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# Hydrothermal synthesis of 3D cauliflower anatase TiO<sub>2</sub> and bio sourced activated carbon: adsorption and photocatalytic activity in real water matrices

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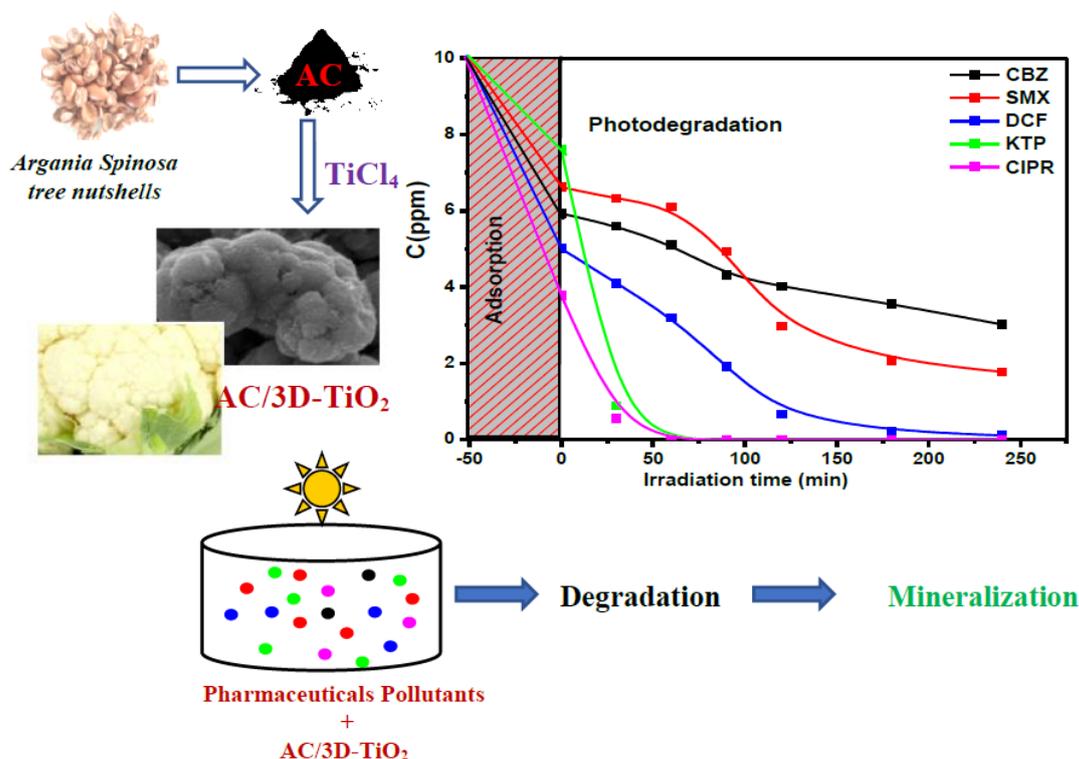
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## Graphical abstract



## Abstract

The development of advanced photocatalyst for the complete and sustainable removal of emerging organic pollutants such as pharmaceuticals in wastewater is still challenging. Thus, a new three-dimensional cauliflower of  $\text{TiO}_2$  immobilized on a bio sourced activated carbon (AC/3D- $\text{TiO}_2$ ) was successfully synthesized by a hydrothermal method. Its morphological and physicochemical properties were well-characterized with a pure 3D- $\text{TiO}_2$  anatase phase, a high surface area ( $763 \text{ m}^2 \cdot \text{g}^{-1}$ ) and a cauliflower-shaped morphology composed of  $\text{TiO}_2$  tubes in a radial direction at a micrometric scale. 3D- $\text{TiO}_2$ -AC photocatalytic activity on carbamazepine (CBZ), in water showed that around 90% of CBZ elimination is obtained after 4h of exposure, that is 1.5 times more efficient than commercial  $\text{TiO}_2$  P25. This was confirmed on five pharmaceuticals (CBZ, ketoprofen, sulfamethoxazole, ciprofloxacin and diclofenac) by

measuring their adsorption, elimination, and mineralization in wastewater highlighting the promising application of AC/3D-TiO<sub>2</sub> in the treatment of wastewaters.

**Keywords:** Hydrothermal, composite material, titanium dioxide anatase, photocatalysis, adsorption, pharmaceuticals.

## 1. Introduction

Titanium dioxide is considered as the most photoactive photocatalyst that gives the best results in the photodegradation of pollutants in both liquid and gas phases. This is due to its wide band gap (3.2 eV), strong oxidizing power, low cost, non-toxic and high resistance to photo-induced corrosion [1,2]. Thus, it has been widely used in photocatalysis, self-cleaning glass, photovoltaics, sensors, solar energy, paint, textiles, cosmetic, etc.[3].

To date, various strategies have been conducted, such as the control of the crystalline structure, dimensions, and morphology with the purpose of having a very distinguished photocatalytic application and improvement of TiO<sub>2</sub> activity [4–9]. Naturally, TiO<sub>2</sub> exists in three different crystalline phases: anatase, rutile, and brookite. Among these phases, anatase and rutile are the most current ones and it is well known that the anatase phase has the greatest photocatalytic activity compared with others [10,11]. Many studies have proved out that TiO<sub>2</sub> crystals with different phase percentages present a distinguished photocatalytic activity [12,13]. Recently, many researchers focused their efforts to discover a new method that controls the anatase TiO<sub>2</sub> synthesis. Several types of morphology have been prepared, such as nanoflowers, nanorods, nanosheets, nanobelts, nanosphere, nanowires, etc [14–18]. Three-dimensional (3D) nanostructures (e.g., TiO<sub>2</sub> nanosheet spheres or TiO<sub>2</sub> nanorod spheres) have good light absorption capability by permitting more light reflection and multiple scattering inside their structures. They also have the enhanced charge transfer facilitated by 1D or 2D nanostructure, thus retarding the recombination of photogenerated electrons and holes. [17,19,20].

Several methods can be used to prepare TiO<sub>2</sub> anatase such as hydrothermal method [21–23], sol-gel [24–27], electrochemistry [28], chemical vapor deposition [29,30], liquid phase deposition [31] spray deposition [32], and others. The hydrothermal method has been widely used for synthesized the TiO<sub>2</sub> anatase nanostructure because it is simple, inexpensive[33,34]. It is easy to control the shape and size of synthesized nanoparticles with high chemical purity[35–37]. The hydrothermal process provides many possibilities to tune the morphological, optical, and structural properties of TiO<sub>2</sub>[38].

