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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
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., $\text{H}_2\text{O}_2$, OH, $\text{O}_2$, $\text{O}_3$) 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 ($\text{TiO}_2$) 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 $\text{TiO}_2$ surface, under conditions of photon energy ($hv$) greater than or equal to the bandgap energy of $\text{TiO}_2$, 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 $\text{TiO}_2$-based photocatalysis is given by the necessity of the further separation phase to remove $\text{TiO}_2$ from water, in order to avoid the loss of catalyst particles and introduction of the new pollutant of contamination of $\text{TiO}_2$ 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 $\text{TiO}_2$. According to the obtaining methods, there are a large variety of composites [14], from which in this chapter will be discussed:

- Composites with $\text{TiO}_2$ 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 $\text{TiO}_2$ and the support of carbon nanotubes or nanofibers are dispersed [22–24]
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$_2$.](http://dx.doi.org/10.5772/intechopen.80803)
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 2$\theta$ 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 (2$\theta$ ~ 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.
3.2. Pseudo-second-order kinetic model

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

\[ \frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \]  

(3)

where, \( k_2 \) is the rate constant of the pseudo-second-order adsorption kinetics (g·mg\(^{-1}\)·min\(^{-1}\)) and \( q_e \) is the equilibrium adsorption capacity (mg·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 \( \frac{t}{q_t} \) vs. \( t \) show that the experimental data agree with the pseudo-second-order kinetic model for the HA adsorption. The calculated \( q_e \) 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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Parameters</th>
<th>Adsorption</th>
<th>Photocatalysis</th>
</tr>
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<tbody>
<tr>
<td>PAC-TiO(_2)</td>
<td>( q_e ) (mg·g(^{-1}))</td>
<td>38.34</td>
<td>44.25</td>
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<td>( k_2 ) (g·mg(^{-1})·min(^{-1}))</td>
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<td>( R^2 )</td>
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<td>0.996</td>
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<td>GAC-TiO(_2)</td>
<td>( q_e ) (mg·g(^{-1}))</td>
<td>25.59</td>
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<td>( k_2 ) (g·mg(^{-1})·min(^{-1}))</td>
<td>0.00381</td>
<td>0.0170</td>
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<td></td>
<td>( R^2 )</td>
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<td>0.998</td>
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<tr>
<td>Z-TiO(_2)</td>
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<td>( k_2 ) (g·mg(^{-1})·min(^{-1}))</td>
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<td>( R^2 )</td>
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<tr>
<td>CNT-TiO(_2)-Epoxy</td>
<td>( q_e ) (mg·g(^{-1}))</td>
<td>20.68</td>
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<td>0.996</td>
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<td></td>
<td>( R^2 )</td>
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<td>0.943</td>
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Table 1. Pseudo-second-order kinetic parameters for HA sorption and photocatalysis.


