

# Effectiveness of photocatalysis of MMT-supported TiO2 and TiO2 nanotubes for rhodamine B degradation

Thi Bang Tam Dao, Thi Thu Loan Ha, Trung Do Nguyen, Hon Nhien Le, Chi Nhan Ha-Thuc, Thi Mai Loan Nguyen, Patrick Perré, Dang Mao Nguyen

## ▶ To cite this version:

Thi Bang Tam Dao, Thi Thu Loan Ha, Trung Do Nguyen, Hon Nhien Le, Chi Nhan Ha-Thuc, et al.. Effectiveness of photocatalysis of MMT-supported TiO2 and TiO2 nanotubes for rhodamine B degradation. Chemosphere, 2021, 280 (1), pp.130802. 10.1016/j.chemosphere.2021.130802. hal-03547560

# HAL Id: hal-03547560 https://hal.science/hal-03547560

Submitted on 9 May 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Version of Record: https://www.sciencedirect.com/science/article/pii/S004565352101273X Manuscript\_d5bec6a1c37972305827230bebb2b705

1	Effectiveness of photocatalysis of Montmorillonite-supported $TiO_2$ and $TiO_2$					
2	nanotubes for rhodamine B degradation					
3	Thi Bang Tam Dao <sup>a,b</sup> , Thi Thu Loan Ha <sup>a,b</sup> , Trung Do Nguyen <sup>a,b</sup> , Hon Nhien Le <sup>a,b</sup> , Chi					
4	Nhan Ha-Thuc <sup>a,b*</sup> , Thi Mai Loan Nguyen <sup>c</sup> , Patrick Perre <sup>d*</sup> , Dang Mao Nguyen <sup>d*</sup>					
5	<sup>a</sup> Faculty of Materials Science and Technology, University of Science, VNU-HCM, 227					
6	Nguyen Van Cu Street, Ward 4, District 5, Ho Chi Minh City, 700000, Viet Nam					
7	<sup>b</sup> Vietnam National University – Ho Chi Minh City, Linh Trung Ward, Thu Duc District,					
8	Ho Chi Minh City, 700000, Viet Nam					
9	<sup>c</sup> Institute of Research and Development, Duy Tan University, Da Nang 550000, Viet					
10	Nam.					
11	<sup>d</sup> Université Paris-Saclay, CentraleSupélec, Laboratoire de Génie des Procédés et					
12	Matériaux, SFR Condorcet FR CNRS 3417, Centre Européen de Biotechnologie et de					
13	Bioéconomie (CEBB), 3 rue des Rouges Terres 51110 Pomacle, France					
14	* Corresponding authors: htcnhan@hcmus.edu.vn (C.N. Ha-Thuc);					
15	patrick.perre@centralesupelec.fr (P. Perré); dang-mao.nguyen@centralesupelec.fr (D.M.					
16	Nguyen).					
17						
18	ABSTRACT					
19	The aim of this paper is to synthesize montmorillonite/TiO2-nanoparticles (MMT/TiO2					
20	and montmorillonite/TiO <sub>2</sub> -nanotubes (MMT/TiO <sub>2-NTs</sub> ) photocatalysts through a simple					

22 accumulate the effect of adsorption and photodegradation. Then, the photocatalysts are

wet agitation method based on TiO2 nanoparticles and MMT. They are likely to

1

applied to degrade the rhodamine B in dye effluents. The structural characterizations of 23 photocatalysts are investigated using transmission electron microscopy (TEM), scanning 24 electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared 25 (FTIR) and energy-dispersive X-ray spectroscopy (EDX). spectroscopy 26 The photocatalytic activities and effectiveness of photocatalysts are evaluated through 27 rhodamine B degradation at different concentrations under dark and UV-C irradiation 28 conditions. The results show that the synthesized TiO<sub>2-NTs</sub> have an average tube diameter 29 of 5 nm and a tube length at least about 110 nm, which are intercalated into MMT sheets 30 in MMT/TiO<sub>2-NTs</sub> photocatalyst. Meanwhile, TiO<sub>2</sub> nanoparticles are immobilized on the 31 surface of MMT sheets in the MMT/TiO<sub>2</sub> photocatalyst. The photocatalytic effectiveness 32 of rhodamine B degradation of TiO<sub>2-NTs</sub> shows a significantly enhance compared to that 33 of TiO<sub>2</sub> nanoparticles. However, photocatalytic performance of MMT/TiO<sub>2-NTs</sub> is lower 34 than that of MMT/TiO<sub>2</sub>. The degradation effectiveness of MMT/TiO<sub>2</sub> photocatalyst 35 reaches to 100% for 3ppm and 90% at 10ppm of rhodamine B, while these values are 36 97.5% and 85.5%, respectively, recorded for MMT/TiO<sub>2-NTs</sub>. 37

38 *Keywords: Photocatalysts, UV-C irradiation, TiO*<sub>2</sub> *nanotubes, MMT*/TiO<sub>2</sub> and
39 MMT/TiO<sub>2-NTs</sub>, and rhodamine B.

40

#### 41 **1. Introduction**

Synthetic dyes are widely used in various applications in the industries as paper, leather,
and textile due to their color-giving properties (Gupta and Suhas, 2009; Abdi et al., 2017;
Katheresan et al., 2018; Wang et al., 2020). They are responsible for environmental

pollutions and human health (Charumathi and Das, 2012) due to the presence of dye in 45 effluents. It was stated that some of the following industries are mainly responsible for 46 environmental pollution from dye effluent such the textile (54%), the dyeing industry 47 (21%), paper and pulp (10%), tannery and paint (8%) and the dye manufacturing (7%) 48 (Rauf and Salman Ashraf, 2012) and other activities as dyes degradation (dos Santos et 49 al., 2007). Rhodamine B is a xanthene dye, which is widely used as a colorant in textiles 50 industry, wool, silk, dye cells in biotechnology and food stuffs. However, it is harmful to 51 human and animal as skin, eves and respiratory tract irritation, carcinogenicity as well as 52 reproductive and developmental toxicity (Kingsley et al., 1990; Nagaraja et al., 2012). 53 Therefore, the removal of rhodamine B from dyes effluents must be given priority before 54 they are released into environment. Until now, there was some methodologies of 55 removing of the dyes from wastewaters including chemical, physical methods and 56 biological processes, however, they still have many disadvantages such as low efficiency 57 and high cost (Robinson et al., 2001). Photocatalyst approaches are currently being 58 investigated for the removal of impurities in wastewater. Photocatalytic is a new and 59 potential discovery that uses renewable energy sunlight to decompose organic pollutants 60 into low-cost but highly efficient fuels and removal of trace contaminant from water 61 (Malato et al., 2009). This approach is also environmentally friendly, compared to 62 previous traditional methods such as advanced oxidation, filters, and solar evaporation. In 63 recent years, the use of semiconductor photocatalytic materials for treatment of organic 64 compounds has achieved remarkable achievements and attracted from basic research to 65 application. Some of them have been studied and used as photocatalysts such as ZnO, 66

CdS, and  $Fe_2O_3$  (Hassani et al., 2017; Pannak et al., 2018). Titanium dioxide (TiO<sub>2</sub>) is 67 known as a potential photocatalyst in the field of environmental cleaning because of its 68 chemical and biological inertness, ease of fabrication, non-toxicity, abundance in 69 availability and low cost (Hassani et al., 2017; Chinh et al., 2018; Chinh et al., 2019). In 70 particular, TiO<sub>2</sub> has been widely studied for photocatalysis (Fan et al., 2014; Huang et al., 71 2016; Tahir and Amin, 2016). However, TiO<sub>2</sub> has limitations in photocatalytic 72 applications due to the rapid recombination between electron and holes pairs, which 73 cause to reduce photocatalytic efficiency. Moreover, it also has a wide band gap that only 74 active photocatalyst in the ultraviolet light (less than 5% of the entire solar energy), 75 inducing a lower photocatalytic activity (Leong et al., 2014; Diamond et al., 2017). To 76 overcome the above limitations, some approaches are proposed to improve the 77 photocatalytic activity. Specifically, TiO<sub>2</sub> nanosheets were used as an electron mediator 78 to prepare the CdSe/graphene/TiO<sub>2</sub> nanosheet composite photocatalysts. They provided a 79 great efficient charge separation, extended visible-light absorption range and stability for 80 the degradation of methylene blue in aqueous solutions (Ma et al., 2018). Moreover, the 81 TiO<sub>2</sub> nanosheets were combined with small plasmonic Au nanoparticles to improve the 82 photocatalytic rate of hydrogen production through the large surface adsorptive sites for 83 reactant adsorption and enhancing the charge separation through the Schottky transfer 84 hub to neighboring TiO<sub>2</sub> nanosheets (Cheng et al., 2019). It could be combined with 85 different semiconducting materials (Zhang et al., 2020) to prevent reuniting the 86 photogenerated electron-hole pairs (Dao et al., 2020) and improve the photocatalytic 87 activities (Low et al., 2018). TiO<sub>2-NTs</sub> are synthesized through hydrothermal method from 88

