



HAL
open science

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-03547560v1>

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 CC BY-NC 4.0 - Attribution - Non-commercial use - International License

1 **Effectiveness of photocatalysis of Montmorillonite-supported TiO₂ and TiO₂**
2 **nanotubes for rhodamine B degradation**

3 Thi Bang Tam Dao^{a,b}, Thi Thu Loan Ha^{a,b}, Trung Do Nguyen^{a,b}, Hon Nhien Le^{a,b}, Chi
4 Nhan Ha-Thuc^{a,b*}, Thi Mai Loan Nguyen^c, Patrick Perre^{d*}, Dang Mao Nguyen^{d*}

5 ^aFaculty 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 ^bVietnam National University – Ho Chi Minh City, Linh Trung Ward, Thu Duc District,
8 Ho Chi Minh City, 700000, Viet Nam

9 ^cInstitute of Research and Development, Duy Tan University, Da Nang 550000, Viet
10 Nam.

11 ^dUniversité 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/TiO₂-nanotubes (MMT/TiO₂-NTs) photocatalysts through a simple
21 wet agitation method based on TiO₂ nanoparticles and MMT. They are likely to
22 accumulate the effect of adsorption and photodegradation. Then, the photocatalysts are

23 applied to degrade the rhodamine B in dye effluents. The structural characterizations of
24 photocatalysts are investigated using transmission electron microscopy (TEM), scanning
25 electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared
26 spectroscopy (FTIR) and energy-dispersive X-ray spectroscopy (EDX). The
27 photocatalytic activities and effectiveness of photocatalysts are evaluated through
28 rhodamine B degradation at different concentrations under dark and UV-C irradiation
29 conditions. The results show that the synthesized $\text{TiO}_2\text{-NTs}$ have an average tube diameter
30 of 5 nm and a tube length at least about 110 nm, which are intercalated into MMT sheets
31 in $\text{MMT/TiO}_2\text{-NTs}$ photocatalyst. Meanwhile, TiO_2 nanoparticles are immobilized on the
32 surface of MMT sheets in the MMT/TiO_2 photocatalyst. The photocatalytic effectiveness
33 of rhodamine B degradation of $\text{TiO}_2\text{-NTs}$ shows a significantly enhance compared to that
34 of TiO_2 nanoparticles. However, photocatalytic performance of $\text{MMT/TiO}_2\text{-NTs}$ is lower
35 than that of MMT/TiO_2 . The degradation effectiveness of MMT/TiO_2 photocatalyst
36 reaches to 100% for 3ppm and 90% at 10ppm of rhodamine B, while these values are
37 97.5% and 85.5%, respectively, recorded for $\text{MMT/TiO}_2\text{-NTs}$.

38 **Keywords:** *Photocatalysts, UV-C irradiation, TiO_2 nanotubes, MMT/TiO_2 and*
39 *$\text{MMT/TiO}_2\text{-NTs}$, and rhodamine B.*

40

41 **1. Introduction**

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

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

67 CdS, and Fe₂O₃ (Hassani et al., 2017; Pannak et al., 2018). Titanium dioxide (TiO₂) is
68 known as a potential photocatalyst in the field of environmental cleaning because of its
69 chemical and biological inertness, ease of fabrication, non-toxicity, abundance in
70 availability and low cost (Hassani et al., 2017; Chinh et al., 2018; Chinh et al., 2019). In
71 particular, TiO₂ has been widely studied for photocatalysis (Fan et al., 2014; Huang et al.,
72 2016; Tahir and Amin, 2016). However, TiO₂ has limitations in photocatalytic
73 applications due to the rapid recombination between electron and holes pairs, which
74 cause to reduce photocatalytic efficiency. Moreover, it also has a wide band gap that only
75 active photocatalyst in the ultraviolet light (less than 5% of the entire solar energy),
76 inducing a lower photocatalytic activity (Leong et al., 2014; Diamond et al., 2017). To
77 overcome the above limitations, some approaches are proposed to improve the
78 photocatalytic activity. Specifically, TiO₂ nanosheets were used as an electron mediator
79 to prepare the CdSe/graphene/TiO₂ nanosheet composite photocatalysts. They provided a
80 great efficient charge separation, extended visible-light absorption range and stability for
81 the degradation of methylene blue in aqueous solutions (Ma et al., 2018). Moreover, the
82 TiO₂ nanosheets were combined with small plasmonic Au nanoparticles to improve the
83 photocatalytic rate of hydrogen production through the large surface adsorptive sites for
84 reactant adsorption and enhancing the charge separation through the Schottky transfer
85 hub to neighboring TiO₂ nanosheets (Cheng et al., 2019). It could be combined with
86 different semiconducting materials (Zhang et al., 2020) to prevent reuniting the
87 photogenerated electron-hole pairs (Dao et al., 2020) and improve the photocatalytic
88 activities (Low et al., 2018). TiO₂-NTs are synthesized through hydrothermal method from

89 TiO₂. They can improve the photocatalytic activity due to large specific surface area, ion
90 exchange capacity, and fast electronic transfer over a long distance, and high adsorption
91 of light due to a large ratio between the length and diameter of the tubes. Specially, all
92 these properties could be obtained and controlled through the synthesis method (Casu et
93 al., 2018; Niu et al., 2020). Unfortunately, similar to most semiconductor materials used
94 as photocatalyst, TiO₂-TN_s are also difficult in separating the electron–hole pairs, leading
95 to reduce photocatalytic activity. Therefore, some strategies have been proposed to
96 extend the lifetime of photoinduced charge carriers and enhance photocatalytic activities
97 including doping metal (Park et al., 2011; Sasani et al., 2016), metal oxides (Xu et al.,
98 2014; Habila et al., 2016) and non-metals such as Zeolite, and Carbon and
99 Montmorillonite (MMT) (Yin et al., 2014; Hassani et al., 2016). MMT is purified from
100 bentonite and available in large reserves from natural mineral sources (Thuc et al., 2010).
101 Specially, it combines a low cost with interesting properties due to its layered structure,
102 large surface area, cation exchange ability and high heat resistance. It is considered as
103 potential material to be combined with TiO₂ and TiO₂-NT_s to create novel materials, which
104 could be used to degrade and store pollutants and toxic agents in wastewater (Hassani et
105 al., 2017; Szczepanik, 2017a; Shan et al., 2020). In the literature, a study has successfully
106 synthesized MMT/TiO₂ from Tetraethyl orthotitanate for Ciprofloxacin (CIP) treatment.
107 The results showed that the CIP degradable efficiency of MMT/TiO₂ nanocomposites
108 reached up to 65.01% after 120 min adsorption time, which was much higher than that of
109 MMT or TiO₂ only (Hassani et al., 2017). The photocatalytic effect of TiO₂/MMT doping
110 with Y³⁺ (Yttrium) into TiO₂ for Methyl Orange (MO) treatment was reported (Bing et

111 al., 2015). Thus, Y^{3+} reduces the band gap to increase the photocatalytic capacity of TiO_2 ,
112 leading to increase the efficiency of MO degradation. In addition, MMT/ TiO_2
113 nanocomposite was produced by hydrothermal method to obtain the TiO_2 particles range
114 about 40-60 nm to treat Basic Blue 3 (BB3) (Khataee et al., 2015). The results showed
115 that the photocatalytic performance of MMT/ TiO_2 was much higher than that of MMT
116 and TiO_2 under different pH and BB3 concentration. In addition, it was reported that
117 rhodamine B was degraded by various photocatalysts, which was clearly described in
118 previous literature (Natarajan et al., 2011; Shi et al., 2014; Wang et al., 2020). The
119 degradation process could be explained by the fact that the active radicals such as
120 hydroxyl free radicals ($\bullet OH$), and free superoxide radicals ($\bullet O_2^-$), attack the central
121 carbon in the rhodamine B molecules and oxidize them to low-weight intermediates. In
122 the opening-ring process, the active radicals attack the simple intermediates that are
123 produced, which results in the formation of small and broken-ring compounds. The
124 smaller compounds are degraded to CO_2 and H_2O .

125 In this paper, we will synthesis of MMT/ TiO_2 and MMT/ TiO_{2-NTs} photocatalysts with a
126 low-cost hydrothermal method. These combinations could maximize the photocatalytic
127 capabilities under dark and UV-C irradiation conditions for rhodamine B degradation at
128 different concentrations from dyeing wastewater compared to TiO_2 and TiO_{2-TNs} only,
129 because they are likely to slowdown of electron and holes pairs recombination.

130 Moreover, the reusability of MMT/ TiO_2 and MMT/ TiO_{2-NTs} for the rhodamine B
131 degradation was repeated three time under the same conditions to evaluate the stability of
132 the photocatalytic activities.

133 **2. Materials and experiment**

134 **2.1. Materials**

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

138

139 **2.2. MMT preparation**

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

148

149 **2.3. Preparation of TiO₂-NTs**

150 TiO₂-NTs were synthesized by hydrothermal method from TiO₂ powder with particle size
151 in the range of 50-60 nm. 4.2 g of TiO₂ powder was added slowly into 10M NaOH
152 solution with TiO₂/NaOH molar ratio of 1/30 and stirred for 4 hours at 50°C. The
153 suspension solution obtained was poured into a Teflon flask, which was then inserted into
154 a stainless-steel jar and sealed. Hydrothermal process was then performed at 130°C for 24

155 hours in an autoclave before cooling to the room temperature. The product after
156 hydrothermal process was filtered and washed with deionized water to reach a pH = 9.
157 The solid product was then dispersed in deionized water and adjusted to pH = 7 with 2M
158 HNO₃ solution and stirring for 2 hours before centrifuging to obtain solid product. Once
159 again, the product was dispersed into deionized water at 80°C and stirred to remove the
160 salt formed during the above reaction. The solid product was then obtained by
161 centrifugation for 15 min and dried at 60°C for 24 hours. Finally, the product was heated
162 at 400°C with a heating rate of 5 °/min and maintained at the final temperature for 2 hours
163 to obtain TiO_{2-TNs} (Wong et al., 2011; Farghali et al., 2014).

