Application of doped-titanate nanotubes in (1) the photodegradation of Tannic Acid, Methyl Orange and Malachite Green and (2) the inhibition of bacteria and fungus.

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Abstract
The purpose of this article is to study the photocatalytic properties of doped titanate nanotubes prepared by hydrothermal treatment using different metals: Ce, Fe, Zn and Zr at 2 wt% content. The textural and morphological properties of the nanopowders were determined by different analysis techniques such as: XRD, RD/UV–Vis, FTIR and TG-DTA. The results of the characterizations showed that nanotubes can be obtained with a hollow structure, and an important thermal stability of whatever element nature. However, the photocatalytic activity ends with the photodegradation under UV-Visible irradiation of the three industrial molecules: Malachite Green, Methyl Orange and Tannic Acid having different molecule charges. It was noted that the degradation rates of the order of 98% were obtained in fairly short times. The final results obtained revealed that the dopant nature and the solution pH play a major role in determining the photocatalytic degradation of pollutants using TiNTs. However the application of TiNTs and doped TiNTs show that these materials have an inhibitory power of fungi and bacteria quite important.

Keywords: Titanate; Nanotube; Heterogeneous catalysis; Environmental chemistry; Photocatalysis.
1. Introduction

In recent years, photocatalytic technology has become one of the most effective methods against environmental pollution[1, 2]. TiO$_2$-based photocatalysts are widely used to combat this pollution because of many of their advantages, such as high photocatalytic activity, high physical and chemical stability, low cost and non-toxicity [3, 4]. However, it has two disadvantages, to name the low separation and migration efficiency of electron-hole (e$^-$/h$^+$) pairs and the narrow range of light absorption only under UV irradiation which will limit its application on a large industrial scale [5]. Currently, controlling the morphology of TiO$_2$-based photocatalysts is usually one of the most important research directions.

Several new types of TiO$_2$-based photocatalysts have emerged in recent years, including nanorods [6], nanotubes [7, 8], nanofibers [9], nanowires [10, 11], etc. Hydrothermal reaction under highly concentrated alkaline conditions has been used as a simple and a practical method for preparing TiNTs [12] which generate a hollow structure with an internal and external diameter vary from 2 and 8 nm [8, 13, 14] and a thickness of multiple walls varying from 2 to 3 nm as well as a good crystal structure [13, 14].

However, TiNTs also have similar disadvantages to ordinary titanium oxide, that is, the low separation efficiency of (e$^-$/h$^+$) pairs [15], as well as a narrow range of light absorption only under UV radiation[16, 17]. It was reported that TiNTs band gap energy ($E_g$)(3.34 eV) is higher than that of ordinary TiO$_2$ anatase (3.20 eV) due to the quantum size effect which is probably due to the decrease in crystallite sizes as well as the transition from a 3D crystal structure to a 1D crystal structure [8, 18]. Doping of TiNTs by metals such as, Au, Ag, V, Ce, Zn, Fe, Zn and Zr will decrease their $E_g$ and improve their absorption in the visible region[8, 19, 20]. Sekino et al. [21] evoked an $E_g$ value around 3.40 eV for TiNTs. In the same concept, Qu et al. [22] calculated the $E_g$ of ZrO$_2$/TiNTs and found it equal to 3.22 eV while that of the TiNTs was 3.13 eV. This slight increase in the $E_g$ value is probably due to the substitution of Zr$^{4+}$ ions (radius around 0.87 Å) by Ti$^{4+}$ (radius around 0.64 Å) [23]. In addition, Zhu et al. [24] estimated the $E_g$ value for TiNTs and ZnO/TiNTs at different atomic ratios (1:6; 1:4 and 1:2) around 3.47 eV, 3.35 eV, 3.31 eV and 3.43 eV, respectively. Therefore, doping TiNTs with ZnO decreased the $E_g$ and improved their absorption in the visible region.

