

1 Optimized photodegradation of palm oil agroindustry waste 2 effluent using multivalent manganese–modified black titanium 3 dioxide

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Abbreviations

AOPs	Advanced oxidation processes	MSE	Mean square error
ANOVA	Analysis of variance	Mn	Manganese
CB	Conduction band	OPIs	Organic pollution indicators
CCD	Central composite design	PCs	Phenolic compounds
DOE	Design of experiments	POME	Palm oil mill effluent
Df	Degree of freedom	RMSE	Root mean square error
FFT	Fast Fourier transform	RSM	Response surface methodology
GA	Gallic acid	TOC	Total organic carbon
GAE	Gallic acid equivalent	TPOME	Treated palm oil mill effluent
MAD	Mean average deviation	UV	Ultraviolet
MAE	Mean average error	VB	Valence band
MAPE	Mean absolute percentage error		

28

29 ABSTRACT

30 This paper describes a systematic approach to optimizing and improving visible-light-driven
31 photodegradation of treated effluent of the palm oil agroindustry (TPOME) using
32 manganese(Mn^{3+} – Mn^{7+})-modified black titanium dioxide ($Mn/BTiO_2$) as a photocatalyst. The
33 $BTiO_2$ was fabricated using a modified wet-chemical process, which was then wet impregnated
34 with Mn and subjected to an hour-long calcination $300^\circ C$. The activity of $Mn/BTiO_2$ was
35 examined for photo-assisted elimination of chemical oxygen demand (COD), phenolic
36 compounds (PCs), color and the total organic carbon (TOC). The conditions of the
37 photocatalytic process including the photocatalyst loading, Mn concentration, hydrogen
38 peroxide (H_2O_2) dosage and irradiation time were optimized using design of experiments
39 (DOE). Under optimized conditions of 0.85 g/L photocatalyst loading, 0.048 mol/L H_2O_2
40 dosage, 0.301wt% Mn concentration, and 204 min of visible-light treatment, exceptionally
41 improved COD, PCs, color, and TOC removal efficiencies of 88.87%, 86.04%, 62.8% and
42 84.66% were obtained. According to the statistical analysis, the response variables had a high
43 R^2 and lower RMSE, MSE, MAD, MAE and MAPE, indicating high reliability in estimating
44 their removal from TPOME. This study established that the developed photocatalytic system
45 has a high-level potential for the treatment of waste effluent produced by the palm oil and other

46 agro-industries, with the ability to abate multiple organic pollution indicators (OPIs)
47 simultaneously.

48 **Keywords:** Manganese-doped black TiO₂, photodegradation of POME, comparative
49 performance, design of experiments, statistical optimization

50 **1. Introduction**

51 In nations like Indonesia and Malaysia, the palm oil agroindustry is quickly becoming a
52 significant industry and the foundation of the local economy. POME production has increased
53 due to the undeniable rise in demand for edible palm oil. The yearly production of POME in
54 Malaysia is estimated to be between 48 and 72 million tonnes (Chia et al., 2020). POME has
55 been identified as a key polluter of the environment because of its undesirable characteristics
56 such as high BOD₅ of 10,250–43,750 mg/L, COD of 15,000–100,000 mg/L, and PCs of more
57 than 1000 mg/L (Iskandar et al., 2018). When the standard discharge limits stipulated by the
58 Department of Environment Malaysia for some of the parameters were compared to the
59 characteristics of untreated POME and TPOME (Table S1), it became clear that the pollutant
60 concentration was still significantly higher than the permitted limit even after treatment. The
61 high concentrations of these pollutants suggest that the methods of POME treatment currently
62 in use fall short of the required standard.

63 Undoubtedly, over the years, various technologies for TPOME remediation have been
64 explored at the laboratory scale to bring the levels of organic pollutants under the acceptable
65 limits (Cheng et al., 2021, Aris et al., 2019, Nawaz et al., 2021), but they have some drawbacks
66 such as high operational and maintenance costs, high energy and chemical inputs requirements
67 and secondary pollution. In order to remediate recalcitrant pollutants in TPOME, advanced
68 oxidation processes (AOPs) offer a desirable and sustainable alternative solution (Miklos et al.,
69 2018, Kamyab et al., 2022, Bello and Abdul Raman, 2017). Among AOPs, the TiO₂ based
70 photocatalysis has illustrated technical and economic feasibility for TPOME remediation

71 (Bello and Abdul Raman, 2017, Ng, 2021, Chowdhury et al., 2017, Moradeeya et al., 2022).
72 Employed as a stand-alone technology, TiO₂ based photocatalysis has successfully reduced the
73 concentrations of BOD, COD, and color of TPOME by 79, 95, and 83%, respectively, in 360
74 minutes of UV irradiation (Alhaji et al., 2018). When exposed to visible light, the system
75 performed very poorly, but when exposed to UV light, it performed very well. Several methods,
76 such as doping TiO₂ with metals (Ag, Cu, Au, Pt, Nd) (Ng et al., 2016b, Sin et al., 2020b,
77 Cheng et al., 2015), modifying the morphology (Wong et al., 2019), heterojunction fabrication,
78 and coupling (Sin et al., 2020a, Sin et al., 2019) have been proposed to increase the remediation
79 efficiency of TPOME using visible irradiations. However, for industrial scale implementation,
80 higher removal efficiencies of the various OPIs, specifically PCs using visible or solar
81 radiations, are still required.

82 Fabricating black TiO₂ (BTiO₂) and Mn/TiO₂ could be potential approaches to improve the
83 remediation of TPOME. The majority of researchers seem to agree that BTiO₂ performs better
84 than other photocatalytic materials in a variety of applications, such as organic pollution
85 abatement (Kouhail et al., 2022, Liang et al., 2021). For example, after only 10 minutes of
86 visible-light irradiation, BTiO₂ synthesized via hydrogen plasma removed 89% of phenol from
87 wastewater (Zhang et al., 2020). Mn doping, on the other hand, is another effective approach
88 because Mn incorporation into TiO₂ matrix can make it efficiently utilize visible-light and
89 significantly lessen the reunification of electron-hole pairs, thereby improving photocatalytic
90 performance (Choi and Han, 2014). For example, Mn/TiO₂ has been shown to remove 91.7%
91 of 2-chlorophenol after 240 minutes of solar irradiation (Sharotri et al., 2019). However, the
92 performance of BTiO₂ and Mn/TiO₂ has been mainly investigated for model pollutants. As a
93 result, it is critical to investigate BTiO₂ and Mn doping of TiO₂ and BTiO₂ for improving
94 visible-light assisted TPOME photocatalytic remediation efficiency.



95 The photodegradation process parameters may be optimized using DOE and statistical
96 modelling as a further means of enhancing TPOME's remediation. The impact of process
97 variables such as O₂ flowrate, initial TPOME concentration, and photocatalyst loading on the
98 remediation of TPOME has been carefully examined using a variety of machine learning and
99 quadratic polynomial models approaches (Ng et al., 2016a, Ng et al., 2020, Jiang et al., 2020).
100 According to optimization techniques, the optimum conditions for removing 52.52% of COD
101 from TPOME were 70 g/L TiO₂ loading, 70 mL/L O₂ flowrate, and 250 mg/L initial COD
102 concentration. Although the final COD removal efficiency is still low and the required TiO₂
103 loading of 70 g/L is very high, the models are adequate in terms of generalizability and
104 accuracy. More importantly, no estimation or optimization of PC photodegradation in TPOME
105 has ever used such models.

106 Based on the preceding discussion, the current study aimed to develop and test a
107 photocatalytic system based on Mn/BTiO₂ and driven by light in the visible range for the
108 remediation of TPOME. The synthesis of visible-light active BTiO₂ was carried out using a
109 facile sol-gel process assisted by glycerol, which also served as a co-solvent and reductant. The
110 top-performing BTiO₂ was further modified with Mn based on preliminary performance
111 results. The photocatalytic process in RSM was optimized using CCD. The process
112 performance was evaluated based on its ability to reduce OPIs in TPOME.

113 **2. Materials and methods**

114 *2.1 Reagents and chemicals*

115 Ammonium hydroxide (NH₄OH, 25%), Folic-Ciocalteau (F-C) reagent ($\geq 98\%$), glycerol
116 (C₃H₈O₃, 85%), gallic acid (C₇H₆O₅, 99%), hydrogen peroxide (H₂O₂, 35%), sodium carbonate
117 (Na₂CO₃, $\geq 99.5\%$), potassium permanganate (KMnO₄, $\geq 99\%$), and Titanium(IV) chloride



118 (TiCl₄, 99.9%) were purchased from Merck (Darmstadt, Germany) that were of highest purity
119 grade and used directly.

120 2.2 TPOME sampling and analysis

121 TPOME liquid samples were gathered from a local palm oil industry's stabilization pond
122 (final pond) in Perak, Malaysia. Sampling locations are presented in Fig. S1. To avoid changes
123 in its properties, TPOME was kept in a cold storage at 4°C. Prior to analysis, the solid residues
124 were removed by centrifuging the sample. The characteristics of TPOME are listed in Table
125 S2. With gallic acid (GA) serving as a reference standard, the PCs concentration in TPOME
126 was measure spectrophotometrically through a slightly modified F-C analytical technique. This
127 method is used because it is quick, easy, and does not require expensive or toxic reagents (Chen
128 et al., 2015). GA was selected as the standard because it is a pure and stable substance that is
129 also more readily available and less costly than other options.

130 In a sample vial, 500 µL of diluted F-C reagent (1:4) and 100 µL of diluted TPOME were
131 typically mixed. The mixture was then treated with 500 µL of 200 g/L Na₂CO₃ solution. To
132 complete the reaction, the mixed solution was kept at 25–28°C for about 1 hour. A SpectroVis
133 Plus instrument was then used to record the solution's absorbance at 765 nm. The absorbance
134 values were converted into PCs concentrations by comparing them to the standard GA
135 calibration (10–50 mg/L) and represented in mg/L of GAE. All measurements were taken three
136 times and the average was reported.

137 With a spectrophotometer DRB5000, COD was monitored in accordance with the protocol
138 for examining water and wastewater (Ahmad et al., 2005). The current study utilized H₂O₂ in
139 optimization studies. However, it can affect COD tests, which could lead to an overestimation
140 of COD measurements (Wu and Englehardt, 2012). Therefore, comparing the COD
141 concentration in TPOME before and after the addition of H₂O₂, Eq. (1) was used to counteract
142 the effects of residual H₂O₂ (Khraisheh et al., 2012):

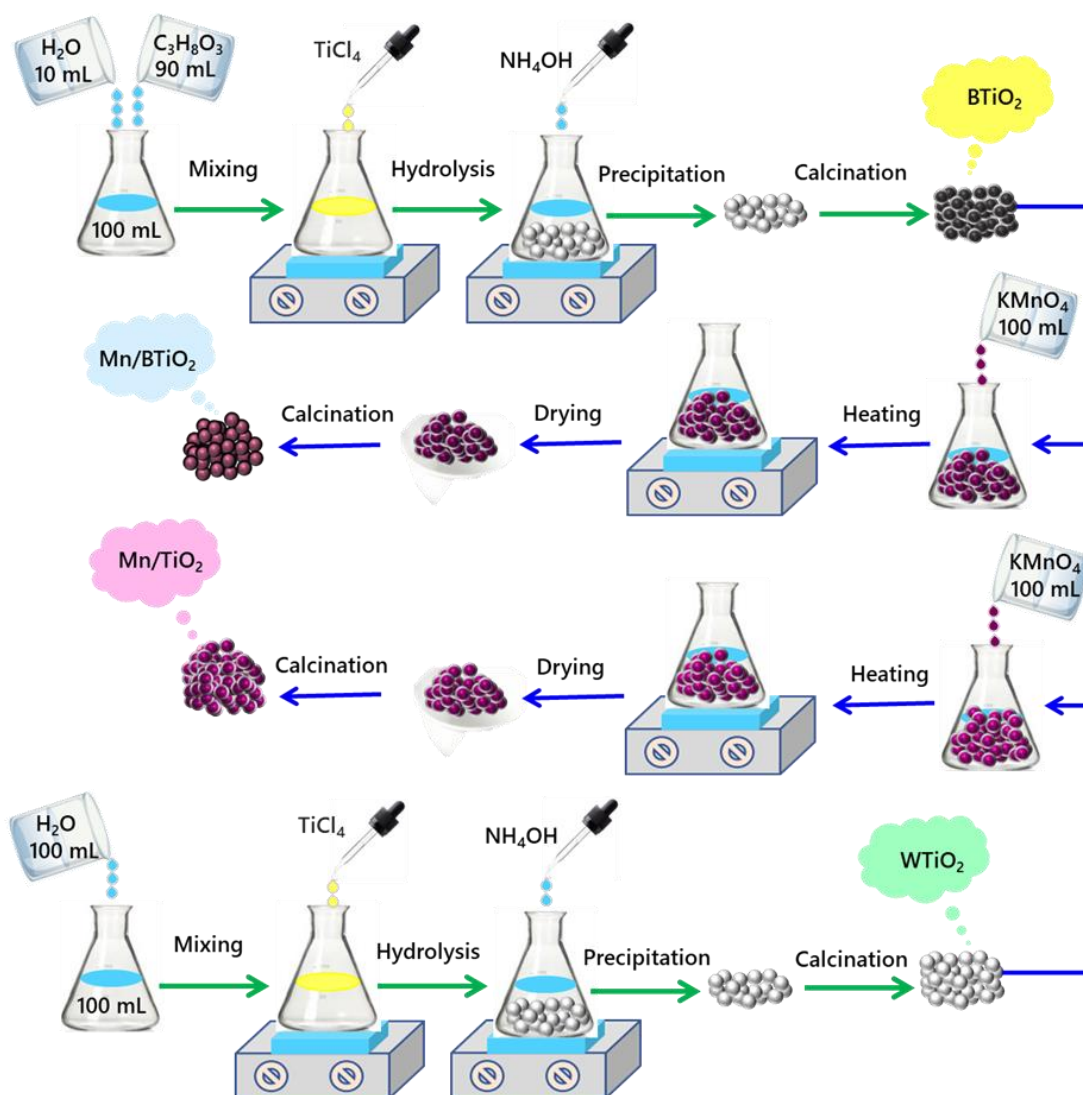
$$COD_{(true)} = COD_{measured} - 0.4514C_{H_2O_2} \quad (1)$$

143 where, COD_{true} is the COD concentration in TPOME before adding H_2O_2 , COD_m is the
144 measured COD after the addition of H_2O_2 and $C_{H_2O_2}$ is the H_2O_2 concentration in mg/L.