164

165 **2.4. Preparation of MMT/TiO₂ and MMT/TiO_{2-TNs} photocatalysts**

166 2.00 g of MMT was slowly added to 100 mL of deionized water and mechanical stirred
167 500rpm for 24 hours to allow MMT to expand completely. Then, 0.206 g TiO₂ was added
168 slowly to the above MMT suspension and stirred 500 rpm for 4 hours. This suspension
169 solution was then treated by ultrasound (UPH100) at 100 W and frequency 30 kHz for 1
170 hour . The product was obtained through centrifugation process with a rotating speed of
171 3500 rpm for 15 min. Finally, the product was dried at 80°C in an oven for 24 hours to
172 obtain MMT/TiO₂ photocatalyst. MMT/TiO_{2-NTs} photocatalyst was synthesized with
173 similarly process and proportion for MMT/TiO₂ photocatalysts. The contents of
174 MMT/TiO_{2-NTs} and MMT/TiO₂ were calculated based on the cation exchange capacity of
175 montmorillonite clay (CEC_{MMT} = 86 mmol/100g).

176

2.5. Photocatalysts characterizations

The characteristic vibration of functional groups in photocatalysts was characterized using a Fourier transform infrared (FT-IR) spectrometer Nicolet iS 50 (FT-IR, Thermo, USA) in the range 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} . The structure of TiO_2 , $\text{TiO}_2\text{-NTs}$, MMT and nanocomposites was evaluated by X-ray diffraction using D2-PHASER diffractometer (Bruker, Germany) with a Ni-filtered CuK radiation ($\lambda=1.54 \text{ \AA}$) at 40 kV, 40 mA, scan rate 0.030 $^\circ/\text{sec}$, and scan angle $2\theta = 5\text{-}80^\circ$. The SEM technique was used to evaluate the surface morphology of materials using a S4800 (Hitachi co., Japan). Samples were fixed on an aluminum stub for scanning electronic microscope using a carbon double-side tape. The following conditions were applied to obtain the images: secondary electron detector, high vacuum mode, an accelerating voltage of 10 kV, a spot size of 3 and a work distance of approximate 9 mm. The non-conductive samples were first coated with gold before being scanned. Finally, the structure of $\text{TiO}_2\text{-NTs}$ and the state of $\text{TiO}_2\text{-TNs}$ intercalation into MMT sheets in $\text{MMT}/\text{TiO}_2\text{-TNs}$ photocatalyst are observed by JEM-1400 Transmission Electron Microscope (TEM) equipment (JEOL, Japan) with an acceleration voltage 120kV. Energy-dispersive X-ray (EDX) spectroscopy (HORIBA H-7593) was used to detect and quantify the metallic elemental compositions in materials. The X-ray peak intensity is proportional to the percentage of elements present in the test sample.

196

197

198

199 **2.6. Evaluation of the photocatalytic activity of materials**

200 The adsorption ability and degradation of rhodamine B from dyeing wastewater of
201 nanocomposites was evaluated in dark condition and irradiation condition by UV-C lamp,
202 respectively. In the dark condition, 10 mg of each photocatalyst was slowly added to 100
203 mL of rhodamine B solution at an initial concentration of 10 ppm (C_0) and stirred for 60
204 min. Then, every 30 min, 5 mL of the solution was extracted and centrifuged at 3500 rpm
205 for 15 min to separate the material from the dye solution. The portion of the obtained
206 solution was used to measure UV-Vis and calculate the decomposition efficiency.

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

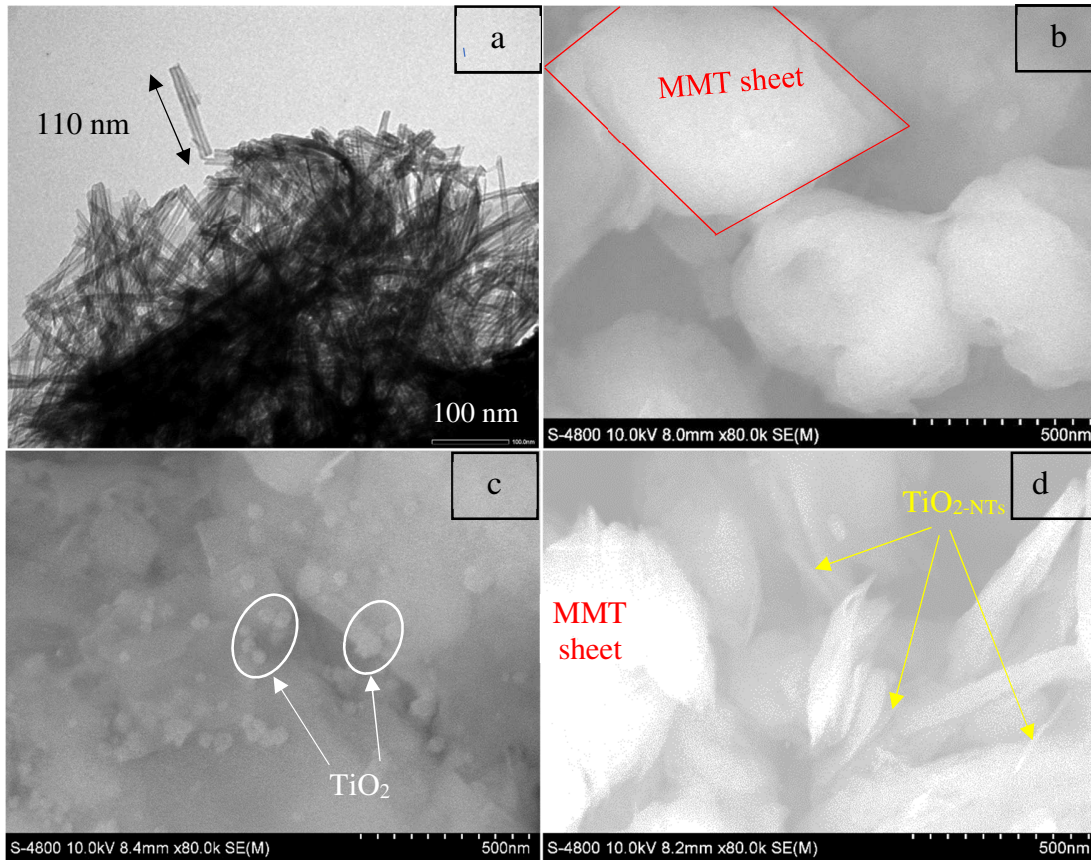
215

216 **3. Results and discussion**

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

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

221 and formation of $\text{TiO}_2\text{-TNs}$. The Ti-O-Ti bonds are created after water removal and heated
222 for 2 hours at 400°C (Cui et al., 2012). TEM image of $\text{TiO}_2\text{-NTs}$ is presented in Figure 1a.
223 The $\text{TiO}_2\text{-TNs}$ are formed from different directions with relatively uniform size as an
224 average tube diameter of about 5 nm and tube length at least about 110 nm. The SEM
225 analysis of pure MMT, MMT/ TiO_2 and MMT/ $\text{TiO}_2\text{-NTs}$ photocatalysts is displayed in
226 Figure 1 (b-d), respectively. As showed in Figure 1b, the MMT is stacked by sheets with
227 different sizes and shapes. Figure 1c clearly displays the morphology of MMT
228 immobilized TiO_2 particles. The TiO_2 particles are evenly dispersed on the surface of
229 MMT sheets with nanosized range from 30 to 45 nm. This result is suitable with previous
230 observations (Yin et al., 2014; Shiding Miao et al., 2016; Mishra et al., 2017). However,
231 the dispersion and morphology of MMT/ $\text{TiO}_2\text{-NTs}$ is much differential to MMT/ TiO_2 ,
232 where $\text{TiO}_2\text{-NTs}$ are intercalated and dispersed randomly between MMT sheets to produce
233 heterogeneous structure. The nanotubes morphology can be observed as presented in
234 Figure 1d. In addition, the clearly structure and morphology of MMT/ $\text{TiO}_2\text{-NTs}$
235 photocatalyst is described through the TEM analysis in Figure 2.



236

237 Figure 1. The TEM image of TiO₂-NTs structure synthesized through hydrothermal method

238 (a); and the SEM analysis of pure MMT (b), MMT/TiO₂ (c) and (d) MMT/TiO₂-NTs.

239 This Figure highlights that TiO₂-NTs and MMT sheets are intercalated in MMT/TiO₂-NTs

240 photocatalyst compared to MMT sheets immobilized TiO₂ particles in the MMT/TiO₂

241 photocatalyst. The MMT sheets are presented as the red-edged black blocks are

242 surrounded by TiO₂-NTs. Moreover, the TEM images also presents the interface between

243 MMT sheets and TiO₂-NTs as well as interface between TiO₂-NTs, which also allow to

244 evaluate the connection, alignment and orientation of the TiO₂-NTs in the MMT/TiO₂-NTs

245 photocatalyst.