TiO<sub>2</sub>. They can improve the photocatalytic activity due to large specific surface area, ion 89 exchange capacity, and fast electronic transfer over a long distance, and high adsorption 90 of light due to a large ratio between the length and diameter of the tubes. Specially, all 91 these properties could be obtained and controlled through the synthesis method (Casu et 92 al., 2018; Niu et al., 2020). Unfortunately, similar to most semiconductor materials used 93 as photocatalyst, TiO<sub>2-TNs</sub> are also difficult in separating the electron-hole pairs, leading 94 to reduce photocatalytic activity. Therefore, some strategies have been proposed to 95 extend the lifetime of photoinduced charge carriers and enhance photocatalytic activities 96 including doping metal (Park et al., 2011; Sasani et al., 2016), metal oxides (Xu et al., 97 2014; Habila et al., 2016) and non-metals such as Zeolite, and Carbon and 98 Montmorillonite (MMT) (Yin et al., 2014; Hassani et al., 2016). MMT is purified from 99 bentonite and available in large reserves from natural mineral sources (Thuc et al., 2010). 100 Specially, it combines a low cost with interesting properties due to its layered structure, 101 102 large surface area, cation exchange ability and high heat resistance. It is considered as potential material to be combined with TiO<sub>2</sub> and TiO<sub>2-NTs</sub> to create novel materials, which 103 could be used to degrade and store pollutants and toxic agents in wastewater (Hassani et 104 al., 2017; Szczepanik, 2017a; Shan et al., 2020). In the literature, a study has successfully 105 106 synthesized MMT/TiO<sub>2</sub> from Tetraethyl orthotitanate for Ciprofloxacin (CIP) treatment. 107 The results showed that the CIP degradable efficiency of MMT/TiO<sub>2</sub> nanocomposites reached up to 65.01% after 120 min adsorption time, which was much higher than that of 108 MMT or TiO<sub>2</sub> only (Hassani et al., 2017). The photocatalytic effect of TiO<sub>2</sub>/MMT doping 109 with  $Y^{3+}$  (Yttrium) into TiO<sub>2</sub> for Methyl Orange (MO) treatment was reported (Bing et 110

al., 2015). Thus,  $Y^{3+}$  reduces the band gap to increase the photocatalytic capacity of TiO<sub>2</sub>, 111 leading to increase the efficiency of MO degradation. In addition, MMT/TiO<sub>2</sub> 112 nanocomposite was produced by hydrothermal method to obtain the TiO<sub>2</sub> particles range 113 about 40-60 nm to treat Basic Blue 3 (BB3) (Khataee et al., 2015). The results showed 114 that the photocatalytic performance of MMT/TiO<sub>2</sub> was much higher than that of MMT 115 and TiO<sub>2</sub> under different pH and BB3 concentration. In addition, it was reported that 116 rhodamine B was degraded by various photocatalysts, which was clearly described in 117 previous literature (Natarajan et al., 2011; Shi et al., 2014; Wang et al., 2020). The 118 degradation process could be explained by the fact that the active radicals such as 119 hydroxyl free radicals (•OH), and free superoxide radicals (• $O_2^-$ ), attack the central 120 carbon in the rhodamine B molecules and oxidize them to low-weight intermediates. In 121 the opening-ring process, the active radicals attack the simple intermediates that are 122 produced, which results in the formation of small and broken-ring compounds. The 123 smaller compounds are degraded to CO<sub>2</sub> and H<sub>2</sub>O. 124

In this paper, we will synthesis of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> photocatalysts with a 125 low-cost hydrothermal method. These combinations could maximize the photocatalytic 126 capabilities under dark and UV-C irradiation conditions for rhodamine B degradation at 127 different concentrations from dyeing wastewater compared to TiO<sub>2</sub> and TiO<sub>2-TNs</sub> only, 128 because they are likely to slowdown of electron and holes pairs recombination. 129 Moreover, the reusability of MMT/TiO2 and MMT/TiO2-NTs for the rhodamine B 130 degradation was repeated three time under the same conditions to evaluate the stability of 131 the photocatalytic activities. 132

#### 133

## 2. Materials and experiment

## 134 **2.1. Materials**

Rhodamine B was purchased from Sigma-Aldrich in highest purity. Montmorillonite
(purity > 95%) was purified from bentonite in Lam Dong Province, Vietnam. Acid nitric,
Sodium hydroxide, Ethanol, Sodium Chloride were purchased from Merck (Germany).

138

139 **2.2. MMT preparation** 

200 g Bentonite and 5L distilled water were stirred for 24 hours and settled for 5 hours. 1 140 g of NaCl was added and mechanical stirred for 3 hours and settled for 24 hours. The 141 suspension obtained was centrifuged for 30 min with a speed of 3500 rpm. The collected 142 solids were washed with distilled water for 4 hours and settled for 8 hours. Ethanol (30%) 143 was added to the above solution and stirred for 30 min before being settled for 24 hours. 144 Then, the suspension was centrifuged for 30 min at 3500 rpm to obtain high purity MMT. 145 Finally, MMT was dried at 60 °C for 72 hours. The purification of MMT from Bentonite 146 could be referenced in previous studies (Thuc et al., 2010; Nguyen Van et al., 2020). 147 148

140

149 **2.3. Preparation of TiO<sub>2-NTs</sub>** 

TiO<sub>2-NTs</sub> were synthesized by hydrothermal method from TiO<sub>2</sub> powder with particle size in the range of 50-60 nm. 4.2 g of TiO<sub>2</sub> powder was added slowly into 10M NaOH solution with TiO<sub>2</sub>/NaOH molar ratio of 1/30 and stirred for 4 hours at 50°C. The suspension solution obtained was poured into a Teflon flask, which was then inserted into a stainless-steel jar and sealed. Hydrothermal process was then performed at 130°C for 24

hours in an autoclave before cooling to the room temperature. The product after 155 hydrothermal process was filtered and washed with deionized water to reach a pH = 9. 156 The solid product was then dispersed in deionized water and adjusted to pH = 7 with 2M 157 HNO<sub>3</sub> solution and stirring for 2 hours before centrifuging to obtain solid product. Once 158 again, the product was dispersed into deionized water at 80°C and stirred to remove the 159 salt formed during the above reaction. The solid product was then obtained by 160 centrifugation for 15 min and dried at 60°C for 24 hours. Finally, the product was heated 161 at 400°C with a heating rate of 5 °/min and maintained at the final temperature for 2 hours 162 to obtain TiO<sub>2-TNs</sub> (Wong et al., 2011; Farghali et al., 2014). 163

164

165

## 2.4. Preparation of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-TNs</sub> photocatalysts

2.00 g of MMT was slowly added to 100 mL of deionized water and mechanical stirred 166 500rpm for 24 hours to allow MMT to expand completely. Then, 0.206 g TiO<sub>2</sub> was added 167 slowly to the above MMT suspension and stirred 500 rpm for 4 hours. This suspension 168 solution was then treated by ultrasound (UPH100) at 100 W and frequency 30 kHz for 1 169 hour. The product was obtained through centrifugation process with a rotating speed of 170 3500 rpm for 15 min. Finally, the product was dried at 80°C in an oven for 24 hours to 171 obtain MMT/TiO<sub>2</sub> photocatalyst. MMT/TiO<sub>2-NTs</sub> photocatalyst was synthesized with 172 173 similarly process and proportion for MMT/TiO<sub>2</sub> photocatalysts. The contents of MMT/TiO<sub>2-NTs</sub> and MMT/TiO<sub>2</sub> were calculated based on the cation exchange capacity of 174 montmorillonite clay ( $CEC_{MMT} = 86 \text{ mmol}/100\text{g}$ ). 175