145 TOC was measured according to APHA Standard Method using a TOC Analyzer (TOC-
146 VCSH SHIMADZU). A closed reflux colorimetric method was used to determine the color
147 concentration of the TPOME before and after the reaction with help of DR3900 HACH
148 spectrometer (Saeed et al., 2015). The color concentration was determined using platinum-
149 cobalt (PtCo) as the standard at 455 nm.

150 2.3 Synthesis of $BTiO_2$ and $WTiO_2$ photocatalysts

151 Fig. 1 depicts a schematic of the $BTiO_2$ and $WTiO_2$ synthesis processes. A modified
152 precipitation technique that involved hydrolyzing $TiCl_4$ in 100 mL of an aqueous glycerol, then
153 calcining the resultant material was used to produce the $BTiO_2$ photocatalyst. Aqueous glycerol
154 solution (1.18 mol/L) was prepared by mixing water and glycerol at 9:1 (v/v: 90:10 mL). Then
155 approximately 18 mL of $TiCl_4$ was added to the solution drop by drop. The reaction vessel was
156 kept in an ice bath to control the temperature of the reaction at around $5^\circ C$. To maximize the
157 precipitation of TiO_2 particles, nearly 300 mL of 2.5 M NH_4OH were added to the reaction
158 mixture during the precipitation process. The precipitates were centrifuged and repeatedly
159 washed with deionized water until the washing was pH-neutral and free of chloride. The
160 precipitates were converted to amorphous white TiO_2 powder after drying in an oven at $80^\circ C$
161 for 12 hours. Anatase phase $BTiO_2$ was produced by calcining the dried powder for one hour
162 at a temperature of $300^\circ C$. The $WTiO_2$ photocatalyst was synthesized in only water following
163 the procedure as described for the synthesis of $BTiO_2$.



164

165 Fig. 1. Process flow diagram for the synthesis of WTiO_2 , BTiO_2 , Mn/TiO_2 , and Mn/BTiO_2 .

166 *2.4 Synthesis of Mn/TiO_2 and Mn/BTiO_2 photocatalysts*

167 Wet impregnation synthesis technique, which was used to prepared Mn/TiO_2 and
 168 Mn/BTiO_2 , is shown in Fig. 1. Stock solution was prepared by dissolving 1.438 g of KMnO_4
 169 in 0.1 L of deionized water. A specific quantity of the synthesised WTiO_2 (4.995, 4.985, and
 170 4.975 g) was homogenised after being suspended in 100 mL of deionized water. Then, a
 171 predetermined volume from the stock solution, such as 1.0, 3.0, and 5.0 mL, was added to the
 172 homogeneous suspension to make various Mn weight percentages, such as 0.1, 0.3, and
 173 0.5wt%, respectively. The resulting solution was heat up to 60°C until it became a slurry with
 174 constant stirring, and it was then allowed to dry for 24 hours at 80°C . The dehydrated sample

175 was calcined at 300°C for one hour to produce Mn/TiO₂. The Mn/BTiO₂ sample was prepared
176 in the same manner as the Mn/TiO₂ sample for comparison purposes.

177 2.5 Characterization of the photocatalysts

178 XRD analysis was used to analyze the crystallinity, crystallite size, and crystalline structure
179 of the photocatalysts. A powder X-ray diffraction spectrometer (PANalytical X'Pert3 Powder)
180 was used to detect the XRD patterns. They were recorded in the range of 20 to 80°(2θ) with a
181 0.001° step size and a 2 second acquisition time per step using Cu Kα irradiation (λ=1.5406 Å).
182 The Debye-Scherrer method was employed to find the average crystallite size of the
183 photocatalysts, as shown in Eq. (2).

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

184 where, λ is the wavelength of the incident rays is 1.5406 Å, K is known as the Scherrer constant,
185 which accounts for the shape factor of particles, is typically taken to be 0.9, D is the crystallite
186 size (nm), β is the reflection peak's full width at half maximum (FWHM), expressed in radians,
187 and θ is the Bragg angle.

188 HRTEM micrographs were taken using Transmission Electron Microscope (Tecnai G2-
189 F20 X-Twin TMP) equipped with Gatan Digital-Micrograph software. The HRTEM images
190 were used to create 2-dimension and 3-dimension view surface plots of TiO₂ in order to
191 determine the surface characteristics of the photocatalysts. HRTEM images were subjected to
192 Fast Fourier Transform (FFT) analysis to distinguish crystalline from amorphous phases. The
193 energy dispersive x-ray spectroscopy (EDX) instrument (Carl Zeiss SUPRA 55VP) was used
194 to identify and quantify the chemical elements of the synthesized materials.

195 XPS analysis were carried out via Thermo Scientific spectrometer. Al Kα X-rays were
196 employed as the source of excitation and the calibration C1s correction was applied at 284.5
197 eV. The Gaussian fitting was performed to obtain the XPS fitting parameters using Advantage

198 Software. DRUV-Vis measurements were carried out in UV-Visible spectrum ($\lambda=200-800$
199 nm) using UV-Vis spectrometer (Agilent Carry100). The reflectance spectra were used to
200 calculate the bandgap energies of the materials using the KM (Kubelka-Munk) function, as
201 shown in Eq. (3):

$$[F(R)h\nu]^{1/2} = K(h\nu - E_g) \quad (3)$$

202 where K has a constant value and characteristic of semiconductor, $h\nu$ is the energy of the
203 photon, and E_g is the energy gap.

204 The PL spectra of the materials were recorded with a spectrometer (Horiba LabRam HR
205 Evolution). The spectra were measured at room temperature and ranged in wavelength from
206 300 to 700 nm with an excitation wavelength of 325 nm. The physio-sorption isotherms were
207 measured with the Micromeritics ASAP 2020 analyzer (Micromeritics Corps). Based on the
208 adsorption measurement at a relative pressure (P/P_o) range of 0.1 to 1.0, the bet surface area of
209 each sample was determined using the Brunauer, Emmett, and Teller (BET) method. For the
210 acquisition of adsorption isotherms, the photocatalyst was placed in sample tube and cooled to
211 -196.0°C . On the other hand, the N_2 desorption isotherms were acquired by desorption of N_2
212 gas from the saturated sample taking similar precautions as for adsorption process. The pore
213 size of the TiO_2 photocatalysts were estimated from the data obtained for desorption using
214 Barret-Joyer-Halenda (BJH) method.

215 *3.6 Recyclability tests of the photocatalysts*

216 In the present work, the recyclability of Mn/BTiO_2 photocatalyst, which is used in
217 optimization study and performed better than other synthesized samples were evaluated. The
218 Mn/BTiO_2 photocatalyst was exposed to visible spectrum range for five consecutive cycles for
219 removing PCs and COD from TPOME. After each run, the used photocatalyst was recovered,
220 thoroughly cleaned with deionized water, and then allowed to dry overnight before being used

221 in the following run. Once more suspended in TPOME solution, the recovered photocatalyst
222 was exposed to visible light for 204 minutes.

223 *3.7 Preliminary photocatalytic performance tests*

224 To assess the efficiency of the synthesized photocatalysts for the photo-assisted degradation
225 of PCs from TPOME using visible radiation, preliminary photocatalytic reactions were carried
226 out. To achieve a photocatalyst loading of 0.5 g/L, a precisely weighted quantity of each
227 photocatalyst (WTiO₂, BTiO₂, Mn/TiO₂, and Mn/BTiO₂) was suspended in 0.05 L of TPOME
228 solution. For 30 minutes without any light, the suspension was stirred to achieve equilibrium
229 state. After that, the suspension was subjected to visible portion of light for 180 minutes.
230 Throughout the course of reaction, an aliquot of 1.0 mL was taken out of the photoreactor at
231 regular intervals using a highly precise syringe. Each sample was pass through a filter (Nylon,
232 0.2 m) before analysis. The removal of PCs from TPOME was estimated according to the Eq.
233 (4).

$$X\% = \frac{C_i - C_f}{C_i} \times 100\% \quad (4)$$

234 where C_i is the initial concentration, C_f is the final concentration of PCs, and $X\%$ denotes
235 the degradation efficiency after a specific period of 30, 60, 90, 120, and 180 min of reaction.

236 *3.8 Design of photodegradation experiments*

237 Another series of photoreactions employing DOE were conducted in the presence of
238 photocatalysts for a rigorous analysis and optimization of the independent process variables.
239 The photodegradation experiments were designed using a statistical software (Design Expert
240 12.0.0, State-Eas Inc). It was also used for carrying out statistical modeling, analysis, and
241 optimization of process variables. Independent factors such as TiO₂ loading (X_1) in g/L, H₂O₂
242 dosage (X_2) in mol/L, Mn concentration (X_3) in wt%, and irradiation time (X_4) in minutes were



243 considered in the current study. The response variables were PCs as GAE and COD removal
 244 (%) represented as Y_1 and Y_2 , respectively. Other variables like light intensity, initial
 245 concentration, pH of the solution, and temperature (28-30°C) remained constant. The chosen
 246 factors were converted into dimensionless values using Eq. (5) and coded as follows $A \rightarrow X_1$,
 247 $B \rightarrow X_2$, $C \rightarrow X_3$, and $D \rightarrow X_4$. This will make it easier to compare various factors of various
 248 natures and units. This will also help reducing the possibility of statistical analysis error and
 249 make up for a lack of mathematical model fit.

$$x_i = \frac{x_i - X_0}{\Delta X} \quad (5)$$

250 where X_0 is the center point value of x_i , x_i is the dimensionless coded value assigned to i th
 251 factor, and ΔX is the value assigned to the step change.

252 According to the CCD principle, the minimum, center, and maximum points of each input
 253 variable were designated as -1, 0, and +1, respectively. The actual and coded values as well as
 254 range of the independent variables are presented in Table 1. The CCD principle was employed
 255 during the experimental design. Table 5 depicts the experimental design matrix. The design
 256 had '2ⁿ' fractional factorial points, '2ⁿ' axial points, and '1' center point, with four (n) variables.
 257 Thus, 30 experiments with 10 fractional factorial points, 10 axial points, and 10 center points
 258 were carried out. In order to calculate the experimental error, reduce it, and obtain reliable
 259 results, three replicates were obtained, and the average is reported.

260 **Table 1.**
 261 Symbols, coded values, real values, and range of independent factors.

Factors	Symbols	Coded Values	Unit	Range		
				-1	0	+1
TiO ₂ loadings	A	X ₁	g/L	0.4	0.9	1.4
H ₂ O ₂ dosage	B	X ₂	mole/L	0.02	0.05	0.08
Mn concentration	C	X ₃	wt%	0.1	0.3	0.5
Irradiation Time	D	X ₄	min	60	180	300

262 RSM based on CCD was used to specify the optimal levels of the independent factors and
 263 demonstrate the output nature of the response surface. Eq. (6) denotes an empirical second-
 264 order quadratic polynomial model that describes the behavior patterns of the photocatalytic
 265 system.

$$Y = \beta_o + \sum_{i=1}^n \beta x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^n \times \sum_{i \neq j=1}^n \beta_{ij} x_i x_{ij} + \varepsilon \quad (6)$$

266 where, Y represents PCs and COD removal efficiency, β is the coefficient for linear effects
 267 (main effects) of the chosen variables, β_o represents the error, β_{ii} is the quadratic β_{ij} is
 268 interaction effects of the independent factors.