This work aims to develop 3D-TiO<sub>2</sub> anatase supported on activated carbon with easy hydrothermal method using TiCl<sub>4</sub> as a titanium precursor. Different techniques fully characterized the AC/3D-TiO<sub>2</sub> anatase to assess its morphology, elemental composition, crystal structure, and specific surface area. Its photocatalytic properties were assessed using carbamazepine as a model molecule and compared to a commercial TiO<sub>2</sub> Degussa P25 photocatalyst as a control. An application is carried out on a matrix of five medications (CBZ, SMX, DCF, KTP, and CIPR) in the wastewater of Aix-en-Provence, France, to demonstrate the feasibility of employing AC/3D-TiO<sub>2</sub> to treat a mixture of persistent pharmaceuticals.

## **2. Material and Methods**

### **2.1 Chemicals**

Carbamazepine, ciprofloxacin, sulfamethoxazole, diclofenac and ketoprofen were purchased from Sigma-Aldrich. Hydrochloric acid (37%) and titanium tetrachloride (TiCl<sub>4</sub>) (99.99%) were provided from Sigma-Aldrich and isopropanol and acetonitrile (HPLC grade) were provided by Fischer Scientific SAS.

### **2.2 Synthesis AC/3D-TiO<sub>2</sub>**

The preparation of activated carbon was adopted from previous work described by El Mouchtari et al [39]. The AC/3D-TiO<sub>2</sub> composite was prepared by the hydrothermal method. A known amount of TiCl<sub>4</sub> (200 μL) was added to 20 mL of a concentrated hydrochloric acid solution (18.5%). After magnetic stirring for 30 min, 1 g of activated carbon was added to the solution and allowed to stir for 30 min. The mixture was transferred to a stainless-steel autoclave, equipped with sealed Teflon<sup>®</sup> tubes, at 180°C for 16 h under autogenous pressure. After cooling to room temperature (depending on the inertia of the autoclave), the solid was recovered, cleaned several times with distilled water, and dried at 100°C for 24 h. Finally, the material was calcined at 500°C in a muffle furnace for two hours under atmospheric conditions without fresh air regeneration, then washed and dried at 100°C overnight. The 3D-TiO<sub>2</sub> was prepared by the same synthesis method without adding the activated carbon.

### **2.3 Characterization of AC and AC/3D-TiO<sub>2</sub>**

The surface morphology of the produced pastes was observed by Scanning Electron Microscopy (SEM) using a FEI Quanta 450 FEG operating at an accelerating voltage

of 200 kV. Thermogravimetric analysis (TGA) was performed in air atmosphere using TGA Q500 (TA 1000) equipment. The specimens (approximately 20 mg) were weight in the platinum crucible. The samples were heated at a rate of  $5^{\circ}\text{C}\cdot\text{min}^{-1}$  from ambient temperature to  $1000^{\circ}\text{C}$ . X-ray diffraction patterns were taken at ambient temperature using a Bruker D8 advance diffractometer operating at 20 kV and 10 mA with Cu  $K\alpha$  radiation ( $\lambda = 1.540593$  nm) with a scan speed of  $2^{\circ}\text{min}^{-1}$ . Radials cans were recorded in the reflection scanning mode with  $2\theta$  being changed from  $5$  to  $80^{\circ}$  with a scan step  $0.02^{\circ}$ . The data were collected between  $5$  and  $80^{\circ}$  in  $2\theta$  with a step size of  $0.02^{\circ}$  at a scanning rate of  $5^{\circ}\cdot\text{min}^{-1}$ . The phase composition of the synthesized products was determined using DIFFRAC.EVA software and PDF-4+2019 database. The measurements of the specific surfaces of the prepared pastes were carried out on an apparatus "A micromeritics 3Flex" by nitrogen adsorption at its liquid temperature ( $77$  K) with previous dry of the samples, and degasification at  $100^{\circ}\text{C}$  for 12 hours. This allows the measurement of the specific surface in the range of  $0.01$  to  $>2000$   $\text{m}^2/\text{g}$  and the porosity in the range of  $2$  to  $200$  nm.

#### **2.4 Photocatalysis and adsorption experiments**

Irradiation was performed with the same system used by EL Mouchtari et al [40–42]. The adsorption capacity of the composite material for CBZ was evaluated in a dark environment at  $25^{\circ}\text{C}$  with a CBZ concentration of  $50$  mg/L and  $0.1\text{g L}^{-1}$  of AC/3D-TiO<sub>2</sub> anatase cauliflower. Magnetic stirring was used to achieve the adsorption-desorption equilibrium during the experiment (2 h). The residual concentration of CBZ was determined by LC to analyse.

#### **2.5 Application in wastewater**

Wastewater was collected from wastewater treatment plant of Aix-en-Provence (Pioline, France), which serves 175 000 inhabitants and operates through primary and biological treatment. The collected wastewater corresponds to the final effluent after the biological treatment. The wastewater was filtered through  $0.45$   $\mu\text{m}$  membrane filter using Whatman glass microfiber filter, Binder-free GF/C  $1.2$   $\mu\text{m}$  and immediately stored in the dark at  $-20^{\circ}\text{C}$ . Before starting the treatment, we determined the organic and inorganic matter in the wastewater using total organic carbon (TOC) analysis. We found that the water contains  $21.79$  and  $34.66$   $\text{mg}\cdot\text{L}^{-1}$  of organic and inorganic matter, respectively.

50 mg.L<sup>-1</sup> solutions of each standard have been prepared by dissolving 12.5 mg of each substance in 250 mL of wastewater. The solutions are stored between 0 and 4°C. A solution of the mixture is prepared by diluting the 50 mL mother solutions of ciprofloxacin, carbamazepine, diclofenac sulfamethoxazole and ketoprofen to a mixing concentration of 10 mg.L<sup>-1</sup>.

