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Chapter 6

Carbon-/Zeolite-Supported TiO_2 for Sorption/Photocatalysis Applications in Water Treatment

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Additional information is available at the end of the chapter

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Abstract

The role of various carbon forms, i.e., activated carbon and carbon nanotubes/nanofibers as support for TiO_2 in drinking water treatment, is discussed. Also, TiO_2 supported onto zeolite that acts bifunctionally as a sorbent/photocatalyst for drinking water treatment is presented. The main contaminants of natural organic matter (NOM), arsenic species, and nitrogen compounds from drinking water sources by the type of groundwater and surface water can be removed/degraded by sorption/photocatalysis using TiO_2 supported onto carbon and/or zeolite. TiO_2 supported on powdered activated carbon (PAC-TiO_2), granular activated carbon (GAC-TiO_2), and zeolite (Z-TiO_2), namely, *supported* TiO_2, was synthesized through the sol-gel method, and TiO_2 and multiwall carbon nanotubes/carbon nanofibers dispersed within epoxy matrix (CNT-TiO_2-Epoxy, CNF-TiO_2-Epoxy), namely, TiO_2 *composite*, were obtained through the two-roll mill method. Kinetic study results through specific mathematic models allowed to elucidate some mechanistic aspects for sorption and photocatalysis for the application in drinking water. The intercalation of the carbon- and zeolite-supported TiO_2 layers into a filtering system allows to develop a self-cleaning filtering system in drinking water.

Keywords: carbon-supported TiO_2, zeolite-supported TiO_2, sorption, photocatalysis, drinking water treatment

1. Introduction

Water pollution is a concern for the European population, and the quality objectives for the water protection are set through the EU Water Framework Directive. Also, one of the targets of the Clean Water and Sanitation Goal within the Millennium Sustainable Development

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Goals of the 2030 Agenda is to achieve universal and equitable access to safe and affordable drinking water for all by 2030 [1].

The challenges in treating drinking water are dependent on the water sources, mainly consisted of surface and groundwater. Problematic substances in the drinking water sources can include organic matter and/or different inorganic contaminants, e.g., nitrite, nitrate, and ammonium.

One of the common and advanced unitary processes used in drinking water technology is sorption designed as activated carbon- or zeolite-based filtering. Due to more hydrophobic nature of the activated carbon, it has been recognized for elimination of a broad range of hazardous materials belong to the organic class from aqueous solutions. Activated carbon is less efficiently applied for removal of simple inorganic metallic ions or small-size anions [2].

Zeolite is also a known filtering material that exhibits a high sorption capacity [3] characterized by a selectivity degree in relation with the type of zeolite based on its specific properties of molecular sieve and ionic exchanger [4–6]. The main disadvantage is represented by the fouling of the filtering material surface.

Photocatalysis process is considered very promising for advanced water treatment based on the oxidation and reduction reaction for in situ generation of highly reactive transitory species (i.e., H_2O_2, OH, O_2, O_3) for mineralization of organic compounds and disinfection by-products [7–8], through the electron-hole pair formation under UV or solar irradiation.

Among various semiconductors that have been investigated in photocatalysis application, titanium dioxide (TiO_2) has attracted much attention due to its physical and chemical stability, negligible toxicity, the resistance to corrosion, redox selectivity, high photostability, and easy preparation [3, 9–10]. By UV irradiation onto TiO_2 surface, under conditions of photon energy (hv) greater than or equal to the bandgap energy of TiO_2, the electron will be photoexcited from the valence band to the empty conduction band leading to an empty unfilled valence band that corresponded to the hole and thus creating the electron-hole pair. The electron-hole pair is involved within various oxidative/reductive reactions including the degradation of organics.

For the drinking water treatment, the main disadvantage of TiO_2-based photocatalysis is given by the necessity of the further separation phase to remove TiO_2 from water, in order to avoid the loss of catalyst particles and introduction of the new pollutant of contamination of TiO_2 in the treated water [11]. A solution to avoid the introduction of a new separation phase includes catalyst fixation onto various supports, e.g., activated carbon [12] and mesoporous clays [13]. The catalyst immobilization on different supports allows getting catalyst composites, which are considered a new generation of catalyst with different properties in relation with those of solely TiO_2. According to the obtaining methods, there are a large variety of composites [14], from which in this chapter will be discussed:

- Composites with TiO_2 coated (supported) on the support of activated carbon by the type of powder and granular and zeolite [15–21]
- Hybrid composites, which comprise a matrix material of polymer (epoxy) in which TiO_2 and the support of carbon nanotubes or nanofibers are dispersed [22–24]

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Taking into account that the catalyst represents the key of the performance of the photocatalytic application, the catalyst-based composite should exhibit various effects related to the components and the obtaining methods [14], such as simple supporting effect, stabilizing the microstructure or active components, formation of new compounds which act as active components or stabilizers, having two or more functions, controlling of redox performances, and influencing the kinetics of adsorption/desorption and diffusion of molecules.

In this chapter, two types of composites obtained by two different methods and applied in the drinking water treatment are presented:

- TiO_2 supported on powdered activated carbon (PAC-TiO_2), granular activated carbon (GAC-TiO_2), and zeolite (Z-TiO_2), namely, *supported TiO_2*.
- TiO_2 and multiwall carbon nanotubes and carbon nanofibers dispersed within epoxy matrix (CNT-TiO_2-Epoxy, CNF-TiO_2-Epoxy), namely, *TiO_2 composite*. The carbon and zeolite components were selected taking into account their utility as sorbent for natural organic matter [20–24].

2. TiO_2-based composites obtaining and morphostructural properties

The granular, powdered activated carbon and natural zeolite were functionalized with TiO_2 using titanium tetraisopropoxide (TTIP) as TiO_2 precursors by sol-gel method (**Figure 1**).

