particles, leading to less reactive oxidizing species. Otherwise, the high photocatalytic of TiO₂ under UV light may be attributed to the optical properties and the superfine network structure of cellulose that facilitates the dispersion of catalyst nanoparticles on its surface. So, TiO₂ irradiated by light within the membrane matrix was maximal [16]. Additionally, the high surface area (317 m² g⁻¹) and the small particle size (1.5 μm) of TiO₂ impregnated on the cellulosic paper ensured favourable conditions for better photocatalytic performance.

Unlike the first photocatalyst, the synthesized ZnO nanoparticles impregnated on polystyrene were not as significantly effective as those under UV, visible and sunlight. With the conditions selected for these assays (10 mg l⁻¹ of acetaminophen), the light radiations could not be absorbed by this oxide to generate electron/hole (e⁻/h⁺) pairs. This can be explained by a great absorption of applied light by the concentrated solution limiting consequently the diffusion step of the photo-excited species to the TiO₂ surface [16,30]. To extend the photosensitivity of this semiconductor, several studies suggested adding oxidants which are able to increase the effect of catalysts in the degradation of organic molecules. This is the objective of the paragraph "Effect of oxidants on acetaminophen photodegradation".

Kinetic Degradation of Acetaminophen

Initial acetaminophen concentrations of 2-10 mg l⁻¹ were considered in order to follow the kinetic degradation in the presence of TiO₂/cellulose after 240 min of UV-light irradiation (The kinetic degradation with ZnO/polystyrene was not considered since the catalyst was not efficient without oxidants; significant degradation of the pollutant was only observed when oxidants were added in solution). As indicated in Fig. 5, in the presence of TiO₂/cellulose, the pollutant abatement from the aqueous solution decreases