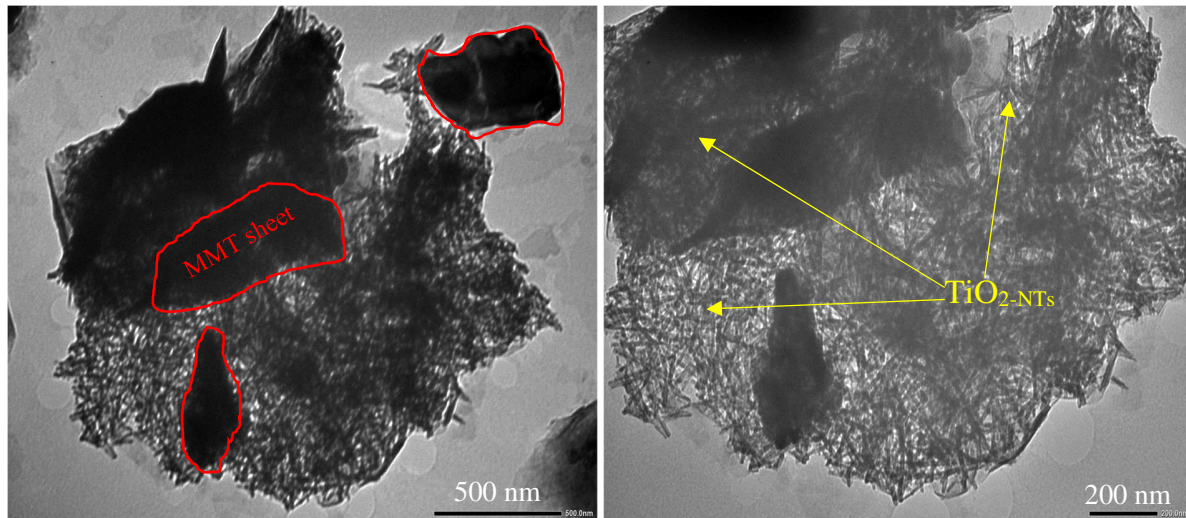


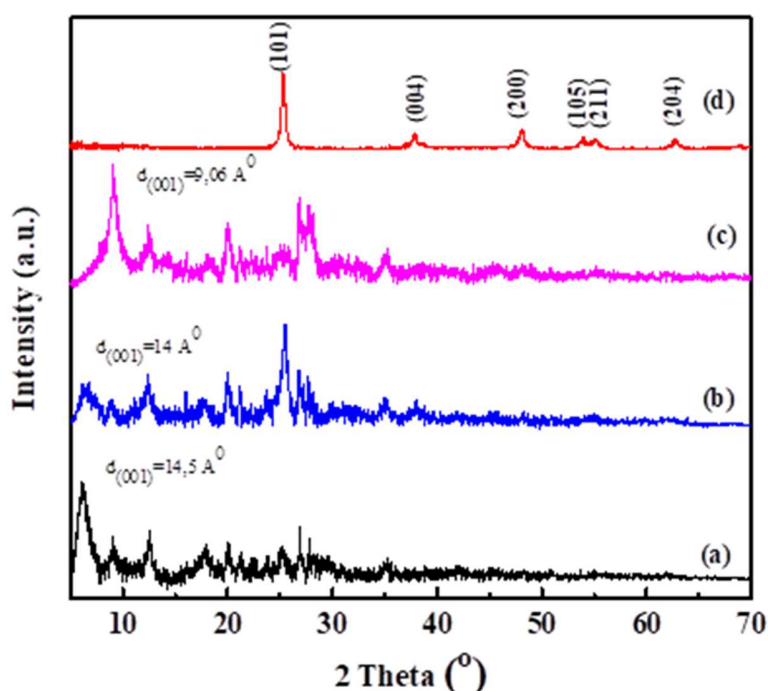
Figure 2: TEM images of MMT/TiO₂-NTs at different magnifications

3.2. XRD diffraction of photocatalysts

The structure of MMT, TiO₂, MMT/TiO₂ and MMT/TiO₂-NTs was also studied by X-ray diffraction as shown in Figure 3. The TiO₂ nanoparticles show the planes of anatase crystallization consisting of the diffraction peaks at (2 θ) 25.3°; 37.9°; 47.8°; 54.3°; 55° and 62.7° corresponding to the network surfaces (101), (004), (200), (105), (211) and (204), respectively, with a strongest peak A(101). This structure corresponds to the highest photocatalytic activity of TiO₂ (Ayoubi-Feiz et al., 2014). For the MMT sample, it has the d₀₀₁ spacing about 14.5 Å at (2 θ) 6,1° and other diffraction peaks are observed at (2 θ) 9.1°; 12.7°; 19.6°; 21.9°; 26.6°; and 35.0°. The two peaks at (2 θ) 20.5° and 27.6° characterize the quartz structure in MMT, which is consistent with the literature (Szczepanik, 2017b).

The XRD pattern of MMT/TiO₂ nanocomposite shows the existence of mainly three phases: MMT at (2 θ) 5-20°, SiO₂ at (2 θ) 26.6° and anatase at (2 θ) 25.3°, in which, the

262 phases MMT and SiO₂ are typical for MMT, and anatase represents for TiO₂. In addition,
 263 the d₀₀₁ spacing of MMT at (2θ) 6.1° was shifted to an angle at (2θ) 6.3° in MMT/TiO₂
 264 nanocomposite, which corresponds to d₀₀₁ spacing to 14 Å. This result shows that the
 265 immobilization of TiO₂ nanoparticles on the surface of MMT (Khataee et al., 2015) and a
 266 small part of TiO₂ has entered inside the layer structure of the MMT.



267
 268 Figure 3. XRD diffraction patterns of different samples: (a) MMT; (b) nanocomposite
 269 MMT/TiO₂; (c) nanocomposite MMT/TiO₂-NTs; and (d) nano TiO₂

270
 271 The XRD pattern of MMT/TiO₂-NTs nanocomposite shows also the existence in three
 272 main phases as MMT/TiO₂ nanocomposite. However, the peak A (101) has a low
 273 intensity compared to that of TiO₂ sample, corresponding to a lower crystallization. This
 274 shows that during the hydrothermal process at 130°C, the crystal structure of TiO₂-NTs has

275 been changed to reduce the anatase phase in TiO₂. Moreover, the d₀₀₁ spacing of MMT
276 was reduced to 9.06 Å corresponding to a larger angle (2θ) 9.2° compared to pure MMT
277 and MMT/TiO₂ nanocomposite. This could be explained by the TiO₂-TNs having entered
278 the layer structure of MMT, leading to decrease the d₀₀₁ spacing of MMT.

279

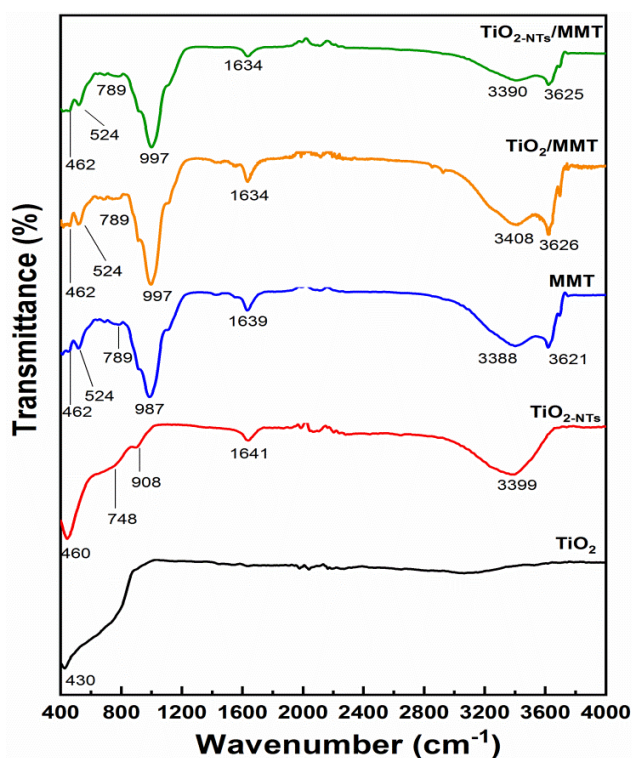
280 **3.3. FTIR spectroscopy analysis of photocatalyst**

281 Characterization of variations on functional groups and chemical bonds of TiO₂, TiO₂-NTs,
282 pure MMT and their nanocomposites were evaluated through FTIR spectrum as shown in
283 Figure 4. TiO₂ nanoparticles has only one peak at wavenumbers of 430 cm⁻¹,
284 corresponding to stretching vibration of Ti-O, meanwhile TiO₂-NTs have adsorption band
285 at 460-908 cm⁻¹ corresponding to stretching vibration of Ti-O band (Pang and Abdullah,
286 2013; Khataee et al., 2015). TiO₂-NTs has also a peak at wavenumber of 1641 cm⁻¹ could
287 be attributed to interlayer H-O-H molecules (Wang et al., 2009). A wide-bulb peak at
288 wavenumber of 3390 cm⁻¹ characterizes for the stretching vibration of -OH group on
289 surface of TiO₂-TNs.

290 The pure MMT has absorbance peaks at wavenumbers 3388 cm⁻¹ and 3621 cm⁻¹ that
291 characterize the symmetrical stretching vibration of the -OH group of H₂O molecules
292 absorbed in MMT. A vibration at wavenumber of 1639 cm⁻¹ characterizes for
293 deformation of interlayer H-O-H molecules. A strong peak at wavenumber of 987 cm⁻¹
294 characterizes asymmetrical stretching vibration of -Si-O group. A peak at wavenumber of
295 789 cm⁻¹ characteristics of Al-O stretching vibration, a peak at wavenumber of 524 cm⁻¹
296 represents the Al-O-Si deformation vibration and a peak at wavenumber of 462 cm⁻¹

297 characteristics of Si–O–Si deformation (Liu et al., 2007; Aber et al., 2009; Khataee et al.,
298 2015).

299 In comparison to FTIR spectra of pure TiO₂, TiO₂-NTs, MMT and their nanocomposites, it
300 seems that component peaks are present in the FTIR spectra of nanocomposites. It is also
301 confirmed that the wide absorbance band of 462 – 789 cm⁻¹ correspond to the adsorption
302 of Ti-O. However, they did not show the stretching vibration of Si-O-Ti at wavenumber
303 around 935 cm⁻¹ (Iwasaki et al., 1994) as expected or this peak is overlapped with the
304 strong peak of MMT or this might be due to the small proportion of TiO₂ in MMT.



305
306 **Figure 4.** FT-IR spectra of different samples: (a) MMT, (b) nanocomposite MMT/TiO₂,
307 (c) nanocomposite MMT/TiO₂-NTs, (d) nano TiO₂ and (e) TiO₂-NTs

308
309

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

311 The EXD results of MMT, MMT/TiO₂ and MMT/TiO₂-NTs photocatalysts are shown in
312 Figure 5. The chemical compositions of MMT include Al, C, Fe, K, Mg, Na, O, Si. The
313 presence of elements K and Fe is due to the isomorphous substitution of metal cations such
314 as K⁺, Fe²⁺. The EDX spectra of MMT/TiO₂ and MMT/TiO₂-TNs photocatalyst show the
315 same chemical compositions as MMT (Al, C, Fe, K, Mg, Na, O, Si) including the
316 appearance of Ti element. This confirms the existence of Ti in these photocatalysts.