The literature comprises several works that dealt with TiNTs application in the photodegradation of different synthetic dyes present in the effluents of many industries which involve leather, textile, plastic, cosmetics, printing paper decomposed into toxic compounds...
for living organisms and are discharged directly into the rivers, lakes and other places without any pre-treatment [8, 20, 25]. Methyl orange (MO) and Malachite green (MG) are anionic and cationic dyes which present an azo group (N=N) in their chemical structure [25, 26]. They are used in the textile, printing, paper, pharmaceuticals, food industries [25], and the dyeing of cotton, leather and silk [26]. In addition, MG is found to be mainly a useful fungicide to combats aprolegia (a very current disease in aquaculture) [26]. However, tannic acid (TA) is a neutral organic substance which presents many functional groups, like hydroxyl and phenolic hydroxyl [27] constituted by the decomposition of a natural organic matter (NOM) which are detected in natural water sources, industrial and domestic waste-waters [28]. It is also detected in bananas, sorghum, coffee and tea [27]. Its high toxicity and carcinogenic properties can cause liver, kidney and central nervous system problems [27]. So, the removal of each dye from industrial wastewater has been a topic of great interest in recent years. Table 1 shows some examples of the application of nanotubes in the water decontamination. It is worth noting that the TA degradation has never been studied in the literature.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conditions</th>
<th>Yield (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂/TiNTs</td>
<td>[MO]= 5 ppm, λ = 254 nm, t=180 min</td>
<td>96</td>
<td>[22]</td>
</tr>
<tr>
<td>ZnO/TiNTs (1 : 4)</td>
<td>[MO]= 10 ppm, λ = 365 nm, t=50 min</td>
<td>90</td>
<td>[24]</td>
</tr>
<tr>
<td>TiNTs</td>
<td>[MO]= 20 ppm, λ = 365 nm, t= 90 min</td>
<td>80</td>
<td>[29]</td>
</tr>
<tr>
<td>Ce-TiNTs</td>
<td>[Reactivebrilliantred X-3B]= 25 ppm, t=80 min, λ &lt; 400 nm</td>
<td>92.3</td>
<td>[30]</td>
</tr>
<tr>
<td>ZnO-TiNTs</td>
<td>[Rhodamine B]=12 ppm, λ = 365 nm, t=40 min</td>
<td>90</td>
<td>[31]</td>
</tr>
<tr>
<td>Fe/TiNTs</td>
<td>[MO]= 20 ppm, λ = 200 – 1000 nm, t=180 min</td>
<td>99.7</td>
<td>[32]</td>
</tr>
<tr>
<td>TiNTs</td>
<td>[MG]= 5.10⁻⁵ mol.L⁻¹, 0.1 g.L⁻¹ of catalyst, t=105 min</td>
<td>100</td>
<td>[33]</td>
</tr>
<tr>
<td>TiNTs</td>
<td>[MG]= 0.3 mmol.L⁻¹, 25 mg of catalyst, λ&lt;310 nm, t = 120 min</td>
<td>~ 20</td>
<td>[34]</td>
</tr>
<tr>
<td>TiNTs</td>
<td>[MG]= 15 ppm, 10 mg of catalyst, t= 180 min, λ = 254 nm</td>
<td>67,77</td>
<td>[35]</td>
</tr>
</tbody>
</table>
The aim of this study is to prepare for the first time mixed oxide nanotubes based on Ti, Ce, Zn, Fe and Zr by hydrothermal way and then tested their activities in the photodegradation of MO, MG and TA under UV-Visible irradiation. In addition, these materials will be tested in the inhibition of bacteria and fungi that exist in aquatic environments.

2. Experimental

2.1. Preparation of materials

2.1.1. Materials

Most of the used products come from Sigma Aldrich and are: commercial titanium dioxide (TiO\textsubscript{2}, anatase, 97%, M=284.22 g.mol\textsuperscript{-1}), Sodium hydroxide (NaOH, ≥98%, M=40 g.mol\textsuperscript{-1}), Hydrochloric acid (HCl, 37%, d=0.789, M=36.46 g.mol\textsuperscript{-1}), Malachite Green (C\textsubscript{23}H\textsubscript{25}ClN\textsubscript{2}, 364.91 g.mol\textsuperscript{-1}), Cerium nitrate hexahydrate (Ce(NO\textsubscript{3})\textsubscript{3}.6H\textsubscript{2}O, ≥ 99%, M = 434.22 g.mol\textsuperscript{-1}), Zinc oxide (ZnO, ≥ 99%, M= 81.39 g.mol\textsuperscript{-1}), Iron oxide, (Fe\textsubscript{2}O\textsubscript{3}, ≥ 99%, d = 5.12, M = 159.69 g.mol\textsuperscript{-1}), Zirconium oxide providing from Merck, (ZrO\textsubscript{2}, ≥ 99%, M = 123.22 g.mol\textsuperscript{-1}), Methyl orange (C\textsubscript{14}H\textsubscript{14}N\textsubscript{3}NaO\textsubscript{3}S, M = 327.33 g.mol\textsuperscript{-1}), Tannic acid (C\textsubscript{76}H\textsubscript{52}O\textsubscript{46}, M = 1702.2 g.mol\textsuperscript{-1}).