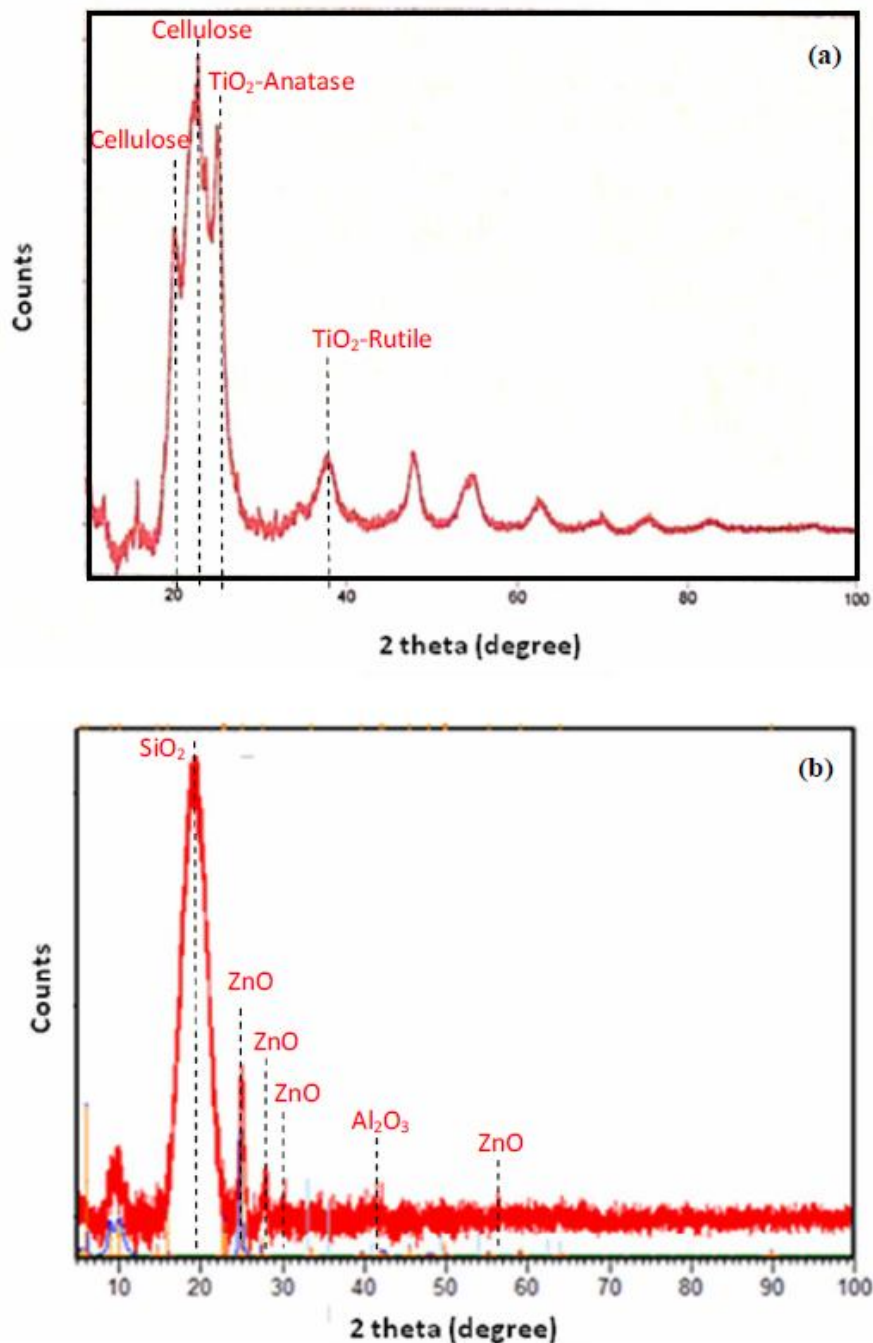


Fig. 2. XRD patterns of (a) TiO₂/cellulose and (b) ZnO/polystyrene.

significantly with increasing the initial concentration. The low concentration of 2 mg l⁻¹ allowed catalyst particles to absorb maximum exciting photons to generate higher

concentrations of Reactive Oxygen Species at the surface of the semiconductor. In case of higher initial concentration, the photons get intercepted before they can reach the surface