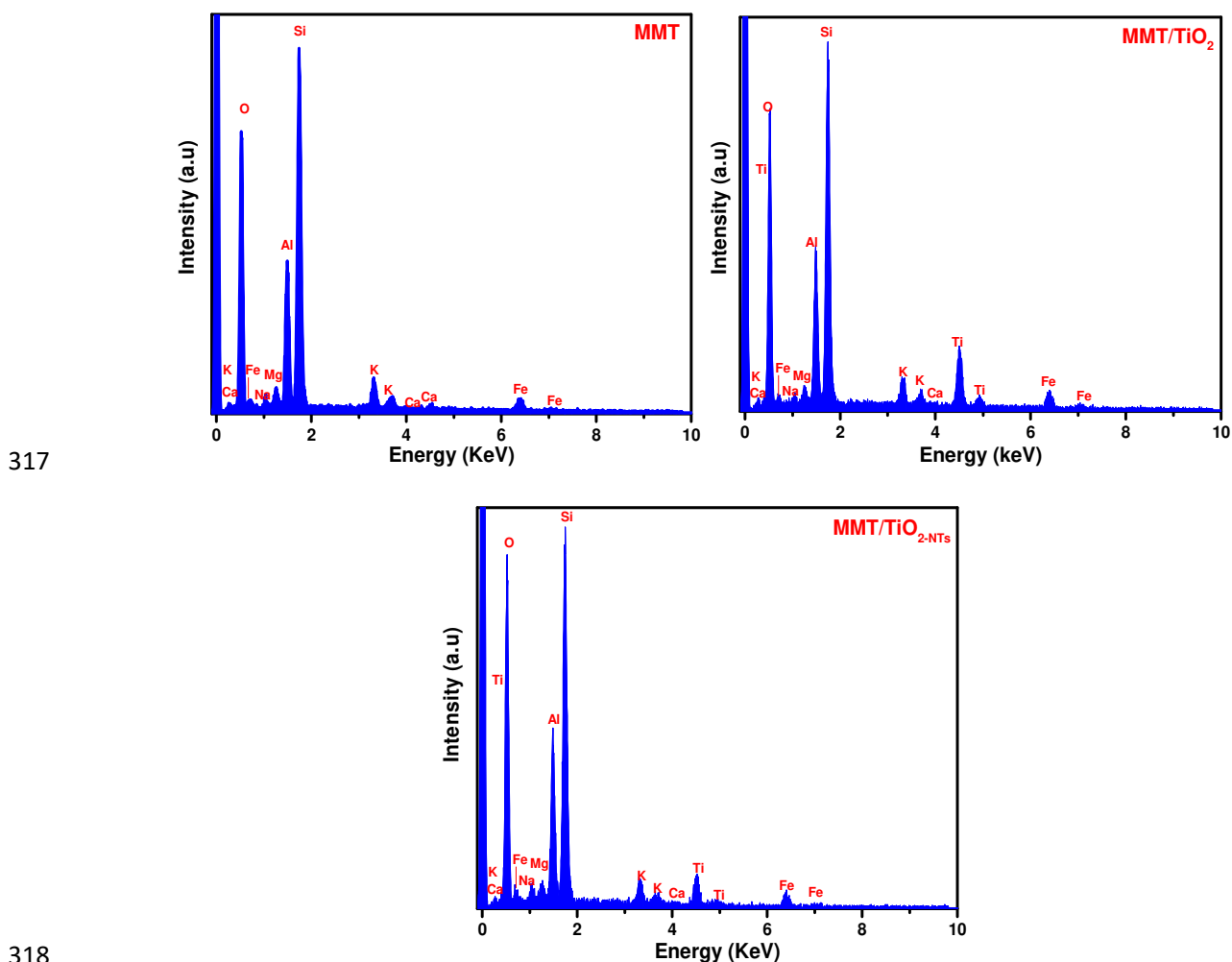
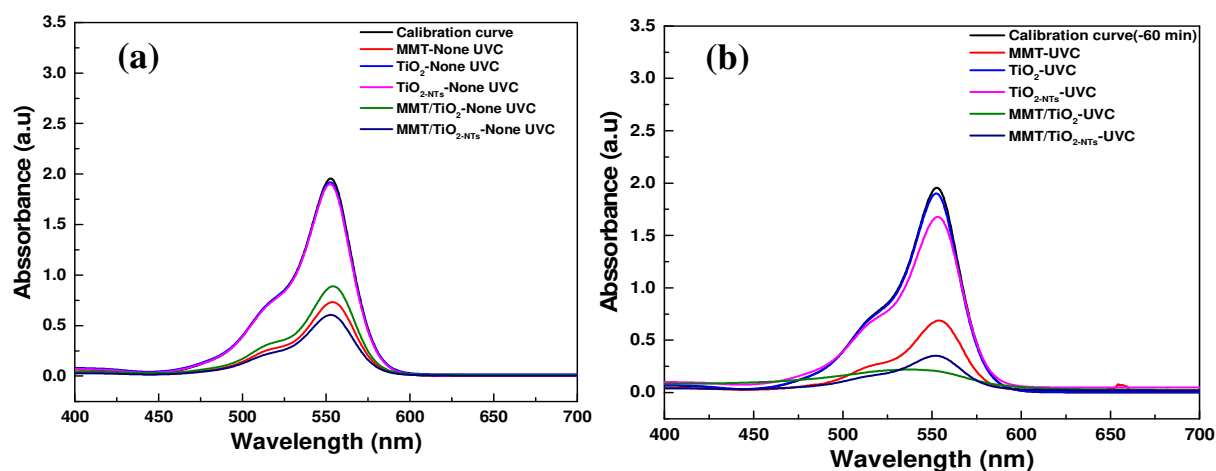


Figure 5: The EXD spectra of MMT, MMT/TiO₂, and MMT/TiO₂-TNs photocatalysts

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

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



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

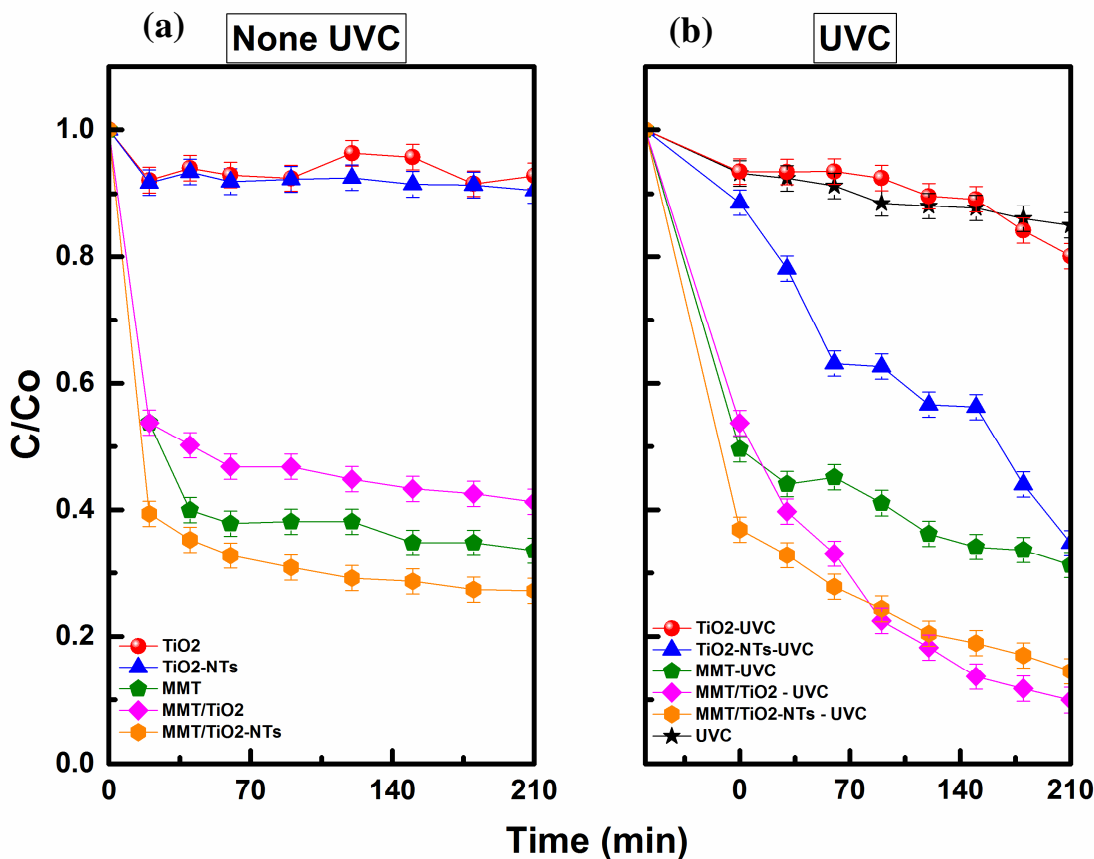
334 Accordingly, the photocatalytic activities and efficiencies of photocatalysts are calculated
335 and exhibited in Figure 7. The photocatalytic activities in rhodamine B degradation of

336 MMT, TiO₂, TiO_{2-NTs}, MMT/TiO₂, and MMT/TiO_{2-NTs} in dark condition is shown in
337 Figure 7a. The adsorption capacity of TiO₂ and TiO_{2-NTs} is very low and has equal
338 efficiency (<10%). After incorporating with MMT, the adsorption efficiency is changed
339 in the following order: MMT/TiO₂ < MMT < MMT/TiO_{2-NTs}. This result shows that, when
340 incorporated to MMT, TiO_{2-NTs} has demonstrated their capacity to absorb rhodamine B
341 compared to that of MMT/TiO₂. In addition, adsorption equilibrium time of MMT,
342 MMT/TiO₂, and MMT/TiO_{2-NTs} photocatalysts is about 40, 60 and 60 min, respectively.
343 The integration of TiO₂ and TiO_{2-NTs} into MMT lead to increase in adsorption equilibrium
344 time, which is probably due to the dispersion of TiO₂ particles and TiO_{2-TNs} into MMT
345 interlayers structure, reducing pores size, thereby extending the adsorption equilibrium
346 time.