269 The analysis of variance (ANOVA), which was CCD's default method of data analysis, was
 270 used to statistically validate the model. Based on the results of the ANOVA, the complex
 271 relations between the two response variables and the four independent factors of the overall
 272 data scenario were deduced. The performance of the quadratic polynomial model fit was
 273 interpreted using the coefficient of determination (R^2), which is the primary output of the
 274 multiple regression. Based on statistical tests like the Fisher's test (F -value), probability test (p -
 275 value), alpha ($\alpha=95\%$, 0.05) 0.05), and others, the results were evaluated. The performance of
 276 the RSM prediction was also assessed by estimating mean square error (MSE), root mean
 277 square error (RMSE), Mean average error (MAE), mean average deviation (MAD), and mean
 278 absolute percentage error (MAPE) as described in Eq.7 to 11.

$$R^2 = \frac{\sum_{t=1}^n (A_t - P_t)^2}{\sum_{t=1}^n (A_m - P_t)^2} \quad (7)$$

$$MSE = \frac{\sum_{t=1}^n (A_t - P_t)^2}{n} \quad (8)$$

$$RMSE = \sqrt{\frac{\sum_{t=1}^n (A_t - P_t)^2}{n}} \quad (9)$$

$$MAD = \frac{1}{n} \sum_{t=1}^n (A_t - P_t) \quad (10)$$

$$MAPE = \frac{\sum_{t=1}^n \left| \frac{A_t - P_t}{A_t} \right|}{100} \times 100\% \quad (11)$$

279 Where, A_m represents the mean values of PCs and COD removal, A_t represents the actual
 280 values, P_t represents the predicted values, and n represents the total number of observations
 281 made for the current study.

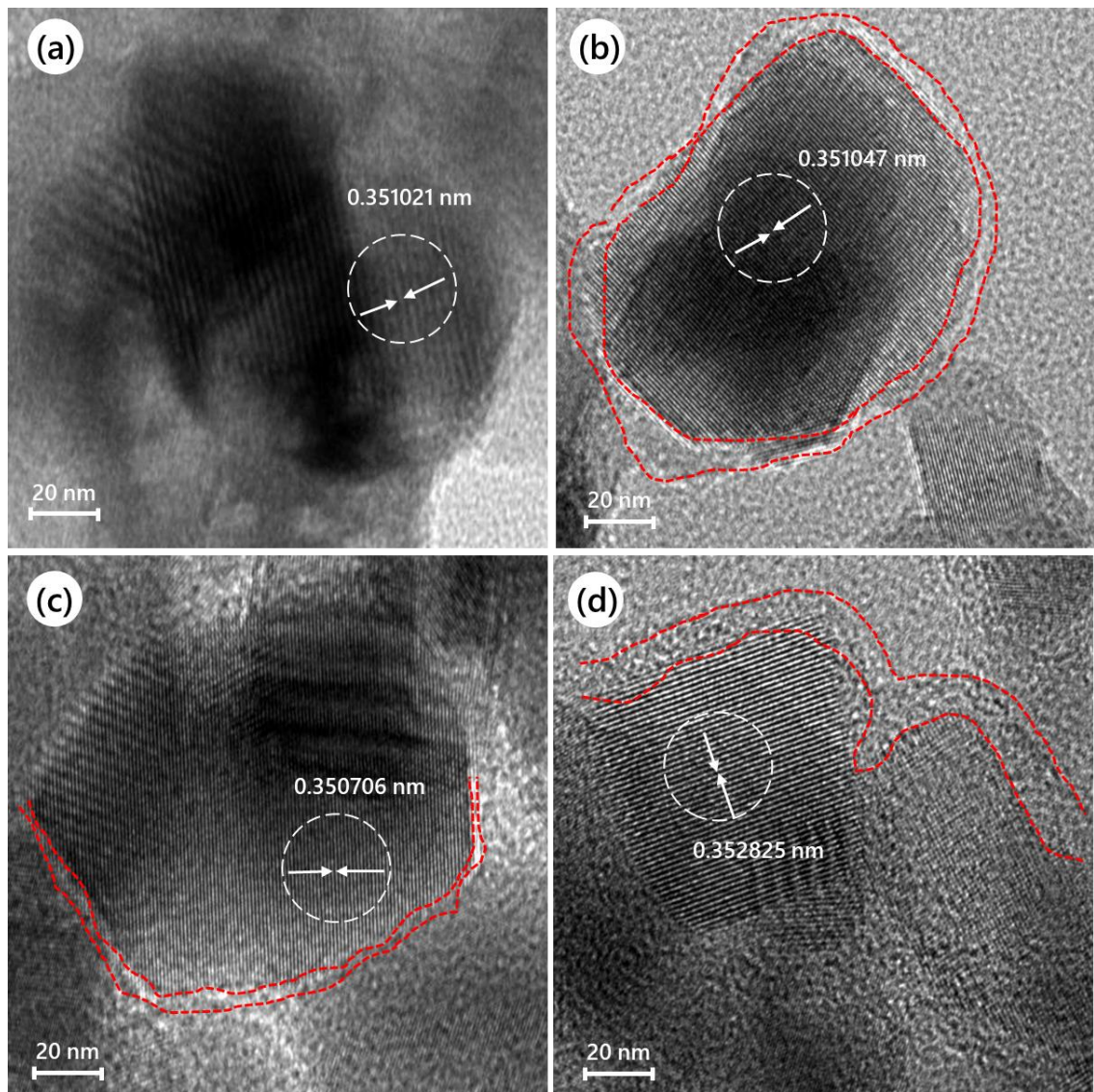
282 According to the impact of the independent input variables on photocatalytic removal of
 283 PCs and COD, 3-D response surface graphs and their corresponding contour plots,
 284 and perturbation plots were produced. To determine the precise figures of the simulated values
 285 of the independent variable for the photocatalytic removal of PCs and COD from TPOME, an
 286 overlay plot was created.

287 3. Results and discussion

288 3.1. Structural properties

289 HRTEM was used to determine the crystal structures of the synthesized photocatalysts. All
 290 of the photocatalysts have well-resolved lattice leading edge and other features, according to
 291 analysis of HRTEM images, which were taken at a scale of 20 nm and shown in Fig. 2. The d -
 292 spacing, a measurement of the separation between the two lattice neighboring fringes, was
 293 approximately 0.35 nm, and it can be attributed to the 101 planes of the crystalline structure of
 294 anatase. The crystal structure was intact in the current work in both cases, either doping WTiO_2
 295 and BTiO_2 with Mn, unlike the complete crystal destruction. However, it can be seen that when
 296 compared to WTiO_2 , the d -spacing of BTiO_2 , Mn/TiO_2 , and Mn/BTiO_2 slightly increased. The
 297 tensile strain generated by defects like SOVs, or Ti^{3+} may be the cause of the increase in d -
 298 spacing (Kong et al., 2015). Since the mobility and effective mass of excitons are inversely

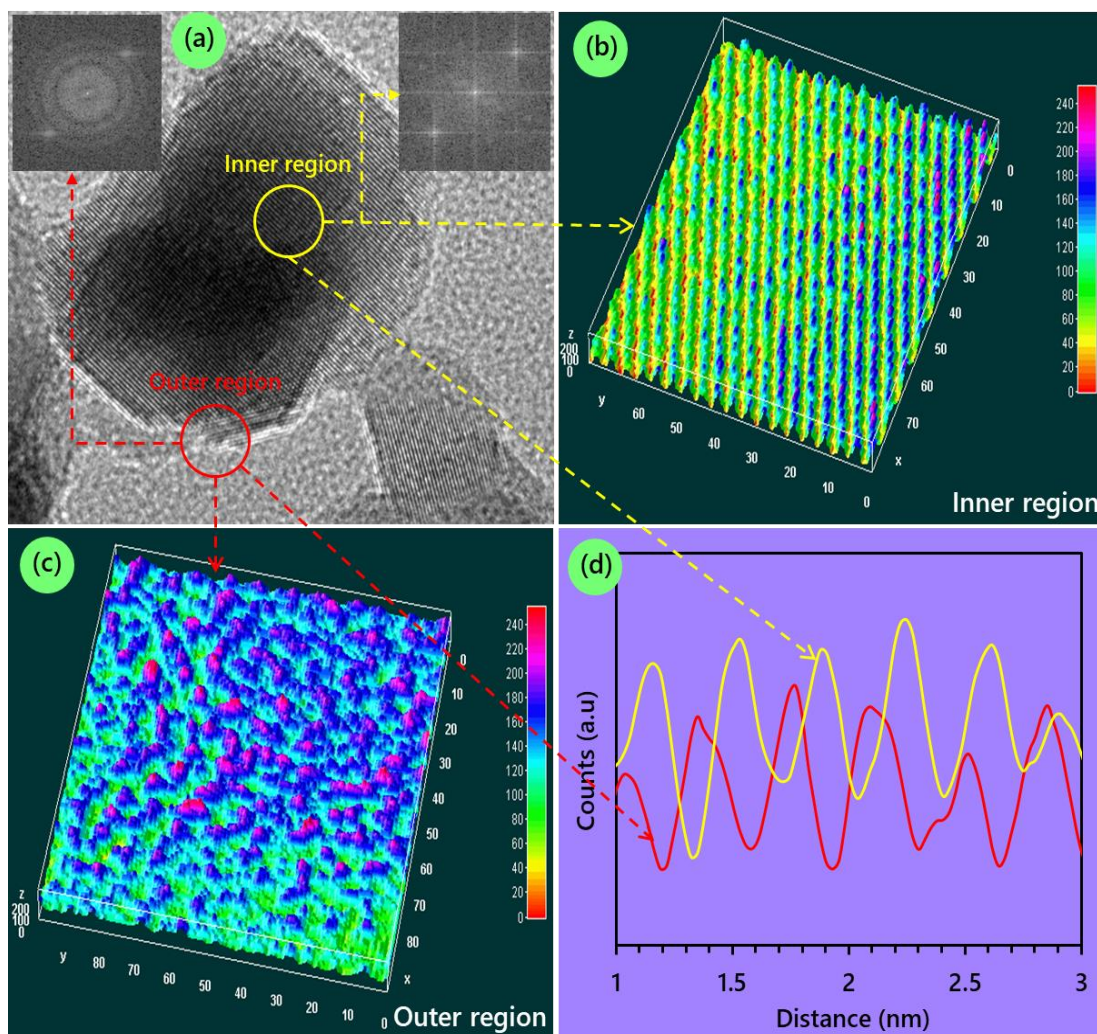
299 related, the strain induced by the defect states will essentially increase the mobility of the
300 carriers.



301
302 Fig. 2. HRTEM micrographs of the synthesized photocatalysts (a) WTiO_2 , (b) BTiO_2 , (c) Mn/TiO_2 and (d)
303 Mn/BTiO_2 .

304 Intriguingly, the crystalline core of BTiO_2 , and Mn/BTiO_2 was surrounded by an
305 amorphous shell, as shown by the red color line in Fig. 2(b–d). The core-shell structure
306 framework was further analyzed using FFT, 3D-view surface and line analysis and the results
307 are presented in Fig. 3. The FFT images of the particle's inner and outer surfaces are shown in
308 the inset of Fig. 3(a). While the bright spots (each arising from Bragg reflection from a single

309 crystallite) in the inner zone of the FFT view confirmed that the core is crystalline, the diffuse
310 rings in the FFT image of the particle outer region indicated that the shell is amorphous.



311
312 Fig. 3. (a) HRTEM image and the corresponding 3D-view surface plots of the (b) inner surface and (c) outer
313 surface, and the line profiles of the inner and outer surface (d), inset of (a) FFT images of interior and outer
314 surfaces.

315 The HRTEM images were further examined using 3D surface analysis for cross validation.
316 The interior surface of the particle, which is indicated by the circular yellow line in Fig. 3(a),
317 was used to generate the 3D view surface plots. The clear lattice fringes and appropriate atomic
318 arrangement with flat surface in Fig. 3(b) suggest the inner core is perfectly crystalline.
319 However, the 3D image of the particle's outer surface taken from the region indicated by the
320 red colored circular line in Fig. 3(a) reveals a disorganized outer layer, emphasizing the

321 unstructured nature of the shell (Fig. 3(c)). The displacement of the interstitial Ti atom from its
 322 base and the ongoing loss of Ti atoms from the lattice, which disrupt the normal order of the
 323 atoms, lead to the formation of an amorphous structure (Tian et al., 2015, Yang et al., 2016).
 324 The line profiles created from the particle's inner and outer surfaces and displayed in Fig. 3(d)
 325 further supported the formation of the core-shell assembly with a disordered shell and
 326 crystalline core. As can be seen, the line profile created from the inner region is no longer
 327 consistent with the line profile of the outer surface.

