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# Modeling and Box-Behnken design optimization of photocatalytic parameters for efficient removal of dye by lanthanum-doped mesoporous TiO<sub>2</sub>

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1           **Modeling and Box-Behnken design optimization of photocatalytic parameters for**  
2                           **efficient removal of dye by lanthanum-doped mesoporous TiO<sub>2</sub>**

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18   **Abstract**

19   In the present study, the Box-Behnken design in the response surface methodology (RSM)  
20   was availed to investigate the modelization and optimization of Methyl Orange (MO)  
21   mineralization parameters. The process was carried out in the presence of lanthanum (La)  
22   doped mesoporous titanium dioxide (TiO<sub>2</sub>) by a simple impregnation method using various  
23   La doping amounts (0.5, 1.5 and 3 wt%). The physico-chemical characteristics of each  
24   catalysts are studied under several approaches. The effects of the wavelength of irradiation  
25   light, catalysts weight and MO concentration on the yield of MO mineralization were  
26   investigated. Based on ANOVA analysis, the results show that the response of MO  
27   mineralization (R) in photocatalytic process was significantly affected by a positive individual  
28   effect of wavelength and catalyst weight. However, the individual effect of MO concentration

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\* Corresponding author

29 has an antagonist impact through the whole process. The optimum conditions were achieved  
 30 for the light irradiation wavelength of 310 nm, catalyst weight of 80 mg, and MO  
 31 concentration of 20 ppm, which allowed reaching 99.89% of mineralization. Overall, the  
 32 adjusted coefficient of determination ( $R^2$ ) value of 0.9956 indicated that the used model was  
 33 quite suitable and the selected RSM was successful in optimizing the mineralization  
 34 conditions of MO.

### 351. Introduction

36 Over the past few years, semiconductor  $TiO_2$  has been widely used in many applications,  
 37 especially in photocatalytic wastewater treatment processes [1-4]. The photocatalytic activity  
 38 of  $TiO_2$  can be improved through doping with different types of elements like metals (Au, Ag,  
 39 Co, etc), non-metals (N, Mg, S, etc.) and rare earths (Ce, La, Eu, etc.) [5-9]. In particular, La,  
 40 which has the electron configuration of [Xe], i.e.  $4f^{14}5d^16s^2$ , is an efficient dopant for  
 41 improving the photocatalytic properties of  $TiO_2$  because its d and f orbitals are incomplete  
 42 [10, 11]. It is widely admitted that the presence of La engenders electron trapping and  
 43 therefore limits their recombination with holes to prevent the formation of electron-hole ( $e^-$   
 44  $/h^+$ ) pairs. This leads to improve the photodegradation efficiency [12, 13]. Furthermore, the  
 45 presence of La offers several advantages among which is the reduction in the crystallite size,  
 46 the increase in the number of oxygen vacancies, and the delay in phase transformation of  
 47 anatase into rutile [12, 14]. **Table 1** shows some applications of La-doped  $TiO_2$  in the  
 48 photodegradation of organic pollutants.

49

50 **Table 1.** Applications of La-doped  $TiO_2$  materials in the photodegradation of organic  
 51 molecules from the literature

Photocatalysts	Pollutants	Degradation efficiency (%)	Eg (eV)	Reaction conditions	References
$TiO_2$	Methyl	18	3.2	180 min, visible light, 25ppm,	[15]
Co-La/ $TiO_2$	Orange	98	3.0	pH=5	

<b>P25</b>		85	3.2	150min, sunlight, 50 ppm, pH=5.	[16]
<b>Anatase</b>		71	/		
<b>0.25% La/ TiO<sub>2</sub></b>	Ibuprofen	67.6	3.35		
<b>0.5% La- TiO<sub>2</sub></b>		81.9	3.15		
<b>1% La- TiO<sub>2</sub></b>		93.7	3.01		
<b>2% La- TiO<sub>2</sub></b>		96.9	2.90		
<b>TiO<sub>2</sub></b>	Methyl	11	3.2	60 min, visible light, 10 ppm.	[17]
<b>La<sup>3+</sup>/Y<sup>3+</sup>/Eu<sup>3+</sup> co-doped TiO<sub>2</sub></b>	Orange	49	/	60 min, visible light, 10 ppm.	
		58		60 min, UV irradiation, 10 ppm.	
<b>0.5% La/TiO<sub>2</sub></b>	Methyl	98.7	/	120min, UVC irradiated 20 ppm.	[18]
	Orange				
<b>0.1% La/TiO<sub>2</sub></b>	Methyl	82.5	2.99	180 min, UVC irradiation, 10 ppm.	[19]
	Orange	38		180 min, visible light, 10 ppm.	
<b>La/N-TiO<sub>2</sub></b>	Methyl	78	3.04	150 min, visible light, 5ppm.	[20]
	Orange				
<b>TiO<sub>2</sub> (P25)</b>	Oily waste	88	/	pH =5.5, full UV light (200–430 nm), [Oily waste]	[21]
	Phenol	76		=480±36 , [phenol]=69±15 mg/L	

52

53 RSM is one of the most popular experimental design methods applied by researchers in a  
54 wide range of fields, especially in chemistry where several parameters are often needed to  
55 investigate chemical processes[21-24]. The main purpose of using the RSM is to create an an  
56 experiment design that allows achieving the optimal operating conditions. In addition, it is  
57 widely acknowledged that RSM is an effective statistical and analytical tool for modeling and  
58 optimizing various processes and in various research fields, particularly in photocatalysis[25-  
59 27].

60 It was found that the Box-Behnken experimental design is well suited for the RSM; it is quite  
61 appreciated for its fast and economic convergence as compared with the traditional  
62 approaches[28, 29]. This technique can provide 3 to 7 factors, along with three levels of  
63 experimental conditions (low, medium and high levels) [30, 31]. It is interesting to note that

64 the Box-Behnken design proved to be much more efficient than the other response surface  
65 designs. Moreover, it is worth recalling that the experimental design efficiency is actually  
66 defined as the number of coefficients in the model under consideration divided by the number  
67 of experiments. For example, while the efficiency in the Box-Behnken design is 0.77, it is  
68 equal to 0.67 in another center composite design (CCD)[32].

69 In this study, UV light-driven photocatalysts of lanthanum-doped mesoporous TiO<sub>2</sub> were  
70 successfully prepared by a common impregnation method using various La doping amounts  
71 (0.5, 1.5 and 3wt %). The photocatalytic activity of the prepared photocatalysts was evaluated  
72 in the mineralization of MO under UV light irradiation. Then, the impacts of three parameters,  
73 namely the light irradiation wavelength, catalyst weight and pollutant concentration, on the  
74 photocatalytic process are investigated by the Box-Behnken design. Further, analysis tried  
75 also to determine the interactions between the parameters under consideration, as well as the  
76 optimal operating conditions for the process to be carried out. This leads to considerably  
77 reduce the number of required tests. It should be pointed out that the main advantage of this  
78 approach lies in its capacity to help save time and money in industrial processes.

## 79 **2. Experimental work**

### 80 **2.1. Reagents**

81 Titanium isopropoxide (IV)[C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti, (97%)], acetic acid [CH<sub>3</sub>COOH, (20%)], Pluronic  
82 P123 [EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, 99.99%], Lanthanum nitrate hexahydrate [La(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O, (99,99%)],  
83 Ethanol [C<sub>2</sub>H<sub>5</sub>OH, (99%)], Methyl orange [C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>NaO<sub>3</sub>S, >98%]. Every chemical  
84 product were purchased from Sigma Aldrich.

### 85 **2.2. Synthesis of materials**

86 Mesoporous TiO<sub>2</sub> was prepared by the hydrothermal-assistant sol-gel method [33]. To do this,  
87 5g of titanium isopropoxidewere added dropwise to the acetic acid solution (20%). The  
88 suspension (Solution 1) obtained was stirred for 4h. Next, Solution 2, which was prepared by

89 adding 3g of Pluronic P123 triblock copolymer into 20 mL of ethanol, was added drop by  
90 drop to Solution 1. The resulting suspension was stirred for 24h at room temperature. The  
91 solution obtained was transferred into a Teflon autoclave which was placed in an oven at  
92 100°C for 48h. Afterwards, it was taken out of the oven to cool down to room temperature. As  
93 a next step, the solution was filtered, and the resulting solid was washed with distilled water  
94 several times. Evaporation of the remaining water took place at the temperature of 80°C,  
95 during 24h. Finally, the recovered solid was calcined at 500°C for 4h, at the heating rate of  
96 1°C/min and a cooling rate of 1°C/min, to obtain the mesoporous TiO<sub>2</sub> material. On the other  
97 hand, La with different amounts, i.e. 0.5, 1.5 and 3%, was impregnated on calcined  
98 mesoporous TiO<sub>2</sub> by means of the incipient wetness impregnation technique using lanthanum  
99 nitrate [8]. Briefly, the calcined mesoporous TiO<sub>2</sub> was mixed with an aqueous solution of  
100 lanthanum nitrate in a rotatory evaporator, at 60°C, and for a period of 2h. The resulting  
101 suspension was first dried at 80°C for 24h and then calcined in air at 400°C for 4h at a heating  
102 rate of 1°C/min and a cooling rate of 1°C/min, to obtain 0.5, 1.5 and 3% La/TiO<sub>2</sub>.