## **2.6 HPLC analysis of pharmaceuticals products (PPs)**

The degradation and adsorption monitoring of pharmaceuticals was performed by high-performance liquid chromatography (UPLC Perkin Elmer Altus 30). Chromatographic separation is performed using a Zorbax Eclipse Plus C18 column (3.5 μm; 2.5 × 150 mm) for pharmaceuticals (CBZ, DCF, SMX, CIP, and KTP) distributed by Agilent. The mobile phase flow rate was set at 0.4 mL/min and the oven temperature at 30°C. The gradient is used to elute all pharmaceutical compounds. A 5 μL volume of sample is injected into the system using a mobile phase composed of two mixtures acidified with 0.1% (v/v) formic acid (FA): an acetonitrile/water mixture (95/5 v/v) (solvent A) and an acetonitrile/water mixture (5/95 v/v) (solvent B) with the following gradient: Isocratic step at 95% B for 4 min, gradient from 95% to 50% B for 2.5 min, isocratic step at 50% B for 1.5 min, gradient from 50% to 100% B for 1.5 min, isocratic step at 100% B for 1 min.

## **3. Results and discussion**

### **3.1 Characterization of AC and AC/3D-TiO<sub>2</sub> composites**

#### **2.1.1 3D-morphology**

SEM images of 3D-TiO<sub>2</sub> (Figure 1) show that this titanium dioxide is composed of deformed balls with quasi-spherical arrangements, designated as a three-dimensional cauliflower-like structure (images a1 and a2). This structure is constituted by an agglomeration of nanometric particles (image a3), as shown in Figure 1.

Furthermore, the images obtained with high resolution show an inside view of the cauliflower structure (image b6), which reveals a three-dimensional growth of TiO<sub>2</sub> in a radial direction at the micrometer scale. When combined with activated carbon, the 3D cauliflower-like morphology was preserved perfectly with an average diameter of 4 micrometers (image b3). On the other hand, the 3D-TiO<sub>2</sub> surface, with a rocky texture

and sharp contours, has undergone a slight alteration forming particles with rounded surface contours (image b6).

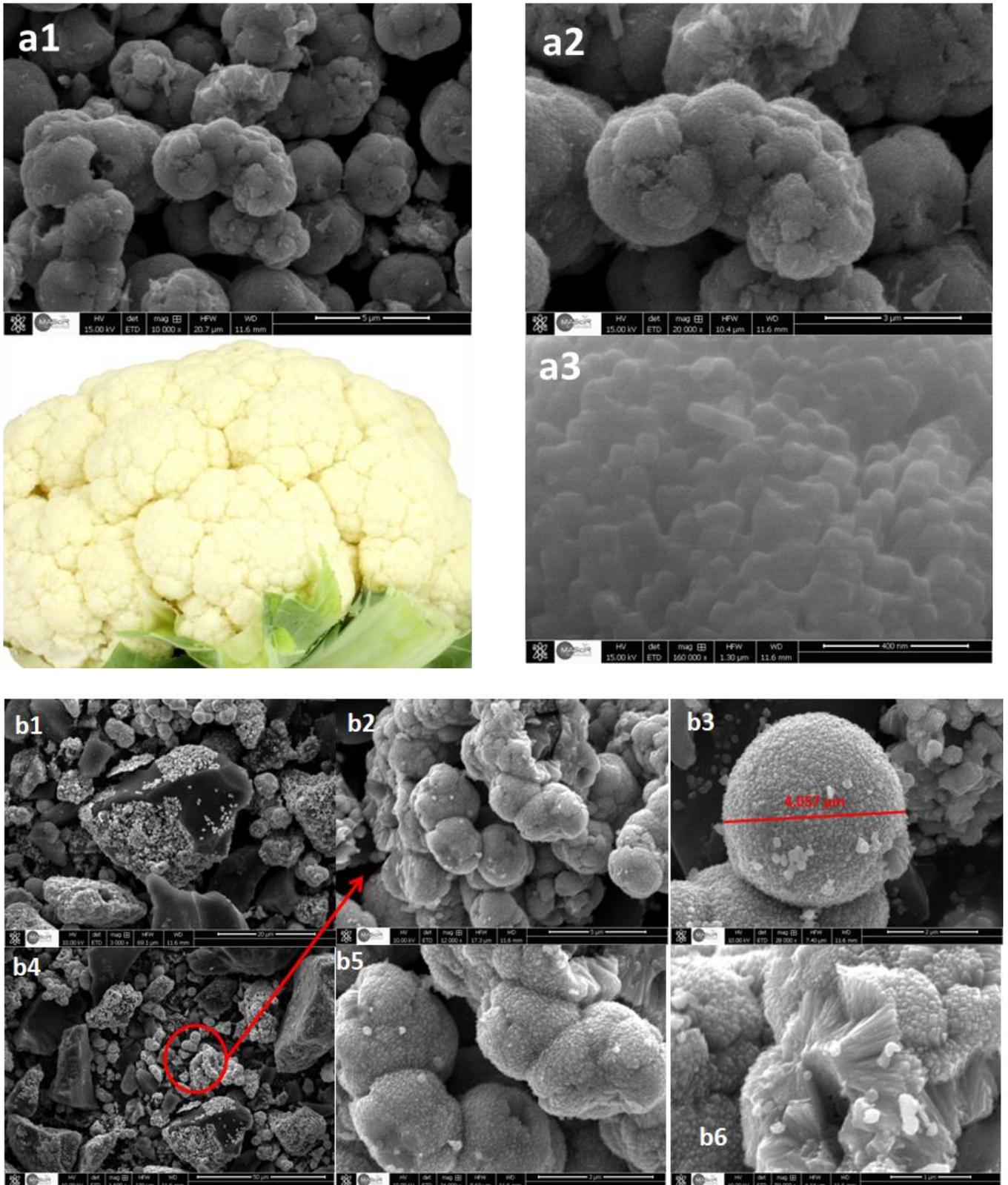
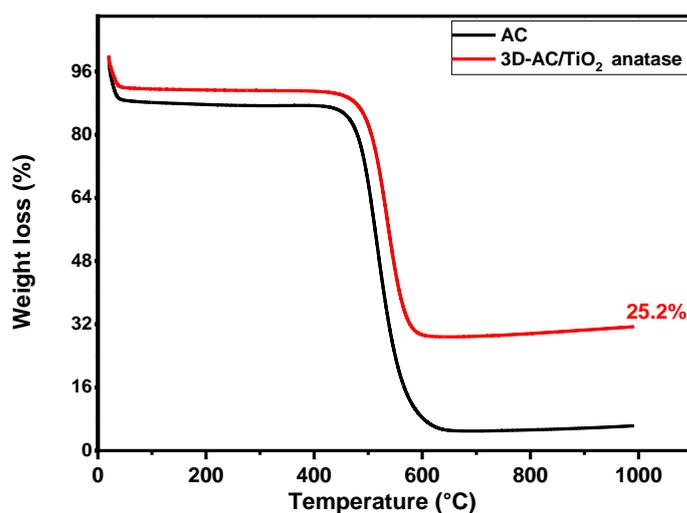


Figure 1. SEM image of 3D-TiO<sub>2</sub> (a) and AC/3D-TiO<sub>2</sub> (b).