328 **Table 2.**

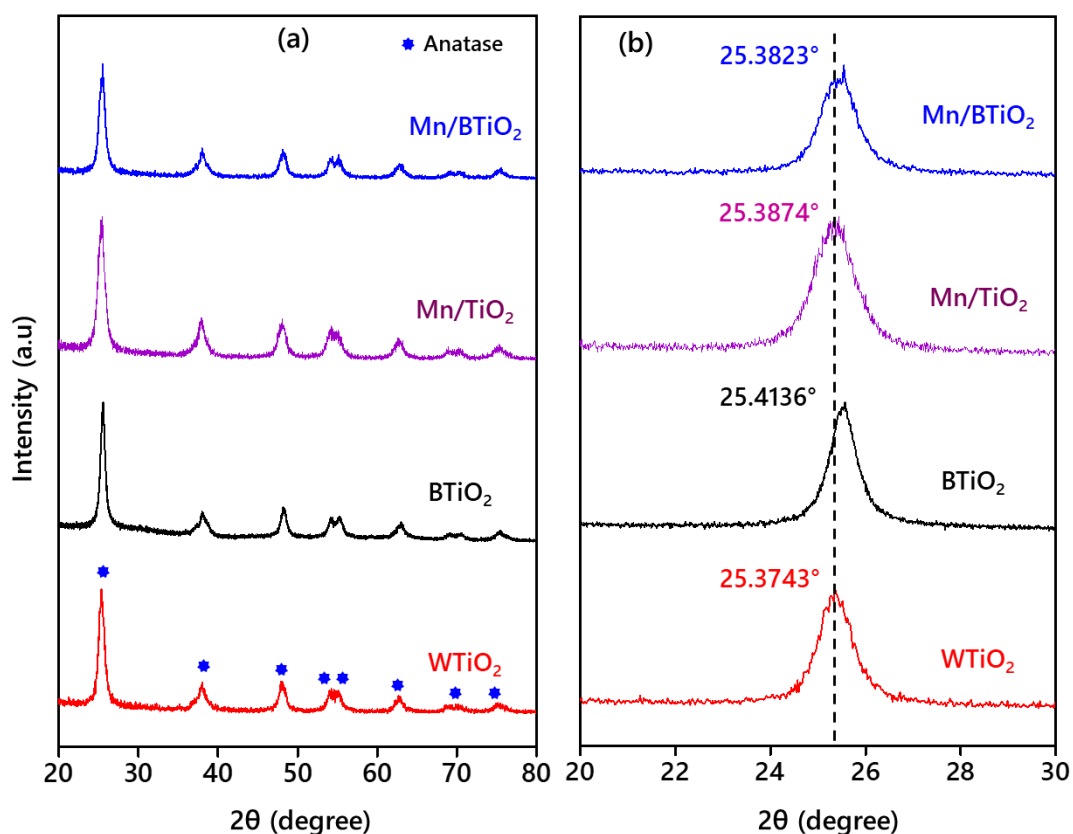
329 Summary of the properties of the synthesized photocatalysts.

Properties	Photocatalysts				
	WTiO ₂	BTiO ₂	Mn/TiO ₂	Mn/BTiO ₂	P25
XRD peak position (°2θ)	25.3743	25.4136	25.3874	25.3823	—
Crystallite size (nm)	47.66	50.87	48.01	47.89	55.10
FWHM	0.3883	0.1872	0.4605	0.5117	0.2558
d-spacing (Å)	0.351021	0.351047	0.350706	0.352825	0.3509
Absorption wavelength (nm)	410	450	>650	>650	388
Bandgap (eV)	3.16	2.96	2.42	2.29	3.20
Surface area (m ² /g)	154.51	99.88	116.41	94.03	50
Pore volumes (cm ³ /g)	0.198	0.161	0.210	0.159	—
Pore size (nm)	4.35	3.06	5.05	5.03	—

330 The XRD diffractogram of the photocatalyst shown in Fig. 4(a) revealed that all the
 331 synthesized photocatalyst are pure anatase phase indicated by the sharp diffraction peaks
 332 around 25° (2θ). A noticeable difference between WTiO₂ and other photocatalysts was
 333 observed when their intense diffraction peak (101 plane) was magnified as depicted in Fig.
 334 4(b). The diffraction peak shifted to higher angle in BTiO₂ and Mn/BTiO₂, which may be
 335 attributed structural deformation due to an expansion in *d*-spacing (Xia and Chen, 2013,
 336 Kunnamareddy et al., 2023). When compared to WTiO₂, the 101 peak of BTiO₂ did, in fact,
 337 shift to a higher angle, moving from 25.3743 to 25.4136° (Table 2). This result is in line with
 338 earlier research, which showed that black TiO₂ and Mn/TiO₂ diffraction peaks (101 plane)
 339 shifted to higher angles than pure TiO₂ (Ullattil and Periyat, 2015). In contrast, yellow TiO₂

340 has been found to have the diffraction peak shift to a lower angle (Bi et al., 2020). The
341 discrepancy between these results and those from prior studies could be attributed to the use of
342 different types of synthesis techniques and starting reagents.

343 The anatase phase was intact even if WTiO_2 or BTiO_2 were impregnated with Mn. No peaks
344 representing oxides of Mn such as Mn_3O_4 or Mn_2O_3 were detected in the XRD patterns
345 suggesting the existence of Mn as impurity (Bousiakou et al., 2022). Due to the close proximity
346 of the ionic radii of the Ti^{4+} (0.06 nm) and Mn^{4+} (0.053 nm), as well as the fact that neither
347 HRTEM nor XRD revealed any evidence of the Mn oxides, it is also likely that Mn is
348 distributed evenly in Mn/TiO_2 and Mn/BTiO_2 matrices. WTiO_2 and BTiO_2 were both doped
349 with Mn, yet there was no meaningful difference in the XRD patterns in either case.



350

351 Fig. 4. (a) XRD diffractogram and (b) enlarged XRD (101) peaks of the synthesized photocatalysts.

352

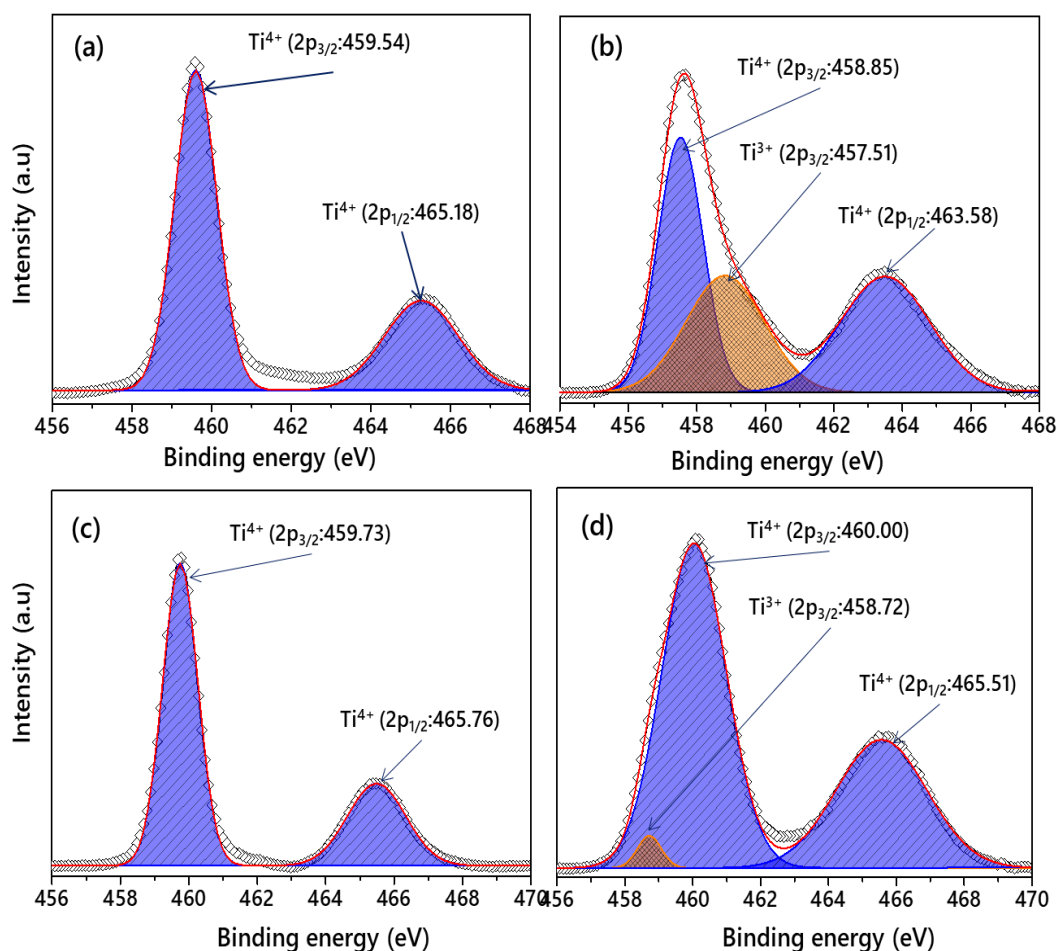
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354

355 3.2 Electronic and optical properties

356 Deconvoluted Ti2p XPS spectra of WTiO₂ are displayed in Fig. 5(a). The Ti2p_{3/2} peak's
357 binding energy (BE) was 459.54 eV, while the Ti2p_{1/2} peak's BE was 465.18 eV. These peak
358 positions represent the typical Ti⁴⁺—O bonds in the common crystalline phase of anatase
359 (Shvab et al., 2017). The WTiO₂ O1s spectrum is depicted in Figure 6(a). The two peaks that
360 were discernible at BE values of 530.81 and 532.15 eV, respectively, are due to lattice O in
361 TiO₂ and surface adsorbed OH. The Ti2p_{3/2} and Ti2p_{1/2} peaks of BTiO₂ had BE values of 458.85
362 and 463.58 eV, respectively, as shown in Fig. 5(b). The peaks may have shifted to their lower
363 BE positions due to an expansion in the Ti—O bond's length brought on by the action of defect
364 species (Pan et al., 2013). There was an extra shoulder peak in the Ti2p XPS spectrum of BTiO₂
365 at a lower BE of 457.51 eV, which is explained by lower oxidation state Ti³⁺ (Bharti et al.,
366 2016). Three peaks at BE 530.32, 531.76, and 532.61 eV in the O1s spectrum of BTiO₂ have
367 been identified as the lattice O in TiO₂, suboxide, and OH, respectively.

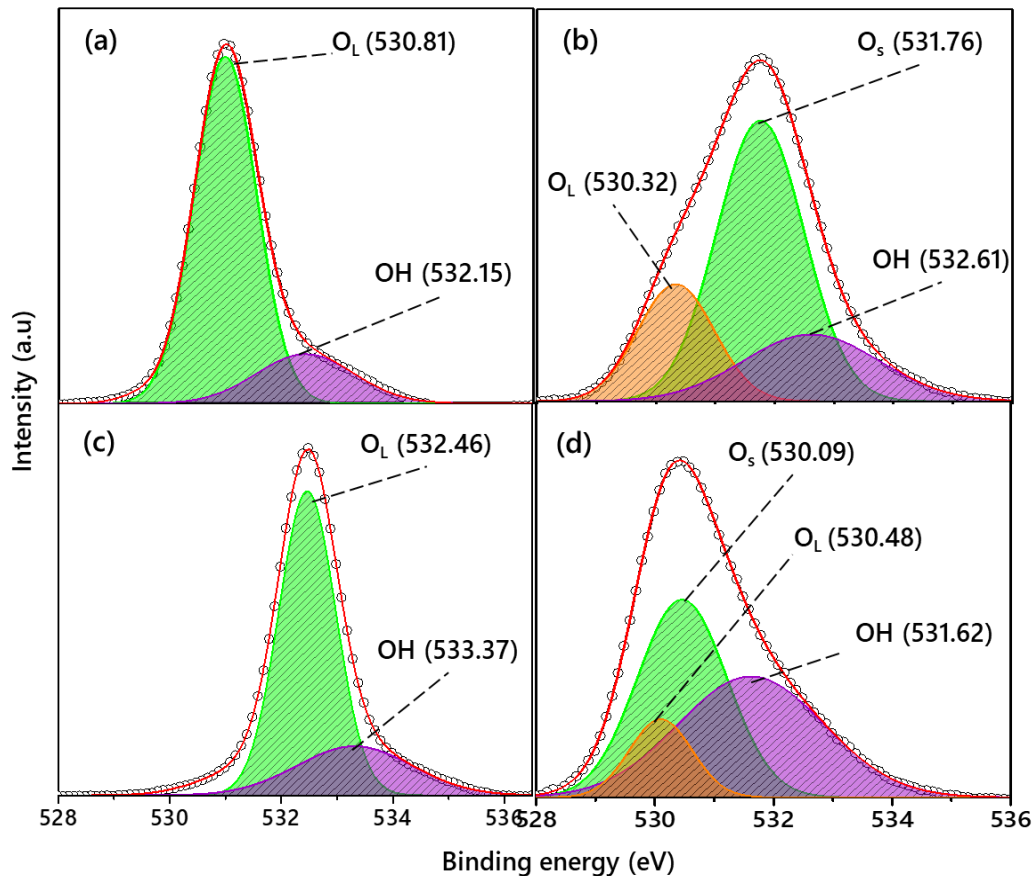
368 The XPS Ti2p spectra for Mn/TiO₂ are shown in Fig. 5(c). The deconvoluted spectra
369 revealed two peaks at BE of 459.73 and 465.76 eV that correspond to the Ti2p_{3/2} and Ti2p_{1/2}
370 orbital doublets and are typical of anatase phase TiO₂. The results are in line with the XRD
371 results shown in Fig. 4 and demonstrate that the synthesized Mn/TiO₂ phase was unaffected by
372 Mn doping. It is important to understand that the Ti2p_{3/2} peak positive shift to the high BE is
373 an indication of the lattice distortion brought on by the inclusion of Mn into the TiO₂ matrix.
374 Fig. 6(c) depicts the Mn/TiO₂ O1s spectra. Two overlapping peaks at BE 532.46 and 533.37
375 eV are visible in the spectra. Lattice oxygen and oxygen vacancies, respectively, were
376 responsible for both of these peak positions. (Qiu et al., 2016). The Ti2p spectra of Mn/BTiO₂
377 in Fig. 5(d), on the other hand, showed two major peaks at BE of 460.00 and 465.51 eV and a
378 shoulder peak at 458.72 eV, which, respectively, represent the Ti⁴⁺ (Ti2p_{3/2} and Ti2p_{1/2}) and
379 Ti³⁺ (Ti2p_{3/2}) states.