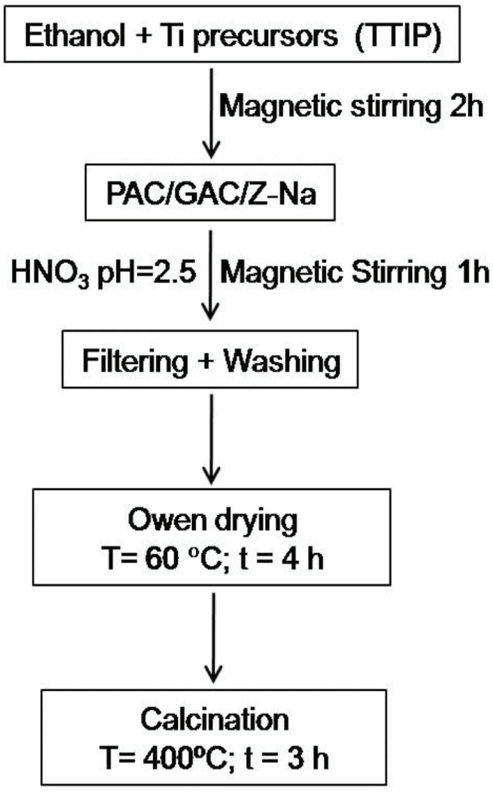


Figure 1. Schematic diagram of obtaining PAC-TiO_2, GAC-TiO_2, and Z-TiO_2.

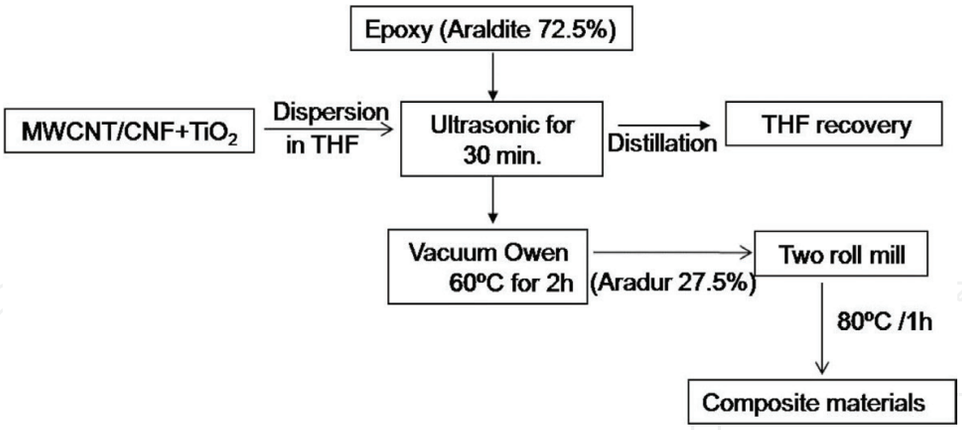


Figure 2. Schematic diagram of obtaining CNT-TiO_2-Epoxy and CNF-TiO_2-Epoxy.

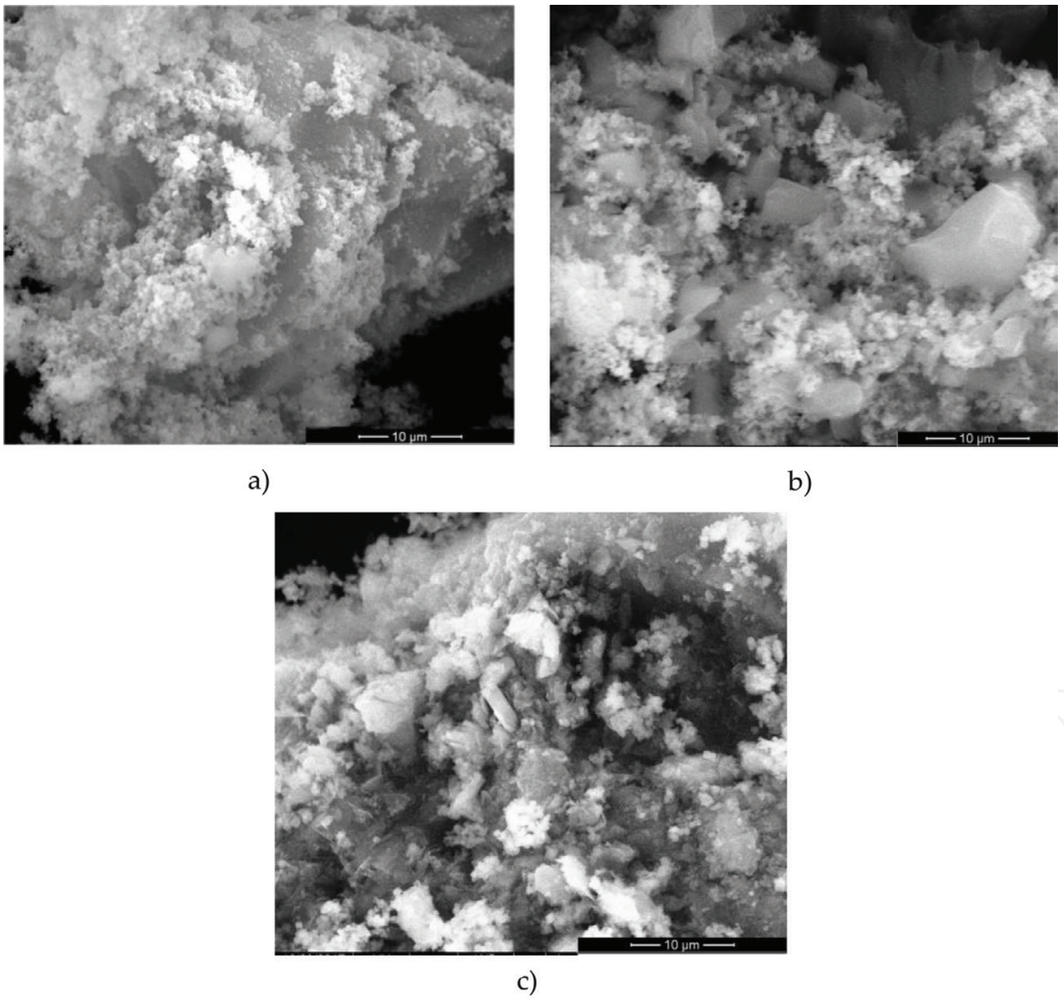


Figure 3. SEM images for (a) PAC-TiO_2, (b) GAC-TiO_2, and (c) Z-TiO_2.