2.1.2. Preparation of TiNTs and doped-TiNTs

The hydrothermal treatment of commercial oxides, i.e. TiO\textsubscript{2} and dopant (i.e: Ce(NO\textsubscript{3})\textsubscript{3}.6H\textsubscript{2}O or Fe\textsubscript{2}O\textsubscript{3} or ZnO or ZrO\textsubscript{2}), was used to prepare doped-titanate nanotubes at 2 wt\%. Briefly, a quantity of 4 g of a commercial material (TiO\textsubscript{2} or a mixture of TiO\textsubscript{2} and dopant) was dissolved in 60 mL of NaOH (10 M). The mixture was kept under ultrasonic stirring, for 10 min. Then, the suspension was transferred into a Teflon autoclave at a temperature of around 120°C, for 48 hours. The resulting solid was washed several times with distilled water, neutralized with an HCl solution (0.1N), and then washed once again with distilled water in order to remove residual ions such as, Na\textsuperscript{+}, Cl\textsuperscript{-}, etc. Finally, the resulting solid was dried at 80 °C, overnight.

2.2. Photocatalytic degradation of organic dyes:
The prepared photocatalysts were tested in the photodegradation of three model organic molecules which are the MO, MG and TA whose structures are shown in Figure 1. The photocatalytic test was carried out in a quartz monolamp photoreactor containing 130mL of the MO, MG and TA solution with a concentration of 30 mg.L⁻¹ and 0.05 g of the catalyst. The irradiation with UVA rays (λ = 350 nm) was only triggered after magnetic stirring of the suspension in the dark for 30 min, in order to achieve the adsorption-desorption equilibrium. The reaction progress was followed by an absorption spectrophotometer of type “Agilent Carry 7000, Universal Measurement Spectrophotometer”. The residual MO, MG and TA concentration in the filtrate at each stage of the reaction was determined by measuring their maximum absorbances at λ = 463 nm, λ = 620 nm and λ = 276 nm respectively. The degradation of MO and MG was calculated using Equation 1:

\[
\text{Degradation efficiency(\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad Eq \ (1)
\]

Where \(C_0\) and \(C_t\) are the initial concentration and the concentration at time \(t\) during the reaction process are \(C_0\) and \(C_t\), respectively.
2.4. Antibacterial and antifungal behaviors of catalysts by disk-diffusion method

All catalysts were tested for their in vitro antimicrobial activity against the Gram positive bacteria *Staphylococcus aureus* (ATCC-25923), *Bacillus cereus* (ATCC 21332), the Gram-negative bacteria, *Pseudomonas aeruginosa* (ATCC-27853), *Escherichia coli* (ATCC-25922), in the nutrient agar media and fungi *Candida albicans* (ATCC 10231), *Trichosporon sp* and *Rhodotorula sp* (ATCC 20837), in Sabouraud chloramphenicol dextrose medium by using serial plate dilution method. The test was conducted by using Whatman filter paper discs (6 mm in diameter) impregnated with 50 μL of the test solutions (10 mg.mL⁻¹) that was placed over the inoculated medium surface and the plates were incubated at 37 °C for 24 h antibacterial test and 72 h of antifungal test. After which they were examined for the existence of inhibition zones. Standard antibiotics Gentamicin (10μg/disc) and amphotericin B.
(100µg/disc) were used as reference drugs for the antibacterial and antifungal activities respectively[23-25].

2.5. Characterization

Powder X-ray diffractograms (XRD) were analyzed using a RigakuDMiniFlexNifiltered 600 diffractometer using Cu Kα radiation (λ = 1.541874 Å), equipped with a secondary monochromator scanning a range between 20-80°(2θ), at room temperature with a step of 0.01° and an acquisition time of 2°.min⁻¹. The average crystallites size was calculated from the Scherrer’s formula (Equation 2).

\[ d = \frac{0.98 * \lambda}{\beta \cos \theta} \quad Eq(2) \]

Where d is the size of the crystallites (nm), λ the wavelength (nm), β the width at mid-height (FWHM)(rad), and θ the angle of Bragg (rad).

The d-spacing (d_{100}) values were calculated using Bragg’s Law (Equation 3):

\[ n \lambda = 2d_{(100)} \sin \theta \quad Eq(3) \]

The optical properties of the samples were analyzed by UV-Vis spectroscopy (200-800 nm) using a PerkinElmer800 UV-Vis spectrophotometer equipped with a set of diffuse reflectance accessories to collect only the diffusion of the reflected light. BaSO₄ was used as a reference. The FTIR spectra were performed using an Agilent Cary600 UV-Vis spectrophotometer with a resolution of 4cm⁻¹, and a scanning area between 4000 and 500 cm⁻¹. Finally, the thermogravimetric analysis (ATG) of the samples was carried out using LINSEIS.STA.PT.1600. A mass of 20 to 30 mg was introduced into a platinum crucible in which it was supported by the plague of a scale located in the oven. The analysis was carried out in air with a temperature ramp of 10 °C.min⁻¹ in an interval from 25 to 1000°C.