380

381 Fig. 5. XPS spectra Ti2p of deconvoluted peaks of (a) WTiO₂, (b) BTiO₂, (c) Mn/TiO₂, and (d) Mn/BTiO₂.

382 The core level XPS spectra of the photocatalysts in Fig. S2 demonstrate the presence of
 383 Mn. EDX was also used to cross validate the existence of Mn in the TiO₂ matrix. The EDX
 384 spectra and mapping of the photocatalyst are shown in Fig. S3. The EDX mapping revealed
 385 the presence of Ti, Mn, O, and C in the Mn/BTiO₂ and the even distribution of the Mn
 386 throughout the TiO₂ matrix. It was found that the experimental Mn concentration of 0.48wt%
 387 matching closely with the theoretical Mn concentration of 0.5wt%. On the surface of
 388 Mn/BTiO₂, the valence state of Mn was examined using XPS analysis.



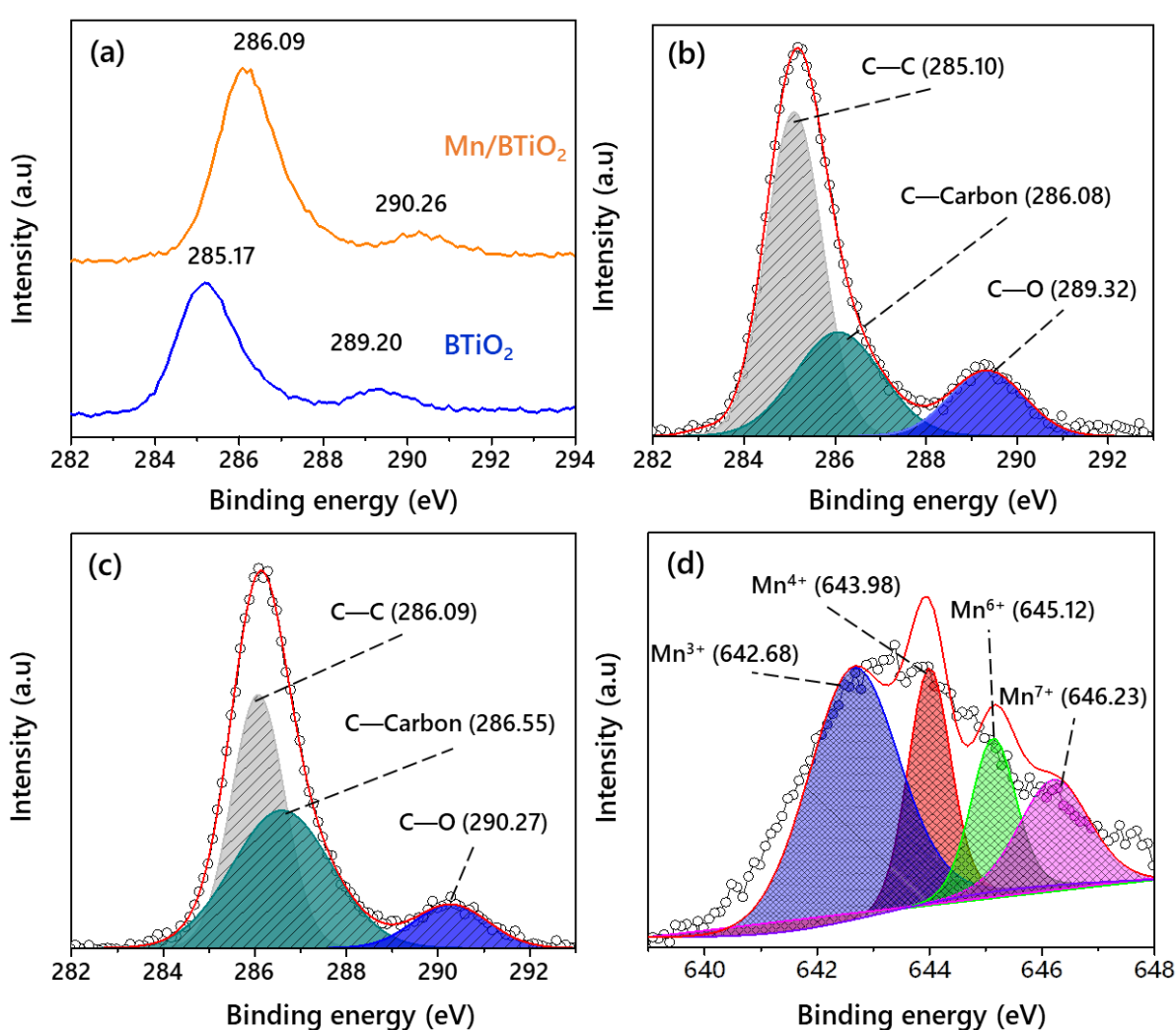
389

390 Fig. 6. Deconvoluted O1s XPS spectra of (a) WTiO₂, (b) BTiO₂, (c) Mn/TiO₂, and (d) Mn/BTiO₂.

391 The Mn2p_{3/2} peak was split into four separate peaks, each of which corresponded to a
 392 different electronic state of Mn as shown in Fig. 7(d). The peaks correspond to Mn³⁺, Mn⁴⁺,
 393 Mn⁶⁺, and Mn⁷⁺ at energies of 642.68, 643.98, 645.12, and 646.23 eV, which agrees with the
 394 theoretical values found in the literature (Zhang et al., 2021, Sun et al., 2020). The absence of
 395 metallic Mn or Mn²⁺ peaks in the spectra suggests that neither substance is present in the
 396 sample. The coexistence of numerous states of Mn on the surface TiO₂ has a major role in the
 397 emergence of surface oxygen because the multivalent-valence state of the metal can encourage
 398 oxygen maneuverability in the semiconductor oxides (Bhardwaj and Pal, 2020, Sharotri et al.,
 399 2019).

400 Fig. 7(a) displays a comparison of the high resolution C1s spectra of Mn/TiO₂ and
 401 Mn/BTiO₂. The Mn/BTiO₂ C1s peak has evidently been moved to a higher BE. The shift of

402 the C1s peak to higher BE is in harmony with the Ti2p and O1s peaks, which both moved
 403 towards higher BE. These findings imply that the addition of Mn to the matrix of the BTiO₂
 404 alters its chemical environment. To better comprehend the photocatalyst chemical
 405 surroundings, the C1s spectra of the samples were deconvoluted. The Mn/TiO₂ high resolution
 406 deconvoluted C1s spectra are shown in Fig. 7(b). The peaks were found at a BE of 285.10,
 407 286.08, and 289.32 eV, and they are attributable to (C—C) with sp² hybridization, coke carbon,
 408 and C atoms, respectively (Piątkowska et al., 2021).



409
 410 Fig. 7. (a) Comparison of C1s spectra of Mn/TiO₂ and Mn/BTiO₂, deconvoluted C1s spectra of (a) Mn/TiO₂ and
 411 (b) Mn/BTiO₂ and (d) deconvoluted Mn2p spectra of the Mn/BTiO₂.

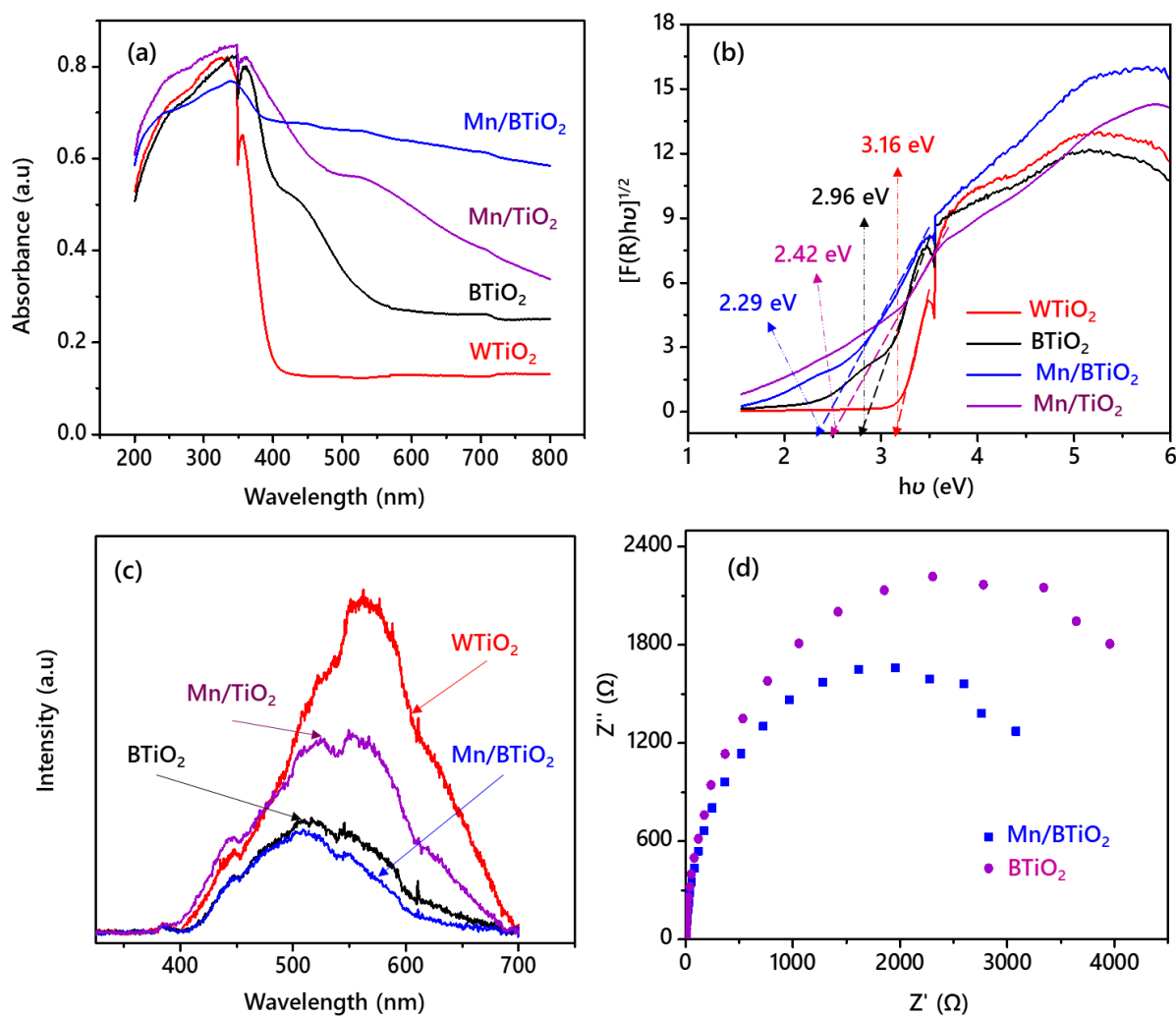
412

413 To gain insight into the optical characteristics of the synthesized photocatalysts, DRUV-
414 Vis analysis was carried out. The photocatalysts' UV-visible spectra are shown in Fig. 8(a).
415 WTiO_2 is only capable of absorption in the near ultraviolet region, in contrast to BTiO_2 ,
416 Mn/TiO_2 , and Mn/BTiO_2 which are all capable of absorption in the visible spectrum. After
417 doping the WTiO_2 and BTiO_2 with Mn, the light absorption was clearly promoted into the
418 visible region. (Choi et al., 2002) explained that a charge exchange between Mn (d electrons)
419 and VB or CB, or a d-d changeover in the crystal field, is what's to intensify the visible light
420 absorption. This is further supported by theoretical research that showed that the creation of
421 intermediate bands into the forbidden gap and the overall reduction of the band gap caused by
422 the replacement of Mn for Ti in the TiO_2 lattice resulted in a dramatic red-shift of the optical
423 absorption edge (Lu et al., 2012). The occupation of the orbital by an unpaired valence electron
424 and the resulting spin polarization give rise to the intermediate bands. Since gap state formation
425 is made easier by orbital occupation, Mn doped material exhibits intermediate bands (Liang
426 and Shao, 2019). These bands serve as steppingstones to increase the effective optical
427 absorption.