For the synthesis process of the composite materials consisting of carbon nanotubes or carbon nanofibers mixed with TiO_2 particles within epoxy matrix, the two-roll mill technique was applied (**Figure 2**).

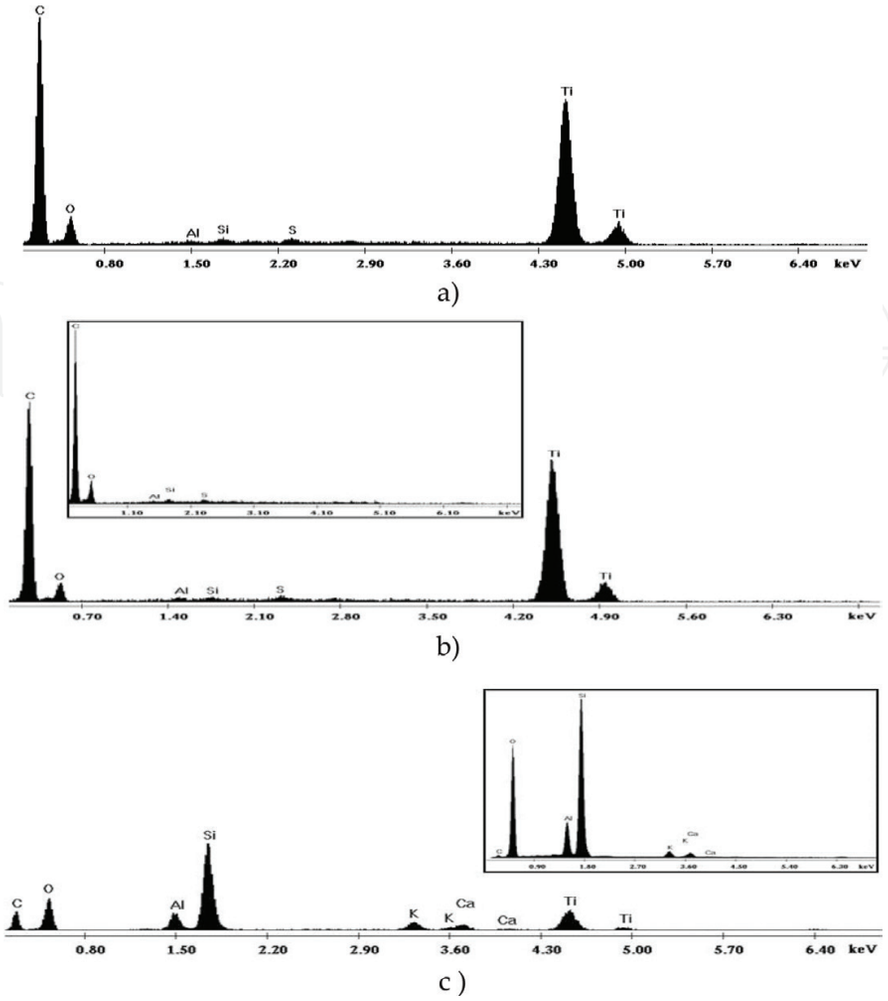


Figure 4. EDX spectra for (a) PAC-TiO_2, (b) GAC-TiO_2, (inset: GAC), and (c) Z-TiO_2 (inset: zeolite).

The morphology of all synthesized materials was observed by a scanning electronic microscope (SEM, Inspect S PANalytical model) coupled with the energy-dispersive X-ray analysis detector (EDX). **Figure 3a–c** presents SEM images for PAC-TiO_2, GAC-TiO_2, and Z-TiO_2, which show the layered structure of activated carbon and a nonuniform distribution and more or less agglomeration of TiO_2 nanoparticles onto the surface. It can be also seen that TiO_2 only adhered to the surface of zeolite without the insight of the inside of the zeolite pores.

The results of semiquantitative elemental analysis of the synthesized material surface were presented by EDX spectra indicating Ti and C presence for PAC-TiO_2 and GAC-TiO_2 and, also, the presence of Ti on the natural zeolite (**Figure 4**). Small amounts of Al, Si, and S were identified within the activated carbon as both powdered and granular as impurities and the presence of K and Ca within the zeolite composition were found.

For composite materials that used epoxy as matrix, it can be noticed that TiO_2 nanoparticles were attached on the nanostructured carbon surface, and, also, a well dispersion of carbon and TiO_2 nanoparticles within epoxy matrix is noticed (**Figure 5a,b**). A slight more uniform distribution of TiO_2 nanoparticles seems to be for CNF in comparison with CNT [22]. The presence of TiO_2 particles in composite materials was confirmed by EDX spectra (**Figure 6**).