347 The influence of UV-C irradiation to trigger a photocatalytic effect likely to degrade
348 rhodamine B of MMT, TiO₂, TiO_{2-TNs} and their incorporation with MMT sheets is shown
349 in Figure 7b. Firstly, it could be seen that the energy of UV-C irradiation alone is not
350 enough to degrade rhodamine B. The rhodamine B degradation efficiency of MMT is the
351 same without and within UV-C irradiation because MMT has only adsorption property
352 without photocatalytic property. TiO_{2-NTs} have higher photocatalytic efficiency to degrade
353 rhodamine B than TiO₂ nanoparticles. In particular, the degradation efficiency of TiO₂
354 nanoparticles increased slightly to ca. 20%, corresponding to C/C₀ = 0.8 compared to less
355 than 10% (C/C₀ = 0.9) without irradiation. Meanwhile, the efficiency of for TiO_{2-NTs}
356 increased significantly to 65% (C/C₀ = 0.35) compared to less than 10% (0.9 C/C₀) of
357 sample without UV-C irradiation. Thus, under UV-C irradiation, TiO₂ and TiO_{2-NTs} are

358 able to absorb photon energy to form hydroxyl free radicals ($\cdot\text{OH}$) free radicals, which are
359 main factors to degrade rhodamine B.

360 The efficiency both MMT/TiO₂ and MMT/TiO_{2-NTs} photocatalyst are also significantly
361 increased under UV-C irradiation. It increased to 90% ($C/C_0 = 0.1$) with irradiation
362 compared to 46% ($C/C_0 = 0.54$) in dark condition for MMT/TiO₂ photocatalyst.
363 Similarly, it is recorded about 85% ($C/C_0 = 0.15$) compared to 73% ($C/C_0 = 0.27$) in dark
364 condition for MMT/TiO_{2-NTs} photocatalyst. Thus, the results showed that under UV-C
365 irradiation, the photocatalytic effective of TiO₂ nanoparticles is increased through more
366 production of free radicals ($\cdot\text{OH}$), leading to capturing and degrading of rhodamine B
367 molecules. In addition, efficiency of MMT/TiO_{2-NTs} photocatalyst is lower than that of
368 MMT/TiO₂. This is due to TiO_{2-NTs} in tubular form, which was intertwined in layer
369 structure of MMT sheets. This limits photon energy absorption of TiO_{2-TNs}, resulting in
370 the less $\cdot\text{OH}$ free radical production, resulting in lower rhodamine B degradation
371 efficiency.



372
 373 Figure 7: Photocatalytic degradation of rhodamine B with 10 ppm using different
 374 photocatalyst: (a) in the dark condition, (b) in the UV-C irradiation condition.
 375 In addition, the photocatalytic performance of MMT/TiO₂ and MMT/TiO₂-NTs to
 376 rhodamine B degradation is compared to that of the TiO₂ based photocatalyst in the
 377 literature as exhibited in Table 1. Thus, the photocatalytic performance of MMT/TiO₂
 378 and MMT/TiO₂-NTs have shown a superior efficiency in rhodamine B degradation
 379 compared to other TiO₂ based photocatalysts in the literature. Basically, the efficiency of
 380 rhodamine B degradation is dependent on many factors such as light source, rhodamine B
 381 concentration, and catalyst amount, etc. Indeed, these results suggest that the combination

382 of TiO₂ and TiO₂-NTs with MMT has significantly increased the photocatalytic efficiency
 383 to eliminate rhodamine B from dye effluent.

384 Table 1. Photocatalytic performance of TiO₂ and TiO₂-NTs based photocatalyst to
 385 rhodamine B degradation compared to previous studies

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

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

386

387 The reusability of MMT/TiO₂ and MMT/TiO_{2-NTs} for the rhodamine B degradation was
388 performed by repeating the reaction for three cycles using the recovered photocatalyst
389 under the same conditions, as shown in Figure 8. After three consecutive runs, the
390 photocatalytic activity of MMT/TiO₂ was decreased by 18% and the photocatalytic
391 activity of MMT/TiO_{2-NTs} was decreased by 23.5%. This might be ascribed to the
392 accumulation of photodegradation products and rhodamine B molecules on the catalyst
393 surface which resulted in decreasing the active sites (Pannak et al., 2018).

394

395

396

397

398

399

400

401

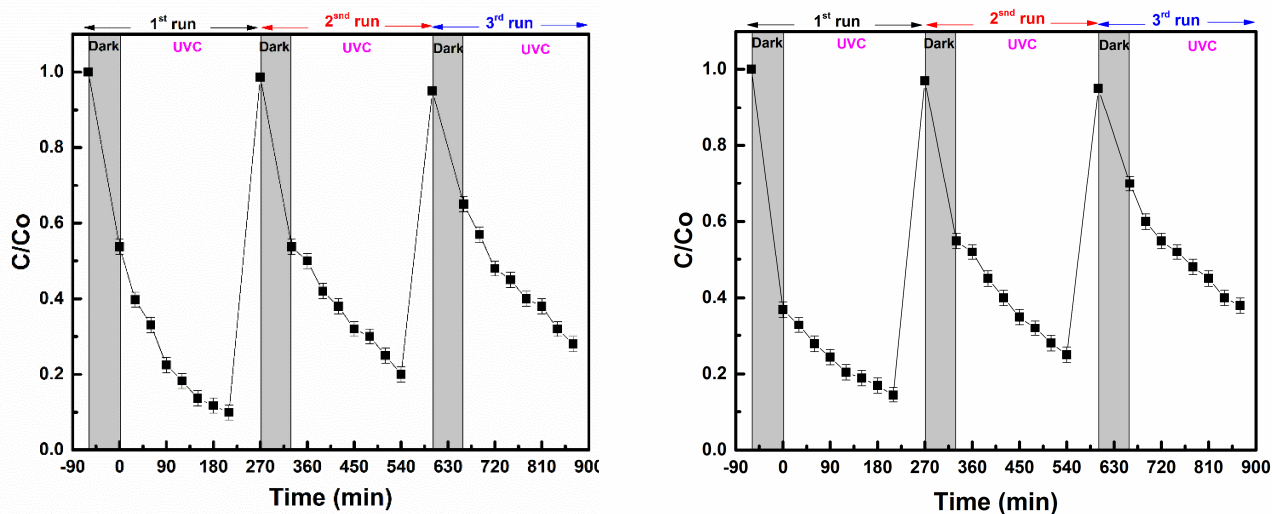
402

403

404

405

406



407

408

409

410

3.6. Photocatalytic performance at different rhodamine B concentrations

411

412

413

414

415

416

417

418

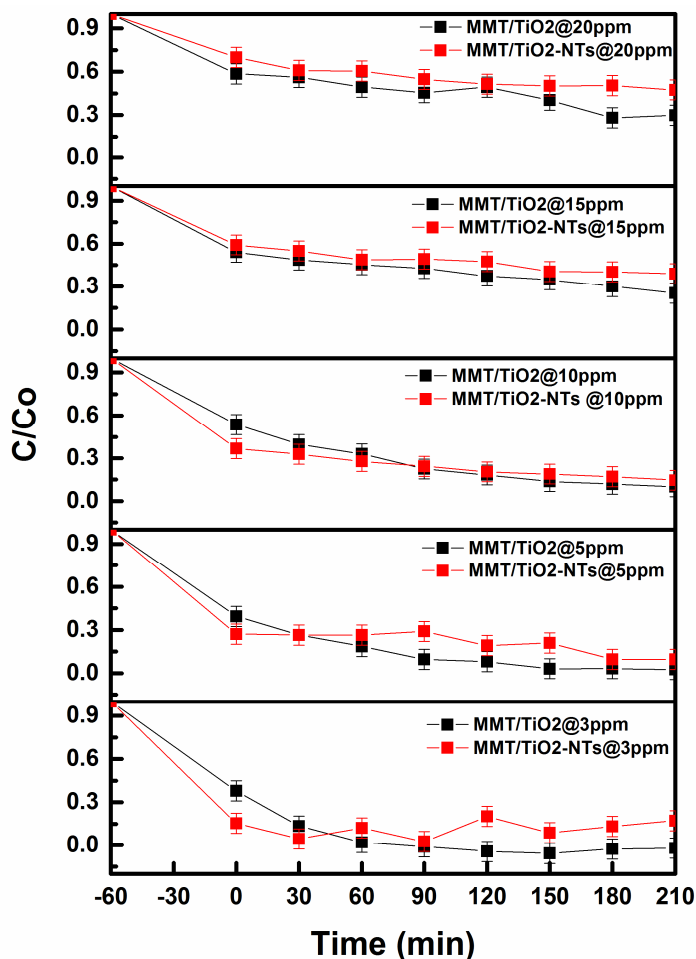
419

420

Figure 8: Photocatalytic activity of (a) MMT/TiO₂ and (b) MMT/TiO₂-NTs photocatalyst for three consecutive runs with 10 ppm rhodamine B.

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

421 presents a decreased efficiency at long term but seems to be slightly higher efficient at
422 short term for low concentration of rhodamine B. This is probably the dominant effect of
423 the $\text{TiO}_2\text{-TNs}$ located on the surface of MMT sheets. In general, at increasing rhodamine B
424 concentrations, the photocatalytic activity and degradation efficiency of TiO_2/MMT and
425 $\text{TiO}_2\text{-NTs}/\text{MMT}$ photocatalysts decreases because of the smaller length of penetration of
426 UV in the rhodamine B solution. This means that rhodamine B molecules are adsorbed
427 onto the surface of MMT/TiO_2 and $\text{MMT}/\text{TiO}_2\text{-TNs}$ photocatalysts, which interferes with
428 the photon energy exposure of TiO_2 and $\text{TiO}_2\text{-TNs}$ on MMT surface, leading to decrease in
429 photocatalytic ability to rhodamine B degradation. In addition, it could be observed that
430 there are the combined effects; at high rhodamine B concentration, the adsorption of
431 rhodamine B by MMT is saturated, which can be seen by the attenuation observed at
432 short time. But we can still see the better effect of MMT/TiO_2 to degrade rhodamine B
433 over time, which is much less pronounced with $\text{MMT}/\text{TiO}_2\text{-NTs}$.