### 103 **2.3. Characterization method**

104 The X-ray powder diffraction (XRD) patterns were recorded on a RigakuD/max2500  
105 diffractometer, using CuK $\alpha$  radiation ( $\lambda = 1.541874$  Å), with an acquisition time of 1 s, in the  
106 range of  $2\theta = 20^\circ - 80^\circ$ , in steps of 0.02°/min. In addition, the surface area and pore size  
107 analysis of the samples were carried out through nitrogen adsorption–desorption  
108 measurements on a Quantachrome NOVA1000 Series instrument, at the temperature of -  
109 196°C. The prepared catalysts overnight at 250°C, under vacuum. In addition, the UV-Vis  
110 reflectance diffuse (RD/UV-Vis) spectra of the catalysts were recorded on a Varian Cary 100  
111 Scan UV–Vis Spectrophotometer equipped with an integrating sphere accessory in the diffuse  
112 reflectance mode (R). Note that the inorganic compound of Barium sulfate (BaSO<sub>4</sub>) was used  
113 as the reference material.

#### 114 2.4. Photocatalytic properties

115 The photocatalytic properties of the prepared catalysts were evaluated through the  
116 photodegradation of MO ( $[MO]=30\text{ppm}$ ,  $m_{\text{catalyst}}=20\text{ mg}$ ,  $V_{\text{solution}}=100\text{ mL}$  for preliminary  
117 tests). The tests were carried out in a MULTIRAYS photoreactor (Heliosquartz, Italy)  
118 (**Figure 1**) that was fitted with ten exchangeable UV lamps (15 W each): (UVC, 254 nm),  
119 (UVB, 310 nm) and (UVA, 366 nm). For the most optimal catalyst, a series of experimental  
120 parameters, involved in the photodegradation and mineralization of MO, were chosen for the  
121 described modeling approach. For this, the studied solution was kept in darkness under  
122 stirring for 30 min, until the adsorption/desorption equilibrium was reached. Then, this  
123 solution was irradiated, and samples were taken every 5min. For each sample, the  
124 measurement of absorbance was made at  $\lambda=463\text{ nm}$ , using the Perkin Elmer Lambda 2S  
125 spectrophotometer. Note that each test was repeated three times. At the end of the experiment,  
126 the total organic carbon (TOC) content was measured by means of a Shimadzu TOC-VCSH  
127 analyzer. The same procedure was repeated for all the catalysts previously prepared. For the  
128 recyclability experiments, the optimal material was reused (6 times) after drying at  $80^{\circ}\text{C}$ .



138 **Fig. 1.** Schematic of photocatalysis experiment.

139 The following equation was used to calculate the yield (%) for the TOC conversion:

$$140 \quad \text{Yield}(\%) = \frac{C_0 - C_{\text{residue}}}{C_0} * 100 \quad \text{Eq. 1}$$

141 Where  $C_0$  is the initial TOC concentration and  $C_{\text{residue}}$  is the TOC concentration at the end of  
142 the experiment.

### 143 **2.5. Box-Behnken design**

144 Broadly speaking, the photocatalytic process depends on several operating parameters. For  
145 better monitoring the experiments, the photocatalytic reactions were designed on the basis of  
146 an experimental approach through the use of the most optimal catalyst. Furthermore, the  
147 empirical quadratic polynomial model was used, and all the experimental data were compiled  
148 by means of the Box-Behnken design using the Design-Expert Software, Version 12.0.3.0,  
149 from Stat-Ease, Inc. It is worth mentioning that the Box-Behnken design is a factorial  
150 combination of a minimum of three parameters with incomplete block designs. In each block,  
151 one factor is held at the central point, while the others vary according to four different  
152 combination values with respect to the upper and lower limits[34]. The experiments were  
153 conducted according to a three level scale, i.e. low (-1), central (0) and high (+1). Note that  
154 one level was set for each variable (**Table 2**). It is worth recalling that the independent  
155 variables in this experiment were the light irradiation wavelength  $\lambda$  (nm), catalyst weight  $m$   
156 (mg) and MO concentration [MO] (ppm), labeled  $X_1$ ,  $X_2$  and  $X_3$ , respectively. Therefore, the  
157 total number of experiments to be carried out was 15. It may be calculated as follows[35]:

$$158 \quad N = k^2 + k + cp \quad \text{Eq.2}$$

159

160 Where  $k$  is the factor number and  $cp$  is the replicate number of the central point[36, 37].

161 The coded values of the independent variables were obtained using the Equation 3[28]:

$$162 \quad x_i = \frac{X_i - X_{i0}}{\Delta X_i} \quad i = 1,2,3, \dots, k \quad \text{Eq. 3}$$

163



164 Where  $x_i$  are the coded values,  $X_i$  the real values of independent variables,  $X_{io}$  is the real value  
 165 in the center plane, and  $\Delta X_i$  the step change. Moreover, a polynomial regression model was  
 166 utilized to analyze the causal relationship between the dependent and independent variables.  
 167 The regression equation was expressed as follows:

$$168 \quad Y = \beta_0 + \sum_{i=1}^K \beta_i x_i + \sum_{i=1}^K \beta_{ii} x_i^2 + \sum_{i=1}^{K-1} \sum_{j=2}^K \beta_{ij} x_i x_j + \varepsilon \quad \text{Eq. 4}$$

169 Where  $Y$  is a response variable,  $\beta$  represents a set of regression coefficients (also called  
 170 constants),  $k$  is the number of exogenous variables (independent variables), and  $\varepsilon$  an unknown  
 171 constant error vector.

172 It must be noted that the positive sign in the regression equation represents the synergistic  
 173 effect between parameters, whereas the negative sign indicates an antagonistic effect. The  
 174 optimal values of the parameters were obtained through the estimation of the regression  
 175 equation and the interpretation of the response of the contour plots.

176 **Table 2.** Experimental ranges and levels of independent variables

Variables design	Factors	Range and levels		
		-1	0	1
$X_1$	$\lambda$ (nm)	254	310	366
$X_2$	$m_{\text{catalyst}}$ (mg)	20	50	80
$X_3$	[MO] (ppm)	20	40	60

177

### 178 3. Results and discussions

#### 179 3.1. Physicochemical properties of the prepared materials

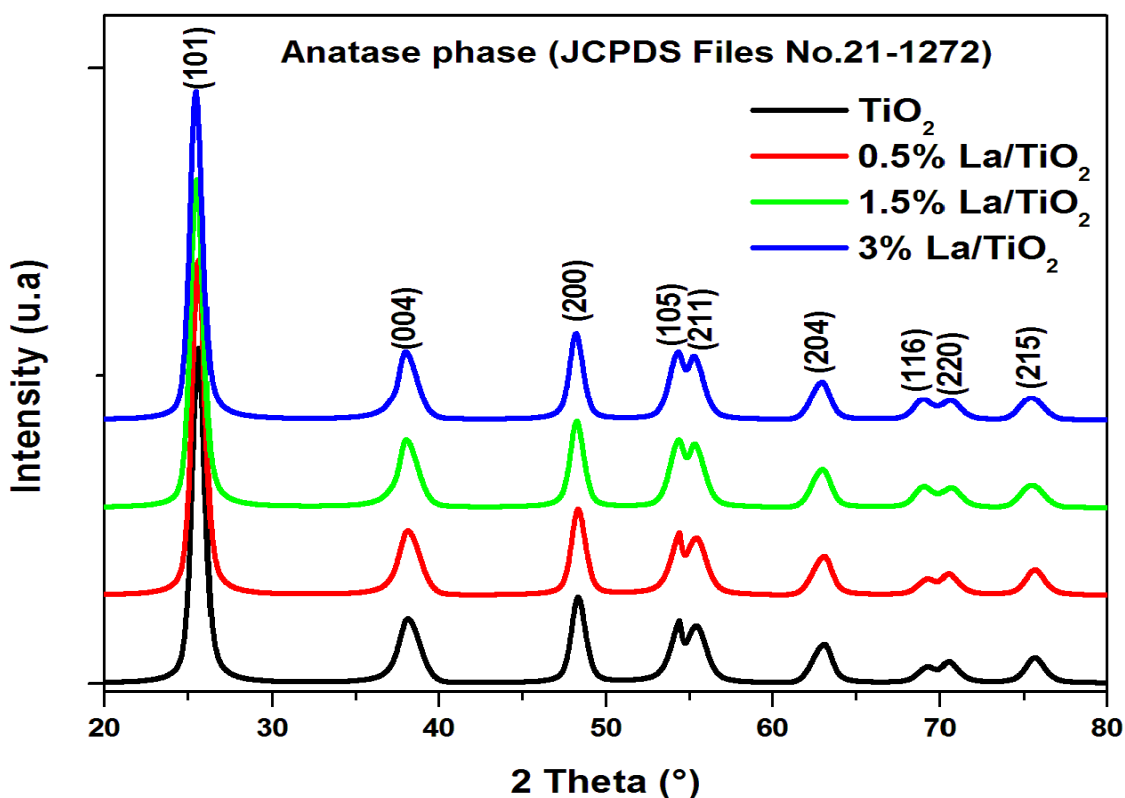
##### 180 3.1.1. X-ray diffraction characterization