## 177 **2.5.** Photocatalysts characterizations

The characteristic vibration of functional groups in photocatalysts was characterized 178 using a Fourier transform infrared (FT-IR) spectrometer Nicolet iS 50 (FT-IR, Thermo, 179 USA) in the range 4000 to 400 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>. The structure of TiO<sub>2</sub>, 180 TiO<sub>2-NTs</sub>, MMT and nanocomposites was evaluated by X-ray diffraction using D2-181 PHASER diffractometer (Bruker, Germany) with a Ni-filtered CuK radiation ( $\lambda$ =1.54 Å) 182 at 40 kV, 40 mA, scan rate 0.030 °/sec, and scan angle  $2\theta = 5-80^\circ$ . The SEM technique 183 was used to evaluate the surface morphology of materials using a S4800 (Hitachi co., 184 Japan). Samples were fixed on an aluminum stub for scanning electronic microscope 185 using a carbon double-side tape. The following conditions were applied to obtain the 186 images: secondary electron detector, high vacuum mode, an accelerating voltage of 10 187 kV, a spot size of 3 and a work distance of approximate 9 mm. The non-conductive 188 samples were first coated with gold before being scanned. Finally, the structure of TiO<sub>2</sub>-189 NTs and the state of TiO<sub>2-TNs</sub> intercalation into MMT sheets in MMT/TiO<sub>2-TNs</sub> photocatalyst 190 are observed by JEM-1400 Transmission Electron Microscope (TEM) equipment (JEOL, 191 Japan) with an acceleration voltage 120kV. Energy-dispersive X-ray (EDX) spectroscopy 192 (HORIBA H-7593) was used to detect and quantify the metallic elemental compositions 193 in materials. The X-ray peak intensity is proportional to the percentage of elements 194 195 present in the test sample.

196

197

## **2.6.** Evaluation of the photocatalytic activity of materials

The adsorption ability and degradation of rhodamine B from dyeing wastewater of nanocomposites was evaluated in dark condition and irradiation condition by UV-C lamp, respectively. In the dark condition, 10 mg of each photocatalyst was slowly added to 100 mL of rhodamine B solution at an initial concentration of 10 ppm ( $C_o$ ) and stirred for 60 min. Then, every 30 min, 5 mL of the solution was extracted and centrifuged at 3500 rpm for 15 min to separate the material from the dye solution. The portion of the obtained solution was used to measure UV –Vis and calculate the decomposition efficiency.

For experiment with UV-C irradiation, a light source at a wavelength of 254 nm with 207 15W was used. Similar to the dark condition, 10 mg of test materials were added to 100 208 mL of rhodamine B solution. The solution was first stirred in the dark condition for 60 209 min. Then, UV-C lamp (UVC 16W - Philip) was used to light the solution. Every 30 min, 210 5 ml of solution was extracted and centrifuged at 3500 rpm for 15 min to eliminate the 211 212 solid to remove the solid. The obtained solutions in dark and UV-C irradiation conditions were then measured with UV–Vis spectrometer (Jasco V-670) with a range of 400 to 700 213 nm, step size of 0.5 nm, and scanning speed of 400 nm/min. 214

215

## 216 **3. Results and discussion**

## 217 **3.1. SEM and TEM images analysis of photocatalysts**

The mechanism of  $TiO_{2-NTs}$  formation is assumed that under hydrothermal condition, the Ti-O-Na and Ti-OH bonds are gradually formed under the influence of high concentrated NaOH solution. Then, the high surface energies of Ti-O-Na and Ti-OH lead to the coiling

and formation of TiO<sub>2-TNs</sub>. The Ti-O-Ti bonds are created after water removal and heated 221 for 2 hours at 400°C (Cui et al., 2012). TEM image of TiO<sub>2-NTs</sub> is presented in Figure 1a. 222 The TiO<sub>2-TNs</sub> are formed from different directions with relatively uniform size as an 223 average tube diameter of about 5 nm and tube length at least about 110 nm. The SEM 224 analysis of pure MMT, MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> photocatalysts is displayed in 225 Figure 1 (b-d), respectively. As showed in Figure 1b, the MMT is stacked by sheets with 226 different sizes and shapes. Figure 1c clearly displays the morphology of MMT 227 immobilized TiO<sub>2</sub> particles. The TiO<sub>2</sub> particles are evenly dispersed on the surface of 228 MMT sheets with nanosized range from 30 to 45 nm. This result is suitable with previous 229 observations (Yin et al., 2014; Shiding Miao et al., 2016; Mishra et al., 2017). However, 230 the dispersion and morphology of MMT/TiO<sub>2-NTs</sub> is much differential to MMT/TiO<sub>2</sub>, 231 where TiO<sub>2-NTs</sub> are intercalated and dispersed randomly between MMT sheets to produce 232 heterogeneous structure. The nanotubes morphology can be observed as presented in 233 234 Figure 1d. In addition, the clearly structure and morphology of MMT/TiO<sub>2-NTs</sub> photocatalyst is described through the TEM analysis in Figure 2. 235



Figure 1. The TEM image of  $TiO_{2-NTs}$  structure synthesized through hydrothermal method (a); and the SEM analysis of pure MMT (b), MMT/TiO<sub>2</sub> (c) and (d) MMT/TiO<sub>2-NTs</sub>.

This Figure highlights that  $TiO_{2-NTs}$  and MMT sheets are intercalated in MMT/TiO<sub>2-NTs</sub> photocatalyst compared to MMT sheets immobilized  $TiO_2$  particles in the MMT/TiO<sub>2</sub> photocatalyst. The MMT sheets are presented as the red-edged black blocks are surrounded by  $TiO_{2-NTs}$ . Moreover, the TEM images also presents the interface between MMT sheets and  $TiO_{2-NTs}$  as well as interface between  $TiO_{2-NTs}$ , which also allow to evaluate the connection, alignment and orientation of the  $TiO_{2-NTs}$  in the MMT/TiO<sub>2-NTs</sub> photocatalyst.





247

Figure 2: TEM images of MMT/TiO<sub>2-NTs</sub> at different magnifications

248

## 249 **3.2. XRD diffraction of photocatalysts**

The structure of MMT, TiO<sub>2</sub>, MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> was also studied by X-ray 250 diffraction as shown in Figure 3. The TiO<sub>2</sub> nanoparticles show the planes of anatase 251 crystallization consisting of the diffraction peaks at  $(2\theta)$  25.3°; 37.9°; 47.8°; 54.3°; 55° 252 and  $62.7^{\circ}$  corresponding to the network surfaces (101), (004), (200), (105), (211) and 253 (204), respectively, with a strongest peak A(101). This structure corresponds to the 254 highest photocatalytic activity of TiO<sub>2</sub> (Ayoubi-Feiz et al., 2014). For the MMT sample, 255 it has the  $d_{001}$  spacing about 14.5 Å at (2 $\theta$ ) 6,1° and other diffraction peaks are observed 256 at (2 $\theta$ ) 9.1°; 12.7°; 19.6°; 21.9°; 26.6°; and 35.0°. The two peaks at (2 $\theta$ ) 20.5° and 27.6° 257 characterize the quartz structure in MMT, which is consistent with the literature 258 (Szczepanik, 2017b). 259

The XRD pattern of MMT/TiO<sub>2</sub> nanocomposite shows the existence of mainly three phases: MMT at  $(2\theta)$  5-20°, SiO<sub>2</sub> at  $(2\theta)$  26.6° and anatase at  $(2\theta)$  25.3°, in which, the

phases MMT and SiO<sub>2</sub> are typical for MMT, and anatase represents for TiO<sub>2</sub>. In addition, the d<sub>001</sub> spacing of MMT at (2 $\theta$ ) 6.1° was shifted to an angle at (2 $\theta$ ) 6.3° in MMT/TiO<sub>2</sub> nanocomposite, which corresponds to d<sub>001</sub> spacing to 14 Å. This result shows that the immobilization of TiO<sub>2</sub> nanoparticles on the surface of MMT (Khataee et al., 2015) and a small part of TiO<sub>2</sub> has entered inside the layer structure of the MMT.