3. Results and discussion:

3.1. Physicochemical characterization

Figure 2 illustrates the XRD spectra. The titanate phase characteristic of nanotubes and layered materials (JCPDS Files No. 01-080-9016), of formula H₂Ti₃O₇·H₂O, appeared
principally at $2\theta \approx 10.34^\circ$, $24.58^\circ$, $28.70^\circ$ and $48.62^\circ$, corresponding to faces (100), (201), (111) and (020). However, the picks related to cerium, iron, zinc and zirconium species were detected as is shown in Table 2. This confirms that doping was successful.

![XRD analysis of the prepared materials.](image)

**Figure 2.** XRD analysis of the prepared materials.

**Table 2.** Spectral lines of the different dopants with their corresponding reticular planes.

<table>
<thead>
<tr>
<th>Dopants</th>
<th>$2\theta$ (°)</th>
<th>hkl</th>
<th>JCPDS Files</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>28.64</td>
<td>111</td>
<td>01-073-6318</td>
</tr>
<tr>
<td></td>
<td>33.25</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td></td>
<td>48.46</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td></td>
<td>56.56</td>
<td>311</td>
<td></td>
</tr>
<tr>
<td></td>
<td>59.20</td>
<td>222</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>33.35</td>
<td>104</td>
<td>01-076-1821</td>
</tr>
<tr>
<td></td>
<td>35.74</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td></td>
<td>54.38</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>32.56</td>
<td>100</td>
<td>01-078-4606</td>
</tr>
<tr>
<td></td>
<td>35.66</td>
<td>002</td>
<td></td>
</tr>
</tbody>
</table>
The d-spacing ($d_{100}$) of various materials are shown in Table 3. The values obtained for these materials are in good agreement with those found in the literature (between 0.77 and 1.7 nm) [8, 38, 39]. The changes in the value of interlayer spaces are due to the exchange of Na$^+$ ions by different dopants.

**Table 3.** Properties of prepared materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$d_{100}$ (nm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiNTs</td>
<td>0.86</td>
<td>3.28</td>
</tr>
<tr>
<td>Ce-TiNTs</td>
<td>0.83</td>
<td>3.03</td>
</tr>
<tr>
<td>Fe-TiNTs</td>
<td>0.86</td>
<td>3.45</td>
</tr>
<tr>
<td>Zn-TiNTs</td>
<td>0.84</td>
<td>3.40</td>
</tr>
<tr>
<td>Zr-TiNTs</td>
<td>0.84</td>
<td>3.35</td>
</tr>
</tbody>
</table>

Figure 3 shows the RD/UV-Vis spectra of the prepared materials. All the materials showed a strong absorption in the UV region (< 400 nm), which is linked to the titanium species [8, 38, 40]. The presence of metal species in the doped-TiNTs led to an enhancement of the absorption in the visible region of the spectrum, especially in the case of the Fe-TiNTs.
The deconvolution of all RD/UV-Vis spectra is shown in Figure 4. A significant absorption was noted in the intervals 209-215, 232-244, 264-299 and 321-332 nm. They can be related to the charge transfer between tetrahedral Ti$^{4+}$ and oxygenated ligand like: O$^{2-}$, O-H, O-Ti or even H$_2$O and to the Ti$^{4+}$ cations in an octahedral environment [8, 38, 40]. Ce-TiNTs showed a band at 402 nm. This band is related to the energy level (4f) of Ce, which generates (e$/h^+$) pairs under visible light irradiations[41]. However, Fe-TiNTs powder showed bands between 250 and 400 nm; which are assigned to the small (FeO)$_n$ and the bands in the region 400-650 nm are related to larger particles of iron oxide or the polymeric species [42, 43]. In the case of Zn-TiNTs, it should be noted that the adsorption band at 323 nm may be attributed to Zn species and is almost shielded by that for TiNTs [44]. Compared with TiNTs spectrum, the absorption intensity of Zr-TiNTs sample is obviously bigger in the UV-light region.
We can employ Equation 4 given below for finding out the values of the gap energy values ($E_g$):