428 The T -plot in Fig. 8(b) was used to estimate the bandgap energies. The bandgap of BTiO_2
429 (2.96 eV) is lower than that of WTiO_2 (3.16 eV). When Mn was doped into both photocatalysts,
430 their bandgap energies were significantly lowered to 2.42 and 2.29 eV, which may be
431 associated to the curved transitional bands inside the bandgap (Xia et al., 2012). The increased
432 electron concentration in the shape of Mn cations, which results in the hybridization of the d-
433 states of Mn with the CB edge of TiO_2 , may be the reason why the bandgap has shrunk. This
434 bandgap narrowing does not, however, ensure increased photocatalytic activity. Instead,
435 narrow bandgaps that increase light absorption and decrease electron and hole recombination
436 are essential for improving photocatalytic activity.



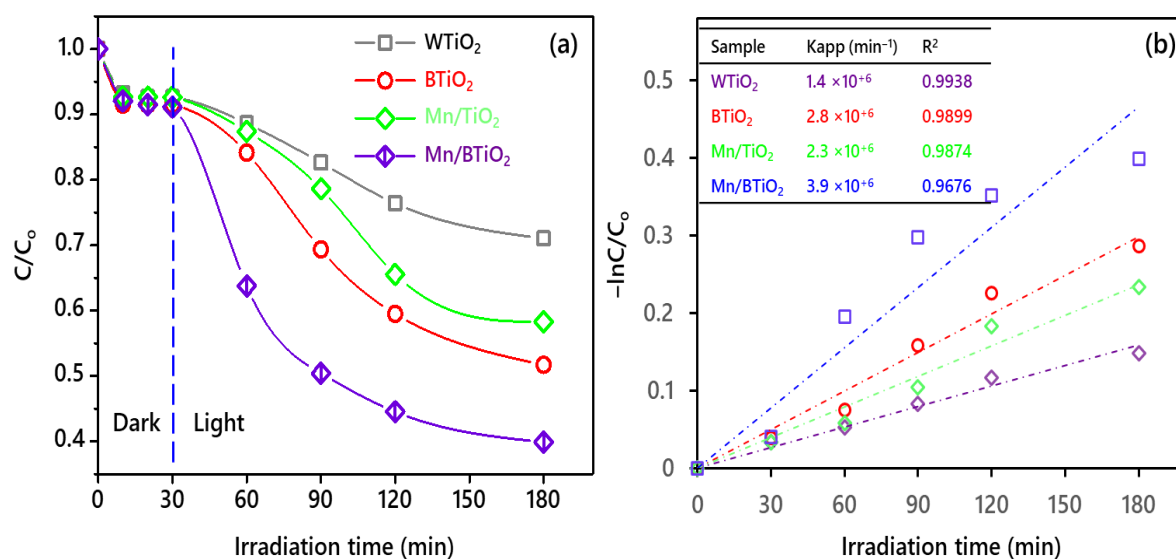
437 To better comprehend the behavior of charges recombination, the PL spectra of the
 438 synthesized photocatalysts were measured and displayed in Fig. 8(c). The fact that the peak
 439 intensities of the modified samples were noticeably lower than those of WTiO_2 suggesting that
 440 the recombination of photoexcited electron-hole has been significantly reduced (Moya et al.,
 441 2015). BTiO_2 and Mn/BTiO_2 were further studied using EIS to determine the rate of electron
 442 and hole recombination and the resistance to charge transfer in them. Fig. 8(d) displays the EIS
 443 spectra revealing higher separation, a slower rate of recombination, and less resistance to
 444 charge transfer are all indicated by smaller semicircle radius (Sigcha-Pallo et al., 2022) in the
 445 spectrum of Mn/BTiO_2 compared to BTiO_2 .



446
 447 Fig. 8. UV-Visible absorption spectra, T-plot of the bandgaps, PL of the synthesized photocatalysts, and PI spectra
 448 of the BTiO_2 and Mn/BTiO_2 .

449 3.3 Preliminary photodegradation studies

450 To determine the efficacy of the photocatalysts for the degradation of PCs from TPOME,
 451 preliminary photodegradation experiments were conducted. Fig. 9(a) displays the normalised
 452 concentration of PCs in TPOME following 180 minutes of photocatalytic treatment under
 453 visible light. The WTiO₂ was capable of eliminating 28.96% of PCs with an apparent removal
 454 rate constant of $1.4 \times 10^{-6} \text{ min}^{-1}$. With a higher apparent removal rate constant of $2.8 \times 10^{-6} \text{ min}^{-1}$,
 455 the PCs removal efficiency rose to 48.30% when BTiO₂ was used as the photocatalyst. WTiO₂
 456 is less efficient than all other photocatalyst at removing PCs despite having a larger surface
 457 area than the other samples (Table 2). This is due to the fact that the wide bandgap of 3.16 eV
 458 of WTiO₂ prevents it from utilising existing light in the visible spectrum. In addition, WTiO₂
 459 has higher charged species recombination and a shorter lifespan (Fig. 8c), which may also
 460 contribute to its poor performance in the visible light spectrum.



461
 462 Fig. 9. (a) Normalized concentration of PCs after 180 min of photocatalytic treatment and and (b) corresponding
 463 pseudo first order kinetic plots.

464 The improved PCs removal by BTiO₂ is a result of both the presence of Ti³⁺ species and
 465 the material's distinctive core-shell structure. The shell might provide the active sites for
 466 effective PC adsorption, whereas the sustained Ti³⁺ species within the crystalline core make up

467 an inter-band energy level. Since BTiO₂ has a lower bandgap than WTiO₂, the electrons can
468 easily be excited from the Ti³⁺ centres to the CB with the aid of visible light absorption, and
469 the shell acts as a trap for the electrons to minimise their interaction with the hole (Rostami et
470 al., 2022). As a result, free electrons and holes are available for a longer period of time to
471 further react with atomic oxygen and water to produce reactive radicals that attack and degrade
472 PC molecules.

473 The removal efficiency of PCs was further enhanced by doping Mn into the WTiO₂,
474 reaching 41.69% with an increase in apparent rate constant to $2.3 \times 10^{-6} \text{ min}^{-1}$. When the BTiO₂
475 was doped with Mn, the PC removal gradually increased to 60.12%, with the highest apparent
476 rate constant being $3.9 \times 10^{-6} \text{ min}^{-1}$. The increased removal of PCs by Mn/TiO₂ and Mn/BTiO₂
477 over WTiO₂ may be attributable to the addition of intermediate curvy bands within the bandgap
478 that make it easier for electrons and holes to be separated under the visible light energy (Deng
479 et al., 2011). Interband levels introduced by Mn also extend the life span of charged species,
480 accelerating the elimination of PCs. It should be noted that Mn/TiO₂ is less effective at
481 removing PCs than BTiO₂. Mn ions, however, add additional positive charge to the surface of
482 WTiO₂, increasing the repulsive interaction between the particles and making Mn/TiO₂ highly
483 stable in wastewater treatment applications (Bhardwaj and Pal, 2020). Higher oxidation state
484 Mn (>2+) impurities enhance TiO₂ capacity for light absorption, pollutant adsorption, and
485 subsequent photodegradation in addition to providing stability (Choi et al., 2010).

486 ***3.4 Process optimization for photodegradation of TPOME***

487 Since the preliminary results of removing PCs from TPOME confirmed the higher
488 performance of Mn/BTiO₂, Therefore, the photocatalytic process for PCs and COD removal
489 from TPOME matrix optimization studies used Mn/BTiO₂. Then the optimized process was
490 also tested for TOC and color removal from the TPOME.

491 3.4.1 Model fit summary statistics and statistical significance

492 Analysis of variance (ANOVA) was used to assess the model's statistical significance and
 493 is shown in Table 3. Overall model p -values for PCs and COD elimination were 0.0001, which
 494 was less than the 0.05 level of significance. So, it was determined that there was a relationship
 495 between the independent variables and the outcome variables, rejecting the null hypothesis.
 496 Because of this, the PCs and COD removal are significantly impacted by the full quadratic
 497 model of the selected independent factors. The fact that the p -value for the factors linear term
 498 is below the level of significance suggests that the factors have a significant impact on PCs and
 499 COD removal (Table S3).

500 **Table 3.**

501 ANNOVA output table for COD and PCs as GAE removal.

Source	Sum of squares	Mean square	df	F -value	Prob> F/P -values	Remarks
For PCs as GAE						
Model	4669.76	333.55	14	64.78	0.0001	Significant
Lack of fit	30.30	3.03	11	1.16	0.0507	Insignificant
For COD						
Model	3424.41	244.60	14	63.46	0.0001	Significant
Lack of fit	45.90	4.59	10	3.28	0.1790	Insignificant

502 Regarding PCs and COD removal, the p -value for the interactions of the independent
 503 factors is found to be significant. The p -values for the PCs (0.0507) and COD (0.1790) removal
 504 models were greater than the level of significance, there is no lack-of-fit in these models. As a
 505 result, the quadratic models with the independent variables shown in Eqs. 12 and Eq. 13 have
 506 a considerable impact on the photodegradation of PCs (Y_1) and COD (Y_2) removal from
 507 TPOME. The direction and strength of the relationship were denoted by the sign and value of
 508 the coefficients, respectively.

509 The model summary output shown in Table 4 is used to run the practical significance test.
 510 While the adjusted R^2 values for the response variables were 98% and 97%, the observed R^2

511 values for PCs and COD were 99% and 98%, respectively. These findings suggest that the
 512 model's parameters are very effective at explaining variation in PCs and COD removal.
 513 Furthermore, high R^2 values for both the response variables ensure a satisfactory agreement
 514 between the observed and predicted PCs and COD removal and a good model fit (Glaz and
 515 Yeater, 2020) . As a result, the model has strong practical relevance.

$$(Y_1) = 87.66 + 0.032A - 0.18B + 1.21C + 2.75D - 0.37AB - 1.97AC - 4.14AD - 0.93BC + 0.028BD - 0.29CD - 5.69A^2 - 4.35B^2 - 13.35C^2 - 13.23D^2 \quad (12)$$

$$(Y_2) = 93.53 - 1.03A - 1.08B - 0.84C + 2.81D - 0.29AB - 3.16AC - 3.16AD + 1.24BC - 0.27BD + 0.023CD - 7.22A^2 - 3.77B^2 - 14.69C^2 - 3.75D^2 \quad (13)$$

516 **Table 4.**

517 RSM output model fit summary for COD and PCs as GAE removal.

Statistical key figure	Acronym	GAE removal	COD removal
Predicted residual error sum of square	PRESS	321.26	329.52
Coefficient of determination	R^2	0.99	0.98
Mean average percentage error	MAPE	0.952	0.046
Mean average deviation	MAD	2.112	1.560
Root mean square error	RMSE	2.542	1.857
Mean average error	MAE	2.110	1.506
Mean square error	MSE	6.459	3.448
Coefficient of variance	C.V.	2.58	2.77
Standard deviation	St. Dev.	1.71	21.96
Adequate precision	A.P.	37.60	25.78
Predicted – R^2	Pre. R^2	0.95	0.90
Adjusted – R^2	Adj. R^2	0.98	0.97
Mean	Mean	66.28	76.10

518

Table 5.

Experimental design matrix (DOE), experimental and predicted values for PCs as GAE and COD removal from TPOME.

Run no.	A: TiO ₂ loading (g/L)	B: H ₂ O ₂ dosage (mol/L)	C: Mn conc. (wt%)	D: Time (min)	PCs as GAE removal (%)		COD removal (%)	
					Experimental	Predicted	Experimental	Predicted
1	0.4	0.02	0.5	60	59.21	61.98	76.17	73.62
2	1.4	0.08	0.1	300	52.41	51.99	61.64	59.15
3	1.4	0.02	0.1	60	54.86	53.05	64.26	63.84
4	0.9	0.05	0.3	180	57.31	54.48	69.81	69.79
5	1.4	0.08	0.5	60	59.27	56.76	74.19	71.05
6	0.4	0.08	0.5	300	48.51	50.27	62.89	60.74
7	0.4	0.08	0.1	60	88.79	89.56	94.58	93.67
8	1.4	0.02	0.5	300	90.13	89.56	93.25	93.73
9	0.9	0.05	0.3	180	48.94	52.39	58.97	59.54
10	0.4	0.02	0.1	300	43.29	43.66	55.17	55.09
11	0.9	0.05	0.3	180	64.73	62.63	70.48	73.28
12	0.4	0.02	0.5	300	52.79	54.42	64.39	65.12
13	1.4	0.02	0.1	300	48.52	51.45	68.41	69.58
14	0.4	0.08	0.1	300	57.21	57.30	63.78	66.46
15	1.4	0.02	0.5	60	41.34	40.68	56.32	58.62
16	0.9	0.05	0.3	180	53.19	54.64	58.43	59.27
17	1.4	0.08	0.5	300	87.34	88.71	91.67	93.53
18	0.4	0.08	0.5	60	48.12	48.31	57.13	58.35
19	1.4	0.08	0.1	60	51.36	47.96	59.81	62.16
20	0.4	0.02	0.1	60	86.13	88.79	93.69	93.62
21	0.9	0.05	0.3	60	72.34	74.16	90.45	92.59
22	0.4	0.05	0.3	180	75.12	80.46	88.73	90.83
23	0.9	0.05	0.3	300	68.45	68.66	90.13	86.97
24	0.9	0.05	0.3	180	74.23	72.49	77.18	78.00
25	0.9	0.05	0.5	180	89.93	84.63	93.16	93.54
26	0.9	0.05	0.1	180	87.46	84.64	94.76	93.91
27	0.9	0.08	0.3	180	81.61	78.98	85.46	85.28
28	1.4	0.05	0.3	180	83.43	80.13	91.77	87.67
29	0.9	0.05	0.3	180	74.25	78.91	88.15	87.33
30	0.9	0.02	0.3	180	66.31	68.07	81.49	79.68

Table 3 displays the Fisher's (F -values) for the models. F -values of 64.78 and 63.46 indicated that the models were significant for effective PCs and COD removal, respectively. The percentage of models with large F -values that are susceptible to noise is less than 1% (0.01). In other words, there is a strong argument that the models were accurate and that there is a very low likelihood that the large F -values are the result of pure chance (p -value=0.0001). Table S4 contains the detailed ANOVA table with the p -values for each model term. The adequate precision (AP), which assesses "signal to noise ratio," was discovered to be 37.60% and 25.78%, respectively, for PCs and COD removal (Table 4). When the AP value exceeded 4, it meant that both modes could be used to maneuver in the space that had been previously defined by the CCD/RSM.