267

Figure 3. XRD diffraction patterns of different samples: (a) MMT; (b) nanocomposite
MMT/TiO<sub>2</sub>; (c) nanocomposite MMT/TiO<sub>2-NTs</sub>; and (d) nano TiO<sub>2</sub>

The XRD pattern of MMT/TiO<sub>2-NTs</sub> nanocomposite shows also the existence in three main phases as MMT/TiO<sub>2</sub> nanocomposite. However, the peak A (101) has a low intensity compared to that of TiO<sub>2</sub> sample, corresponding to a lower crystallization. This shows that during the hydrothermal process at 130°C, the crystal structure of TiO<sub>2-NTs</sub> has

been changed to reduce the anatase phase in TiO<sub>2</sub>. Moreover, the  $d_{001}$  spacing of MMT was reduced to 9.06 Å corresponding to a larger angle (2 $\theta$ ) 9.2° compared to pure MMT and MMT/TiO<sub>2</sub> nanocomposite. This could be explained by the TiO<sub>2-TNs</sub> having entered the layer structure of MMT, leading to decrease the  $d_{001}$  spacing of MMT.

279

## 280 **3.3. FTIR spectroscopy analysis of photocatalyst**

Characterization of variations on functional groups and chemical bonds of TiO<sub>2</sub>, TiO<sub>2-NTs</sub>, 281 pure MMT and their nanocomposites were evaluated through FTIR spectrum as shown in 282 Figure 4. TiO<sub>2</sub> nanoparticles has only one peak at wavenumbers of 430 cm<sup>-1</sup>, 283 corresponding to stretching vibration of Ti-O, meanwhile TiO<sub>2-NTs</sub> have adsorption band 284 at 460-908 cm<sup>-1</sup> corresponding to stretching vibration of Ti-O band (Pang and Abdullah, 285 2013; Khataee et al., 2015). TiO<sub>2-NTs</sub> has also a peak at wavenumber of 1641 cm<sup>-1</sup> could 286 be attributed to interlayer H-O-H molecules (Wang et al., 2009). A wide-bulb peak at 287 wavenumber of 3390 cm<sup>-1</sup> characterizes for the stretching vibration of -OH group on 288 surface of TiO<sub>2-TNs</sub>. 289

The pure MMT has absorbance peaks at wavenumbers 3388 cm<sup>-1</sup> and 3621 cm<sup>-1</sup> that characterize the symmetrical stretching vibration of the -OH group of H<sub>2</sub>O molecules absorbed in MMT. A vibration at wavenumber of 1639 cm<sup>-1</sup> characterizes for deformation of interlayer H–O–H molecules. A strong peak at wavenumber of 987 cm<sup>-1</sup> characterizes asymmetrical stretching vibration of -Si-O group. A peak at wavenumber of 789 cm<sup>-1</sup> characteristics of Al-O stretching vibration, a peak at wavenumber of 524 cm<sup>-1</sup> represents the Al–O–Si deformation vibration and a peak at wavenumber of 462 cm<sup>-1</sup> characteristics of Si–O–Si deformation (Liu et al., 2007; Aber et al., 2009; Khataee et al.,
2015).

In comparison to FTIR spectra of pure TiO<sub>2</sub>, TiO<sub>2-NTs</sub>, MMT and their nanocomposites, it seems that component peaks are present in the FTIR spectra of nanocomposites. It is also confirmed that the wide absorbance band of 462 - 789 cm<sup>-1</sup> correspond to the adsorption of Ti-O. However, they did not show the stretching vibration of Si-O-Ti at wavenumber around 935 cm<sup>-1</sup> (Iwasaki et al., 1994) as expected or this peak is overlapped with the strong peak of MMT or this might be due to the small proportion of TiO<sub>2</sub> in MMT.



305



308

## **310 3.4.** The chemical compositions of photocatalysts

The EXD results of MMT, MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> photocatalysts are shown in Figure 5. The chemical compositions of MMT include Al, C, Fe, K, Mg, Na, O, Si. The presence of elements K and Fe is due to the isomorphic substitution of metal cations such as  $K^+$ ,  $Fe^{2+}$ . The EDX spectra of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-TNs</sub> photocatalyst show the same chemical compositions as MMT (Al, C, Fe, K, Mg, Na, O, Si) including the appearance of Ti element. This confirms the existence of Ti in these photocatalysts.





#### 320 **3.5.** Photocatalytic performance of photocatalyst under UV-C irradiation

The photocatalytic performance of photocatalyst was determined through the 321 photodegradation of rhodamine B by measuring the UV-Vis adsorption spectra in dark 322 and UV-C irradiation. The UV-Vis adsorption spectra of rhodamine B at different 323 concentrations are shown a linear of intensity absorbance peak with rhodamine B 324 concentration with the maximum adsorption peak at a wavelength of 550 nm after 210 325 min of UV-C irradiation. This result also confirms that rhodamine B is not degraded 326 under UV-C irradiation during exposition time. In addition, UV-Vis curves of rhodamine 327 B (10 ppm) with photocatalyst under dark and UV-C irradiation conditions after 210 min 328 are plotted in Figure 6a and 6b, respectively. 329



Figure 6: UV-Vis adsorption spectra of Rhodamine B: (a) 10 ppm rhodamine B with different photocatalysts under dark condition and (b) 10 ppm rhodamine B with different photocatalysts under UV-C irradiation condition after 210 min.

Accordingly, the photocatalytic activities and efficiencies of photocatalysts are calculated and exhibited in Figure 7. The photocatalytic activities in rhodamine B degradation of

MMT, TiO<sub>2</sub>, TiO<sub>2-NTs</sub>, MMT/TiO<sub>2</sub>, and MMT/TiO<sub>2-NTs</sub> in dark condition is shown in 336 Figure 7a. The adsorption capacity of TiO<sub>2</sub> and TiO<sub>2-NTs</sub> is very low and has equal 337 efficiency (<10%). After incorporating with MMT, the adsorption efficiency is changed 338 in the following order: MMT/TiO<sub>2</sub> <MMT <MMT/TiO<sub>2-NTs.</sub> This result shows that, when 339 incorporated to MMT, TiO<sub>2-NTs</sub> has demonstrated their capacity to absorb rhodamine B 340 compared to that of MMT/TiO<sub>2</sub>. In addition, adsorption equilibrium time of MMT, 341 MMT/TiO<sub>2</sub>, and MMT/TiO<sub>2-NTs</sub> photocatalysts is about 40, 60 and 60 min, respectively. 342 The integration of TiO<sub>2</sub> and TiO<sub>2-NTs</sub> into MMT lead to increase in adsorption equilibrium 343 time, which is probably due to the dispersion of TiO<sub>2</sub> particles and TiO<sub>2-TNs</sub> into MMT 344 interlayers structure, reducing pores size, thereby extending the adsorption equilibrium 345 time. 346

The influence of UV-C irradiation to trigger a photocatalytic effect likely to degrade 347 rhodamine B of MMT, TiO<sub>2</sub>, TiO<sub>2-TNs</sub> and their incorporation with MMT sheets is shown 348 in Figure 7b. Firstly, it could be seen that the energy of UV-C irradiation alone is not 349 enough to degrade rhodamine B. The rhodamine B degradation efficiency of MMT is the 350 same without and within UV-C irradiation because MMT has only adsorption property 351 without photocatalytic property. TiO<sub>2-NTs</sub> have higher photocatalytic efficiency to degrade 352 rhodamine B than TiO<sub>2</sub> nanoparticles. In particular, the degradation efficiency of TiO<sub>2</sub> 353 354 nanoparticles increased slightly to ca. 20%, corresponding to  $C/C_0 = 0.8$  compared to less than 10% (C/C<sub>0</sub> = 0.9) without irradiation. Meanwhile, the efficiency of for  $TiO_{2-NTs}$ 355 increased significantly to 65% (C/C0 = 0.35) compared to less than 10% (0.9 C/C<sub>0</sub>) of 356 sample without UV-C irradiation. Thus, under UV-C irradiation, TiO<sub>2</sub> and TiO<sub>2-NTs</sub> are 357

able to absorb photon energy to form hydroxyl free radicals ('OH) free radicals, which aremain factors to degrade rhodamine B.