181 **Figure 2** shows the XRD spectra of  $\text{TiO}_2$  and  $X\% \text{La/TiO}_2$  materials. For all the samples, it  
 182 seems that  $\text{TiO}_2$  is present in the anatase phase (JCPDS Files No.21-1272) with a crystallite  
 183 size around 12 nm, as calculated using the formula of Debye Scherrer given by Equation 5:

$$184 \quad d = \frac{0.98 \cdot \lambda}{\beta \cdot \cos(\theta)} \quad \text{Eq.5}$$

185 Where  $d$  is the crystallite size (nm),  $\lambda$  the wavelength of light (nm),  $\beta$  the full width at half  
186 maximum (FWHM) (Rad), and  $\theta$  is Bragg's angle (Rad) corresponding to the most intense  
187 peak characteristic of  $\text{TiO}_2$ ; this peak is located at  $25^\circ$ .

188 On the other hand, no characteristic peak of La species was found in the recorded XRD  
189 patterns, implying that either La ions were incorporated into the bulk of mesoporous  $\text{TiO}_2$ , or  
190 the La particles were very small and highly dispersed on the mesoporous  $\text{TiO}_2$  surface. Note  
191 that the ionic radius of  $\text{La}^{3+}$  ( $1.15\text{\AA}$ ) is bigger than that of  $\text{Ti}^{4+}$  ( $0.68\text{\AA}$ ) [5, 10], which  
192 indicates that these lanthanide ions cannot really be incorporated within the lattice structure of  
193  $\text{TiO}_2$  [5, 10].



194

195

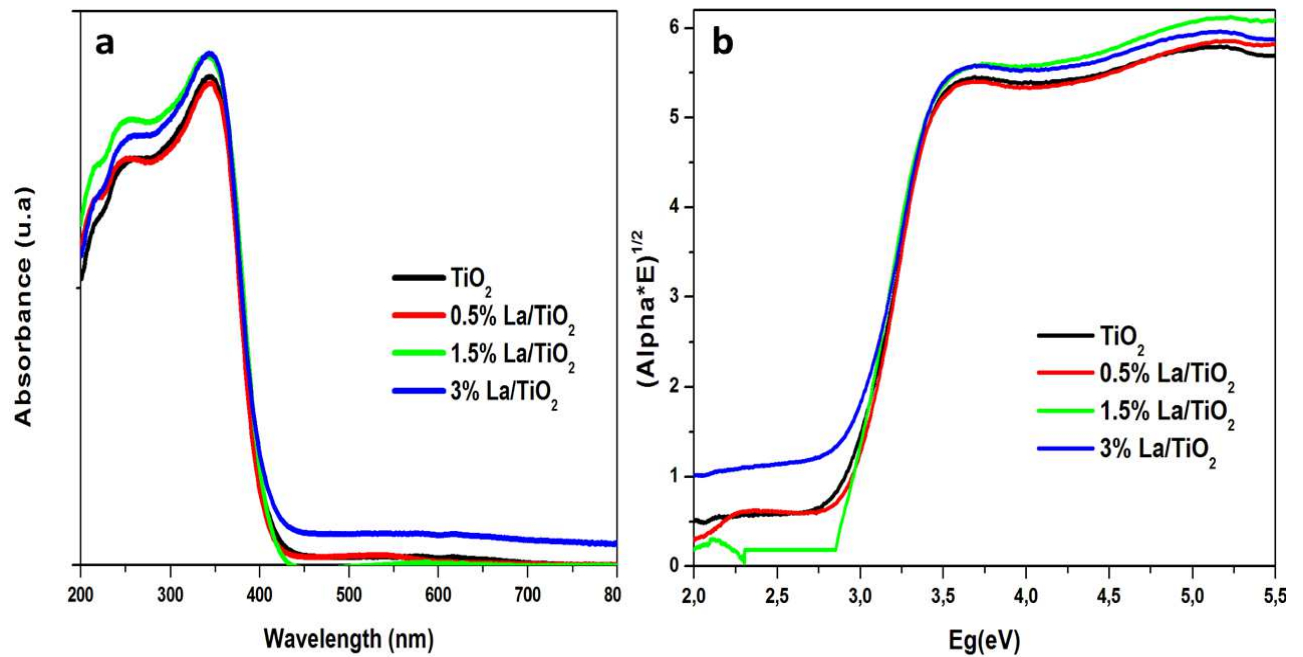
Fig. 2. XRD patterns of  $\text{TiO}_2$  and X%  $\text{La/TiO}_2$  materials.

196

### 197 3.1.2. RD/UV-Vis characterization

198 **Figure 3** displays the RD/UV-Vis spectra of the prepared materials. All samples show an  
199 important absorption within the UV range ( $< 400$  nm) [38-40]. Besides, **Figure 4** indicates

200 that the deconvolution spectra of mesoporous TiO<sub>2</sub> shows the presence of intense absorbance  
201 bands around 210-250 nm and 300-350 nm. The first region might be associated with the  
202 ligand–metal charge transfer between tetrahedral Ti<sup>4+</sup> and an oxygenated ligand such as O<sup>2-</sup>,  
203 while the second one is ascribed to the Ti<sup>4+</sup> cations in the octahedral environment and to the  
204 anatase phase as well[38-40].



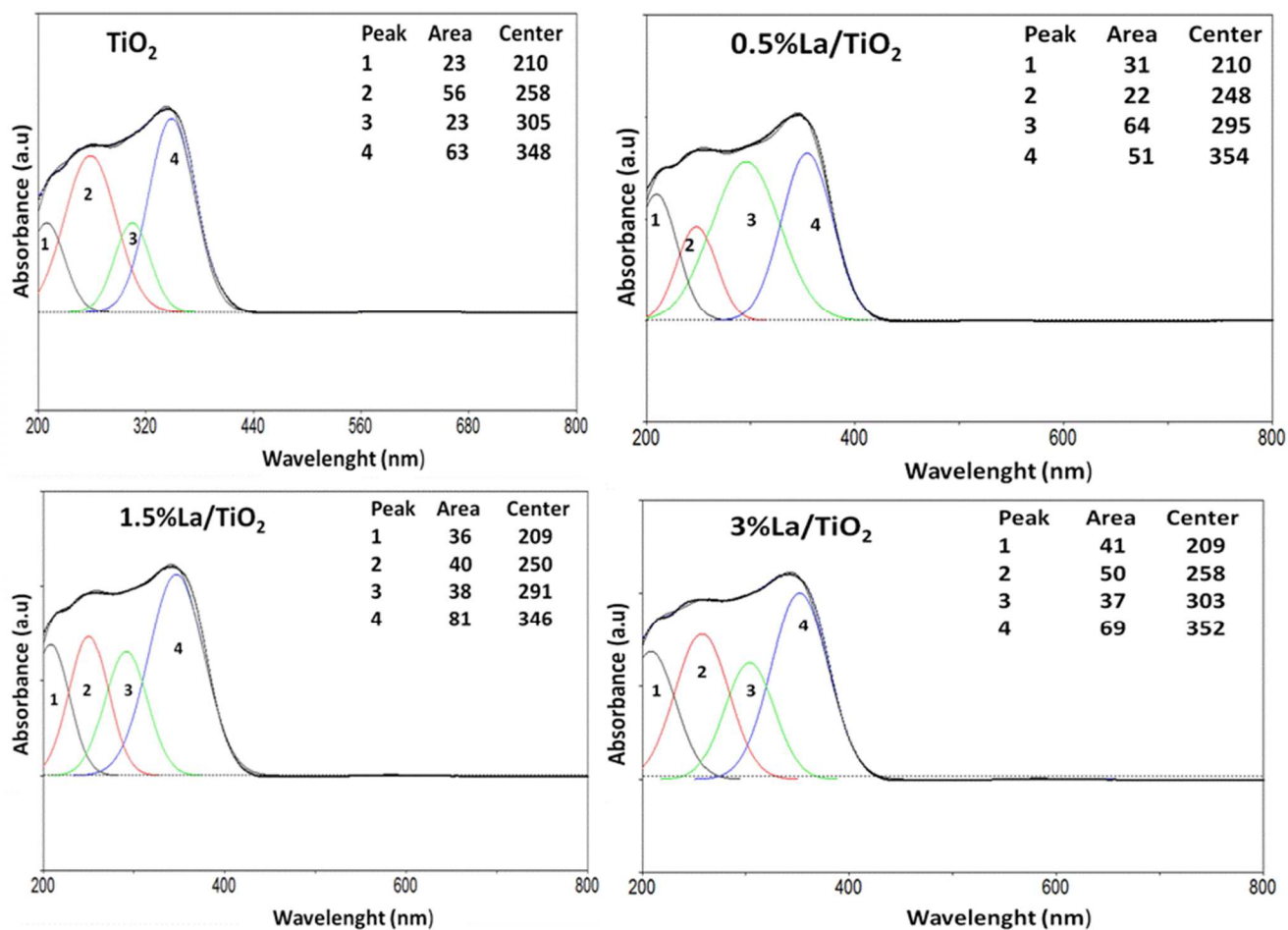
205

206 **Fig. 3. (a)** RD/UV-Vis absorption spectra and **(b)** the variation of  $(\alpha * E)^{1/2}$  as a function of  $E_g$   
207 of TiO<sub>2</sub> and X %La/TiO<sub>2</sub> materials.  
208