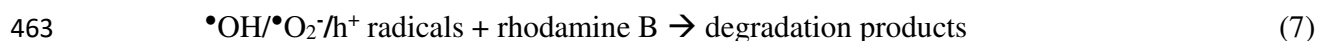
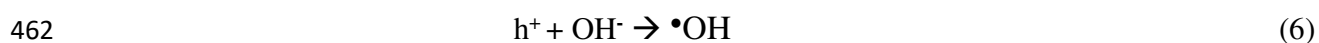
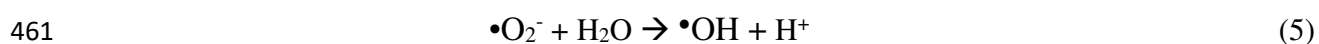
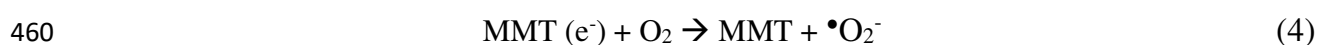
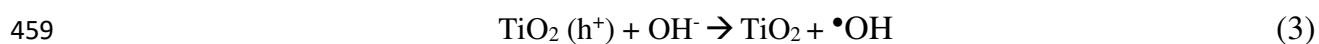


434
 435 **Figure 9.** Degradation effectiveness of MMT/TiO₂ and MMT/TiO_{2-NTs} photocatalysts at
 436 different concentrations of rhodamine B under UV-C irradiation.

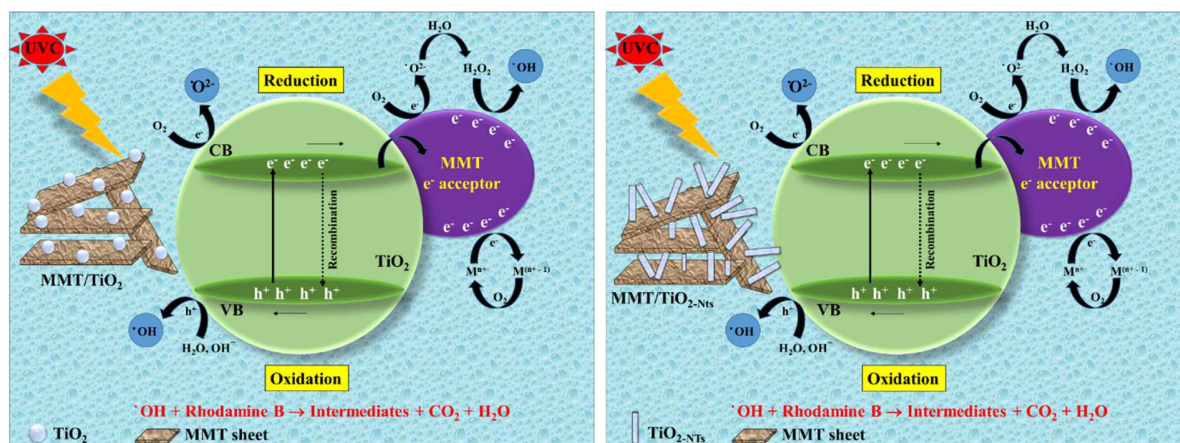
437
 438 **3.7. The mechanism of rhodamine B degradation of photocatalyst**

439 The mechanism of rhodamine B degradation by photocatalysts is proposed in Figure 10.
 440 The TiO₂ components of MMT/TiO₂ act as photocatalyst. Initially, the UV-C irradiation
 441 source produced high-energy photons activates to create photoinduced electrons (e⁻) and
 442 leave holes (h⁺) of the TiO₂. The negatively charged electrons are excited to cross the
 443 band gap (E_g) and jump into the conduction band (CB) leaving holes with positively

444 charged charges in the valence region (VB). In the presence of MMT, the generated
 445 electrons move to the empty d-orbital of the metals in MMT structure. This electron
 446 transfer process can prevent the $e^- - h^+$ pair from recombination. Then, electrons trapped
 447 in MMT react with O_2 to produce free superoxide radicals ($\bullet O_2^-$) (Xu et al., 2021). At the
 448 same time, photogenerated holes react with H_2O or the adsorbed hydroxyl ions (OH^-)
 449 molecules to produce hydroxyl radicals ($\bullet OH$) (Sun et al., 2021). Finally, the produced
 450 free radicals ($\bullet OH$, $\bullet O_2^-$, h^+) with strong oxidizing ability will degrade rhodamine B
 451 molecules into degradation products (Wang et al., 2020; E et al., 2021). Thus, the free
 452 radicals ($\bullet OH$ and $\bullet O_2^-$) attack the central carbon in the rhodamine B molecules and
 453 oxidize them to low-weight intermediates, which results in the formation of small and
 454 broken-ring compounds. In addition, the smaller compounds are degraded to CO_2 and
 455 H_2O (Isari et al., 2018). All steps of photocatalytic process to degrade rhodamine B are
 456 summarized in following equations (1-5):



464



465

466 Figure 10: The photocatalytic mechanism of MMT/TiO₂ (left) and MMT/TiO_{2-NTs} (right)

467 photocatalysts for rhodamine B degradation.

468

469 The degradation products with rhodamine B for at 30 min during photocatalytic process

470 were investigated using LC-MS spectrum and presented in Figure 11. Firstly, the

471 rhodamine B (A₁, m/z 443) was attacked by a large number of e⁻, which was created by

472 MMT/TiO₂ or MMT/TiO_{2-NTs}, to produce N, N, N-diethyl-N'-ethylrhodamine (A₂, m/z

473 415) (Wermuth et al., 2019). Then, A₂ was degraded into two isomers N, N'-ethyl-

474 ethylrhodamine (A₃, m/z 388) and N, N- diethyl-rhodamine (A₄, m/z 388)

475 (Hegazey et al., 2020). Next, A₃ and A₄ were degraded into N, N'-monomethyl-

476 ethylrhodamine (A₅, m/z 360) and N, N'-ethylrhodamine (A₆, m/z 332) (E et al.,

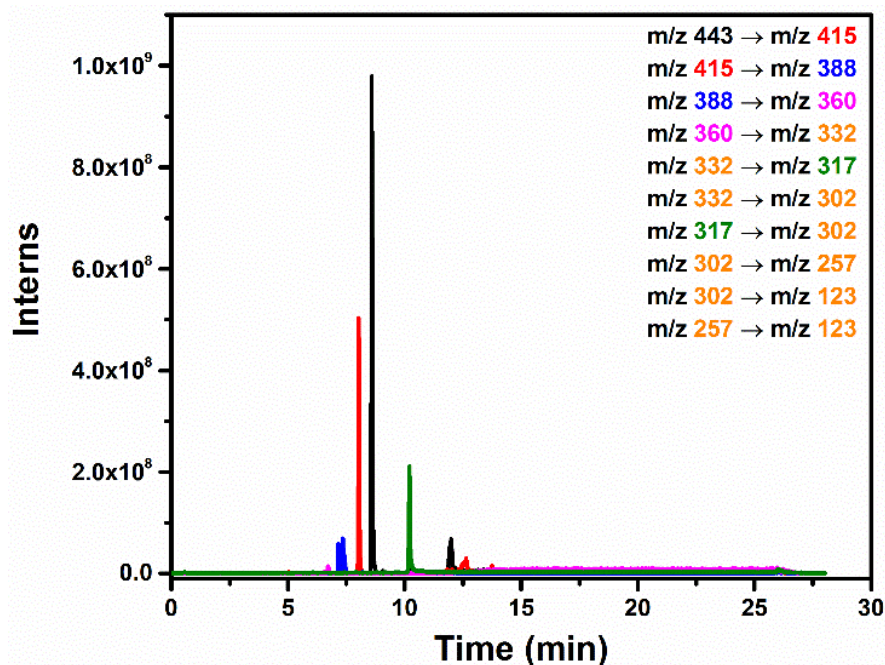
477 2021). Then, -NH bond of A₆ was broken to form N'-ethylrhodamine (A₇, m/z

478 317) and 2-(3H-xanthen-9-yl) benzoic acid (A₈, m/z 302) was generated when all

479 -NH bonds were broken (E et al., 2021). 9-phenyl-3H-xanthene (A₉, m/z 257) was

480 produced by breaking carboxyl group from A₈. The degradation products were

481 benzoic acid (A_{10} , m/z 123) (Guo et al., 2020). Finally, A_{10} was degraded by h^+ ,
482 $\cdot O_2$ and $\cdot OH$ to produce CO_2 and H_2O (Hegazey et al., 2020).