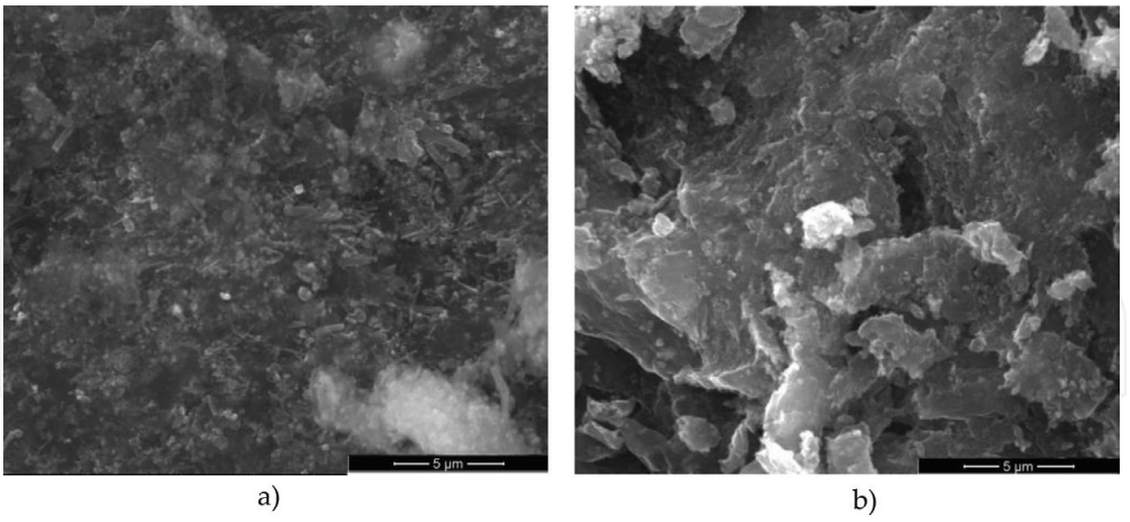


Figure 5. SEM images for (a) CNF-TiO_2-Epoxy and (b) CNT-TiO_2-Epoxy.

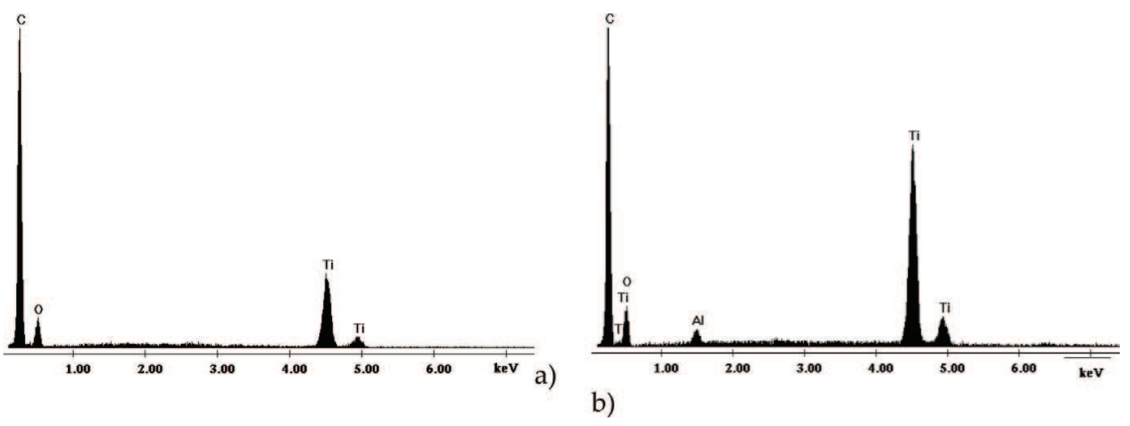


Figure 6. EDX spectra for (a) CNF-TiO_2-epoxy and (b) CNT-TiO_2-epoxy.

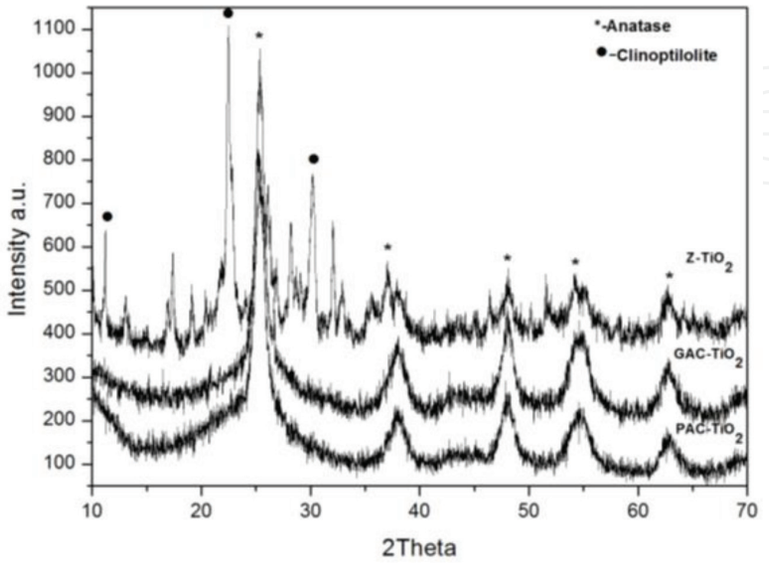


Figure 7. XRD pattern for PAC-TiO_2, GAC-TiO_2, and Z-TiO_2.