209

210 It can clearly be seen that the intrinsic absorption band of La-doped TiO<sub>2</sub>, unlike the undoped  
211 TiO<sub>2</sub>, shifts towards the infrared region. The absorption band changes with the doping levels,  
212 and the red shift is greater when the quantity of La is important. The improvement in the La-  
213 doped mesoporous TiO<sub>2</sub> absorption in the visible region of the UV-Vis spectra may be  
214 assigned to the creation of a new energy level near the conduction band of TiO<sub>2</sub> (**Figure 8**)[8,  
215 9]. This energy level makes the transition of electrons from the valence band to the  
216 conduction band of TiO<sub>2</sub> much easier and consequently promotes the absorption of long-wave  
217 photons, which causes the red shift to move into the UV-Visible spectra[11, 41-43].

218



220

221 **Fig .4.** Deconvolution of RD/UV-Vis spectra of TiO<sub>2</sub> and X %La/TiO<sub>2</sub> materials.

222

223 **Figure 3** depicts the reflectance diffuse spectra that were recalculated from the graph  
 224 representing the variation of  $(\alpha E)^{1/2}$  as a function of the energy in order to obtain the band gap  
 225 energy values ( $E_g$ ). These values were determined by extrapolation of the straight line  
 226 representing  $(\alpha E)^{1/2}$  as a function of  $E_g$  to zero. **Figure 3.b** clearly suggests that the presence of  
 227 La<sup>3+</sup> induces a decrease in the band gap energy value of pure TiO<sub>2</sub> as the amount of  
 228 Lanthanum (**Table 3**) this proves the success doping of La in TiO<sub>2</sub> support.

229

230 **Table 3.** Structural and optical characteristics of the materials prepared

Materials	$S_{\text{BET}}(\text{m}^2.\text{g}^{-1})$	Pore volume (cc/g)	Pore diameter (nm)	$E_g(\text{eV})$
<b>TiO<sub>2</sub></b>	102	0.20	2.8	2.88
<b>0.5%La/TiO<sub>2</sub></b>	123	0.27	2.9	2.86
<b>1.5%La/TiO<sub>2</sub></b>	130	0.30	3.1	2.82
<b>3%La/TiO<sub>2</sub></b>	215	0.33	3.5	2.78

231

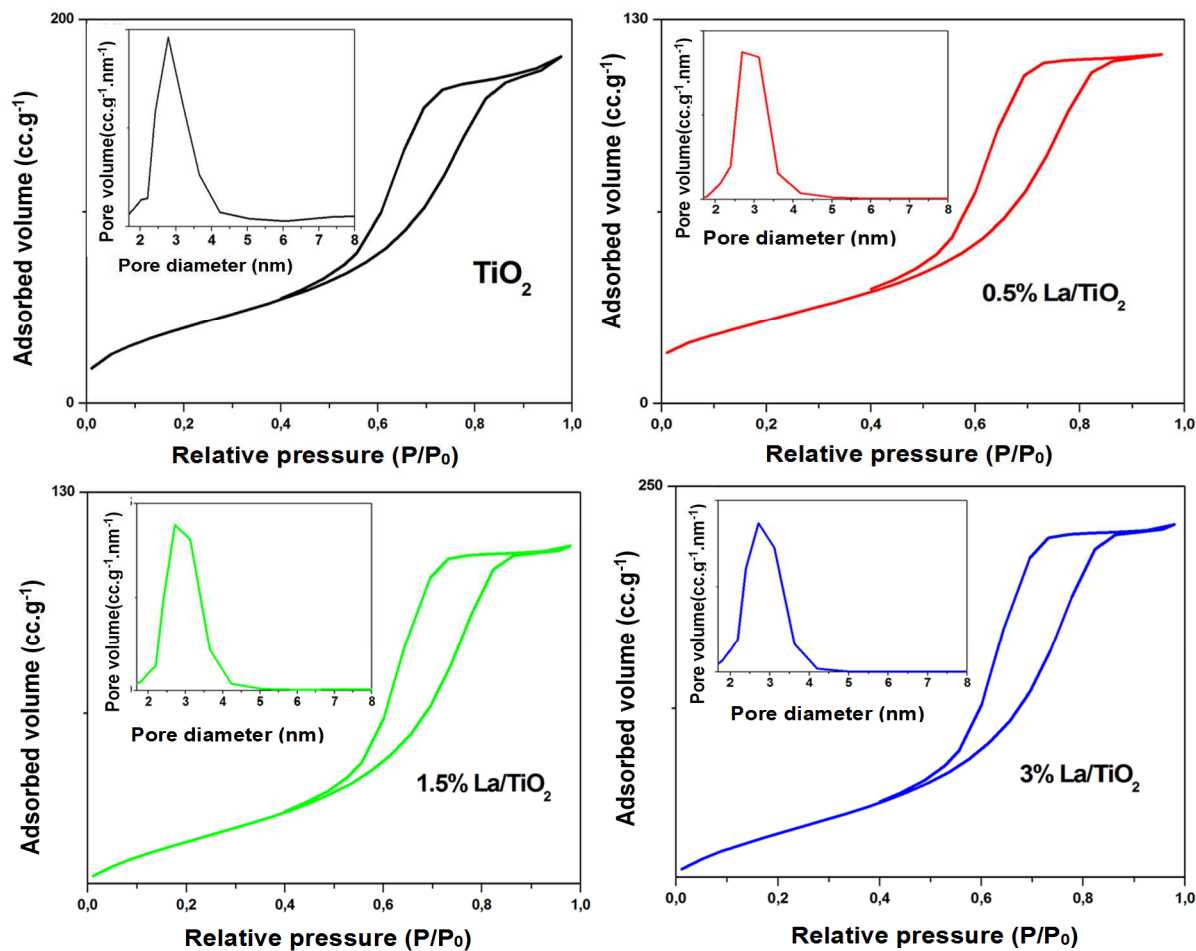
### 232 3.1.3. Textural properties

233 Nitrogen adsorption and desorption analyses were carried out for all materials, and the results  
 234 obtained are illustrated in **Figure 5**. The shape of all isotherms indicates that these are of type  
 235 IV; these isotherms are characteristic of mesoporous materials[8, 9]. However, a typical  
 236 hysteresis B behavior is clearly observed in all materials. Furthermore, the shapes of the  
 237 isotherms and hysteresis suggest the presence of slit-like pores which are thus considered to  
 238 account for the large surface areas of photocatalysts. It is important to mention that the  
 239 measured surface area using BET (Brunauer-Emmett-Teller) method ( $S_{\text{BET}}$ ) of the materials  
 240 was found equal to  $102 \text{ m}^2.\text{g}^{-1}$  for undoped TiO<sub>2</sub>,  $123 \text{ m}^2.\text{g}^{-1}$  for 0.5%La/TiO<sub>2</sub>,  $130 \text{ m}^2.\text{g}^{-1}$  for  
 241 1.5% La/TiO<sub>2</sub>, and  $215 \text{ m}^2.\text{g}^{-1}$  for 3% La/TiO<sub>2</sub>, as shown in **Table 3**. These results suggest that  
 242 there is a clear tendency for the surface area of materials to increase with the amount of the  
 243 dopant La goes up. It is worth noting that the La particles contribute to the increase of the  
 244 specific surface due to the good distribution of these particles and to their small size as well  
 245 [9].

246 Furthermore, the pore size distribution curves of the samples were determined according to  
 247 the BJH (Barrett, Joyner, Halenda) method, are shown in **Figure 5**. In all cases, the intense  
 248 peak that is centered at around 2-4 nm indicates that the pores have an average size of 3 nm.  
 249 The increase in the specific surface of the doped materials may be attributed to the  
 250 introduction of La particles in the TiO<sub>2</sub> pores and consequently increase the pore size.