483

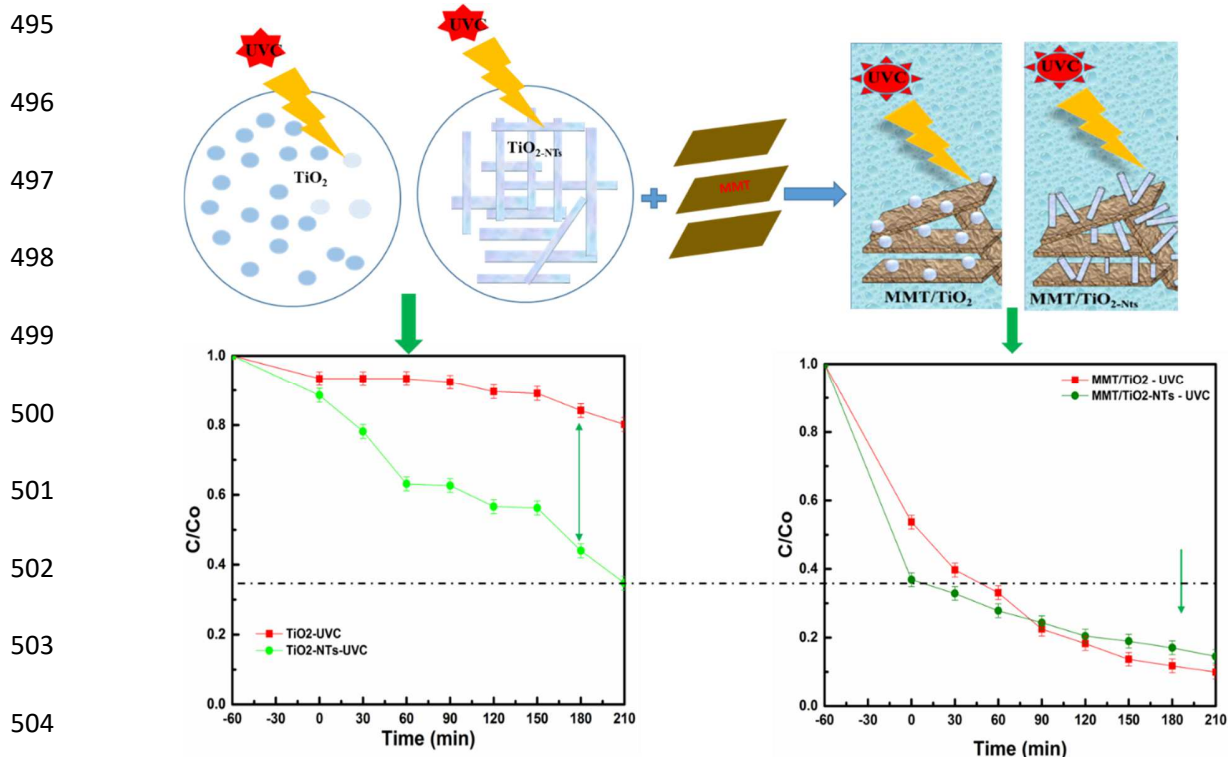
484

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

487

488 In addition, under the UVC irradiation, TiO_{2-NTs} exhibits a higher photocatalytic capacity
489 than TiO_2 . However, the decomposition efficiency of MMT/TiO_{2-NTs} is lower than that of
490 MMT/TiO_2 . This suggests that the addition of TiO_{2-NTs} into MMT leads to decrease the
491 photocatalytic activity of TiO_{2-NTs} . This is due to the MMT has layer structure, when
492 TiO_{2-NTs} are intercalated into MMT layers, the inner surface is not adequately illuminated
493 by UV-C irradiation as described in Figure 12.

494



505 Figure 12: The illustration of photocatalytic activities of MMT/TiO₂ and MMT/TiO_{2-NTs}
 506 for rhodamine B degradation under UV-C irradiation.

507 Therefore, the number of absorbed photons of TiO_{2-NTs} inside is less than the outer
 508 surface, affecting the chemical transformation of the photocatalytic process. Therefore,
 509 the photocatalytic ability of TiO_{2-NTs} is limited in incorporation with MMT sheets
 510 although they have better photocatalytic effectively than TiO₂ nanoparticles.

511

512 4. Conclusions

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

517 of rhodamine B dye in comparison with commercial TiO₂ nanoparticle photocatalyst.
518 However, the efficiency of rhodamine B degradation under UVC light of MMT/TiO₂ is
519 higher than that of MMT/TiO_{2-NTs}. This is due to the immobilization of TiO₂
520 nanoparticles at the surface of MMT sheets, so they are available for UVC light
521 absorption. Besides, the effectiveness of TiO_{2-NTs} is lost in the presence of MMT because
522 TiO_{2-NTs} intercalate into the MMT layers, leading to the inhibition of UVC light
523 absorption. Moreover, MMT/TiO_{2-NTs} nanocomposite still shows a better rhodamine B
524 removal effectiveness in the initial period of 1 hour under UVC light irradiation. As a
525 result, the combination of MMT and TiO_{2-NTs} can be applied for water treatment in short
526 time. The photocatalytic performance of MMT/TiO₂ reached to 100% for 3ppm and 90%
527 at 10ppm of rhodamine B, while these values are 97.5% and 85.5%, respectively,
528 recorded for MMT/TiO_{2-NTs}.

529 **Declarations of interest:** none.

530

531 **Acknowledgments:**

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

537

538

539 **References**

- 540 Abdi, J., Vossoughi, M., Mahmoodi, N.M., Alemzadeh, I., 2017. Synthesis of metal-
541 organic framework hybrid nanocomposites based on GO and CNT with high adsorption
542 capacity for dye removal. *Chemical Engineering Journal* 326, 1145-1158.
- 543 Aber, S., Khataee, A., Sheydaei, M., 2009. Optimization of activated carbon fiber
544 preparation from Kenaf using K₂HPO₄ as chemical activator for adsorption of phenolic
545 compounds. *Bioresource Technology* 100, 6586-6591.
- 546 Ayoubi-Feiz, B., Aber, S., Khataee, A., Alipour, E.J., 2014. Electrosorption and
547 photocatalytic one-stage combined process using a new type of nanosized TiO
548 2/activated charcoal plate electrode. *Environmental Science Pollution Research* 21, 8555-
549 8564.
- 550 Bing, H., Qi, D., Jie, C., Wei, F., Suling, L., He-li, W., 2015. Photocatalytic Degradation
551 of Methyl Orange Over Y³⁺ Doped TiO₂ Pillared Montmorillonite. *Journal of Advanced*
552 *Oxidation Technologies* 18, 98-104.
- 553 Casu, A., Lamberti, A., Stassi, S., Falqui, A., 2018. Crystallization of TiO₂ Nanotubes by
554 In Situ Heating TEM. *Nanomaterials (Basel)* 8, 40.
- 555 Charumathi, D., Das, N., 2012. Packed bed column studies for the removal of synthetic
556 dyes from textile wastewater using immobilised dead *C. tropicalis*. *Desalination* 285, 22-
557 30.
- 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

560 for efficient photocatalytic hydrogen evolution. *Journal of Colloid and Interface Science*
561 555, 94-103.

562 Chinh, V.D., Broggi, A., Di Palma, L., Scarsella, M., Speranza, G., Vilardi, G., Thang,
563 P.N., 2018. XPS Spectra Analysis of Ti²⁺, Ti³⁺ Ions and Dye Photodegradation
564 Evaluation of Titania-Silica Mixed Oxide Nanoparticles. *Journal of Electronic Materials*
565 47, 2215-2224.

566 Chinh, V.D., Hung, L.X., Di Palma, L., Hanh, V.T.H., Vilardi, G., 2019. Effect of
567 Carbon Nanotubes and Carbon Nanotubes/Gold Nanoparticles Composite on the
568 Photocatalytic Activity of TiO₂ and TiO₂-SiO₂. *Chemical Engineering & Technology*
569 42, 308-315.

570 Cui, L., Hui, K., Hui, K., Lee, S., Zhou, W., Wan, Z., Thuc, C.-N.H.J.M.L., 2012. Facile
571 microwave-assisted hydrothermal synthesis of TiO₂ nanotubes. *Materials Letters* 75,
572 175-178.

573 Dao, M.U., Le, H.S., Hoang, H.Y., Tran, V.A., Doan, V.D., Le, T.T.N., Sirotkin, A., Le,
574 V.T., 2020. Natural core-shell structure activated carbon beads derived from *Litsea*
575 *glutinosa* seeds for removal of methylene blue: Facile preparation, characterization, and
576 adsorption properties. *Environmental Research*, 110481.

577 Diamond, S.A., Kennedy, A.J., Melby, N.L., Moser, R.D., Poda, A.R., Weiss, C.A.,
578 Brame, J.A., 2017. Assessment of the potential hazard of nano-scale TiO₂ in
579 photocatalytic cement: application of a tiered assessment framework. *NanoImpact* 8, 11-
580 19.

581 dos Santos, A.B., Cervantes, F.J., van Lier, J.B., 2007. Review paper on current
582 technologies for decolourisation of textile wastewaters: Perspectives for anaerobic
583 biotechnology. *Bioresource Technology* 98, 2369-2385.

584 E, T., Xiao, X., Yang, S., 2021. A new synthesizing method of TiO₂ with
585 montmorillonite: Effective photoelectron transfer to degrade Rhodamine B. *Separation
586 and Purification Technology* 258, 118070.

587 Fan, L., Long, J., Gu, Q., Huang, H., Lin, H., Wang, X., 2014. Single-site nickel-grafted
588 anatase TiO₂ for hydrogen production: Toward understanding the nature of visible-light
589 photocatalysis. *Journal of Catalysis* 320, 147-159.

590 Farghali, A.A., Zaki, A.H., Khedr, M.H., 2014. Hydrothermally synthesized TiO₂
591 nanotubes and nanosheets for photocatalytic degradation of color yellow sunset.
592 *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.

595 Gupta, V.K., Suhas, 2009. Application of low-cost adsorbents for dye removal – A
596 review. *Journal of Environmental Management* 90, 2313-2342.

597 Habila, M.A., Alothman, Z.A., El-Toni, A.M., Labis, J.P., Soylak, M., 2016. Synthesis
598 and application of Fe₃O₄@SiO₂@TiO₂ for photocatalytic decomposition of organic
599 matrix simultaneously with magnetic solid phase extraction of heavy metals prior to ICP-
600 MS analysis. *Talanta* 154, 539-547.

601 Hao, R., Wang, G., Tang, H., Sun, L., Xu, C., Han, D., 2016. Template-free preparation
602 of macro/mesoporous g-C₃N₄/TiO₂ heterojunction photocatalysts with enhanced visible
603 light photocatalytic activity. *Applied Catalysis B-environmental* 187, 47-58.

604 Hassani, A., Khataee, A., Karaca, S., Fathinia, M., 2016. Heterogeneous photocatalytic
605 ozonation of ciprofloxacin using synthesized titanium dioxide nanoparticles on a
606 montmorillonite support: parametric studies, mechanistic analysis and intermediates
607 identification. *RSC Advances* 6, 87569-87583.

608 Hassani, A., Khataee, A., Karaca, S., Karaca, C., Gholami, P., 2017. Sonocatalytic
609 degradation of ciprofloxacin using synthesized TiO₂ nanoparticles on montmorillonite.
610 *Ultrasonics Sonochemistry* 35, 251-262.

611 Hegazey, R.M., Abdelrahman, E.A., Kotp, Y.H., Hameed, A.M., Subaihi, A., 2020.
612 Facile fabrication of hematite nanoparticles from Egyptian insecticide cans for efficient
613 photocatalytic degradation of rhodamine B dye. *Journal of Materials Research and*
614 *Technology* 9, 1652-1661.

615 Hu, Y., Li, D.Z., Wang, H.B., Zeng, G.P., Li, X.H., Shao, Y., 2015. Role of active
616 oxygen species in the liquid-phase photocatalytic degradation of RhB using BiVO₄/TiO₂
617 heterostructure under visible light irradiation. *J. Mol. Catal. A-Chem.* 408, 172-178.