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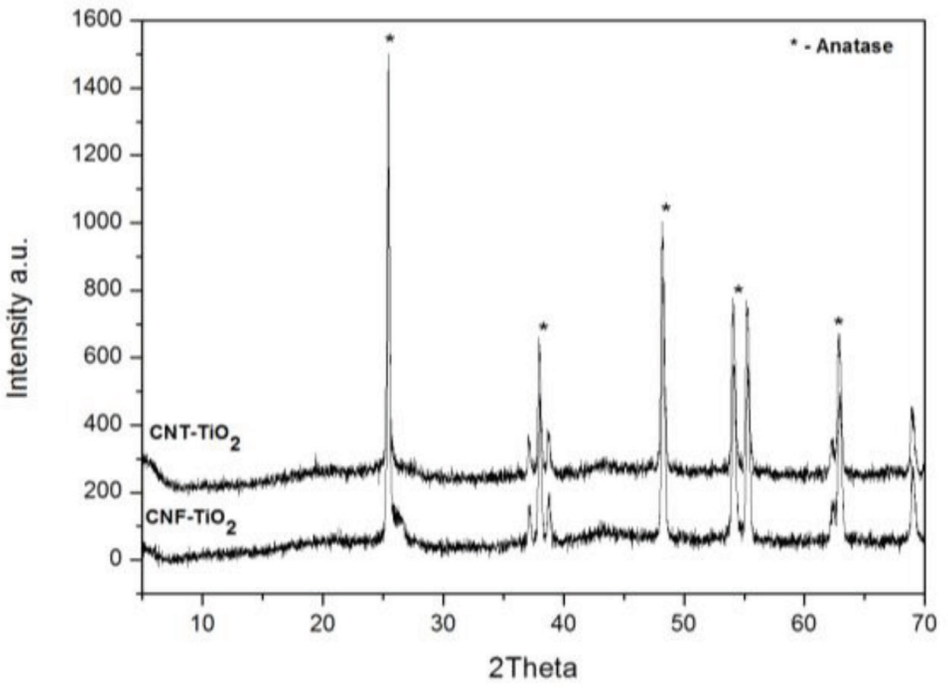


Figure 8. XRD pattern for CNT-TiO_2 and CNF-TiO_2.

X-ray diffraction measurements were carried out to determine the crystal phase composition using a PANalytical X'PertPRO MPD diffractometer. **Figure 7** presents the XRD patterns of GAC-TiO_2, PAC-TiO_2, and Z-TiO_2. The anatase form of TiO_2 is the predominant phase, identified by diffraction lines at 2θ of 25.3, 38.6, 48, 54, and 62.97° [25]. Also, the XRD results revealed that the major component of natural zeolite used in this study is clinoptilolite (2θ ~ 10°; 12°; 22.5°; 30°) [26].

Figure 8 presents the XRD patterns of composite materials based on nanostructured carbon. It is obviously the presence of anatase form of TiO_2 as predominant phase, with the intensity of diffraction lines higher due to the higher TiO_2 loading within the composite composition in comparison with the supported TiO_2.

3. TiO_2-based composite application for sorption and photocatalysis-unitary processes in drinking water treatment

Various types of carbon and zeolite are reported as good sorbents for various types of pollutants from water [2, 15–24]. The easy separation of these materials from water and their good sorption capacity that is important in the first stage of the overall photocatalysis process make them very promising as support for the TiO_2 immobilization.

Humic acids (HAs) represent a main component of natural organic matter that gives the organic loading of drinking water sources, which must be removed or destroyed because of water quality regulations. Also, the presence of HAs before the chlorination step as disinfection could lead to trihalomethane and other toxic by-product generation. The efficiency of *supported TiO_2* materials for the sorption and the photocatalysis of HA from water, expressed as HA removal efficiency, is presented comparatively in **Figure 9**.

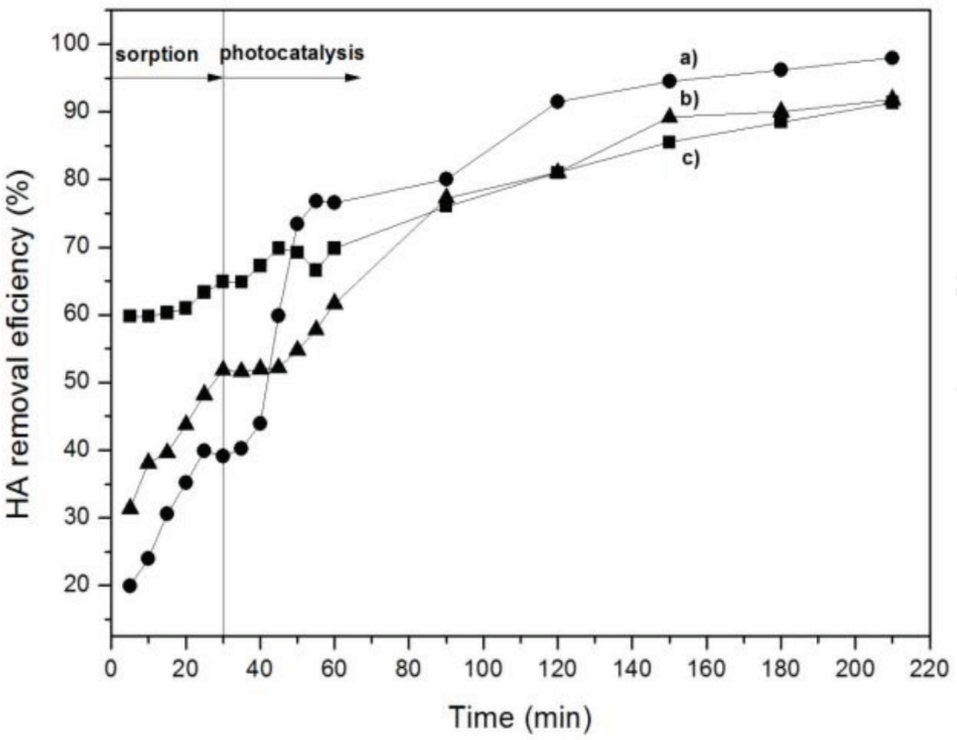


Figure 9. Evolution of HA removal efficiency by sorption and photocatalysis for 50 mg·L^{-1} HA onto (a) GAC-TiO_2, (b) Z-TiO_2, and (c) PAC-TiO_2.