251

252



253

254 **Fig. 5. Nitrogen adsorption-desorption isotherms and pore size distribution of X%La/TiO<sub>2</sub> at**  
 255 **77K.**

256

### 257 3.2. Photocatalytic test

258 First, preliminary tests were carried out for the purpose of selecting the optimal content of

259 lanthanum, and then a comprehensive study was conducted on the optimal catalyst. To do

260 this, the photocatalytic activities of the prepared photocatalysts were evaluated via the

261 photodegradation and mineralization of MO in aqueous solution under UV-Vis light

262 irradiation, as illustrated in **Figures 6.a, 6.b and 6.c**. The photodegradation of MO was

263 followed by light absorption, at regular time intervals, as indicated in the experimental

264 section. In the absence of irradiation and catalysts, only a slight light absorption was observed

265 (less than 2%). The results obtained indicate that both light and the catalyst are necessary for

266 an efficient MO photodegradation. Interestingly, the strong absorption band of MO, located at

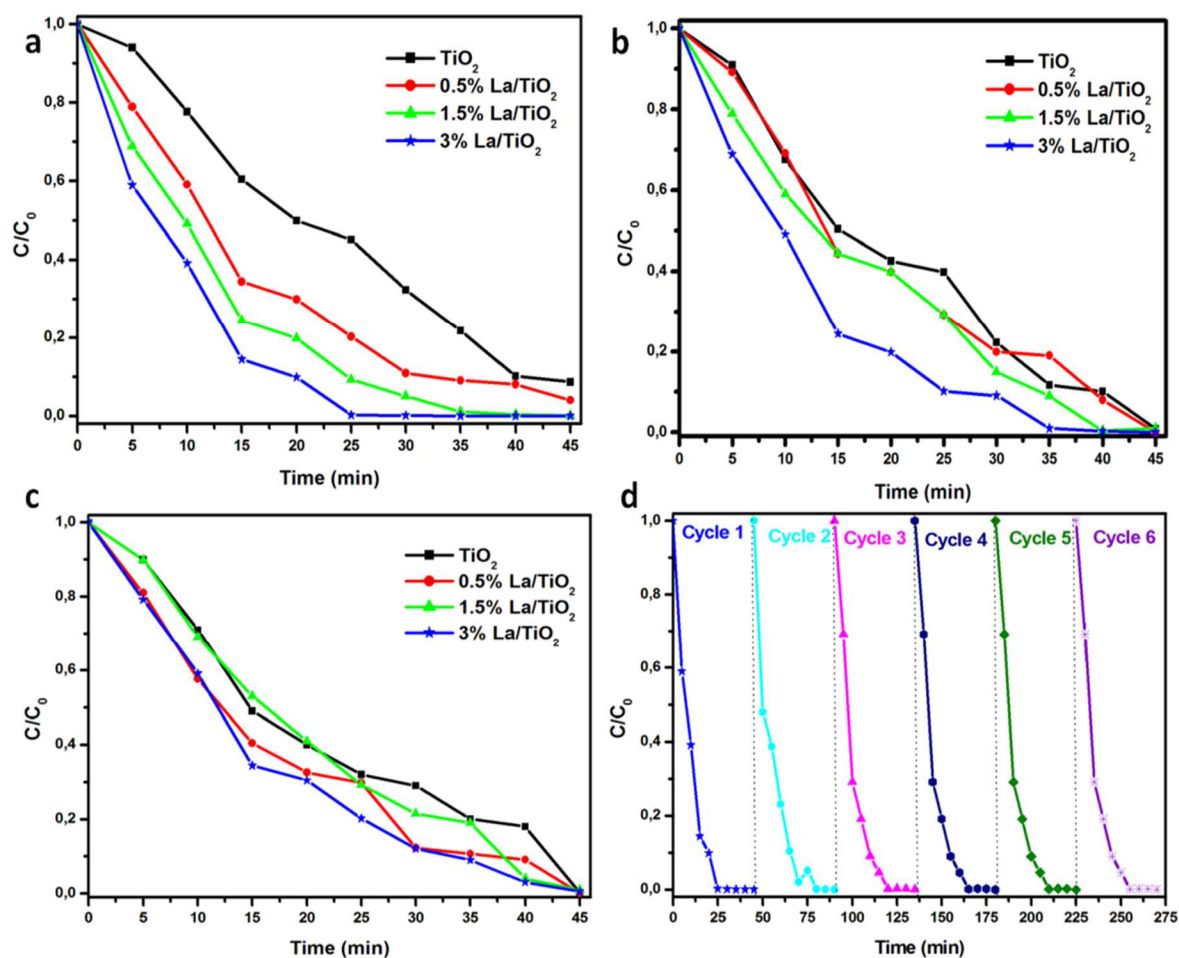
267  $\lambda = 463$  nm, decreased as the number of irradiation times went up; this band finally almost  
268 disappeared within 25min when 3%La/TiO<sub>2</sub> was used as a photocatalyst.

269 Furthermore, **Figures 6.a, 6.b and 6.c** suggest that the photodegradation of MO by La-doped  
270 mesoporous TiO<sub>2</sub> is more efficient than by pure TiO<sub>2</sub>, whatever the light source. The  
271 photocatalytic activity of the prepared photocatalysts, under UV light irradiation, follows the  
272 decreasing order of 3%La/TiO<sub>2</sub> > 1.5%La/TiO<sub>2</sub> > 0.5%La/TiO<sub>2</sub> > TiO<sub>2</sub>. Furthermore, it turned  
273 out that the photodegradation of MO by La-doped mesoporous TiO<sub>2</sub> was faster under UVA  
274 irradiation and varied with the type of light source (UVA > UVB > UVC); this was not the  
275 case for pure TiO<sub>2</sub> for which the photodegradation activity followed the increasing order  
276 UVA < UVB < UVC. It has been largely proven that TiO<sub>2</sub> is more active under UVC  
277 irradiation; this is mainly attributed to its wide band gap[8, 9].

278 The stability of the most performant catalyst, i.e. 3%La/TiO<sub>2</sub>, was assessed during six cycles.  
279 It is useful to know that, after each cycle, the catalyst was recovered by centrifugation, dried  
280 and reused. In addition, it is worth mentioning that MO photodegradation remained almost  
281 unchanged, between 95 and 98% (**Figure 6.d**).

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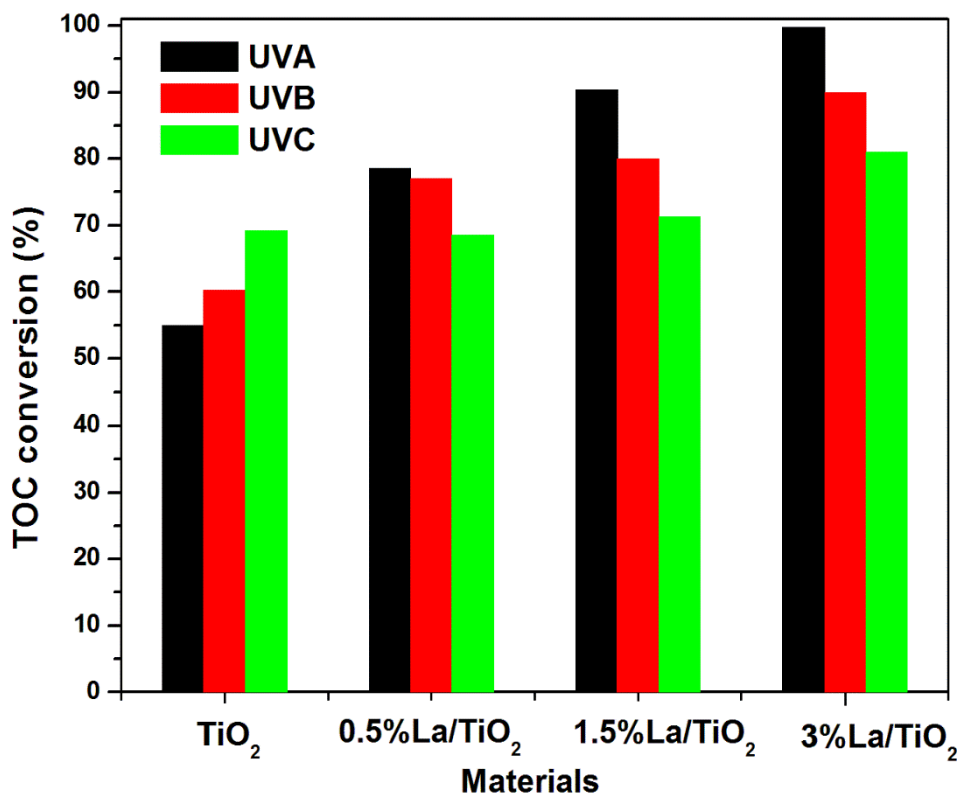
285 **Fig. 6.** (a), (b) and (c) Photodegradation curves of MO using pure and doped mesoporous  
 286 TiO<sub>2</sub> photocatalysts under UVC, UVB and UVA irradiations respectively. (d) Stability test  
 287 result of 3%La/TiO<sub>2</sub> photocatalyst after 6 cycles.  
 288

289

290 To investigate the total mineralization efficiency of prepared photocatalysts, TOC  
 291 measurements were undergone. In fact, the disappearance of the MO coloration is not enough  
 292 to prove its mineralization. The degradation of the organic dye leads to organics by-products  
 293 that will be degraded their turn. These compounds are no more colored and only TOC  
 294 measurements can prove their effective degradation[9].