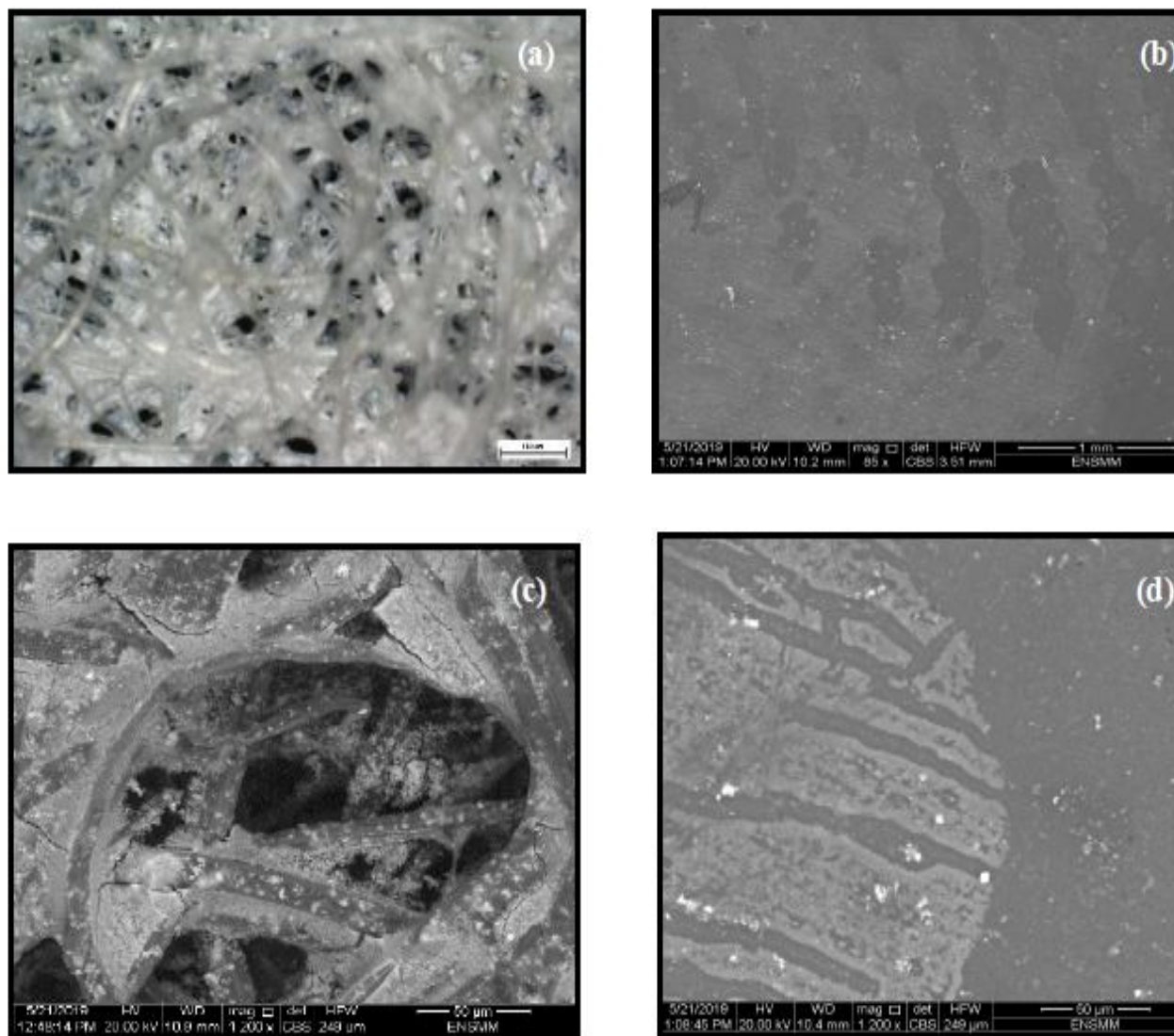


Fig. 3. SEM images of (a-c) TiO₂/cellulose and (b-d) ZnO/polystyrene.

of the saturated catalyst. There, the concentration of photo-generated reactive radicals decreases since the active sites are covered by pollutant molecules, leading to the decrease in the photocatalytic activity [31,32]. The mechanism of the photocatalytic degradation phenomenon using TiO₂ as catalyst has been extensively described in the literature. The several bonds of C-C, C-N and C-O contained in acetaminophen molecule (Fig. 1) are probably attacked by the free radicals ([•]OH and H[•]) produced on the surface of

TiO₂ particles resulting in oxidative products. The final products of the photocatalytic degradation of acetaminophen were identified by HPLC.

Effect of Oxidants on Acetaminophen Photodegradation; Highlighting the Photoactive Efficiency of Supported Catalyst in the Presence of S₂O₈²⁻