The HA removal efficiency was calculated using the following equation:

$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\ (\%) \quad (1)$$

where C_0 and C_t are the concentrations of HA in aqueous solution in terms of A_{254} at initial time and at any time t, respectively (mg·L^{-1}).

The sorption was assessed as the preliminary and compulsory step of the overall photocatalysis process taking into consideration also the possibility to use the supports as simple sorbents and only for self-cleaning to apply the photocatalysis. The sorption capacity for HA is better for PAC-TiO_2, while the photocatalytic activity is better for GAC-TiO_2. This should explain the morphological structure and the sizes of the particles. The lower particle size leads to the higher sorption capacity, while for the photocatalysis application the size of support decreased the photocatalytic activity may be due to the finer suspension should hinder the UV irradiation penetration to the TiO_2 surface.The sorption and the photocatalysis capacities of *TiO_2 composite materials* assessed in terms of HA removal efficiency showed the superiority of CNT-TiO_2-Epoxy versus CNF-TiO_2-Epoxy. It can be noticed that a slight photocatalytic activity was found for both materials (**Figure 10**).

For HA removal, the sorption capacity of tested materials increased in order:

$$\text{PAC} - TiO_2 > \text{Z} - TiO_2 > \text{GAC} - TiO_2 > \text{CNT} - TiO_2 - \text{Epoxy} > \text{CNF} - TiO_2 - \text{Epoxy}$$

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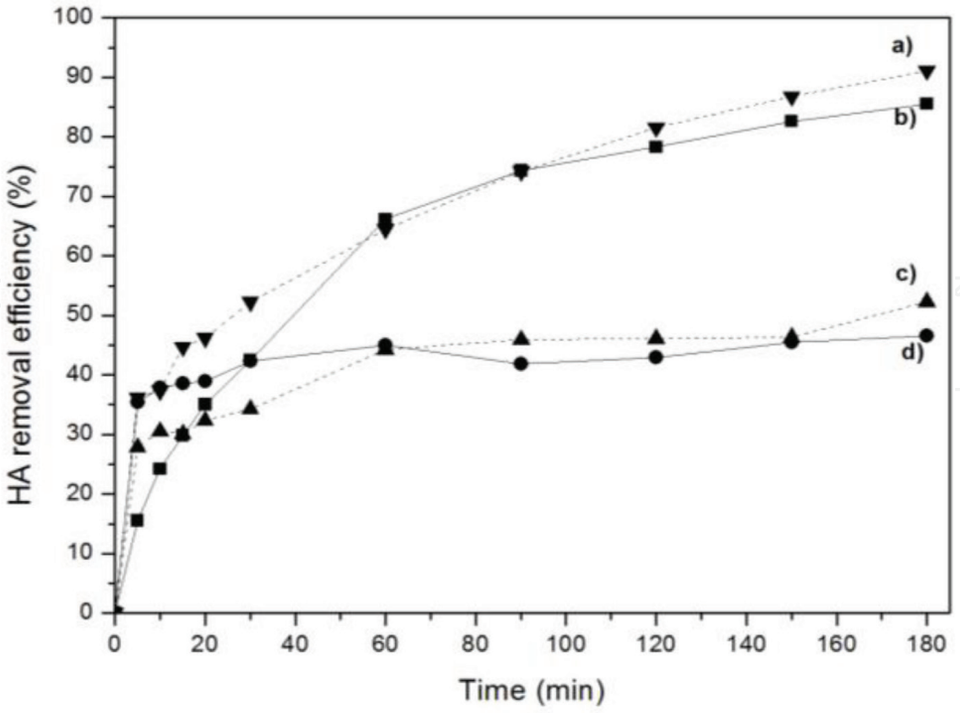


Figure 10. Evolution of removal efficiency of 25 mg·L^{-1} HA using CNT-TiO_2-epoxy by photocatalysis (a), sorption (b), CNF-TiO_2-epoxy by photocatalysis (c), and sorption (d).

The evaluation of photocatalytic activity after the sorption step showed an increasing order:

$$GAC - TiO_2 > Z - TiO_2 > PAC - TiO_2 > CNT - TiO_2 - Epoxy > CNF - TiO_2 - Epoxy$$

These behaviors should be explained by the available sites of the carbon in the sorption process and the available sites of TiO_2 in the photocatalysis process, which are in direct relations with the morphology, size, and the bonding type between TiO_2, carbon, and zeolite support. Also, epoxy resin hindered the available sites, which decreased both sorption capacity and photocatalytic activity of *TiO_2 composite materials*.

In order to determine some mechanism aspects regarding the sorption and photocatalysis processes, several kinetic models must be checked to find the optimum one. Two different kinetic models are used to fit the experimental data, i.e., pseudo-first-order and pseudo-second-order kinetic models [27].

3.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic adsorption was suggested by Lagergren (1898) for the adsorption of solid/liquid systems. It can be expressed in integrated form as shown in Eq. (2):

$$ln(q_e - q_t) = ln(q_e) - k_1 t \quad (2)$$

where, k_1 is the rate constant of adsorption (min^{-1}) and q_t is the adsorption loading of dye (mg·g^{-1}) at time t (min).

3.2. Pseudo-second-order kinetic model

The pseudo-second-order kinetics, proposed by Ho and Mckay [28], is expressed in Eq. (3):

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{3}$$

where, k_2 is the rate constant of the pseudo-second-order adsorption kinetics ($g \cdot mg^{-1} \cdot min^{-1}$) and q_e is the equilibrium adsorption capacity ($mg \cdot g^{-1}$).