It is crucial to assess the reliability and applicability of CCD by calculating important statistical indicators like MSE, RMSE, MAD, MAE and MAPE values which should be as small as possible, and R^2 values should be close to 1, for ideal model fitting (Ateia et al., 2020). The likelihood of error in the estimation of PCs and COD removal from TPOME increases with higher values of statistical indicators. The lower RMSE values of 2.542 and 1.857 for PCs and COD elimination from TPOME showed no departure from the quadratic polynomial model, demonstrating the reliability of the RSM. Low RMSE and high R^2 values for both responses in the fitting analysis results shown in Table 4 imply that the CCD used can more accurately predict and optimize the photodegradation of PCs and COD. Lower values for MAPE, MSE, and MAE as well as higher R^2 values were observed, indicating a lower probability of error.

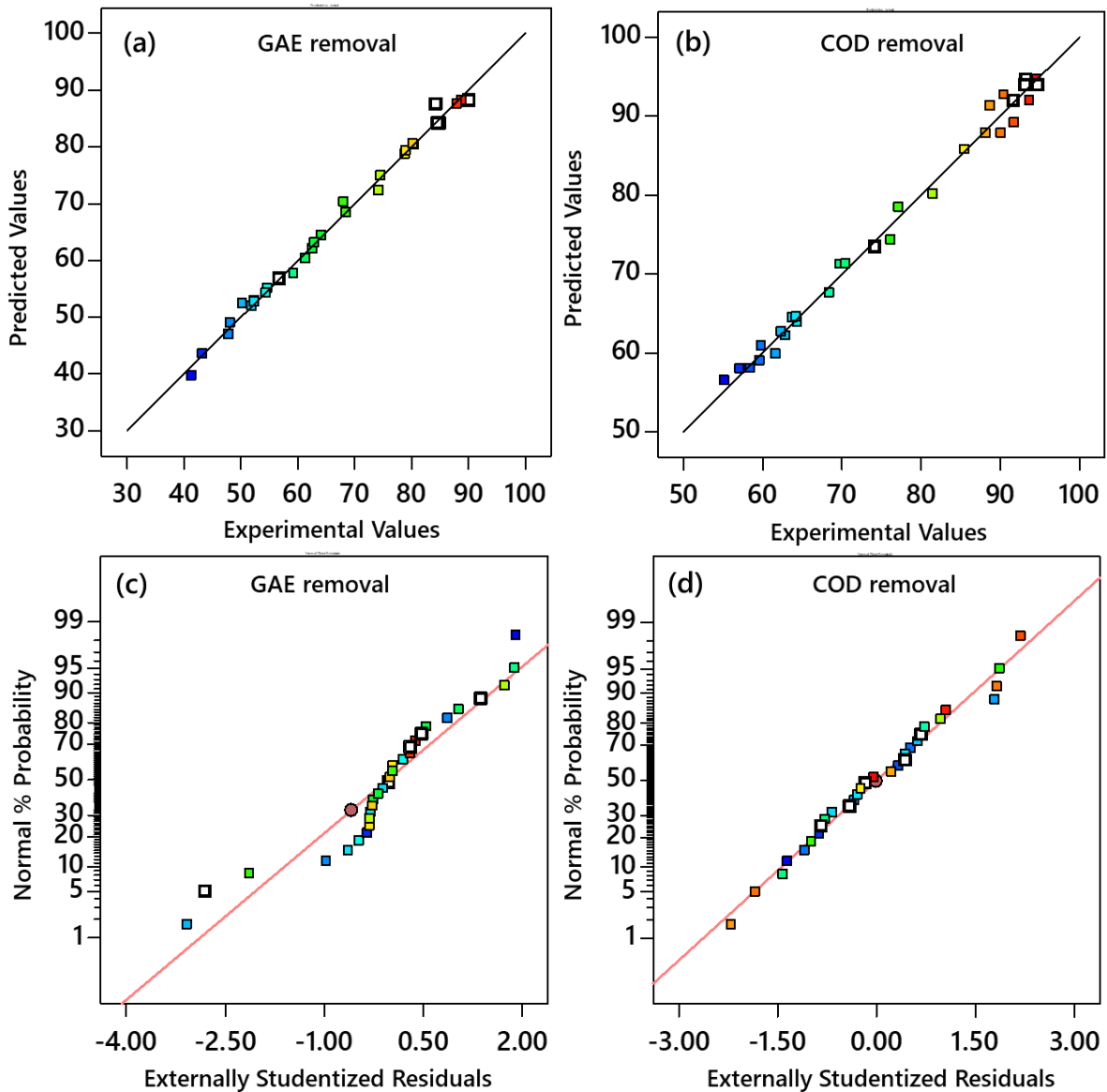


Fig. 10. Experimental and predicted values for (a) PCs as GAE removal and (b) COD removal and residuals Normal distribution plots for (c) PCs as GAE removal and (d) and COD removal.

To learn more about how well the model fit the data, the outcomes of 30 experiments that were designed using CCD in RSM were compared with predicted values as shown in Table 5. Table S4 presents the results of an ANOVA for the response surface quadratic models. The predicted values for PCs and COD removal are displayed in Fig.10(a) and (b), respectively, along with experimental values.

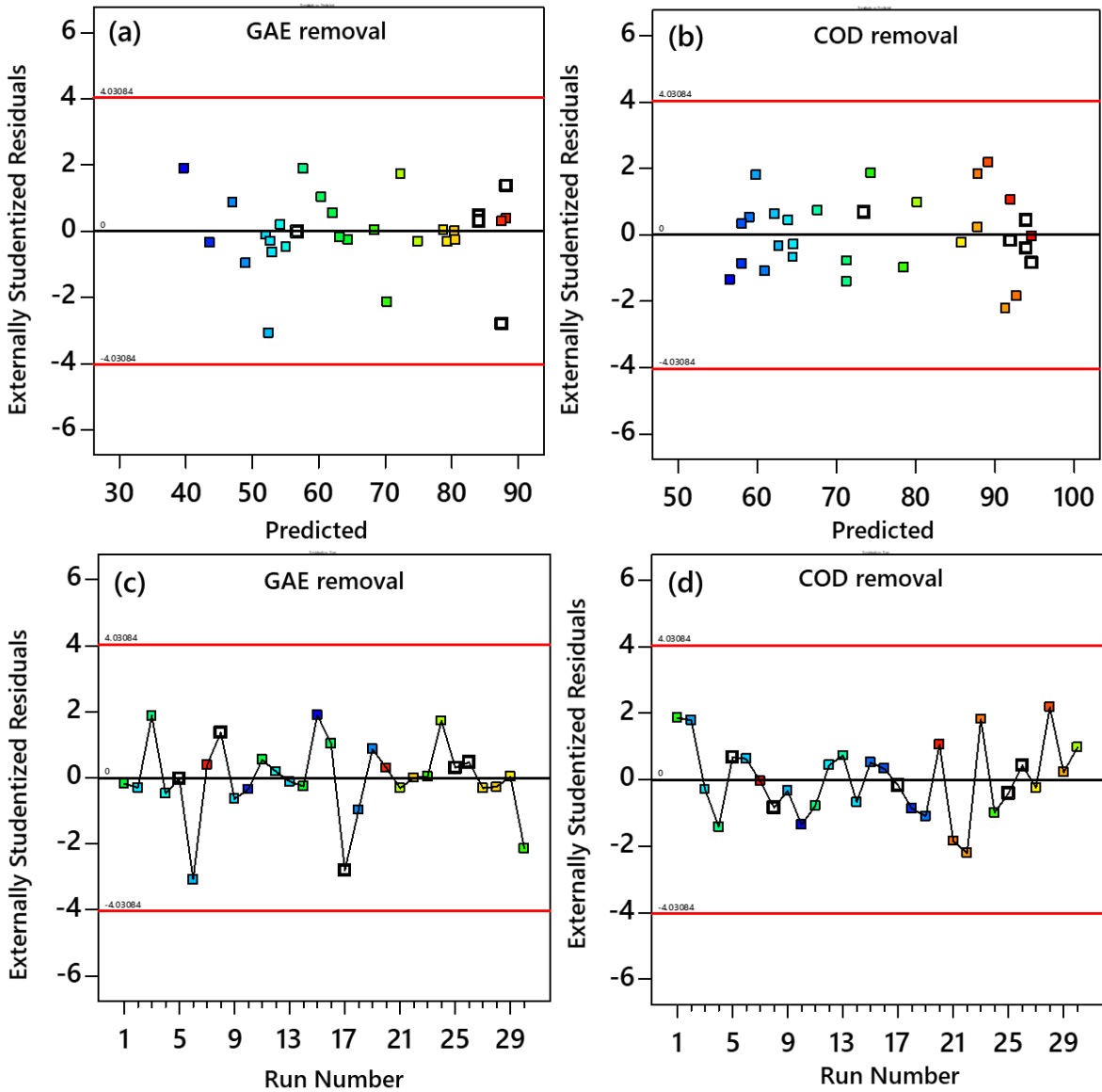


Fig. 11. Externally studentized residuals vs predicted values for (a) PCs removal and (b) COD removal, and externally studentized residuals vs run number for (c) PCs removal and (d) COD removal.

The distribution of the data points is fairly even, and they behave linearly. Plots show a reasonable level of agreement between the predicted and actual data. The fact that the predicted and experimental values were relatively close to one another suggests that the proposed empirical model is appropriate for predicting PCs and COD removal and displayed a reasonable level of agreement with the quadratic model. The residuals for the model for PCs and COD removal are depicted in Fig. 10(c) and (d) as having a normal distribution. The residual plots exhibit linear behavior as well as a straight line can be projected, indicating the accuracy of

model prediction. Fig. 11 presents the residual plots for the two models, PCs and COD removal. The residual vs. predicted values plots in Fig. 11(a) and (b) show that the residuals were distributed normally and random, which clearly indicates good model fitting. The residuals seem to have a normal distribution and be mostly random. Only two data points in Fig. 11(c) deviate from the Normal distribution, and they might not warrant further analysis.

3.4.2 Three-dimension view response surface and contour plots

The response surface can be used to identify a variety of independent variables that will maximise PC and COD photodegradation from TPOME. Maintaining the factors at their highest level could be very expensive, so keeping them within a range is frequently preferred for a process to be cost-effective. To optimize TiO_2 loading and H_2O_2 dosage for maximizing PCs removal, the response surface is plotted in Fig. 12(a). It is evident that the conditions with the maximum PCs removal efficiency (80–85%) were those with TiO_2 loadings between 0.7 and 1.12 g/L and H_2O_2 dosages between 0.03 and 0.065 mol/L. Similar to PCs removal, better COD removal efficiency (85–89%) displayed in Fig.13(a) was maintained when TiO_2 loading and H_2O_2 were within the same range. Fig. S4 displays the individual impact of these two factors on PCs and COD removal. Only the combined positive effects of TiO_2 loading and H_2O_2 dosage could have increased PCs and COD removal to the levels that were reached. This might be due to the synergistic interaction between TiO_2 and H_2O_2 that prevents photogenerated charges recombination by trapping the electron in the CB of TiO_2 and augmenting the amount of $\cdot\text{OH}$ that TiO_2 produces when exposed to visible light (Álvarez et al., 2021). Therefore, more potent $\cdot\text{OH}$ are available to attack the molecules of PCs and COD.