Several studies have claimed that oxidants are able to

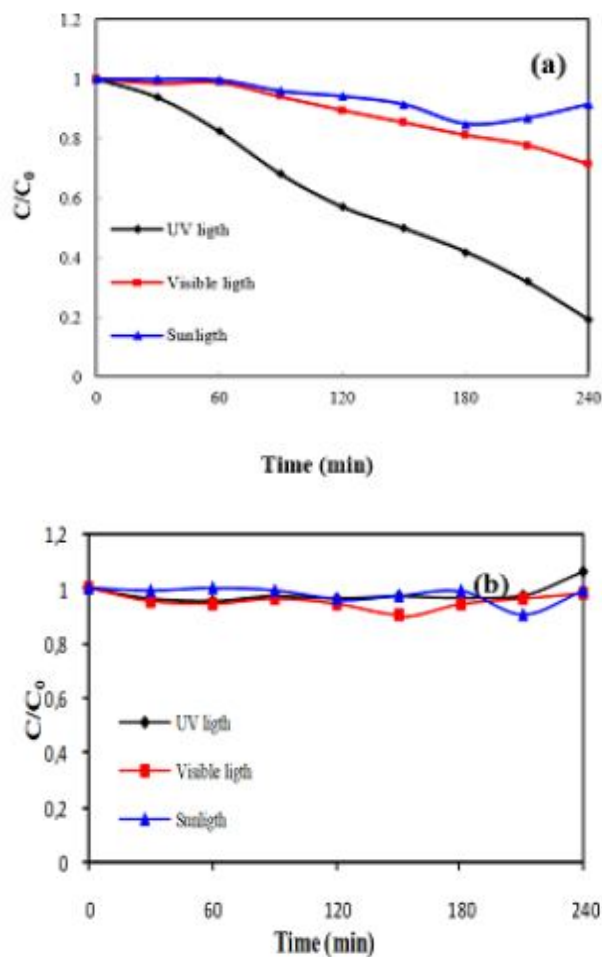


Fig. 4. Photocatalytic degradation of acetaminophen with (a) TiO₂/cellulose and (b) ZnO/polystyrene under UV, visible and sunlight (initial concentration: 5 mg l⁻¹; catalyst dosage: 0.25 g l⁻¹; T = 20 ± 1 °C; natural pH).

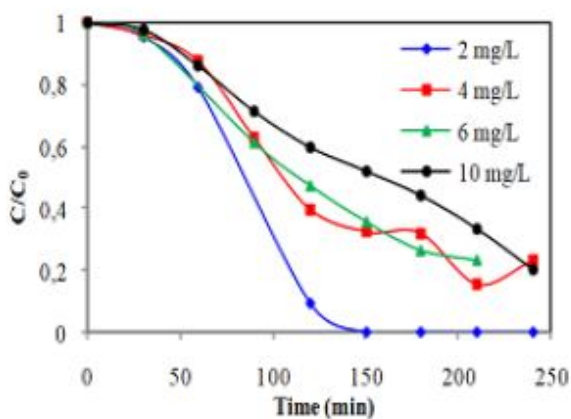


Fig. 5. Kinetic of photocatalytic degradation of acetaminophen with TiO₂/cellulose under UV light (catalyst dosage: 0.25 g l⁻¹; T = 20 ± 1 °C; natural pH).

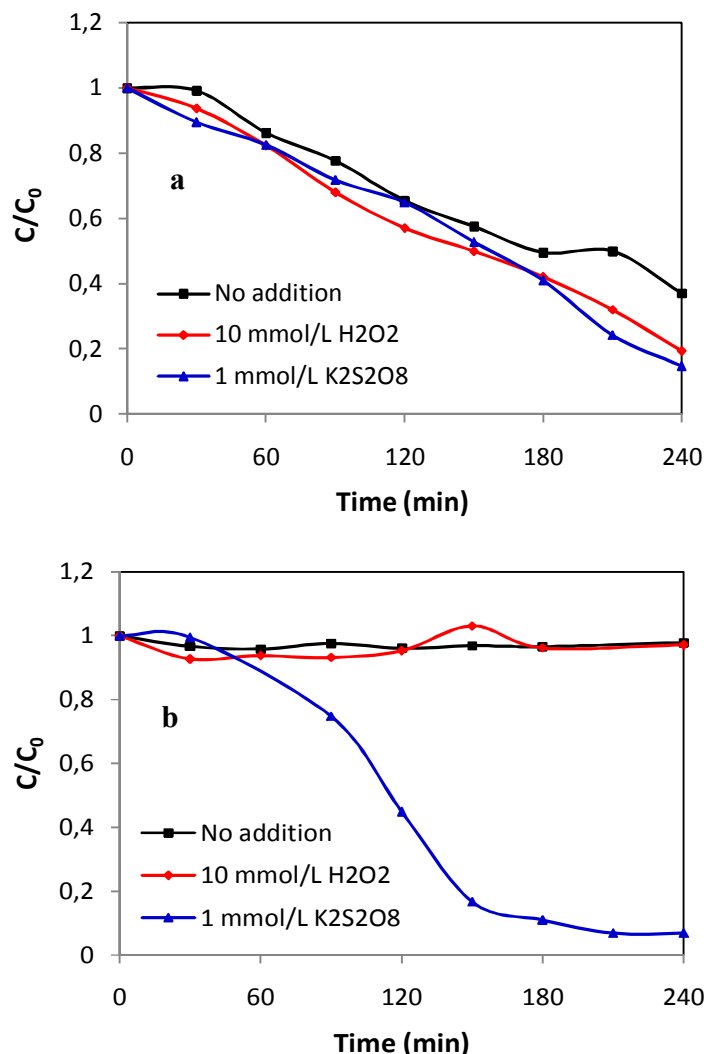


Fig. 6. Effect of oxidants on acetaminophen removal with (a) TiO₂/cellulose and ZnO/polystyrene under UV light (initial concentration: 10 mg l⁻¹; catalyst dosage: 0.25 g l⁻¹; T = 20 ± 1 °C; natural pH).