### 3.1.2 Chemical composition

The percentage of 3D-TiO<sub>2</sub> in the prepared composite material has been calculated by thermogravimetric analysis. The thermogram (Figure 2) reveals the presence of two losses of mass. The first one appears between 20 and 100°C with a mass loss of 8.44%, which is due to the loss of water molecules adsorbed on the solid surface. The second stage, between 100 and 1000°C, with a mass loss of 60.16%, corresponds mainly to the combustion of the organic matter of AC as confirmed by AC thermogram. The incomplete thermal decomposition of AC/3D-TiO<sub>2</sub> can only be explained by the residual mineral part of the composite known for its thermal resistance. Based on these results, the 3D-TiO<sub>2</sub> content is equal to 25.22%, which corresponds to the expected percentage.

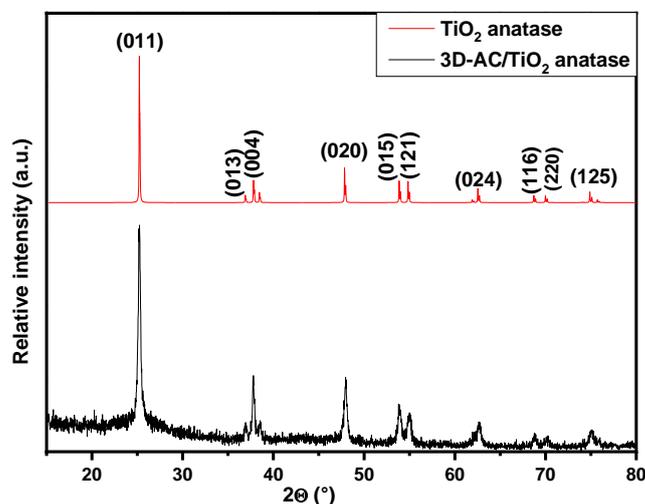


**Figure 2.** TGA profile of AC and AC/3D-TiO<sub>2</sub>.

### 3.1.3 Crystallography

The X-ray diffractograms of 3D-TiO<sub>2</sub> and AC/3D-TiO<sub>2</sub> are shown in Figure 3. Indeed, the characteristic anatase lines are found at 37.86°, 48.17°, 53.83°, 55.03°, 62.64°, 68.91°, 70.25°, and 75.32° on the diffractograms of titanium dioxide and the composite material. This demonstrates the significant formation of the anatase crystal phase of titanium dioxide in both materials. We found a percentage of the AC/3D-TiO<sub>2</sub> phase composition equal to 100% of the anatase phase with a crystallite size of 50 nm from

the Scherrer relation. These results validate the synthesis route that yields the most photoactive phase [43]. It should be noted that Diffraction peak shapes of TiO<sub>2</sub> in the composite material are wider than those of TiO<sub>2</sub> alone. This gives a very fine particle size, which gives it an important photocatalytic efficiency.



**Figure 3.** XRD patterns of 3D-TiO<sub>2</sub> and AC/3D-TiO<sub>2</sub> anatase.

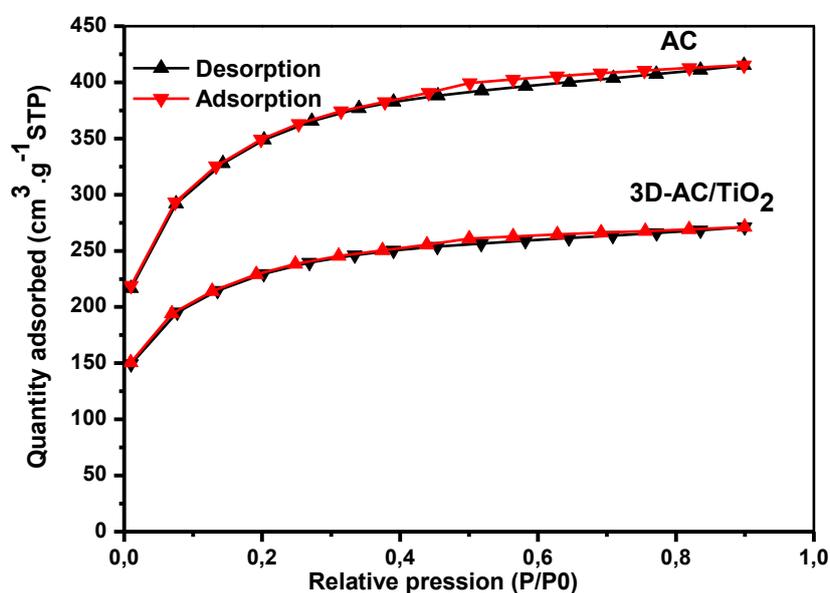
### 3.1.4 Surface area and pore size

From the Figure 4 shows the N<sub>2</sub> adsorption-desorption analyses of activated carbon and composite material AC/3D-TiO<sub>2</sub>, AC and composite were determined and are gathered in Table 1.

The AC and 3D-AC/TiO<sub>2</sub> showed that the isotherms correspond to the type I according to IUPAC classification [44], which indicated the presence of microporous on the materials. Concerning surface area values, activated carbon sample displayed a high surface area (1070 m<sup>2</sup>.g<sup>-1</sup>) and the mixture with the 3D-TiO<sub>2</sub> decreased the surface area of the composite material (very significantly): pore volume decreased and on the other hand, the diameter of the pores remains constant because the larger size of the 3D-TiO<sub>2</sub> particles (4 μm). This indicates that the immobilization of 3D-TiO<sub>2</sub> on the AC surface has been successfully obtained by hydrothermal method.