$$\alpha h\nu = A(h\nu - E_g)^n \quad Eq(4)$$

Where $\alpha$ and $h\nu$ are the absorption coefficient and the photon energy, respectively. It should be noted that $A$ is the invariable characterizing the semiconductor and $n$ denoting the transition nature. For a direct transition $n = 1$, while for an indirect transition $n = 4$, for instance. Also, to determine the $E_g$ values, the graph $(\alpha h\nu)^{1/2}$ as a function of $E_g$ was extrapolated to $\alpha = 0$ (Figure 5).
Table 3 summarizes all the $E_g$ values obtained. It is worth noting that TiNTs have an energy gap value around 3.28 eV. In addition, doping with metals caused a reduction in the $E_g$ values in the case of Ce-TiNTs material. In contrast, Fe-TiNTs, Zn-TiNTs and Zr-TiNTs materials showed bigger $E_g$ values. This may be related to the dopant radius that can replace the Ti$^{4+}$ cations. The literature evoked that the band gap energy of 2%Zn-TiNTs slight increase maybe due to the ionic radii of Zn$^{2+}$ ions (0.88 Å) larger than the ionic radii of Ti$^{4+}$ (0.64 Å) [24].

Figure 6 shows the FTIR spectra of the studied nanotubes. It is worth noting that all the powders have a large band around 640 cm$^{-1}$. This is attributed to the Ti-O-Ti bond vibration [8, 38]. However, the Ti-O tetrahedral coordination is localized around 935 cm$^{-1}$ [8, 38].
Nevertheless, the bands in the region of 1200-1600 cm$^{-1}$ and at 3300 cm$^{-1}$ may be related to the vibration of water molecules (H-O-H) and the O-H groups in the nanotubes surface [8, 38]. However, doped-TiNTs nanopowders showed the appearance of new characteristic bands of the M-O bond elongation vibration (M: Ce, Fe, Zn and Zr) located in the regions 600, 470, 463 and 580 cm$^{-1}$, respectively. This confirms the presence of the crystalline phase of metals [45-49]. The bands detected around 850 cm$^{-1}$ after doping TiNTs indicate the existence of the interaction between M-O-Ti which confirms the strong attraction between the different metals and Ti[26]. The intense band located at 1631 cm$^{-1}$ in the case of Zr-TiNTs indicates that the materials have absorbed moisture [48].

![Figure 7](image.png)

**Figure 7.** Thermal gravimetric analysis of the studied samples.

According to the literature, three processes must take place during the TiNTs thermal transformation which are: dehydration, phase transformation and morphology modification. Each step occurs within a precise temperature interval[8, 50].

**Figure 7** shows DTA-TG of the synthesized materials. The mass loss and the thermal process were analyzed in the temperature range of 25-800°C. In the temperature range of 25-150°C, the loss weight of physisorbed water is estimated to be around 7 and 12%. The increase in temperature up to 200°C is due to the removal of the O-H chemisorbed groups from the interlayer structural water. The O-H from the Ti-OH bond is estimated to be 5% [8,
Beyond 210°C, the TG curve remains stable with no loss of mass which corresponds to the total thermal decomposition of the nanotubes. For the endothermic process which appears between 25-250°C is associated with the O-H dehydration of the interlayer water. Another endothermic peak detected around 440°C is assigned to the TiNTs total dehydration according to the following reaction:

\[
\text{H}_2\text{Ti}_3\text{O}_7 \cdot \text{2H}_2\text{O} \rightarrow \text{H}_2\text{Ti}_3\text{O}_7 \rightarrow \text{TiO}_2 \text{ (anatase)} + \text{H}_2\text{O} \rightarrow \text{TiO}_2 \text{ (rutile)}
\]

In the temperature range of 600-800°C, weak peaks appear which show the transformation of the anatase to the rutile phase[51]. The presence of different dopants in the structure of TiNTs strengthens their thermal stability thanks to the cation exchange in the TiNTs network[8].

### 3.2. Photocatalytic degradation of organic pollutants:

Photocatalytic activities of the prepared materials were tested in the degradation of three model dyes: MO, MG and TA (see Figure 1) under UV-Visible light source. Figures 8, 9 and 10 show the absorbance curve of dyes in the presence of the photocatalysts. The results show that the absorption peak intensity of MO (463 nm), MG (620 nm) and TA (276 nm) gradually decreases with the illumination time and disappears after 35 min for MO, MG and after 150 min for TA. Table 4 evaluates the photodegradation efficiency of all catalysts. Furthermore, the higher photocatalytic activity is achieved in the case of Zn-TiNTs for the three pollutants. This important activity may be related to the following parameters:

i. Large surface of TiNTs (as was proved in our previous work[38]) which insure an excellent transfer of electrons on the TiNTs surface[52].

ii. The good dispersion of dopants in the TiNTs matrix leads to the creation of a new energy level reducing the band gap of TiNTs facilitating the transfer of electrons from one band to another and inhibiting the(e-,h+)recombination that enhances the photocatalytic activity[52].

iii. The presence of Ti-O-dopant bonds (As confirmed by FTIR and RD/UV-Vis deconvoluted spectra) enhances the photodegradation of doped materials[39, 53].
Figure 8. Absorbance spectra of MO dye in the presence of TiNTs and doped-TiNTs.