increase the effect of UV/catalyst in the degradation of an organic molecule by capturing the electrons ejected from the catalyst. It has been reported that H₂O₂ can act as a hole and [•]OH scavenger at high concentrations and that S₂O₈²⁻ ion scavenges electrons [6]. Although many studies have demonstrated the beneficial effect of H₂O₂ at 10 mM [31], this oxidant has shown low effect on the degradation of acetaminophen in the presence of ZnO/polystyrene. Considering the effect of K₂S₂O₈ on the degradation process, Fig. 6 shows that the abatement of

acetaminophen from the contaminated solution was drastically increased in the presence of 1 mM of S₂O₈²⁻. Over TiO₂/cellulose and ZnO/polystyrene catalytic systems, 85.4 and 93.1% of acetaminophen were respectively removed from contaminated solutions containing 10 mg l⁻¹ of paracetamol. The presence of [•]OH radicals as confirmed by several studies is the most necessary element towards the degradation of organic molecules. The photocatalytic degradation of acetaminophen was facilitated through adding S₂O₈²⁻ which reacts with e⁻_{CB} leading to the formation

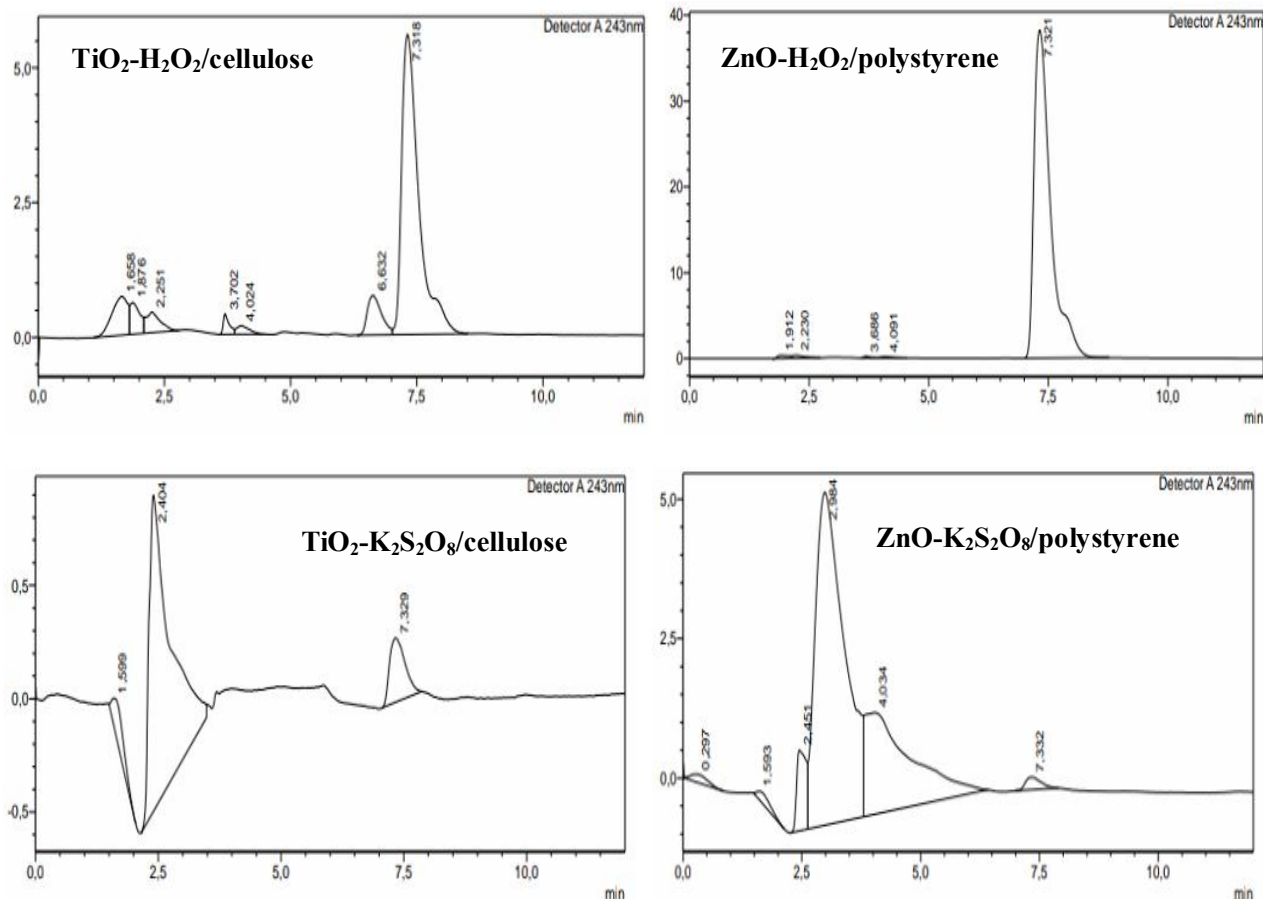
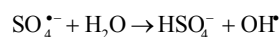
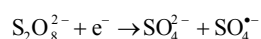