**Table 1.** Textural properties of AC and AC/3D-TiO<sub>2</sub>.

Sample	Phase content (%)		Crystalline size (D) (nm)	S <sub>BET</sub> (m <sup>2</sup> .g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> .g <sup>-1</sup> )	Pore diameter (nm)
	Anatase	Rutile				
AC	-	-	-	1170	0.59	2.21
AC/3D-TiO <sub>2</sub>	100	0	50	763	0.42	2.21

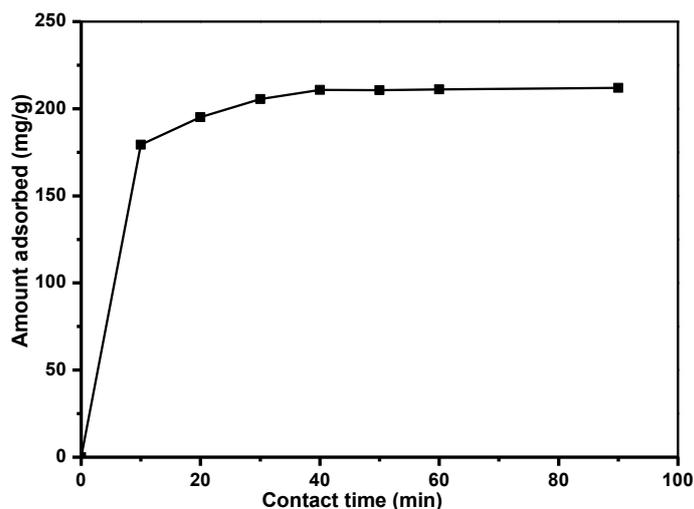


**Figure 4.** N<sub>2</sub> adsorption/desorption isotherms of AC and AC/3D-TiO<sub>2</sub>.

### 3.2 Adsorption kinetic of carbamazepine on AC/3D-TiO<sub>2</sub>

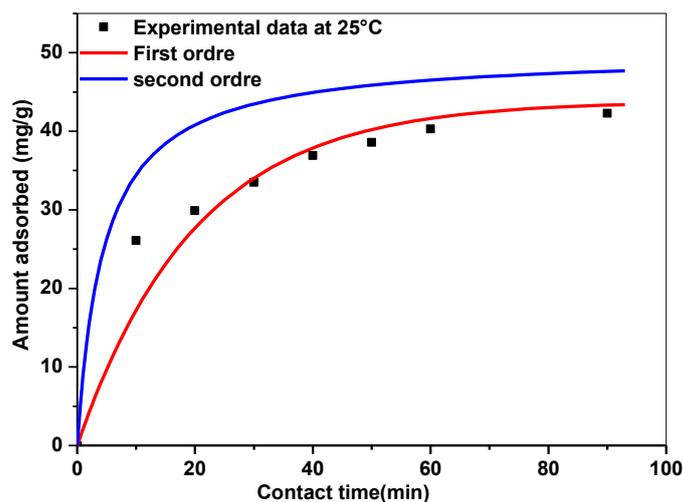
The contact time between the pollutant and the substrate is an important parameter in adsorption treatment. The experiments are carried out at fixed pH (6.5) on 5 mg of AC/3D-TiO<sub>2</sub> and a carbamazepine concentration of 30 mg.L<sup>-1</sup>.

A kinetic study was conducted to determine the contact time required to reach the adsorption equilibrium between the pharmaceutical pollutant molecule and the 3D-AC/3D-TiO<sub>2</sub> material. Figure 5 shows that the adsorption equilibrium is reached after 40 min of contact with a calculated maximum adsorption quantity of about 212 mg.g<sup>-1</sup>.



**Figure 5.** Quantity adsorbed of CBZ on AC/3D-TiO<sub>2</sub> anatase : [CBZ] =30 mg.L<sup>-1</sup>, [AC/3D-TiO<sub>2</sub>] = 0.1 g.L<sup>-1</sup>.

The kinetics presented in Figure 5 shows two distinct stages. Efficient adsorption on CBZ takes place in the first minutes of the experiment and an equilibrium sorption state is reached after 40 min of stirring. This rapid adsorption rate is in good agreement with the high specific surface area attributed to its total pore volume (Table 1). Experimental data of carbamazepine adsorption on AC/3D-TiO<sub>2</sub> were adjusted with pseudo first order and pseudo second order using Origin Pro8 as shown in Figure 6.



**Figure 6.** Non-linear pseudo second order and pseudo-first order models for CBZ adsorption on AC/3D-TiO<sub>2</sub> anatase: [CBZ]=5-30mg.L<sup>-1</sup>

Adsorption isotherms describe the interactions between pollutants and adsorbents and are very interesting for an optimization of the adsorption mechanism. The equilibrium relations between adsorbent and adsorbate are described by the adsorption isotherms.

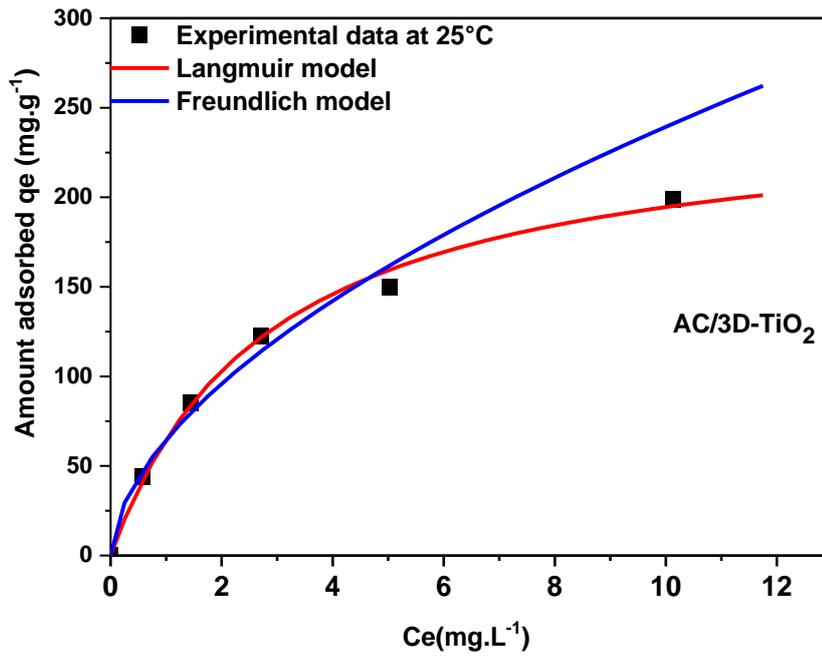
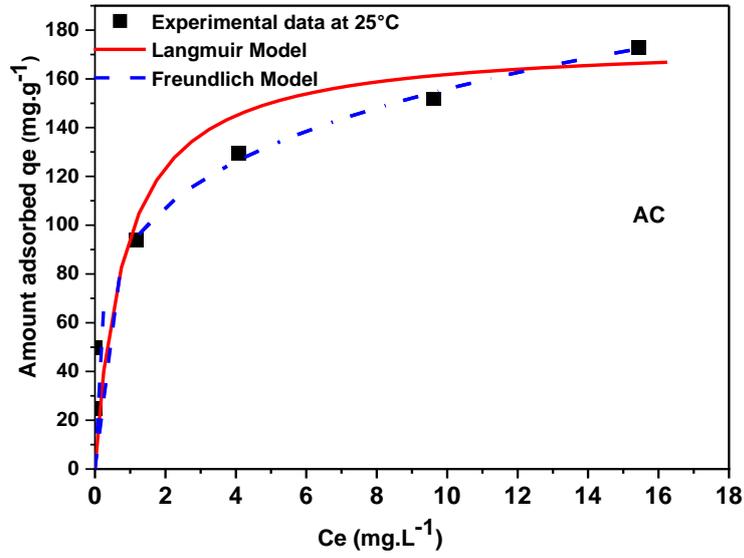
Two widely used mathematical methods of adsorption models, the Langmuir and Freundlich model, have been studied to better understand the mechanism of adsorption of CBZ on the surface of AC and AC/3D-TiO<sub>2</sub>. All parameter values and correlation coefficients for both isotherms are presented in table 2.