The efficiency both MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> photocatalyst are also significantly 360 increased under UV-C irradiation. It increased to 90% (C/C<sub>0</sub> = 0.1) with irradiation 361 compared to 46% (C/C<sub>0</sub> = 0.54) in dark condition for MMT/TiO<sub>2</sub> photocatalyst. 362 Similarly, it is recorded about 85% (C/C<sub>0</sub> = 0.15) compared to 73% (C/C<sub>0</sub> = 0.27) in dark 363 condition for MMT/TiO<sub>2-NTs</sub> photocatalyst. Thus, the results showed that under UV-C 364 irradiation, the photocatalytic effective of TiO<sub>2</sub> nanoparticles is increased through more 365 production of free radicals ('OH), leading to capturing and degrading of rhodamine B 366 molecules. In addition, efficiency of MMT/TiO<sub>2-NTs</sub> photocatalyst is lower than that of 367 368 MMT/TiO<sub>2</sub>. This is due to TiO<sub>2-NTs</sub> in tubular form, which was intertwined in layer structure of MMT sheets. This limits photon energy absorption of TiO<sub>2-TNs</sub>, resulting in 369 the less •OH free radical production, resulting in lower rhodamine B degradation 370 efficiency. 371





Figure 7: Photocatalytic degradation of rhodamine B with 10 ppm using different photocatalyst: (a) in the dark condition, (b) in the UV-C irradiation condition.

In addition, the photocatalytic performance of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> to rhodamine B degradation is compared to that of the TiO<sub>2</sub> based photocatalyst in the literature as exhibited in Table 1. Thus, the photocatalytic performance of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> have shown a superior efficiency in rhodamine B degradation compared to other TiO<sub>2</sub> based photocatalysts in the literature. Basically, the efficiency of rhodamine B degradation is dependent on many factors such as light source, rhodamine B concentration, and catalyst amount, etc. Indeed, these results suggest that the combination of  $TiO_2$  and  $TiO_{2-NTs}$  with MMT has significantly increased the photocatalytic efficiency

to eliminate rhodamine B from dye effluent.

384 Table 1. Photocatalytic performance of TiO<sub>2</sub> and TiO<sub>2-NTs</sub> based photocatalyst to

rhodamine B degradation compared to previous studies

Catalyst	Light source	Concentration	Catalyst	Degradation	Exposed	Ref
		(mg/L) of	amount	(%)	time	
		rhodamine B	(mg)		(min)	
TiO <sub>2</sub>	UV-C lamp	10	10	20.0	210	this
						study
TiO <sub>2-NTs</sub>	UV-C lamp	10	10	65.3	210	this
						study
MMT/TiO <sub>2</sub>	UV-C lamp	10	10	90.0	210	this
						study
MMT/TiO <sub>2</sub>	UV-C lamp	3	10	100	210	This
						study
MMT/TiO <sub>2-NTs</sub>	UV-C lamp	10	10	85.5	210	this
						study
MMT/TiO <sub>2-NTs</sub>	UV-C lamp	3	10	97.5	210	this
						study
10%MWCNT/TNT	HPMV lamp	50	50	89	60	(Natar
						ajan et
						al.,
						2017)
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	Visible	10	1.6 g/L	70	240	(Wang
						et al.,
						2012)
BiVO <sub>4</sub> /TiO <sub>2</sub>	Visible	1	-	85	120	(Hu et

						al.,
						2015)
Polyphyrin/TiO <sub>2</sub>	Incandescent	5	0.75 g/L	55.5	198	(Huan
	light					g et al.,
						2009)
B-doped TiO <sub>2</sub>	Stimulated	-	-	52	210	(Li et
	sunlight					al.,
						2013)
g-C <sub>3</sub> N <sub>4</sub> /TiO <sub>2</sub>	Visible	1		90	78	(Hao et
						al.,
						2016)

386

The reusability of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> for the rhodamine B degradation was performed by repeating the reaction for three cycles using the recovered photocatalyst under the same conditions, as shown in Figure 8. After three consecutive runs, the photocatalytic activity of MMT/TiO<sub>2</sub> was decreased by 18% and the photocatalytic activity of MMT/TiO<sub>2-NTs</sub> was decreased by 23.5%. This might be ascribed to the accumulation of photodegradation products and rhodamine B molecules on the catalyst surface which resulted in decreasing the active sites (Pannak et al., 2018).

394

395

396

397



Figure 8: Photocatalytic activity of (a) MMT/TiO<sub>2</sub> and (b) MMT/TiO<sub>2-NTs</sub> photocatalyst
for three consecutive runs with10 ppm rhodamine B.

409

## 410 **3.6.** Photocatalytic performance at different rhodamine B concentrations

The photocatalytic effectiveness of MMT/TiO2 and MMT/TiO2-NTs photocatalysts to 411 degrade rhodamine B at different concentrations under UV-C irradiation is depicted in 412 Figure 9. The weight of photocatalyst for each experiment is 10 mg. The results show 413 that MMT/TiO<sub>2</sub> photocatalyst has a higher photocatalytic efficiency to degrade 414 rhodamine B than that of MMT/TiO2-NTs photocatalyst for all rhodamine B 415 concentrations. In particular, the degradation efficiency of MMT/TiO<sub>2</sub> photocatalyst is 416 recorded at 100%, 97.5%, 90.1%, 74.8% and 70.1% corresponding to concentration at 3 417 ppm, 6 ppm, 11 ppm, 16 ppm and 18 ppm, respectively. Whereas, these values of TiO<sub>2-</sub> 418 <sub>TNs</sub>/MMT photocatalyst are recorded at 97.5%, 90.5%, 85.5%, 61.2% and 52.6%, for the 419 same concentrations. However, it could be seen that MMT/TiO<sub>2-NTs</sub> photocatalyst 420

presents a decreased efficiency at long term but seems to be slightly higher efficient at 421 short term for low concentration of rhodamine B. This is probably the dominant effect of 422 the TiO<sub>2-TNs</sub> located on the surface of MMT sheets. In general, at increasing rhodamine B 423 concentrations, the photocatalytic activity and degradation efficiency of TiO<sub>2</sub>/MMT and 424 TiO<sub>2-NTs</sub>/MMT photocatalysts decreases because of the smaller length of penetration of 425 UV in the rhodamine B solution. This means that rhodamine B molecules are adsorbed 426 onto the surface of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-TNs</sub> photocatalysts, which interferes with 427 the photon energy exposure of TiO<sub>2</sub> and TiO<sub>2-TNs</sub> on MMT surface, leading to decrease in 428 photocatalytic ability to rhodamine B degradation. In addition, it could be observed that 429 there are the combined effects; at high rhodamine B concentration, the adsorption of 430 rhodamine B by MMT is saturated, which can be seen by the attenuation observed at 431 short time. But we can still see the better effect of MMT/TiO<sub>2</sub> to degrade rhodamine B 432 over time, which is much less pronounced with MMT/TiO<sub>2-NTs</sub>. 433



#### 434

Figure 9. Degradation effectiveness of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub> photocatalysts at
different concentrations of rhodamine B under UV-C irradiation.

437

## **3.7.** The mechanism of rhodamine B degradation of photocatalyst

The mechanism of rhodamine B degradation by photocatalysts is proposed in Figure 10. The TiO<sub>2</sub> components of MMT/TiO<sub>2</sub> act as photocatalyst. Initially, the UV-C irradiation source produced high-energy photons activates to create photoinduced electrons ( $e^{-}$ ) and leave holes ( $h^+$ ) of the TiO<sub>2</sub>. The negatively charged electrons are excited to cross the band gap (E<sub>g</sub>) and jump into the conduction band (CB) leaving holes with positively

charged charges in the valence region (VB). In the presence of MMT, the generated electrons move to the empty d-orbital of the metals in MMT structure. This electron transfer process can prevent the  $e^-$  -  $h^+$  pair from recombination. Then, electrons trapped in MMT react with  $O_2$  to produce free superoxide radicals ( $^{\bullet}O_2^{-}$ ) (Xu et al., 2021). At the same time, photogenerated holes react with H<sub>2</sub>O or the adsorbed hydroxyl ions (OH<sup>-</sup>) molecules to produce hydroxyl radicals (•OH) (Sun et al., 2021). Finally, the produced free radicals ( $^{\circ}OH$ ,  $^{\circ}O_2$ , h+) with strong oxidizing ability will degrade rhodamine B molecules into degradation products (Wang et al., 2020; E et al., 2021). Thus, the free radicals (•OH and  $\bullet O_2^-$ ) attack the central carbon in the rhodamine B molecules and oxidize them to low-weight intermediates, which results in the formation of small and broken-ring compounds. In addition, the smaller compounds are degraded to CO<sub>2</sub> and H<sub>2</sub>O (Isari et al., 2018). All steps of photocatalytic process to degrade rhodamine B are summarized in following equations (1-5): 