Fig. 7. Chromatograms of acetaminophen degradation and its oxidation products in the presence of different catalytic systems (initial concentration: 10 mg l⁻¹; catalyst dosage: 0.25 g l⁻¹; T = 20 ± 1 °C; natural pH).

of sulfate radical anions (SO₄^{•-}) and generation of extra [•]OH according to the following equations [34]:



The [•]OH radicals are formed at the surface of the catalyst when illuminated with UV light of $\lambda \leq 367.9$ nm (larger than ZnO band gap energy) resulting in the creation of electron-hole pairs [35,36]. The addition of peroxydisulfate ion, releasing the extremely active and short-live radical SO₄^{•-} (30-40 μs), was thus responsible for suppression of the

recombination of charge carriers enhancing the molecule photodegradation. Several researchers investigated the degradation process of acetaminophen under UV/catalyst and found that S₂O₈²⁻ oxidant enhances the pollutant photodisparition from water as compared to other oxidants [37,38].

Because [•]OH reacts non-selectively, the formation of by-products may be unavoidable in the photocatalytic degradation. The by-products detected during the degradation of acetaminophen in the presence of the two supported catalysts were identified by HPLC. As can be seen in Fig. 7, about three known by-products were formed when acetaminophen was treated by TiO₂/cellulose and ZnO/polystyrene systems; the following intermediates were