In order to select the model that best fits the experimental data, we took into account the coefficient of determination ( $R^2$ ). The table show that the Freundlich model describes satisfactorily the adsorption of CBZ on activated carbon with a coefficient of determination equal to 0.988 and a heterogeneity factor  $n > 1$  which reveals a high adsorption affinity of carbamazepine on activated carbon. This result is in agreement with those obtained by Zirui Yu et al. on the adsorption of two pharmaceuticals (naproxen and carbamazepine) on coconut-based activated carbon [45], which showed that carbamazepine is the most adsorbed compound and that the isotherm is of Freundlich type.

Based on the correlation coefficients (between 0.99 and 0.97) and the values of  $Q_e$  (the calculated by the Langmuir model which are in good agreement with  $Q_e(\text{exp})$  (figure 7). The Langmuir model is best suited in our case to describe the monolayer adsorption process of CBZ on our composite compared to Freundlich, indicating the homogeneous nature of AC/3D-TiO<sub>2</sub> sites and pharmaceutical molecules. This model is considered the most appropriate to describe the monolayer adsorption of all PPs on an AC/3D-TiO<sub>2</sub> composite[39,46].

**Table 2.** Parameter values of CBZ adsorption on AC and AC/3D-TiO<sub>2</sub> using Langmuir and Freundlich model, [CBZ] = 5 to 50 mg.L<sup>-1</sup>, [composite] = 0.1 g.L<sup>-1</sup>, T = 25°C.

Material	Langmuir model			Freundlich model		
	$Q_{\max}$ (mg.g <sup>-1</sup> )	$R^2$	$K_L$ (L.mg <sup>-1</sup> )	$K_f$ (mg.g <sup>-1</sup> ) (mg.L <sup>-1</sup> ) <sup>-n</sup>	$R^2$	1/n
AC	370	0.988	0.64	181.2	0.995	4.32
AC/3D-TiO <sub>2</sub>	250	0.993	0.25	64.7	0.97	0.56



**Figure 7.** Non-linear Langmuir and Freundlich isotherms obtained for CBZ adsorption on AC and AC/3D-TiO<sub>2</sub> anatase: [CBZ]= 5-30 $\text{mg.L}^{-1}$

### 3.3 Photocatalytic studies

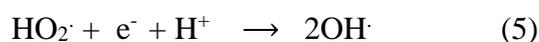
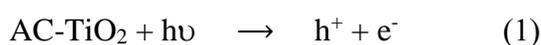
The degradation of the pharmaceutical product by the AC/3D-TiO<sub>2</sub> composite is shown in Figure 8 (blue curve). The photodegradation of the PP was performed after stirring for 50 min in the dark, to reach the adsorption/desorption equilibrium. The percentage of removal in the adsorption process by our composite was about 65%, which proves that the adsorption capacity of AC/3D-TiO<sub>2</sub> is higher than that of naked TiO<sub>2</sub> [47,48].

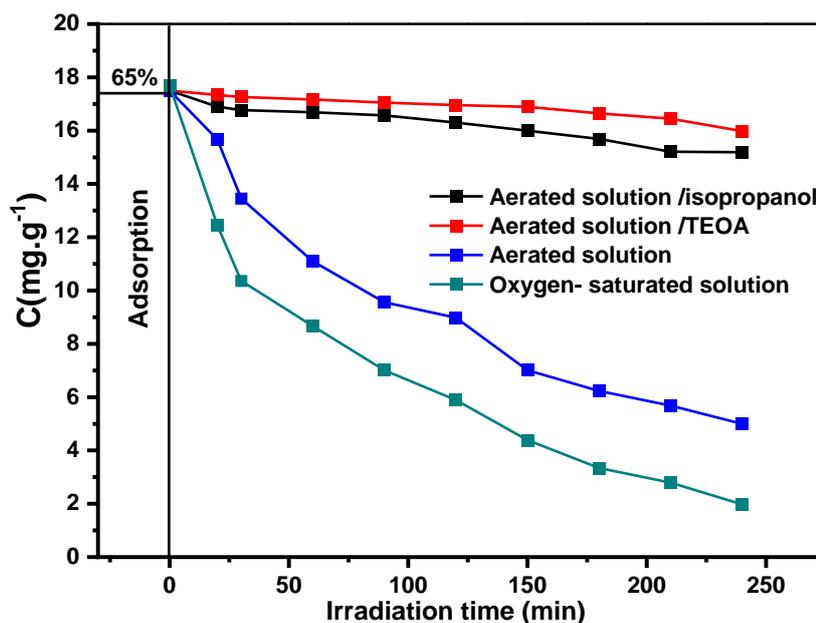
After the adsorption step, exposure to light in the presence of AC/3D-TiO<sub>2</sub> leads to 70% degradation of carbamazepine in the aqueous solution. These results show that the presence of 3D-TiO<sub>2</sub> deposited on the porous surface of the activated carbon unambiguously enhances the removal of CBZ from the aqueous phase by the chemical photo-induced route. This high reactivity is attributable to the favored transfer of PPs from activated carbon to 3D-TiO<sub>2</sub> particles through the surface diffusion phenomenon that results from the difference in concentration of PPs on AC compared to 3D-TiO<sub>2</sub> [49]. In addition, the possible electron charge density transfer from 3D-TiO<sub>2</sub> to activated carbon at the AC/3D-TiO<sub>2</sub> interface limits the recombination of the electron-hole pair, which increases the production rate of hydroxyl radicals by the photocatalyst [50].