Pseudo-first- and pseudo-second-order kinetic models were tested for fitting the sorption and photocatalysis experimental data (**Tables 1** and **2**). The linear plots of *t/qt* vs. *t* show that the experimental data agree with the pseudo-second-order kinetic model for the HA adsorption. The calculated *qe* values agree very well with the experimental data, and the correlation coefficients for the pseudo-second-order kinetic model are higher than 0.90 in almost all cases. These indicate that the adsorption of HA from water onto materials obeys the pseudo-second-order kinetic model that predicts an exponential decay of concentrations as a function of time. The pseudo-first-order kinetic model was not appropriate for fitting the sorption experimental data, while the photocatalysis experimental data were fitted well with both kinetic models with the correlation coefficient

Catalyst	Parameters	Adsorption	Photocatalysis
		HA concentration (50 mg·L^{-1})	
PAC-TiO_2	q_e($mg*g^{-1}$)	38.34	44.25
	k_2($g \cdot mg^{-1} \cdot min^{-1}$)	0.0067	0.0031
	R^2	0.915	0.996
GAC-TiO_2	q_e($mg*g^{-1}$)	25.59	49.78
	k_2($g \cdot mg-1 \cdot min^{-1}$)	0.00381	0.0170
	R^2	0.966	0.998
Z-TiO_2	q_e($mg*g^{-1}$)	28.65	42.32
	k_2($g \cdot mg^{-1} \cdot min^{-1}$)	0.0059	0.0025
	R^2	0.976	0.985
		HA concentration (25 mg·L^{-1})	
CNT-TiO_2-Epoxy	q_e($mg*g^{-1}$)	20.68	19.98
	k_2($g \cdot mg^{-1} \cdot min^{-1}$)	0.0024	0.0015
	R^2	0.986	0.996
CNF-TiO_2-Epoxy	q_e($mg*g^{-1}$)	13.06	12.37
	k_2($g \cdot mg^{-1} \cdot min^{-1}$)	0.0045	0.0001
	R^2	0.996	0.943

Table 1. Pseudo-second-order kinetic parameters for HA sorption and photocatalysis.

Catalyst	Parameters	Value
	HA concentration (50 mg·L^{-1})	
PAC-TiO_2	q_e(mg*g^{-1})	9.95
	k_1(min^{-1})	0.0073
	R^2	0.955
GAC-TiO_2	q_e(mg*g^{-1})	1.64
	k_1(min^{-1})	0.0494
	R^2	0.913
Z-TiO_2	q_e(mg*g^{-1})	2.92
	k_1(min^{-1})	0.0142
	R^2	0.943
	HA concentration (25 mg·L^{-1})	
CNT-TiO_2-Epoxy	q_e(mg*g^{-1})	0.33
	k_1(min^{-1})	0.085
	R^2	0.995
CNF-TiO_2-Epoxy	q_e(mg*g^{-1})	1.66
	k_1(min^{-1})	0.0019
	R^2	0.956

Table 2. Pseudo-first-order kinetic parameters for HA photocatalysis.

higher than 0.90. However, there is a significant difference between calculated and experimental qe using the pseudo-first-order kinetic model that limits its interpretation (**Table 2**), and, thus, it means that the pseudo-second-order kinetic model is most appropriate. Besides the kinetic parameter, the pseudo-second-order kinetic model informed about the significance of the sorption step within the overall photocatalysis process. It is well known that the reaction rate and kinetics are influenced by many experimental parameters, *e.g.*, HA concentration, catalyst dose, and pH [22].

Based on the results presented in **Table 1**, it can be seen that the PAC-TiO_2 exhibited higher sorption capacity and the best kinetics for HA removal and the GAC-TiO_2 exhibited the best photocatalytic kinetics, which are in accordance with the efficiency results. The worse results were achieved for *TiO_2 composite* materials, which can be explained by the presence of epoxy matrix that reduced the active sites for the sorption and the photocatalysis. Also, the main difference was found between CNT-TiO_2-Epoxy and CNF-TiO_2-Epoxy due to the morphology and sizes of the nanostructured carbon component, better for CNT in comparison with CNF. For these types of material, the photocatalytic activity was better also for CNT-TiO_2-Epoxy.

Arsenic is a common contaminant in drinking water supplies especially for groundwater sources. Inorganic arsenic speciation in water consists of arsenite (AsIII) and arsenate (AsV), but As(III) is more problematic because of its high toxicity and the difficulty to be removed from

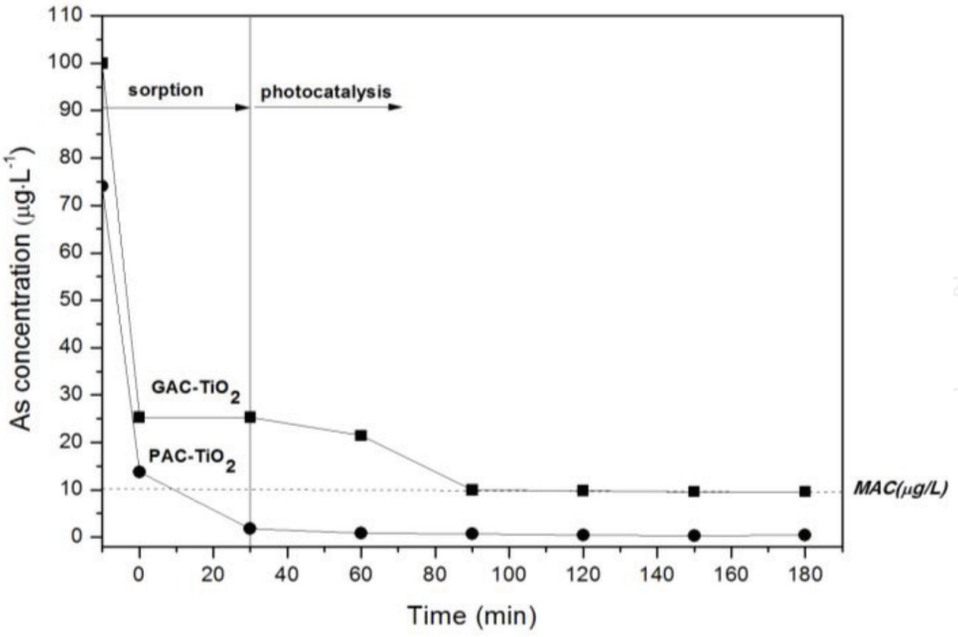


Figure 11. Time evolution of As(III) concentration during sorption and photocatalysis using PAC-TiO_2 and GAC-TiO_2.