295 The mineralization yields calculated after 30 min of irradiation are illustrated in Figure 7. The  
 296 TOC abatement values were significantly higher for La-doped mesoporous TiO<sub>2</sub> whatever the  
 297 light source. The best TOC abatement was 99.80% for 3%La/TiO<sub>2</sub>. These results indicate that  
 298 La loading enhanced the photocatalytic activity of TiO<sub>2</sub> and its mineralization efficiency.





**Fig. 7.** TOC conversion (%) for the photocatalytic degradation of MO under UV light irradiation.

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It should be noted that the highest photocatalytic activity was obtained with 3%La-doped TiO<sub>2</sub>, for all light wavelengths. This could be explained by the transition of the electrons of the 4f subshell of lanthanum ion, which leads to the improvement of the optical properties of the photocatalyst. They support the separation of photo-generated electron-hole ( $e^-/h^+$ ) pairs. Furthermore, the red shift of the optical adsorption edge of TiO<sub>2</sub> by lanthanum-doped TiO<sub>2</sub> was useful for the improvement of the UV-light photocatalytic activity of TiO<sub>2</sub>. In this context, Stengl et al. found out that the optimum content of lanthanum supported on oxides for the photodegradation of azo dyes was  $\sim 3-4$  wt% under UVC irradiation, while the optimum content of lanthanum was around 1–2 wt% under visible light irradiation [44]; these results are in good agreement with our findings. It is useful to recall that increasing the dopant ion content induces a higher surface barrier and a narrower space charge region.

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### 318 3.3. Proposed photocatalytic mechanism

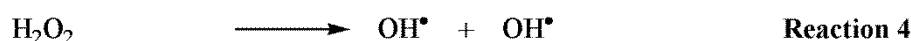
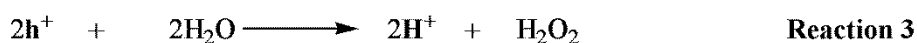
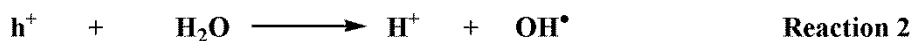
319 TiO<sub>2</sub> is a semiconductor with a large band gap. Nevertheless, the biggest problem of using  
320 TiO<sub>2</sub> lies in the fact that only UV light irradiation can be applied because, as stated before,  
321 this material possesses a wide band gap. This drawback was addressed through the doping of  
322 TiO<sub>2</sub> with La, which allowed reducing the band gap width.

323 Hence, La-doped TiO<sub>2</sub> was capable of absorbing photons from visible light, and the electrons  
324 were excited from the valence band (VB) to the conduction band (CB) of the semiconductor  
325 (Figure 8), hence creating electron-hole pairs (e<sup>-</sup> and h<sup>+</sup>), as shown in reaction 1. It is worth  
326 noting that the holes created in the VB can therefore form hydroxyl radicals (OH<sup>•</sup>) via the  
327 oxidative reactions, expressed in reaction 2.

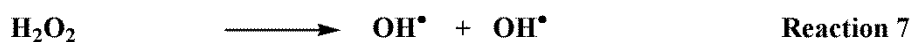
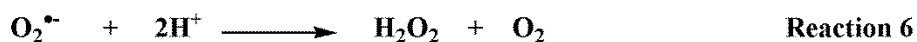
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#### (ii) Oxidative reactions with holes



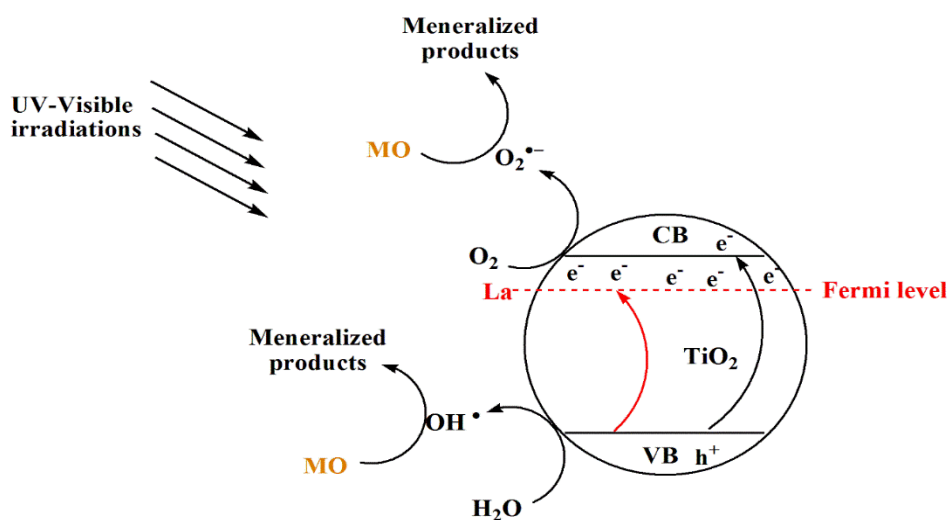
#### (ii) Reductive reaction with O<sub>2</sub>



330 Consequently, the electrons in the CB form super oxide radical anions (O<sub>2</sub><sup>•-</sup>) through the  
331 reductive reactions, as given in reactions 5 and 6. It is important to note that the two radicals  
332 OH<sup>•</sup> and O<sub>2</sub><sup>•-</sup> are strong oxidants that can oxidize the organic compounds. Indeed, O<sub>2</sub><sup>•-</sup> has a

333 sufficient reduction potential that allows oxidizing organic species with strong electron-  
 334 donating groups (such as active azo -N=N- bond); however, radical OH• tends to remove  
 335 hydrogen or attack the C-C unsaturated bonds [45]. Therefore, a model pollutant containing  
 336 unsaturated C-C bonds such as MO can very likely be photocatalytically oxidized or attacked  
 337 with the formation of OH• radicals.

338



339

340 **Fig. 8.** Proposed pathway for photocatalytic degradation of MO using La-doped TiO<sub>2</sub> under  
 341 UV irradiation[46].

342

### 343 3.4. Experimental design and statistical analysis

344 The Box–Behnken design matrix for the real values, along with the experimental (irradiation  
 345 at 30 min) and predicted values for TOC abatement (%) for the optimum photocatalyst are  
 346 summarized in **Table 4**. The maximum abatements (%) were found equal to 99.89% and  
 347 100% for actual and predicted values, respectively.

348 The final quadratic equation (**Equation 6**) generated by the design model with the three  
 349 independent variables and dependent responses (Y) can be expressed as:

$$\begin{aligned}
 \widehat{Y}_2 = & 71.7667 + 2.8625(X_1) + 22.4437(X_2) - 11.6663(X_3) + 0.3(X_1)(X_2) - 0.475(X_1)(X_3) \\
 & + 1.0875(X_2)(X_3) + 5.60792(X_1)^2 - 6.17458(X_2)^2 + 2.60042(X_3)^2 \quad \text{Eq. 6}
 \end{aligned}$$

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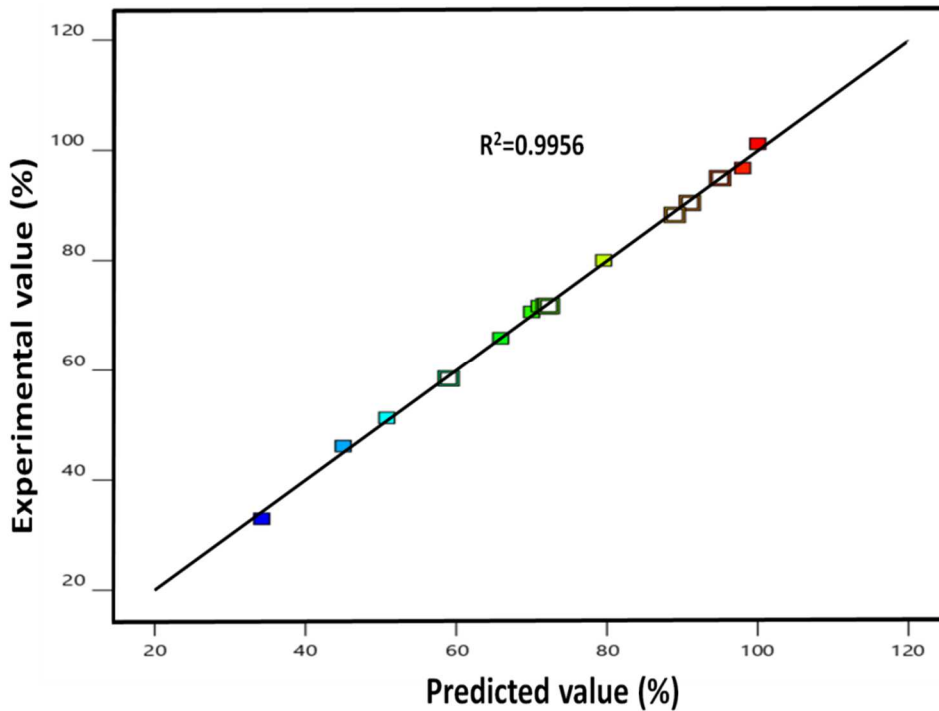
353 **Table 4 .** Box-Behnken design with experimental values for the independent variables