In the presence of the AC/3D-TiO<sub>2</sub> composite, the combined processes of adsorption and photodegradation lead to the efficient removal of CBZ. Other studies have focused on the degradation of pharmaceuticals by AC/TiO<sub>2</sub> composites [51–54]. For example, Gar Alam et al. showed that in the presence of 0.4 g.L<sup>-1</sup> AC/TiO<sub>2</sub> and under solar irradiation, complete removal of amoxicillin and ampicillin, at an initial concentration of 50 mg.L<sup>-1</sup>, was observed after 180 min of exposure while 85% of diclofenac was transformed under these same conditions [47]. Another similar study on the removal of ibuprofen in the presence of the same composite material (AC/3D-TiO<sub>2</sub>) showed that the transformation of 93% of ibuprofen by the adsorption/photocatalysis process with 1.6 g.L<sup>-1</sup> catalyst under irradiation at 254 nm and after 4 h of irradiation [55]. Although these studies emphasized the effectiveness of the AC/3D-TiO<sub>2</sub> irradiation system, our work shows that the AC/3D-TiO<sub>2</sub> composite provides removal that is more effective with a low catalyst loading (0.1 g.L<sup>-1</sup>), a high drug concentration (50 mg.L<sup>-1</sup>) and a reasonable exposure time of about 4 h.

To identify the reactive species photogenerated and responsible for the degradation of CBZ in AC/3D-TiO<sub>2</sub>, two scavengers have been used. Isopropanol (IPA) quenched hydroxyl radicals (OH<sup>•</sup>) and triethanolamine (TEOA) quenched positive holes (h<sup>+</sup>) [56–58]. To show these radicals' involvement, a mixture of CBZ and AC/3D-TiO<sub>2</sub> (50 mg.L<sup>-1</sup> and 0.1 g.L<sup>-1</sup>) with 2% v/v IPA or TEOA were irradiated under the same conditions. The effect of oxygen on the degradation of CBZ, was studied by oxygen bubbling before and during the irradiation experiment. The resulting degradation kinetics are shown on figure 8.

The addition of IPA as well as TEOA inhibits the degradation of carbamazepine as no decrease of the concentration was measured during the experiment. The above results suggest that OH radicals were the principal reactive active species in the photocatalytic reaction process, and are generated by the positive holes according to the reaction (1) and (2) [59,60]. On the contrary, there is a total disappearance of the CBZ with oxygen bubbling after 4 hours of irradiation. This implies that O<sub>2</sub> plays an essential role in the degradation of carbamazepine. It enables the generation of superoxide radical O<sub>2</sub><sup>•-</sup> by reaction 3, which can subsequently produce hydroxyl radicals that are responsible for the degradation of CBZ (reactions 4 and 5). It also participates in slowing down the electron-hole recombination phenomenon, which increases photocatalytic activity [61–63].

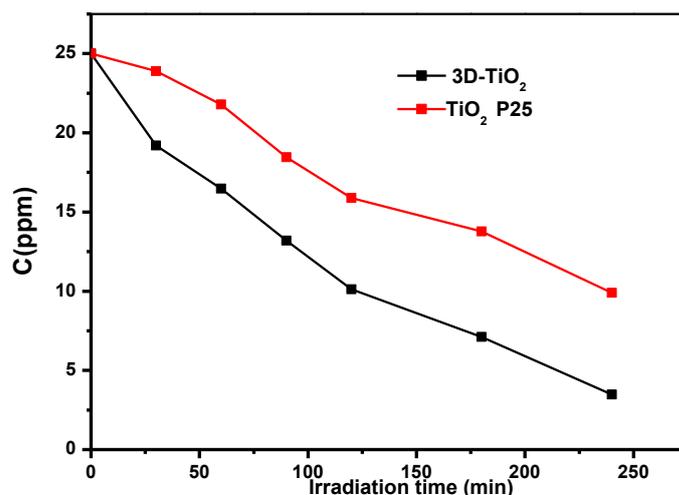




**Figure 8.** CBZ degradation kinetic in aerated (blue) and oxygen saturated (green) conditions in the presence of isopropanol (black) and TEOA (red),  $[CBZ]= 50 \text{ mg.L}^{-1}$ ,  $[AC/3D-TiO_2] = 0.1 \text{ g. L}^{-1}$ , Xe lamp 300W.

The performance of our material synthesized by the hydrothermal method 3D-TiO<sub>2</sub> was compared to the commercial photocatalyst TiO<sub>2</sub> P25. According to the results shown in Figure 9, the degradation of CBZ (25 mg.L<sup>-1</sup>) by UV-vis light is higher for 3D-TiO<sub>2</sub> than for the commercial photocatalyst TiO<sub>2</sub> P25. The percentage of degradation is about to 86%, while in the case of TiO<sub>2</sub>-P25 this percentage is decreased (60%).

Carabin et al. evaluated the removal of carbamazepine in an aqueous solution by a photocatalytic process at 365 nm by TiO<sub>2</sub>-P25. The degradation results showed that the percentage of degradation with 1 g.L<sup>-1</sup> of TiO<sub>2</sub>-P25 after 30 min of irradiation and in an acidic medium (pH = 5) is in the same order than our work, as they reach a degradation percentage of 65% [9]. Other work has studied the degradation of CBZ by graphene oxide/TiO<sub>2</sub> (RGOT) under UV light. In a 10 mg.L<sup>-1</sup> aqueous solution of CBZ, RGOT displayed high adsorption and nearly two-fold higher photodegradation capacity than bare TiO<sub>2</sub>, with more than 99 percent CBZ elimination seen within 90 minutes [64]. This study shows the photocatalysis using 3D-TiO<sub>2</sub> is most efficient compared to TiO<sub>2</sub>-P25.