- $TiO_2 + hv \rightarrow TiO_2 (e^- + h^+)$ (1)
- $TiO_2 (e^- + h^+) + MMT \rightarrow TiO_2 (h^+) + MMT (e^-)$ (2)
- $\operatorname{TiO}_2(h^+) + OH^- \rightarrow \operatorname{TiO}_2 + {}^{\bullet}OH$  (3)
- $\operatorname{MMT}(e^{-}) + O_2 \rightarrow \operatorname{MMT} + {}^{\bullet}O_2^{-}$  (4)
- $\bullet O_2^- + H_2 O \rightarrow \bullet OH + H^+$ (5)
- $h^+ + OH^- \rightarrow \bullet OH$  (6)
- $^{\bullet}OH/^{\bullet}O_2^{-}/h^+$  radicals + rhodamine B  $\rightarrow$  degradation products (7)



466 Figure 10: The photocatalytic mechanism of MMT/TiO<sub>2</sub> (left) and MMT/TiO<sub>2-NTs</sub> (right)
467 photocatalysts for rhodamine B degradation.

468

The degradation products with rhodamine B for at 30 min during photocatalytic process 469 were investigated using LC-MS spectrum and presented in Figure 11. Firstly, the 470 rhodamine B (A<sub>1</sub>, m/z 443) was attacked by a large number of e-, which was created by 471 MMT/TiO<sub>2</sub> or MMT/TiO<sub>2-NTs</sub>, to produce N, N, N-diethyl-N'-ethylrhodamine (A<sub>2</sub>, m/z 472 415) (Wermuth et al., 2019). Then, A<sub>2</sub> was degraded into two isomers N, N'-ethyl-473 ethylrhodamine (A<sub>3</sub>, m/z 388) and N, N- diethyl-rhodamine (A<sub>4</sub>, m/z 388) 474 (Hegazey et al., 2020). Next, A<sub>3</sub> and A<sub>4</sub> were degraded into N, N'-monomethyl-475 ethylrhodamine (A<sub>5</sub>, m/z 360) and N, N'-ethylrhodamine (A<sub>6</sub>, m/z 332) (E et al., 476 2021). Then, -NH bond of A6 was broken to form N'-ethylrhodamine (A7, m/z 477 317) and 2-(3H-xanthen-9-yl) benzoic acid (A<sub>8</sub>, m/z 302) was generated when all 478 -NH bonds were broken (E et al., 2021). 9-phenyl-3H-xanthene (A<sub>9</sub>, m/z 257) was 479 produced by breaking carboxyl group from A8. The degradation products were 480

481 benzoic acid (A<sub>10</sub>, m/z 123) (Guo et al., 2020). Finally, A<sub>10</sub> was degraded by h<sup>+</sup>,
482 O<sub>2</sub> and OH to produce CO<sub>2</sub> and H<sub>2</sub>O (Hegazey et al., 2020).



483 484

Figure 11. LC-MS spectrum of degradation products with Rh-B for at 30 min during
photocatalytic process

487

In addition, under the UVC irradiation,  $TiO_{2-NTs}$  exhibits a higher photocatalytic capacity than TiO<sub>2</sub>. However, the decomposition efficiency of MMT/TiO<sub>2-NTs</sub> is lower than that of MMT/TiO<sub>2</sub>. This suggests that the addition of TiO<sub>2-NTs</sub> into MMT leads to decrease the photocatalytic activity of TiO<sub>2-NTs</sub>. This is due to the MMT has layer structure, when TiO<sub>2-NTs</sub> are intercalated into MMT layers, the inner surface is not adequately illuminated by UV-C irradiation as described in Figure 12.



Figure 12: The illustration of photocatalytic activities of MMT/TiO<sub>2</sub> and MMT/TiO<sub>2-NTs</sub>
for rhodamine B degradation under UV-C irradiation.

Therefore, the number of absorbed photons of  $TiO_{2-NTs}$  inside is less than the outer surface, affecting the chemical transformation of the photocatalytic process. Therefore, the photocatalytic ability of  $TiO_{2-NTs}$  is limited in incorporation with MMT sheets although they have better photocatalytic effectively than TiO<sub>2</sub> nanoparticles.

511

## 512 **4. Conclusions**

In this study, bentonite mineral is purified to produce MMT clay that has good property of organic dye absorption but no photocatalytic activity. In addition, random-orientation  $TiO_{2-NTs}$  were successfully synthesized by a low-cost hydrothermal method. Assynthesized  $TiO_{2-NTs}$  were demonstrated to present much more efficient photodegradation

of rhodamine B dye in comparison with commercial TiO<sub>2</sub> nanoparticle photocatalyst. 517 However, the efficiency of rhodamine B degradation under UVC light of MMT/TiO<sub>2</sub> is 518 higher than that of MMT/TiO<sub>2-NTs</sub>. This is due to the immobilization of TiO<sub>2</sub> 519 nanoparticles at the surface of MMT sheets, so they are available for UVC light 520 absorption. Besides, the effectiveness of TiO<sub>2-NTs</sub> is lost in the presence of MMT because 521 TiO<sub>2-NTs</sub> intercalate into the MMT layers, leading to the inhibition of UVC light 522 absorption. Moreover, MMT/TiO<sub>2-NTs</sub> nanocomposite still shows a better rhodamine B 523 removal effectiveness in the initial period of 1 hour under UVC light irradiation. As a 524 result, the combination of MMT and TiO<sub>2-NTs</sub> can be applied for water treatment in short 525 time. The photocatalytic performance of MMT/TiO<sub>2</sub> reached to 100% for 3ppm and 90% 526 at 10ppm of rhodamine B, while these values are 97.5% and 85.5%, respectively, 527 recorded for MMT/TiO<sub>2-NTs</sub>. 528

## 529 **Declarations of interest**: none.

530

## 531 Acknowledgments:

This research was supported by Vietnam National University Ho Chi Minh City (VNUHCM) [grant number C2021]. The authors would like to thank Departement de la Marne,
Greater Reims, Region Grand Est and European Union with European Regional
Development Fund (ERDF Champagne Ardenne 2014-2020) for their financial support to
the Chair of Biotechnology of CentraleSupélec.

537

#### 539 **References**

- Abdi, J., Vossoughi, M., Mahmoodi, N.M., Alemzadeh, I., 2017. Synthesis of metalorganic framework hybrid nanocomposites based on GO and CNT with high adsorption
  capacity for dye removal. Chemical Engineering Journal 326, 1145-1158.
- Aber, S., Khataee, A., Sheydaei, M., 2009. Optimization of activated carbon fiber
  preparation from Kenaf using K2HPO4 as chemical activator for adsorption of phenolic
  compounds. Bioresource Technology 100, 6586-6591.
- Ayoubi-Feiz, B., Aber, S., Khataee, A., Alipour, E.J., 2014. Electrosorption and
  photocatalytic one-stage combined process using a new type of nanosized TiO
  2/activated charcoal plate electrode. Environmental Science Pollution Research 21, 85558564.
- 550 Bing, H., Qi, D., Jie, C., Wei, F., Suling, L., He-li, W., 2015. Photocatalytic Degradation
- of Methyl Orange Over Y3+ Doped TiO2 Pillared Montmorillonite. Journal of Advanced
  Oxidation Technologies 18, 98-104.
- 553 Casu, A., Lamberti, A., Stassi, S., Falqui, A., 2018. Crystallization of TiO<sub>2</sub> Nanotubes by
- In Situ Heating TEM. Nanomaterials (Basel) 8, 40.
- Charumathi, D., Das, N., 2012. Packed bed column studies for the removal of synthetic
  dyes from textile wastewater using immobilised dead C. tropicalis. Desalination 285, 2230.
- 558 Cheng, L., Zhang, D., Liao, Y., Li, F., Zhang, H., Xiang, Q., 2019. Constructing 559 functionalized plasmonic gold/titanium dioxide nanosheets with small gold nanoparticles