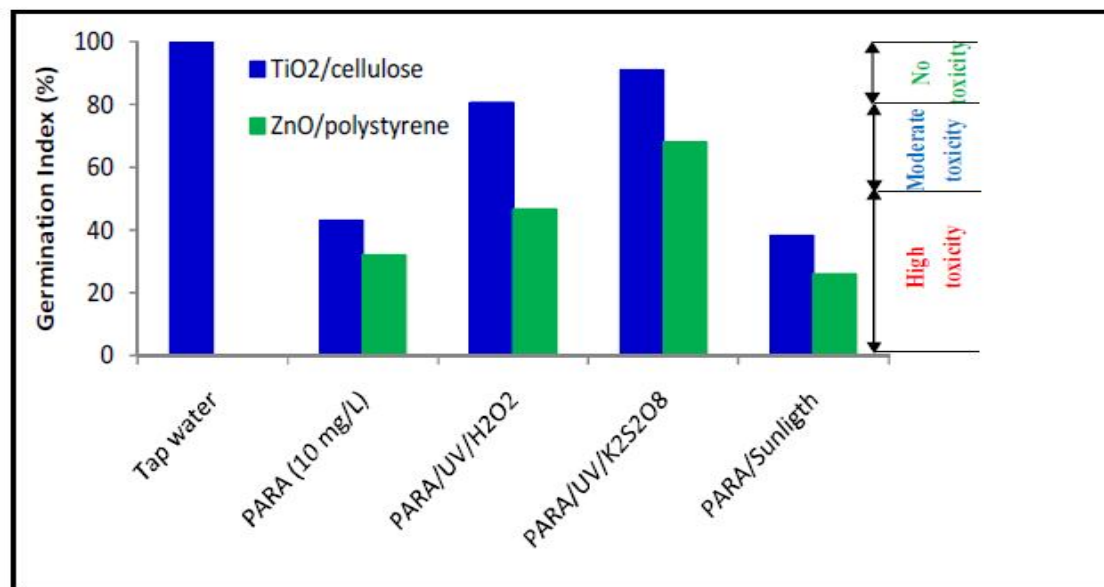


Fig. 8. Germination index (GI) of acetaminophen solutions before and after photocatalysis treatment with different catalytic compounds.

identified: oxalic acid (2.25 min), formic acid (2.2 min), ammonium (6.6 min) and some unknown by-products (1.9, 3.7, 4.1 min); ammonium was produced following the mineralization of the nitrogen present in paracetamol molecule. These intermediates indicate that degradation of acetaminophen involves a cleavage of the benzene ring followed by subsequent reactions to form water and carbon dioxide [39]. On the same figure, we noticed that in the presence of $S_2O_8^{2-}$, the peaks of the different by-products are much less intense.

Phytotoxicity Analysis of By-products

From a toxicological point of view, it is important to establish whether the photocatalyzed samples are able to be discharged into the environment, since it is established that during and/or after photocatalytic decomposition of pollutants, generation of more toxic by-products can occur [40]. Thus, toxicity of the untreated and photocatalytic treated samples using Cresson seeds was evaluated. The highest GI was observed in the case of control (tap water). The tests demonstrated lower percentage of germination in the seeds (GI = 43%) for the untreated sample compared to

the seeds sprayed with water containing by-products. It also shows that only photocatalytic treatments with TiO₂/cellulose in the presence of H₂O₂ (GI = 80.1%) and K₂S₂O₈ (GI = 91.1%) lead to non-toxic degradation by-products (Fig. 8). In parallel, treatment with ZnO-K₂S₂O₈/polystyrene, although it was more than 93% effective, led to a moderate toxicity with a GI value of 68.1%; this is probably due to the photodissolution of Zn during the treatment leading to an increase of toxicity [41]. All these observations suggest that pollutant metabolites produced after photocatalytic treatments in the presence of TiO₂-K₂S₂O₈/cellulose and TiO₂-H₂O₂/cellulose are not toxic for the seeds; these treatments were responsible for the reduction of the phytotoxicity of drug solutions. Similar results were found by Zeghioud *et al.* [42] in the case of dye pollutant treatment with TiO₂-UV-C/polyester photocatalysis. The effluents having undergone these treatments could then be discharged into the environment without concerning about their harmful impacts on animal and plant biodiversity. The photocatalytic treatments under solar irradiation were considered insufficient at this stage.

CONCLUSIONS

The efficiency of supported TiO₂/cellulose and ZnO/polystyrene in the degradation of acetaminophen was evaluated. Unlike ZnO/polystyrene, TiO₂/cellulose exhibited a potential to degrade the pharmaceutical pollutants under ambient temperature and natural pH, and its photocatalytic efficiency was correlated with initial concentration. The UV photocatalysis revealed to be better than visible and solar photocatalyses during the comparative analysis. The addition of oxidants (H₂O₂ and K₂S₂O₈) increased the degradation capacity of the organic pollutants; particularly, the peroxydisulfate ion greatly increased the degradation capacity of acetaminophen in the presence of supported catalysts that guarantees rapid electron transport and homogenous exposure to light. Phytotoxicity tests revealed that photocatalyzed samples were non-toxic for the Cresson seeds, indicating the reuse potential of the treated water in crop irrigation, for example. In a future study, to support such work, it is recommended to examine other phenomena often neglected by the authors such as photodissolution and photocorrosion of the catalysts in order to effectively apply the present process on a large scale.

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Conflict of Interests

The authors declare no conflict of interest.

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