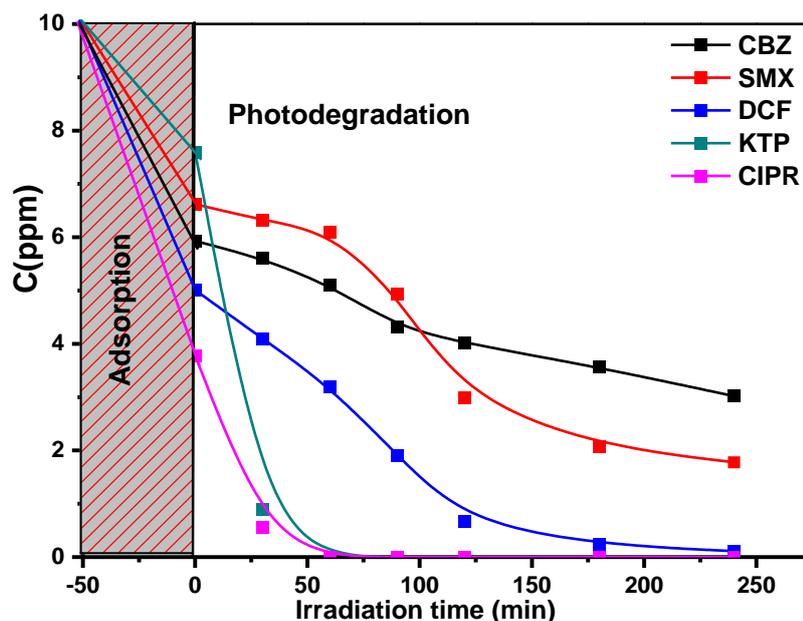


**Figure 9.** The Comparison between 3D-TiO<sub>2</sub> and TiO<sub>2</sub> P25: [CBZ]=25 mg.L<sup>-1</sup>, [TiO<sub>2</sub>-P25] = 0.4 g. L<sup>-1</sup>, [3D-TiO<sub>2</sub>]=0.1g.L<sup>-1</sup>, Xe lamp 300W.

### 3.4 Application in wastewater

An application was realized in the aqueous solution containing a mixture of five pharmaceutical products prepared in a wastewater treatment plant's effluent. First, the direct photolysis of the five pharmaceutical products in wastewater treatment plant water was monitored. The results are illustrated in figure S1. Based on the pollutants' degradation kinetics, under direct excitation, only CBZ was found to be photochemically stable under our experimental conditions. However, approximately 78% DCF, 20% SMX, 90% CIPR, and 99% KTP were degraded in the medium after 4 hours of irradiation.

The photodegradation of PPs was carried out after stirring for 2 hours in the dark to allow the adsorption/desorption equilibrium to be reached. The results illustrated in figure 10, it can be observed the elimination of 40% of CBZ, 50% of DCF, 34% of CIPR and 24% of KTP, and in wastewater effluent, by adsorption process in the presence of AC/3D-TiO<sub>2</sub>.

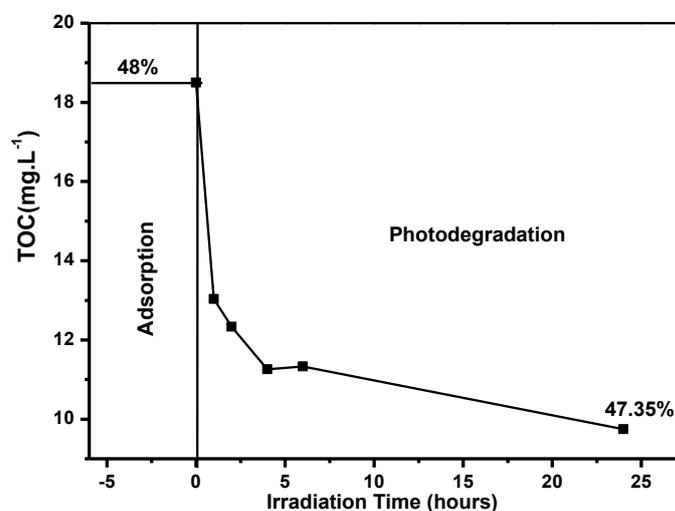


**Figure 10.** Adsorption and photocatalytic degradation of CBZ, DCF, SMX, KTP and CIPR with AC/3D-TiO<sub>2</sub> from aqueous wastewater of the five products: [AC/3D-TiO<sub>2</sub>] = 0.1 g.L<sup>-1</sup>, [PPs] = 10 mg.L<sup>-1</sup>, Xe lamp 300W.

Under irradiation, the adsorption-photodegradation process implies in the removal of PPs mixture from the solution leads to the total disappearance of KTP and CIPR after 60 minutes and 98% of DCF, 73% of SMX, and 50% of CBZ have been eliminated in the solution of wastewater effluent after 4 hours of exposure. These results suggests that the induced degradation process in the presence of AC/TiO<sub>2</sub> 3D is involved in CBZ elimination while for the other PPs (DCF, SMX, KTP and CIPR), the contribution of the direct photodegradation pathway should also be considered.

The kinetics of the total mineralization of the five pharmaceuticals was followed in the aqueous phase using the total organic carbon (TOC) analysis (Figure 11). In the presence of AC/3D-TiO<sub>2</sub> and before irradiation, the preliminary step of adsorption leads to the removal of 48% of five pharmaceuticals from the solution. That is to say, 25.9 mg.L<sup>-1</sup> has transferred to the surface of AC/3D-TiO<sub>2</sub> and the same amount remained in the solution, this concentration was taken as reference. As presented in figure 11, the mineralization of PPs is observed after 4 hours under irradiation at the surface of

AC/3D-TiO<sub>2</sub> but also in the solution even if PPs are not totally degraded (47% degradation).



**Figure 11.** The evolution of TOC as a function of irradiation time in aqueous, [PPs] = 50 mg.L<sup>-1</sup>, [AC/3D-TiO<sub>2</sub>] = 0.1g.L<sup>-1</sup>, Xe 300 W, aerated conditions

#### 4. Conclusion

In summary, a 3D cauliflower-like TiO<sub>2</sub> has been successfully immobilized on a bio sourced activated carbon using hydrothermal method leading to a bio composite with very interesting properties: new 3D morphology, large surface area and exclusive photoactive anatase structure. In addition, AC/3D-TiO<sub>2</sub> material proved its ability to efficiently adsorb pharmaceuticals, induce their degradation and mineralization by photocatalysis in pure water and wastewater. This result shows that this material represents a promising and economically sustainable solution for water depollution.

#### Compliance with ethical standards

##### Competing Interest

There are no conflicts of interest to declare.

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