618 Huang, H., Gu, X., Zhou, J., Ji, K., Liu, H., Feng, Y., 2009. Photocatalytic degradation of
619 Rhodamine B on TiO₂ nanoparticles modified with porphyrin and iron-porphyrin.
620 *Catalysis Communications* 11, 58-61.

621 Huang, J., Shi, Z., Dong, X., 2016. Nickel sulfide modified TiO₂ nanotubes with highly
622 efficient photocatalytic H₂ evolution activity. *Journal of Energy Chemistry* 25, 136-140.

623 Isari, A.A., Payan, A., Fattahi, M., Jorfi, S., Kakavandi, B., 2018. Photocatalytic
624 degradation of rhodamine B and real textile wastewater using Fe-doped TiO₂ anchored
625 on reduced graphene oxide (Fe-TiO₂/rGO): Characterization and feasibility, mechanism
626 and pathway studies. *Applied Surface Science* 462, 549-564.

627 Iwasaki, M., Yasumori, A., Shibata, S., Yamane, M., 1994. Preparation of high
628 homogeneity BaO-TiO₂-SiO₂ gel. *Journal of Sol-Gel Science and Technology* 2, 387-
629 391.

630 Katheresan, V., Kansedo, J., Lau, S.Y., 2018. Efficiency of various recent wastewater
631 dye removal methods: A review. *Journal of Environmental Chemical Engineering* 6,
632 4676-4697.

633 Khataee, A., Sheydaei, M., Hassani, A., Taseidifar, M., Karaca, S., 2015. Sonocatalytic
634 removal of an organic dye using TiO₂/Montmorillonite nanocomposite. *Ultrasonics*
635 *Sonochemistry* 22, 404-411.

636 Kingsley, J.J., Suresh, K., Patil, K.C., 1990. Combustion synthesis of fine particle rare
637 earth orthoaluminates and yttrium aluminum garnet. *Journal of Solid State Chemistry* 88,
638 435-442.

639 Leong, S., Razmjou, A., Wang, K., Hapgood, K., Zhang, X., Wang, H., 2014. TiO₂ based
640 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.

644 Liu, J., Li, X., Zuo, S., Yu, Y., 2007. Preparation and photocatalytic activity of silver and
645 TiO₂ nanoparticles/montmorillonite composites. *Applied Clay Science* 37, 275-280.

646 Low, J., Zhang, L., Tong, T., Shen, B., Yu, J., 2018. TiO₂/MXene Ti₃C₂ composite with
647 excellent photocatalytic CO₂ reduction activity. *Journal of Catalysis* 361, 255-266.

648 Ma, X., Xiang, Q., Liao, Y., Wen, T., Zhang, H., 2018. Visible-light-driven CdSe
649 quantum dots/graphene/TiO₂ nanosheets composite with excellent photocatalytic activity
650 for E. coli disinfection and organic pollutant degradation. *Applied Surface Science* 457,
651 846-855.

652 Malato, S., Fernández-Ibáñez, P., Maldonado, M.I., Blanco, J., Gernjak, W., 2009.
653 Decontamination and disinfection of water by solar photocatalysis: Recent overview and
654 trends. *Catalysis Today* 147, 1-59.

655 Mishra, A., Sharma, M., Mehta, A., Basu, S., 2017. Microwave Treated Bentonite Clay
656 Based TiO₂ Composites: An Efficient Photocatalyst for Rapid Degradation of Methylene
657 Blue. *Journal of nanoscience and nanotechnology* 17, 1149-1155.

658 Nagaraja, R., Kottam, N., Giriya, C.R., Nagabhushana, B.M., 2012. Photocatalytic
659 degradation of Rhodamine B dye under UV/solar light using ZnO nanopowder
660 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
663 decomposition efficiency. *Catalysis Today* 282, 13-23.

664 Natarajan, T.S., Thomas, M., Natarajan, K., Bajaj, H.C., Tayade, R.J., 2011. Study on
665 UV-LED/TiO₂ process for degradation of Rhodamine B dye. *Chemical Engineering*
666 *Journal* 169, 126-134.

667 Nguyen Van, H., Chu Van, H., Luu Hoang, T., Vo Nguyen, D.K., Ha Thuc, C.N., 2020.
668 The starch modified montmorillonite for the removal of Pb(II), Cd(II) and Ni(II) ions
669 from aqueous solutions. *Arabian Journal of Chemistry* 13, 7212-7223.

670 Niu, X., Sun, L., Zhang, X., Sun, Y., Wang, J., 2020. Fabrication and antibacterial
671 properties of cefuroxime-loaded TiO₂ nanotubes. *Applied microbiology and*
672 *biotechnology* 104, 2947-2955.

673 Pang, Y.L., Abdullah, A.Z., 2013. Effect of carbon and nitrogen co-doping on
674 characteristics and sonocatalytic activity of TiO₂ nanotubes catalyst for degradation of
675 Rhodamine B in water. *Chemical Engineering Journal* 214, 129-138.

676 Pannak, P., Songsasen, A., Foytong, W., Kidkhunthod, P., Sirisaksoontorn, W., 2018.
677 Homogeneous distribution of nanosized ZnO in montmorillonite clay sheets for the
678 photocatalytic enhancement in degradation of Rhodamine B. *Research on Chemical*
679 *Intermediates* 44, 6861-6875.

680 Park, D.J., Sekino, T., Tsukuda, S., Hayashi, A., Kusunose, T., Tanaka, S.-I., 2011.
681 Photoluminescence of samarium-doped TiO₂ nanotubes. *Journal of Solid State*
682 *Chemistry* 184, 2695-2700.

683 Rauf, M.A., Salman Ashraf, S., 2012. Survey of recent trends in biochemically assisted
684 degradation of dyes. *Chemical Engineering Journal* 209, 520-530.

685 Robinson, T., McMullan, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in
686 textile effluent: a critical review on current treatment technologies with a proposed
687 alternative. *Bioresource Technology* 77, 247-255.

688 Sasani, A., Baktash, A., Mirabbaszadeh, K., Khoshnevisan, B., 2016. Structural and
689 electronic properties of Mg and Mg-Nb co-doped TiO₂ (101) anatase surface. *Applied*
690 *Surface Science* 384, 298-303.

691 Shan, R., Lu, L., Gu, J., Zhang, Y., Yuan, H., Chen, Y., Luo, B., 2020. Photocatalytic
692 degradation of methyl orange by Ag/TiO₂/biochar composite catalysts in aqueous
693 solutions. *Materials Science in Semiconductor Processing* 114, 105088.

694 Shi, L., Liang, L., Ma, J., Meng, Y., Zhong, S., Wang, F., Sun, J., 2014. Highly efficient
695 visible light-driven Ag/AgBr/ZnO composite photocatalyst for degrading Rhodamine B.
696 *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
699 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
701 fabrication of 1D/2D CdS nanorod@Ti₃C₂ MXene composites for good photocatalytic
702 activity of hydrogen generation and ammonia synthesis. *Chemical Engineering Journal*
703 406, 127177.

704 Szczepanik, B., 2017a. Photocatalytic degradation of organic contaminants over clay-
705 TiO₂ nanocomposites: A review. *Applied Clay Science* 141, 227-239.

706 Szczepanik, B., 2017b. Photocatalytic degradation of organic contaminants over clay-TiO
707 2 nanocomposites: A review. *Applied Clay Science* 141, 227-239.

708 Tahir, M., Amin, N.S., 2016. Performance analysis of nanostructured NiO–In₂O₃/TiO₂
709 catalyst for CO₂ photoreduction with H₂ in a monolith photoreactor. *Chemical*
710 *Engineering Journal* 285, 635-649.

711 Thuc, C.-N.H., Grillet, A.-C., Reinert, L., Ohashi, F., Thuc, H.H., Duclaux, L., 2010.
712 Separation and purification of montmorillonite and polyethylene oxide modified
713 montmorillonite from Vietnamese bentonites. *Applied Clay Science* 49, 229-238.

714 Wang, H., Wang, H.-L., Jiang, W.-F., Li, Z.-Q., 2009. Photocatalytic degradation of 2,4-
715 dinitrophenol (DNP) by multi-walled carbon nanotubes (MWCNTs)/TiO₂ composite in
716 aqueous solution under solar irradiation. *Water Research* 43, 204-210.

717 Wang, R., Shi, M., Xu, F., Qiu, Y., Zhang, P., Shen, K., Zhao, Q., Yu, J., Zhang, Y.,
718 2020. Graphdiyne-modified TiO₂ nanofibers with osteoinductive and enhanced
719 photocatalytic antibacterial activities to prevent implant infection. *Nature*
720 *Communications* 11, 4465.

721 Wang, Y., Zhang, J., Liu, L., Zhu, C., Liu, X., Su, Q., 2012. Visible light photocatalysis
722 of V₂O₅/TiO₂ nanoheterostructures prepared via electrospinning. *Materials Letters* 75,
723 95-98.

724 Wermuth, T.B., Arcaro, S., Venturini, J., Hubert Ribeiro, T.M., de Assis Lawisch
725 Rodriguez, A., Machado, E.L., Franco de Oliveira, T., Franco de Oliveira, S.E., Baibich,
726 M.N., Bergmann, C.P., 2019. Microwave-synthesized KNbO₃ perovskites: photocatalytic
727 pathway on the degradation of rhodamine B. *Ceramics International* 45, 24137-24145.

728 Wong, C.L., Tan, Y.N., Mohamed, A.R., 2011. A review on the formation of titania
729 nanotube photocatalysts by hydrothermal treatment. *Journal of Environmental*
730 *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.,
732 Wang, X., Zhao, M., Cui, H., 2021. Construction of hierarchical 2D/2D Ti₃C₂/MoS₂
733 nanocomposites for high-efficiency solar steam generation. *Journal of Colloid and*
734 *Interface Science* 584, 125-133.

735 Xu, X., Zhou, X., Li, X., Yang, F., Jin, B., Xu, T., Li, G., Li, M., 2014. Electrodeposition
736 synthesis of MnO₂/TiO₂ nanotube arrays nanocomposites and their visible light
737 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.

741 Zhang, J., Zhang, Z., Zhu, W., Meng, X., 2020. Boosted photocatalytic degradation of
742 Rhodamine B pollutants with Z-scheme CdS/AgBr-rGO nanocomposite. *Applied Surface*
743 *Science* 502, 144275.

744