- for efficient photocatalytic hydrogen evolution. Journal of Colloid and Interface Science555, 94-103.
- 562 Chinh, V.D., Broggi, A., Di Palma, L., Scarsella, M., Speranza, G., Vilardi, G., Thang,
- P.N., 2018. XPS Spectra Analysis of Ti2+, Ti3+ Ions and Dye Photodegradation
  Evaluation of Titania-Silica Mixed Oxide Nanoparticles. Journal of Electronic Materials
  47, 2215-2224.
- Chinh, V.D., Hung, L.X., Di Palma, L., Hanh, V.T.H., Vilardi, G., 2019. Effect of
  Carbon Nanotubes and Carbon Nanotubes/Gold Nanoparticles Composite on the
  Photocatalytic Activity of TiO2 and TiO2-SiO2. Chemical Engineering & Technology
  42, 308-315.
- Cui, L., Hui, K., Hui, K., Lee, S., Zhou, W., Wan, Z., Thuc, C.-N.H.J.M.L., 2012. Facile
  microwave-assisted hydrothermal synthesis of TiO2 nanotubes. Materials Letters 75,
  175-178.
- Dao, M.U., Le, H.S., Hoang, H.Y., Tran, V.A., Doan, V.D., Le, T.T.N., Sirotkin, A., Le,
  V.T., 2020. Natural core-shell structure activated carbon beads derived from Litsea
  glutinosa seeds for removal of methylene blue: Facile preparation, characterization, and
  adsorption properties. Environmental Research, 110481.
- Diamond, S.A., Kennedy, A.J., Melby, N.L., Moser, R.D., Poda, A.R., Weiss, C.A.,
  Brame, J.A., 2017. Assessment of the potential hazard of nano-scale TiO2 in
  photocatalytic cement: application of a tiered assessment framework. NanoImpact 8, 1119.

- dos Santos, A.B., Cervantes, F.J., van Lier, J.B., 2007. Review paper on current
  technologies for decolourisation of textile wastewaters: Perspectives for anaerobic
  biotechnology. Bioresource Technology 98, 2369-2385.
- E, T., Xiao, X., Yang, S., 2021. A new synthesizing method of TiO2 with montmorillonite: Effective photoelectron transfer to degrade Rhodamine B. Separation and Purification Technology 258, 118070.
- Fan, L., Long, J., Gu, Q., Huang, H., Lin, H., Wang, X., 2014. Single-site nickel-grafted
  anatase TiO2 for hydrogen production: Toward understanding the nature of visible-light
  photocatalysis. Journal of Catalysis 320, 147-159.
- Farghali, A.A., Zaki, A.H., Khedr, M.H., 2014. Hydrothermally synthesized TiO2
  nanotubes and nanosheets for photocatalytic degradation of color yellow sunset.
  International Journal of Advanced Research 2, 285-291.
- 593 Guo, N., Liu, H., Fu, Y., Hu, J., 2020. Preparation of Fe2O3 nanoparticles doped with 594 In2O3 and photocatalytic degradation property for rhodamine B. Optik 201, 163537.
- Gupta, V.K., Suhas, 2009. Application of low-cost adsorbents for dye removal A
  review. Journal of Environmental Management 90, 2313-2342.
- Habila, M.A., Alothman, Z.A., El-Toni, A.M., Labis, J.P., Soylak, M., 2016. Synthesis
  and application of Fe3O4@SiO2@TiO2 for photocatalytic decomposition of organic
  matrix simultaneously with magnetic solid phase extraction of heavy metals prior to ICPMS analysis. Talanta 154, 539-547.

- Hao, R., Wang, G., Tang, H., Sun, L., Xu, C., Han, D., 2016. Template-free preparation
  of macro/mesoporous g-C3N4/TiO2 heterojunction photocatalysts with enhanced visible
  light photocatalytic activity. Applied Catalysis B-environmental 187, 47-58.
- Hassani, A., Khataee, A., Karaca, S., Fathinia, M., 2016. Heterogeneous photocatalytic
  ozonation of ciprofloxacin using synthesized titanium dioxide nanoparticles on a
  montmorillonite support: parametric studies, mechanistic analysis and intermediates
  identification. RSC Advances 6, 87569-87583.
- Hassani, A., Khataee, A., Karaca, S., Karaca, C., Gholami, P., 2017. Sonocatalytic
  degradation of ciprofloxacin using synthesized TiO2 nanoparticles on montmorillonite.
  Ultrasonics Sonochemistry 35, 251-262.
- Hegazey, R.M., Abdelrahman, E.A., Kotp, Y.H., Hameed, A.M., Subaihi, A., 2020.
  Facile fabrication of hematite nanoparticles from Egyptian insecticide cans for efficient
  photocatalytic degradation of rhodamine B dye. Journal of Materials Research and
  Technology 9, 1652-1661.
- Hu, Y., Li, D.Z., Wang, H.B., Zeng, G.P., Li, X.H., Shao, Y., 2015. Role of active
  oxygen species in the liquid-phase photocatalytic degradation of RhB using BiVO4/TiO2
  heterostructure under visible light irradiation. J. Mol. Catal. A-Chem. 408, 172-178.
- Huang, H., Gu, X., Zhou, J., Ji, K., Liu, H., Feng, Y., 2009. Photocatalytic degradation of
- Rhodamine B on TiO2 nanoparticles modified with porphyrin and iron-porphyrin.Catalysis Communications 11, 58-61.
- Huang, J., Shi, Z., Dong, X., 2016. Nickel sulfide modified TiO2 nanotubes with highly
- efficient photocatalytic H2 evolution activity. Journal of Energy Chemistry 25, 136-140.

- Isari, A.A., Payan, A., Fattahi, M., Jorfi, S., Kakavandi, B., 2018. Photocatalytic
  degradation of rhodamine B and real textile wastewater using Fe-doped TiO2 anchored
  on reduced graphene oxide (Fe-TiO2/rGO): Characterization and feasibility, mechanism
  and pathway studies. Applied Surface Science 462, 549-564.
- Iwasaki, M., Yasumori, A., Shibata, S., Yamane, M., 1994. Preparation of high
  homogeneity BaO-TiO2-SiO2 gel. Journal of Sol-Gel Science and Technology 2, 387391.
- Katheresan, V., Kansedo, J., Lau, S.Y., 2018. Efficiency of various recent wastewater
  dye removal methods: A review. Journal of Environmental Chemical Engineering 6,
  4676-4697.
- Khataee, A., Sheydaei, M., Hassani, A., Taseidifar, M., Karaca, S., 2015. Sonocatalytic
  removal of an organic dye using TiO2/Montmorillonite nanocomposite. Ultrasonics
  Sonochemistry 22, 404-411.
- Kingsley, J.J., Suresh, K., Patil, K.C., 1990. Combustion synthesis of fine particle rare
  earth orthoaluminates and yttrium aluminum garnet. Journal of Solid State Chemistry 88,
  435-442.
- Leong, S., Razmjou, A., Wang, K., Hapgood, K., Zhang, X., Wang, H., 2014. TiO2 based
  photocatalytic membranes: A review. Journal of Membrane Science 472, 167-184.
- 641 Li, L., Yang, Y., Liu, X., Fan, R., Shi, Y., Shuo, L., Zhang, L., Fan, X., Tang, P., Rui, X.,
- 642 Zhang, W., Wang, Y., Ma, L., 2013. A direct synthesis of B-doped TiO2 and its
- 643 photocatalytic performance on degradation of RhB. Applied Surface Science 265, 36-40.

- Liu, J., Li, X., Zuo, S., Yu, Y., 2007. Preparation and photocatalytic activity of silver and
  TiO2 nanoparticles/montmorillonite composites. Applied Clay Science 37, 275-280.
- Low, J., Zhang, L., Tong, T., Shen, B., Yu, J., 2018. TiO2/MXene Ti3C2 composite with
- excellent photocatalytic CO2 reduction activity. Journal of Catalysis 361, 255-266.
- Ma, X., Xiang, Q., Liao, Y., Wen, T., Zhang, H., 2018. Visible-light-driven CdSe
  quantum dots/graphene/TiO2 nanosheets composite with excellent photocatalytic activity
  for E. coli disinfection and organic pollutant degradation. Applied Surface Science 457,
  846-855.
- Malato, S., Fernández-Ibáñez, P., Maldonado, M.I., Blanco, J., Gernjak, W., 2009.
- Decontamination and disinfection of water by solar photocatalysis: Recent overview andtrends. Catalysis Today 147, 1-59.
- Mishra, A., Sharma, M., Mehta, A., Basu, S., 2017. Microwave Treated Bentonite Clay
- Based TiO2 Composites: An Efficient Photocatalyst for Rapid Degradation of Methylene
- Blue. Journal of nanoscience and nanotechnology 17, 1149-1155.
- Nagaraja, R., Kottam, N., Girija, C.R., Nagabhushana, B.M., 2012. Photocatalytic
  degradation of Rhodamine B dye under UV/solar light using ZnO nanopowder
  synthesized by solution combustion route. Powder Technology 215-216, 91-97.
- 661 Natarajan, T.S., Lee, J.Y., Bajaj, H.C., Jo, W.-K., Tayade, R.J., 2017. Synthesis of
- 662 multiwall carbon nanotubes/TiO2 nanotube composites with enhanced photocatalytic
- decomposition efficiency. Catalysis Today 282, 13-23.