Figure 9. Absorbance spectra of MG dye in the presence of TiNTs and doped-TiNTs.
Figure 10. Absorbance spectra of TA dye in the presence of TiNTs and doped-TiNTs.

Table 4. Degradation efficiency of the prepared photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MO dye (35min)</th>
<th>MG dye (35min)</th>
<th>TA (150min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiNTs</td>
<td>90</td>
<td>77</td>
<td>70</td>
</tr>
<tr>
<td>Ce-TiNTs</td>
<td>98</td>
<td>85</td>
<td>47</td>
</tr>
<tr>
<td>Fe-TiNTs</td>
<td>57</td>
<td>82</td>
<td>76</td>
</tr>
<tr>
<td>Zn-TiNTs</td>
<td>99</td>
<td>90</td>
<td>85</td>
</tr>
<tr>
<td>Zr-TiNTs</td>
<td>96</td>
<td>80</td>
<td>44</td>
</tr>
</tbody>
</table>

3.2.1 Photocatalytic mechanism:

In Figure 11, we explain the photocatalytic degradation reaction mechanism of the dyes on the TiNTs and dopant-TiNTs surface. In the case of TiNTs, the \((h^+)^{\star}\) creation in the VB of TiNTs is caused by the transition of the electrons from the valence band (VB) towards the conduction band (CB) by the effect of UV-Vis irradiations, while the electron causes the reduction of oxygen to give the radical anion \(O_2^{\cdot}\). Moreover, it is brought to notice that the \((h^+)^{\star}\) contributes to the water transformation to give the radical ion \(OH^{\cdot}\) [8, 53-55]. These two radicals are among the strongest oxidants enabling the degradation of pollutants (here: MO, MG and TA). It is worth noting that another mechanism intervenes in the presence of dopants. Under UV-Visible irradiation, an electron in the VB of the dopant is excited towards the CB of Ti–and causes \((h^+)^{\star}\) formation in the VB of the dopant. This should further enrich the formation of the radicals \(OH^{\cdot}\) and \(O_2^{\cdot}\) and therefore give better photodegradation of the organic pollutants [8, 53-55].
Figure 11. Mechanism of photodegradation of doped-TiNTs under UV-Visible conditions.

3.2.2 Kinetic studies

Figure 12 shows the linear relationship of Ln (C₀/C) vs. irradiation time (t) for the solution of MO, MG and TA. The regression coefficient (R²) was calculated from a linear fitting line of plot Ln (C₀/C) as shown in Figure 12. The rate constant was calculated from the following equations [56, 57]:

\[
\ln \left( \frac{C_0}{C} \right) = kt; \text{ order 1}
\]

Where C₀ and C represent the concentration of the dye solution at initial (t₀) and time t. The calculated values of R² and k are reported in Table 5 using the Langmuir-Hinshelwood model.

Table 5. Kinetics modeling parameters of the dye photocatalytic degradation for prepared photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MO dye</th>
<th></th>
<th></th>
<th>MG dye</th>
<th></th>
<th></th>
<th>TA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K (min⁻¹)</td>
<td>R²</td>
<td>K (min⁻¹)</td>
<td>R²</td>
<td>K (min⁻¹)</td>
<td>R²</td>
<td></td>
</tr>
<tr>
<td>TiNTs</td>
<td>0.03719633</td>
<td>0.947</td>
<td>0.04735405</td>
<td>0.937</td>
<td>0.00477663</td>
<td>0.950</td>
<td></td>
</tr>
<tr>
<td>Ce-TiNTs</td>
<td>0.05832386</td>
<td>0.967</td>
<td>0.06243699</td>
<td>0.949</td>
<td>0.00189377</td>
<td>0.958</td>
<td></td>
</tr>
<tr>
<td>Fe-TiNTs</td>
<td>0.01231636</td>
<td>0.970</td>
<td>0.0587846</td>
<td>0.960</td>
<td>0.00729602</td>
<td>0.954</td>
<td></td>
</tr>
<tr>
<td>Zn-TiNTs</td>
<td>0.06031415</td>
<td>0.981</td>
<td>0.06845579</td>
<td>0.970</td>
<td>0.00851441</td>
<td>0.962</td>
<td></td>
</tr>
<tr>
<td>Zr-TiNTs</td>
<td>0.05756076</td>
<td>0.952</td>
<td>0.05584384</td>
<td>0.953</td>
<td>0.00238382</td>
<td>0.934</td>
<td></td>
</tr>
</tbody>
</table>
Table 5 describes the degradation kinetics of MO, MG and TA over various catalysts. The results show that all the catalysts have the $R^2$ value in the range of 0.92-0.98 indicating that all prepared catalysts have good first order kinetics because it showed a good fitting with experimental data [58]. The highest value of $R^2$ (0.98) and $k$ (0.06 min$^{-1}$) obtained for Zn-TiNTs was 2 times greater compared with TiNTs ($R^2=0.94$, $k=0.03$ min$^{-1}$) with MO photodegradation. For MG and TA degradation, the $R^2$ values are 0.97 and 0.96 and the $k$ values are 0.07 min$^{-1}$ and 0.008 min$^{-1}$, respectively. The possible reason for this important activity is the higher contact area of the adsorbed material with different dye molecules [56].