Run order	Codedlevel of Variables			Actuallevel of variables			R (%)	
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Observed response	Predicted response
1	0	1	-1	310	80	20	99.89	100
2	-1	0	1	254	50	60	65.9	65.92
3	0	-1	-1	310	20	20	59	58.50
4	-1	1	0	254	80	40	91	90.48
5	0	1	1	310	80	60	79.56	80.05
6	1	0	-1	366	50	20	95	94.97
7	1	-1	0	366	20	40	50.8	51.31
8	0	0	0	310	50	40	71	71.80
9	0	0	0	310	50	40	72	71.76
10	-1	0	-1	254	50	20	89	88.30
11	0	0	0	310	50	40	72.3	71.76
12	0	-1	1	310	20	60	34.21	32.99
13	-1	-1	0	254	20	40	45	46.19
14	1	0	1	366	50	60	70	70.69
15	1	1	0	366	80	40	98	96.80

354

355 The model statistical significance and its validity were tested through the analysis of variance  
356 (ANOVA). The model robustness was evaluated using both the coefficient of determination  
357 ( $R^2$ ) and the adjusted coefficient of determination (adjusted  $R^2$ ). They were both found equal  
358 to 0.9956 approximatively (**Figure 9**).

359



360

361

**Fig. 9.** Predicted response vs. observed response

362

363 Conventionally, the commonly accepted threshold value is equal or greater than 0.80. The

364 closer this value is to one, the more suitable the model is[47]. As it can be seen in **Table 5**, the

365 Fischer value (*F*-value) and probability value (*p*-value) of the yields were quite significant as

366 they were found smaller than 0.05%.

367 **Table 5.** Analysis of Variance for Response surface quadratic model

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
<b>Model</b>	9	9	610.49	349.53	< 0.0001	<b>Significant</b>
<b>X<sub>1</sub></b>	65.55	1	65.55	37.53	0.0017	
<b>X<sub>2</sub></b>	4029.78	1	4029.78	2307.25	< 0.0001	
<b>X<sub>3</sub></b>	1088.81	1	1088.81	623.40	< 0.0001	
<b>X<sub>1</sub>X<sub>2</sub></b>	0.3600	1	0.3600	0.2061	0.6689	
<b>X<sub>1</sub>X<sub>3</sub></b>	0.9025	1	0.9025	0.5167	0.5044	
<b>X<sub>2</sub>X<sub>3</sub></b>	4.73	1	4.73	2.71	0.1607	
<b>X<sub>1</sub><sup>2</sup></b>	116.12	1	116.12	66.48	0.0005	
<b>X<sub>2</sub><sup>2</sup></b>	140.77	1	140.77	80.60	0.0003	
<b>X<sub>3</sub><sup>2</sup></b>	24.97	1	24.97	14.30	0.0129	
<b>Residual</b>	8.73	5	1.75			
<b>Lack of Fit</b>	7.81	3	2.60	5.62	0.1549	<b>not significant</b>

368

R<sup>2</sup>=0.9984, Adj. R<sup>2</sup> =0.9956 and Pred. R<sup>2</sup>= 0.9769.

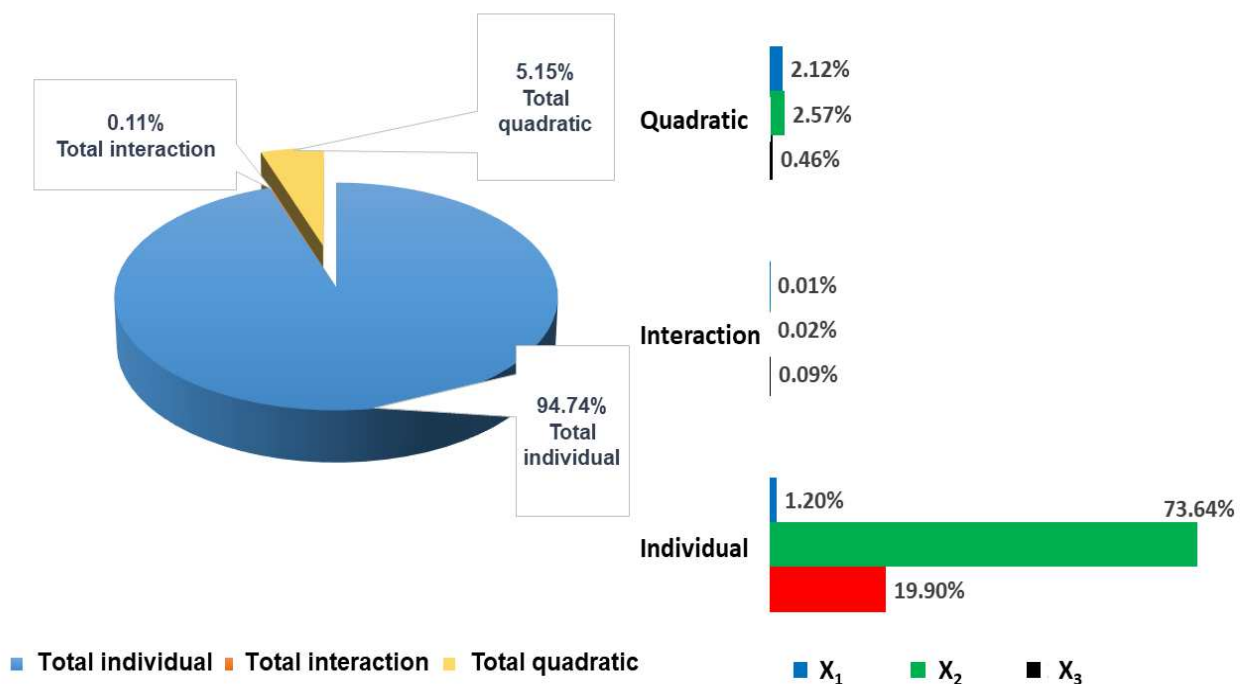
369  
 370 Furthermore, the sum of squares (SS) taken from ANOVA data were used to calculate the  
 371 total percentage contributions (TPC) for each model term. The TPC for the first order,  
 372 interaction, and quadratic terms could be obtained using the following three equations[48]:

$$373 \quad TPC_i = \frac{\sum_{i=1}^n SS_i}{\sum_{i=1}^n \sum_{i=1}^n SS_i + SS_{ii} + SS_{ij}} \times 100 \quad \text{Eq. 7}$$

$$374 \quad TPC_{ij} = \frac{\sum_{i=1}^n \sum_{i=1}^n SS_{ij}}{\sum_{i=1}^n \sum_{i=1}^n SS_i + SS_{ii} + SS_{ij}} \times 100 \quad \text{Eq. 8}$$

$$375 \quad TPC_{ii} = \frac{\sum_{i=1}^n \sum_{i=1}^n SS_{ii}}{\sum_{i=1}^n \sum_{i=1}^n SS_i + SS_{ii} + SS_{ij}} \times 100 \quad \text{Eq. 9}$$

376  
 377 This can be expressed as the factorial weight or the variance part taken by each considered  
 378 factor. As shown in **Figure 10**, the individual effect is more predominant than the interactive  
 379 and quadratic effects, which is consistent with the findings reported in the literature[29].  
 380 Furthermore, the catalyst weight can be considered as the most important factor, followed by  
 381 the MO concentration. However, the light irradiation wavelength is less decisive in our  
 382 model.