- Natarajan, T.S., Thomas, M., Natarajan, K., Bajaj, H.C., Tayade, R.J., 2011. Study on
  UV-LED/TiO2 process for degradation of Rhodamine B dye. Chemical Engineering
  Journal 169, 126-134.
- 667 Nguyen Van, H., Chu Van, H., Luu Hoang, T., Vo Nguyen, D.K., Ha Thuc, C.N., 2020.
- The starch modified montmorillonite for the removal of Pb(II), Cd(II) and Ni(II) ionsfrom aqueous solutions. Arabian Journal of Chemistry 13, 7212-7223.
- Niu, X., Sun, L., Zhang, X., Sun, Y., Wang, J., 2020. Fabrication and antibacterial
  properties of cefuroxime-loaded TiO(2) nanotubes. Applied microbiology and
  biotechnology 104, 2947-2955.
- Pang, Y.L., Abdullah, A.Z., 2013. Effect of carbon and nitrogen co-doping on
  characteristics and sonocatalytic activity of TiO2 nanotubes catalyst for degradation of
  Rhodamine B in water. Chemical Engineering Journal 214, 129-138.
- Pannak, P., Songsasen, A., Foytong, W., Kidkhunthod, P., Sirisaksoontorn, W., 2018.
  Homogeneous distribution of nanosized ZnO in montmorillonite clay sheets for the
  photocatalytic enhancement in degradation of Rhodamine B. Research on Chemical
  Intermediates 44, 6861-6875.
- Park, D.J., Sekino, T., Tsukuda, S., Hayashi, A., Kusunose, T., Tanaka, S.-I., 2011.
  Photoluminescence of samarium-doped TiO2 nanotubes. Journal of Solid State
  Chemistry 184, 2695-2700.
- Rauf, M.A., Salman Ashraf, S., 2012. Survey of recent trends in biochemically assisted
  degradation of dyes. Chemical Engineering Journal 209, 520-530.

- Robinson, T., McMullan, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in
  textile effluent: a critical review on current treatment technologies with a proposed
  alternative. Bioresource Technology 77, 247-255.
- Sasani, A., Baktash, A., Mirabbaszadeh, K., Khoshnevisan, B., 2016. Structural and
  electronic properties of Mg and Mg-Nb co-doped TiO2 (101) anatase surface. Applied
  Surface Science 384, 298-303.
- Shan, R., Lu, L., Gu, J., Zhang, Y., Yuan, H., Chen, Y., Luo, B., 2020. Photocatalytic
  degradation of methyl orange by Ag/TiO2/biochar composite catalysts in aqueous
  solutions. Materials Science in Semiconductor Processing 114, 105088.
- Shi, L., Liang, L., Ma, J., Meng, Y., Zhong, S., Wang, F., Sun, J., 2014. Highly efficient
  visible light-driven Ag/AgBr/ZnO composite photocatalyst for degrading Rhodamine B.
  Ceramics International 40, 3495-3502.
- 697 Shiding Miao, Zhimin Liu, Buxing Han, Jianling Zhang, Xin Yu, Jimin Du, Zhenyu Sun,
- 698 2016. Synthesis and characterization of TiO2–montmorillonite nanocomposites and their
- application for removal of methylene blue. Journal of Materials Chemistry 16, 579-584.
- 700 Sun, B., Qiu, P., Liang, Z., Xue, Y., Zhang, X., Yang, L., Cui, H., Tian, J., 2021. The
- fabrication of 1D/2D CdS nanorod@Ti3C2 MXene composites for good photocatalytic
  activity of hydrogen generation and ammonia synthesis. Chemical Engineering Journal
  406, 127177.
- Szczepanik, B., 2017a. Photocatalytic degradation of organic contaminants over clayTiO2 nanocomposites: A review. Applied Clay Science 141, 227-239.

- Szczepanik, B., 2017b. Photocatalytic degradation of organic contaminants over clay-TiO
  2 nanocomposites: A review. Applied Clay Science 141, 227-239.
- Tahir, M., Amin, N.S., 2016. Performance analysis of nanostructured NiO–In2O3/TiO2
- catalyst for CO2 photoreduction with H2 in a monolith photoreactor. ChemicalEngineering Journal 285, 635-649.
- Thuc, C.-N.H., Grillet, A.-C., Reinert, L., Ohashi, F., Thuc, H.H., Duclaux, L., 2010.
  Separation and purification of montmorillonite and polyethylene oxide modified
  montmorillonite from Vietnamese bentonites. Applied Clay Science 49, 229-238.
- Wang, H., Wang, H.-L., Jiang, W.-F., Li, Z.-Q., 2009. Photocatalytic degradation of 2,4dinitrophenol (DNP) by multi-walled carbon nanotubes (MWCNTs)/TiO2 composite in
  aqueous solution under solar irradiation. Water Research 43, 204-210.
- Wang, R., Shi, M., Xu, F., Qiu, Y., Zhang, P., Shen, K., Zhao, Q., Yu, J., Zhang, Y.,
  2020. Graphdiyne-modified TiO2 nanofibers with osteoinductive and enhanced
  photocatalytic antibacterial activities to prevent implant infection. Nature
  Communications 11, 4465.
- Wang, Y., Zhang, J., Liu, L., Zhu, C., Liu, X., Su, Q., 2012. Visible light photocatalysis
  of V2O5/TiO2 nanoheterostructures prepared via electrospinning. Materials Letters 75,
  95-98.
- Wermuth, T.B., Arcaro, S., Venturini, J., Hubert Ribeiro, T.M., de Assis Lawisch
  Rodriguez, A., Machado, E.L., Franco de Oliveira, T., Franco de Oliveira, S.E., Baibich,
  M.N., Bergmann, C.P., 2019. Microwave-synthesized KNbO3 perovskites: photocatalytic
- pathway on the degradation of rhodamine B. Ceramics International 45, 24137-24145.

- Wong, C.L., Tan, Y.N., Mohamed, A.R., 2011. A review on the formation of titania
  nanotube photocatalysts by hydrothermal treatment. Journal of Environmental
  Management 92, 1669-1680.
- 731 Xu, R., Wei, N., Li, Z., Song, X., Li, Q., Sun, K., Yang, E., Gong, L., Sui, Y., Tian, J.,
- Wang, X., Zhao, M., Cui, H., 2021. Construction of hierarchical 2D/2D Ti3C2/MoS2
  nanocomposites for high-efficiency solar steam generation. Journal of Colloid and
  Interface Science 584, 125-133.
- 735 Xu, X., Zhou, X., Li, X., Yang, F., Jin, B., Xu, T., Li, G., Li, M., 2014. Electrodeposition
- synthesis of MnO2/TiO2 nanotube arrays nanocomposites and their visible light
  photocatalytic activity. Materials Research Bulletin 59, 32-36.
- 738 Yin, J., Guo, H., Liu, Y., Kong, Y., Xia, X., Yao, L., Su, B., Wang, Y., Cao, Y., 2014.
- 739 Effect of MMT content on structure of polyimide/(TiO2+MMT) nanocomposite films.
- 740 2014 9th International Forum on Strategic Technology (IFOST), pp. 475-478.
- Zhang, J., Zhang, Z., Zhu, W., Meng, X., 2020. Boosted photocatalytic degradation of
  Rhodamine B pollutants with Z-scheme CdS/AgBr-rGO nanocomposite. Applied Surface
- 743 Science 502, 144275.
- 744