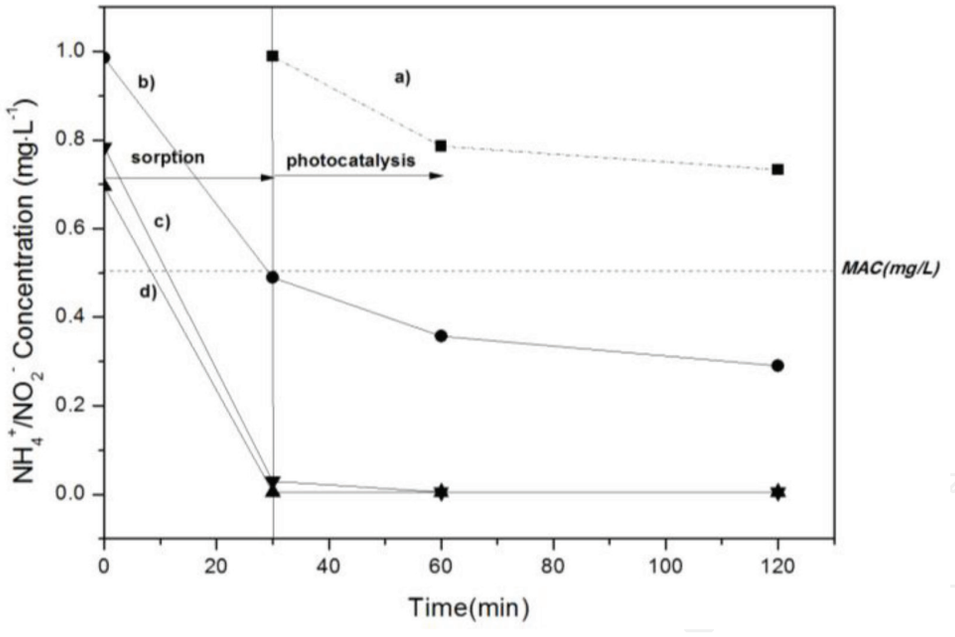


Figure 12. Time evolution of NO_2^- concentration during photolysis (a), photocatalysis using Z-TiO_2 (b), of NH_4^+ concentration during photocatalysis using Z-TiO_2 (c), and natural zeolite (d).

water [29]. The comparative results regarding As(III) removal in the presence of HA showed a good efficiency for both sorption and photocatalysis using *supported TiO_2* material (**Figure 11**).

Another common problem of groundwater source used for drinking water supply is given by the presence of ammonium, nitrite, and nitrate. Nitrate could not be removed from water on these tested materials, while ammonium and nitrate were removed from Z-TiO_2 (**Figure 12**).

The results showed that ammonium is removed by sorption on the zeolite based on ionic exchange, which is proven by comparison with natural zeolite, while the nitrite removal is based on its oxidation process during UV irradiation, which is enhanced by the presence of the Z-TiO_2 photocatalyst.

Since activated carbon is a versatile sorbent class for the retention of a wide spectrum of organic compounds and arsenic(III) and the zeolite exhibited an adsorption/ion-exchange capacity for ammonium, nitrite, and heavy metals, their common presence as mixed materials broadens the spectrum of contaminants that can be removed from the water.

4. Conclusions

In this chapter, two types of composites obtained by two different methods and applied in the drinking water treatment were studied:

a. TiO_2 supported on powdered activated carbon (PAC-TiO_2), granular activated carbon (GAC-TiO_2), and zeolite (Z-TiO_2), namely, *supported TiO_2*, obtained through sol-gel method.

b. TiO_2 and multiwall carbon nanotubes and carbon nanofibers dispersed within epoxy matrix (CNT-TiO_2-Epoxy, CNF-TiO_2-Epoxy), namely, *TiO_2 composite*, obtained through the two-roll mill method.

The sorption and photocatalysis studies showed that for HA removal, the sorption capacity of tested materials increased in order, PAC-TiO_2 > Z-TiO_2 > GAC-TiO_2 > CNT-TiO_2-Epoxy>CNF-TiO_2-Epoxy, and for the photocatalytic activity, GAC-TiO_2 > Z-TiO_2 > PAC-TiO_2 > CNT-TiO_2-Epoxy> CNF-TiO_2-Epoxy.

The removal of pollutants/impurities dissolved in water is based, on the one hand, on the sorption capacity of activated carbon and/or zeolite, which exhibited selectivity for certain impurities dissolved under the lamp-off conditions. On the other hand, but taking into account the sorption phase, by starting the lamp, TiO_2 on the active carbon surface and the zeolite acted by photocatalytic activity generating oxidation and reduction processes that cause the degradation and mineralization of the dissolved organic compounds and the transformation of the inorganic contaminants into the compounds that can be retained on the surface material or compounds that do not affect the quality of the water. Also, the oxidation and reduction processes under irradiation conditions allow the destruction of the contaminants and, implicitly, the cleaning of the sorbent surface. A mixture of zeolite and activated carbon as support for TiO_2 could exhibit bifunctionality, depending on the water features. Thus, for low loading of water with contaminants that can be adsorbed on the filter material, the lamp is not switched on during system operation but only in the washing/regeneration stage, and for a water loaded with contaminants that cannot be adsorbed on the filter material, the system works with the lamp on, ensuring water decontamination and self-cleaning during operation.

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