As shown in Table 6, most of catalysts exhibit an important adsorption rate during adsorption-desorption equilibrium time in the dark, especially in the case of MG and TA. This can be explained by the influence of the solution pH which is a key parameter in the photocatalytic process defining the surface charge properties of photocatalysts, the charge of dye molecules, the adsorption of dyes onto the photocatalyst surface, and the concentration of hydroxyl radicals [59]. There is a relationship between the solution pH and the zero point charge (pH$_{PZC}$) of prepared materials. As we all know, the surface charge is positive at pH<$\text{pH}_{PZC}$, whereas, at pH>$\text{pH}_{PZC}$ it is negative [60]. MO is an anionic dye with a negative charge and the solution pH is about 8.63, MG is a cationic dye with a positive charge and the solution pH is about 8.77. TA is a neutral dye with no charge on its surface and the solution pH is about 9.68. The pH$_{PZC}$ value of TiNTs is 8.5; so the negatively charged surface of TiNTs repulse the MO molecules [61]. In this contest, Ge et al. [59] studied the MO using ZnO/TiO$_2$ composites at various pH conditions. After 60 min, the photodegradation efficiency achieved 98.13% at pH=2, 85.14% in alkaline solution (pH=11) and 87.68% in neutral solution (pH=6).

For the adsorption rates in the dark (for the first 30 min), 30% were at pH=2; 10% at pH=6 and 3.77 at pH=11.

In our case, the MG adsorption efficiency by TiNTs is higher because of the strong interaction between the negative catalyst surface and the positive charges of MG cations [62]. Qu et al. [62] tested the MG photodegradation using activated carbon at various pH conditions. The results showed that the MG elimination rate attains its minimum at pH<4 with a degradation efficiency of 35% and increases at 5<pH<9 with 90%. The degradation efficiency stabilizes if the pH>9. Consequently, better degradation occurs in alkaline condition while the acidic condition has a negative effect.
Figure 12. Plots of $\ln (C_0/C)$ against time: (A) MO, (B) MG, (C) TA using TiNTs and doped-TiNTs.
Finally, TA is a weak organic acid with an ionization strongly depending on the solution pH [63]. It has been noted that the TA surface charge is nearly zero at pH<4.5, which explains that it is in the molecular form. At pH>4.5, the TA dissociation degree highly increases to be negatively charged [63]. In our case, the TA is negatively charged on carboxyl and phenolic hydroxyl groups since the pH of the solution is 9.63, the pH_{PZC} of TiNTs is 8.5 so the electrostatic interaction will not exist due to the negatively charge repulsion but it can form hydrogen bonding or Van Der Waals interaction with OH groups in TiNTs surface favoring the adsorption process [64]. An et al. [63, 64] studied the pH effect on the TA adsorption into Chitosan-Coated Attapulgite(CCATP). The results showed that at 4.5<pH<5.5, the electrostatic attraction between TA and positively charged CCATP determines the adsorption rate of 90%. When the 5.5<pH<8, the electrostatic interaction decreases because of the deprotonation of chitosan at higher pH but the hydrogen bonding or Van Der Waals interaction arises between TA and CCATP. This increase promotes the adsorption rate of 99%. At pH>10, the decrease of the adsorption rate occurs due to TA hydrophilicity and the competitive adsorption of OH- on TiNTs surface [64, 65, 66]. Table 6 shows the adsorption rate of the three dyes on prepared materials.

### Table 6. Adsorption rate in the dark of MO, MG and TA on prepared materials.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>MO Adsorption rate (%)</th>
<th>MG Adsorption rate (%)</th>
<th>TA Adsorption rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiNTs</td>
<td>38</td>
<td>61</td>
<td>32</td>
</tr>
<tr>
<td>Ce-TiNTs</td>
<td>10</td>
<td>73</td>
<td>1</td>
</tr>
<tr>
<td>Fe-TiNTs</td>
<td>12</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>Zn-TiNTs</td>
<td>18</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>Zr-TiNTs</td>
<td>3</td>
<td>66</td>
<td>8</td>
</tr>
</tbody>
</table>

#### 3.2.4. Antibacterial and antifungal activities of the prepared materials

In this work, the biological power of TiNTs and doped-TiNTs was estimated by measuring their antibacterial and antifungal activities. Modified TiNTs with other metal can improve the TiNTs application in biomedical files [39-42].