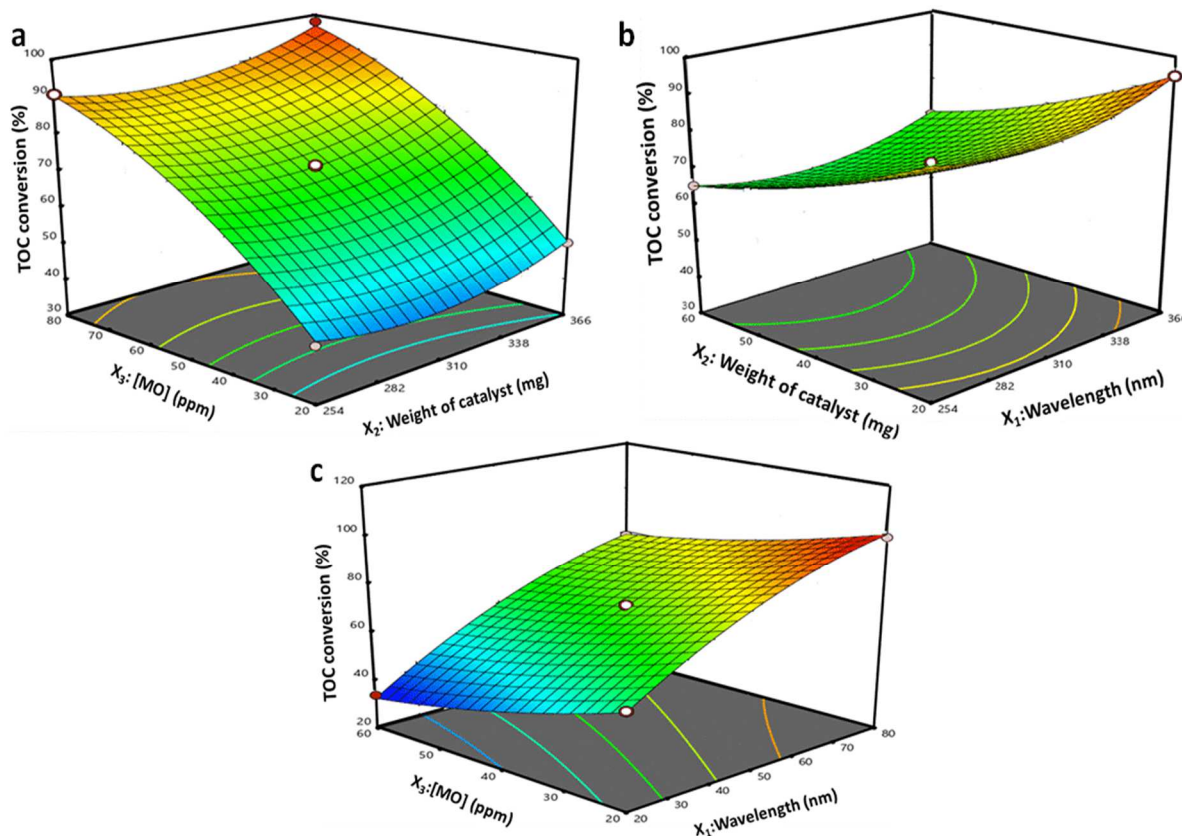


384 **Fig. 10** .Schematic representation of the Percentage Contribution.

385 Based on the data obtained by ANOVA for the quadratic model (**Table 5**), the F-value of the  
386 Lack of Fit (LOF) equal to 5.62 implies that the LOF is quite low as compared to the absolute  
387 error. A non-significant LOF value means that the contribution of the selected variable is  
388 sufficiently high for building the entire model. Therefore, it can be stated that our results are  
389 in good agreement with those reported in several works in the relevant literature [48, 49].  
390 Finally, three dimensional response surface plots are drawn in **Figure 11** to visualize the  
391 interaction effects between the independent variables and the responses.

392 **3.5. Optimization and model validation**

393 **Figure 11** presents the three dimensional (3D) response surface plots of yields as a function  
394 of the independent variables. The 3D surface explains the relationship between the dependent  
395 variables (R) and independent variables ( $X_1$ ,  $X_2$  and  $X_3$ ). With regard to these three variables,  
396 one of them remained constant at its zero level, while the two others were analyzed  
397 separately.



398

399 **Fig. 11.** 3D surface plots of R as a function of (a) X<sub>2</sub> and X<sub>3</sub>, (b) X<sub>1</sub> and X<sub>2</sub>, and (c) X<sub>2</sub> and X<sub>3</sub>

400

401 **Figure 11.a** shows the contour plot of response R as a function of the MO concentration and  
 402 catalyst weight, while the irradiation light wavelength is kept constant. It is worth indicating  
 403 that increasing the MO concentration and catalyst weight leads to increase TOC conversion.  
 404 Similarly, **Figure 11.b** suggests that when the irradiation wavelength and catalyst weight  
 405 increase, the R value goes up too. Unlike the other observations made in **Figure 11.b**,  
 406 increasing the irradiation light wavelength and MO concentration, while the catalyst weight is  
 407 kept constant, results in a decrease of the response R (**Figure 11.c**).

408 However, it should be noted that there is an upper threshold for the yield optimization levels  
 409 for these parameters. This finding goes in the same way with the experimental results  
 410 obtained for other response surfaces works [46-48].

411 **4. Conclusion**



412 This work was mainly focused on the preparation and characterization of nanomaterials based  
413 on mesoporous TiO<sub>2</sub> doped with Lanthanum. Besides, it include a modeling and optimization  
414 framework for the photodegradation and mineralization of MO under UV light irradiation.  
415 The effects of the three parameters, namely the irradiation light wavelength, catalyst weight  
416 and pollutant concentration on the mineralization of MO, were studied using the Box-  
417 Behnken experimental design. The results of the photocatalytic experiments showed that the  
418 3%La/TiO<sub>2</sub> photocatalyst enhances the photocatalytic activity of TiO<sub>2</sub> under UV irradiation.  
419 The activity improvement of TiO<sub>2</sub> can be attributed to the large specific area, good dispersion  
420 of La particles, small size of crystallites, and narrow energy gap, which can likely lead to the  
421 total elimination of MO. The ANOVA data for the quadratic model revealed that the catalyst  
422 weight is the most significant factor influencing the response followed by the pollutant  
423 concentration, and finally the irradiation wavelength. Therefore, the quadratic models using  
424 the Box-Behnken design are quite as they express a very high coefficient of determination R<sup>2</sup>  
425 (0.9956). The optimal conditions after the regression analysis were achieved with an  
426 irradiation wavelength of 310 nm, catalyst weight of 80 mg and MO concentration of 20 ppm,  
427 for a TOC abatement rate of 98.89%. This study confirms that the Box-Behnken design could  
428 be efficiently applied for modeling the MO mineralization process under UV light irradiation  
429 using 3%La/TiO<sub>2</sub>. Furthermore, this strategy is an interesting economic approach to obtain the  
430 targeted information in a short time, with a minimum number of experiments.

431

#### 432 **CRedit authorship contribution statement**

433 **Hanane Chaker** Writing - Review & Editing, Conceptualization, Validation, Investigation,  
434 Methodology. **Nawal Ameur** Resources, Investigation, Formal analysis, Validation. **Karima**  
435 **Saidi-Bendahou** : Project administration. **Mustapha Djennas**: Methodology, Formal  
436 analysis. **Sophie Fourmentin** : Project administration, Supervision.

437 **Declaration of Competing Interest**

438 The authors declare that they have no conflict of interest.

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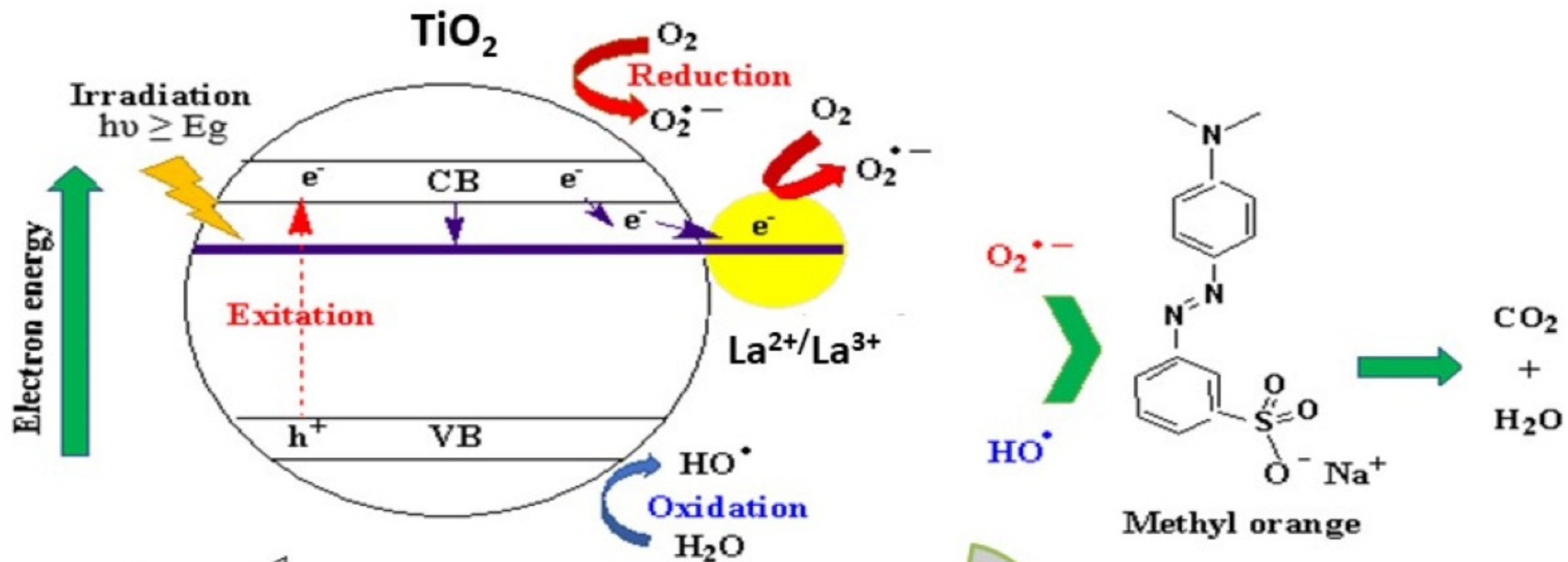
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Weight of catalyst