The results of antimicrobial activities were summarized in Tables 7. The inhibition zones of disc for strains were in the ranges 6.0 – 20.0 mm. Non-doped TiNTs show moderate antifungal activity but no inhibition of bacteria. However, doping with other metals leads to an improvement in their anti-fungal activity and also enriches their inhibition towards bacteria. This was found in the case of the Ce-TiNTs, Fe-TiNTs, Zn-TiNTs and Zn-TiNTs materials;
that exhibited inhibition activities toward Bacillus Cereus and Escherichia Coli bacteria and Candida, Trichosporon and Rhodotorula fungus. This improvement in activity can only be linked to the presence of metal species, i.e. Ce$^{3+}$, Ce$^{4+}$, Fe$^{3+}$, Zn$^{2+}$ and Zr$^{4+}$.

Table 7. Antibacterial and antifungal activities of catalysts at 10 mg.mL$^{-1}$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Bacteria</th>
<th>Fungi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gram - positive</td>
<td>Gram - negative</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>TiNTs</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ce-TiNTs</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Fe-TiNTs</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Zn-TiNTs</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Zr-TiNTs</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Gentamicin</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>amphotericin B</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Key to the inhibition zones activities: Highly active = (21-30 mm) +++; moderately active = (15-20 mm )++; Slightly active = (8 -14 mm ) +; Inactive= (< 6 mm) -

S. a. (Staphylococcus aureus), B. c. (Bacillus cereus), E.c. (Escherichia coli), P. a.(Pseudomonas aeruginosa).

The main mechanism of metal-TiNTs antimicrobial activity is attributed to the release of ions from the nanotube (Na$^+$, Ce$^{3+}$, Ce$^{4+}$, Fe$^{3+}$ and Zn$^{2+}$,...) structure into the surrounding environment[39-42]. Usually, the antimicrobial efficiency mainly depends upon reactive oxygen species (ROS) creation, oxidation state, surface area, irradiation, particle size, etc. The literature evoked that oxide materials produce ROS (O$_2^-$, HO', HO$_2'^•$, H$_2$O$_2$, etc.) via Fenton process inducing lipid peroxidation, protein oxidation and DNA destruction [39, 40].

Undoped TiNTs present Na$^+$ ions which may be the origin of their anti-fungal activity. However, the presence of metal in doped-TiNTs catalysts enriches the activity of the TiNTs. In addition, this catalyst presents metal species that are more available to cross the barriers of the cells studied (bacteria or fungi) and cause damage to their DNA. Note that there is currently no specific mechanism in the literature that explains the inhibition mechanism that metal exerts on bacteria or fungi. However, it was assumed that inhibition occurs by sorption of metal ions and Na$^+$ species on the negatively charged cell wall causing the deactivation of cellular enzymes[39]. Finally, we can say that Na$^+$ and metal ions act side by side to kill bacterial and fungal cells; thanks to the following points[39-42]:
(i) High dispersion of metals over TiNTs enhances the charge separation for generating ROS species that stress the bacterial and fungus,

(ii) Enhances the biocide effect on bacterial and fungus, inhibiting its spread,

(iii) The nanotubes shape and size help the cell wall damages, accelerating vacuolation and invaginations that produce fatal inhibition of the fungus or bacteria.

4. Conclusion

In this work, TiNTs and doped-TiNTs materials were prepared by the hydrothermal method using commercial raw materials. Also, all the prepared materials were fully characterized. Three model dyes were chosen to evaluate the efficiency of photocatalytic activity and adsorption capacity of synthesized materials. TiNTs presented a good improvement in the catalytic activity in presence of Zn compared to the undoped-TiNTs. These excellent results are due to the large surface area, the good dispersion of dopants on TiNTs surface and the appropriate Eg. On the other hand, the adsorption capacity of TiNTs depends strongly on the pH solution and the dopant nature as well as the charge of the pollutant molecule. The present results have showed that Zn-TiNTs were expected to serve as promising and potential photocatalysts to eliminate the effluents present in industrial wastewater with a degradation efficiency achieving 99% in a much reduced time period. Finally we can say that the presence of dopants improves the antibacterial effectiveness of TiNts in addition to their anti-fungal activity.

Acknowledgements

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