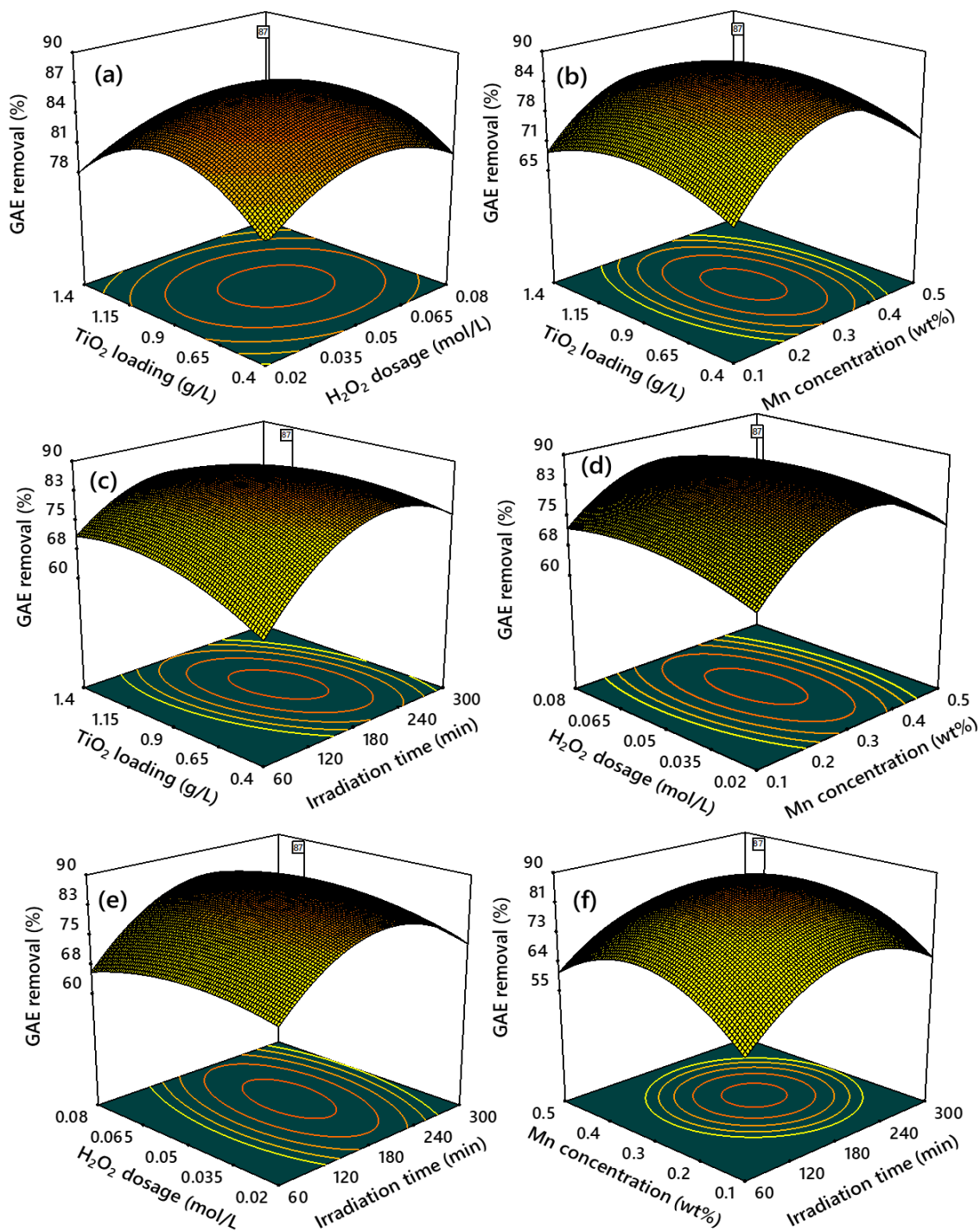


Fig. 12. Response surface plots of (a) TiO_2 loading vs H_2O_2 dosage, (b) TiO_2 loading vs Mn concentration, (c) TiO_2 loading vs irradiation time, (d) H_2O_2 dosage vs Mn concentration, (e) H_2O_2 dosage vs irradiation time, and (f) Mn concentration vs irradiation time for PCs as GAE removal.

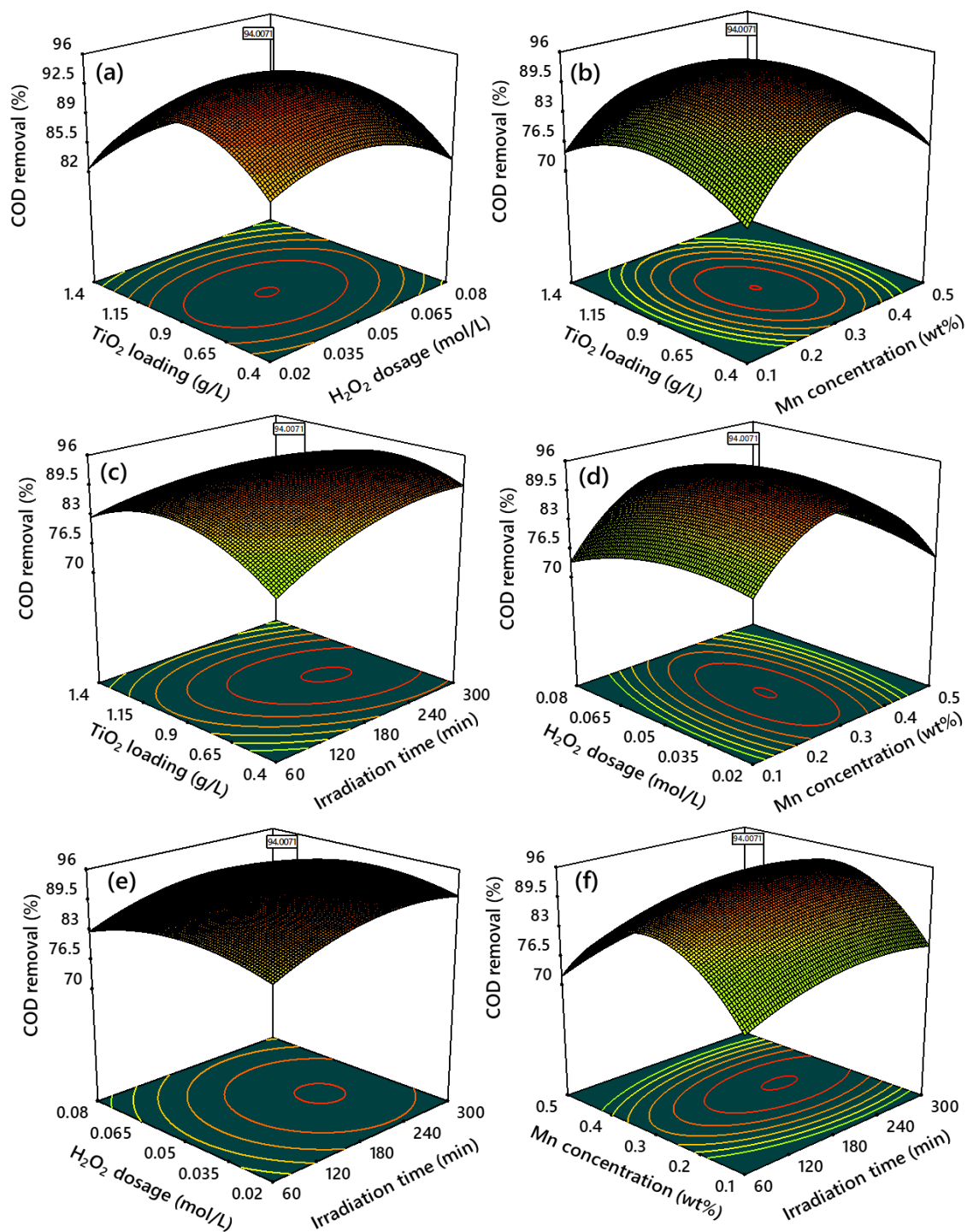


Fig. 13. Response surface plots of (a) TiO_2 loading vs H_2O_2 dosage, (b) TiO_2 loading vs Mn concentration, (c) TiO_2 loading vs irradiation time, (d) H_2O_2 dosage vs Mn concentration, (e) H_2O_2 dosage vs irradiation time, and (f) Mn concentration vs irradiation time for COD removal.

To optimize TiO_2 loading and Mn concentration for maximizing PCs and COD removal, the response surface is plotted in Fig. 12(b) and Fig. 13(b), respectively. The maximum PCs removal (78–86%) was achieved at the TiO_2 loading of 0.7 and 1.12 g/L and Mn concentration

between 0.3–0.45wt%. Maximizing PCs and COD removal efficiency may require maintaining the Mn concentration in the optimum range. Because the Mn concentration has a significant impact on how well the Mn/TiO₂ performs in wastewater treatment applications (Ettireddy et al., 2007). If the Mn concentration is too low, the photocatalytic removal may be reduced because the bandgap may not be narrowed enough to produce an enhanced photoelectric effect under visible light and start photocatalytic reactions. High Mn concentrations caused the higher photocatalytic removal efficiency to lose effectiveness. This might be because there were too many crystal defects, which the photogenerated charge carriers may have used as recombination sites.

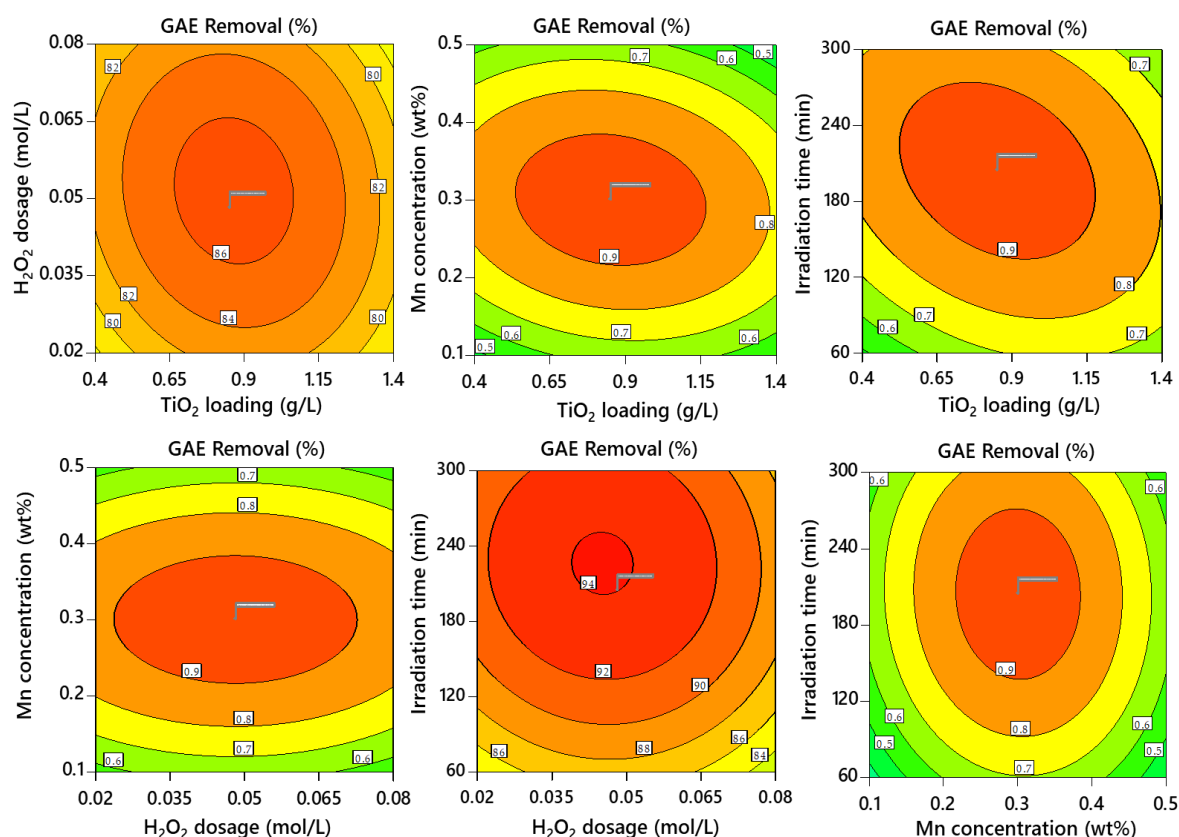


Fig. 14. Contour plots for phenolic compounds (as GAE) removal.

To optimize irradiation time for maximizing PCs and COD removal, the response surface is plotted in Fig. 12(c) and Fig. 13(c), respectively. When the irradiation time was between 180 and 250 min, the best PCs and COD removal efficiency in the range of 75–88% were attained.



When the irradiation time exceeded this range, the removal of both responses decreased, which might be caused by competition between the reactant and intermediate products as well as the deposition of byproducts results in the deactivation of active sites on the photocatalyst's surface (Pillai and Gupta, 2015). Fig. 12 and 13 show that the efficiency of removing PCs and COD begins to plateau, and that points farther away from the optimum perform worse. Due to exceeding and overshooting the optimum, the PCs and COD removal remained constant, if not even decreased, for two or three consecutive jumps. These characteristics led us to realise that the optimum has come into view.

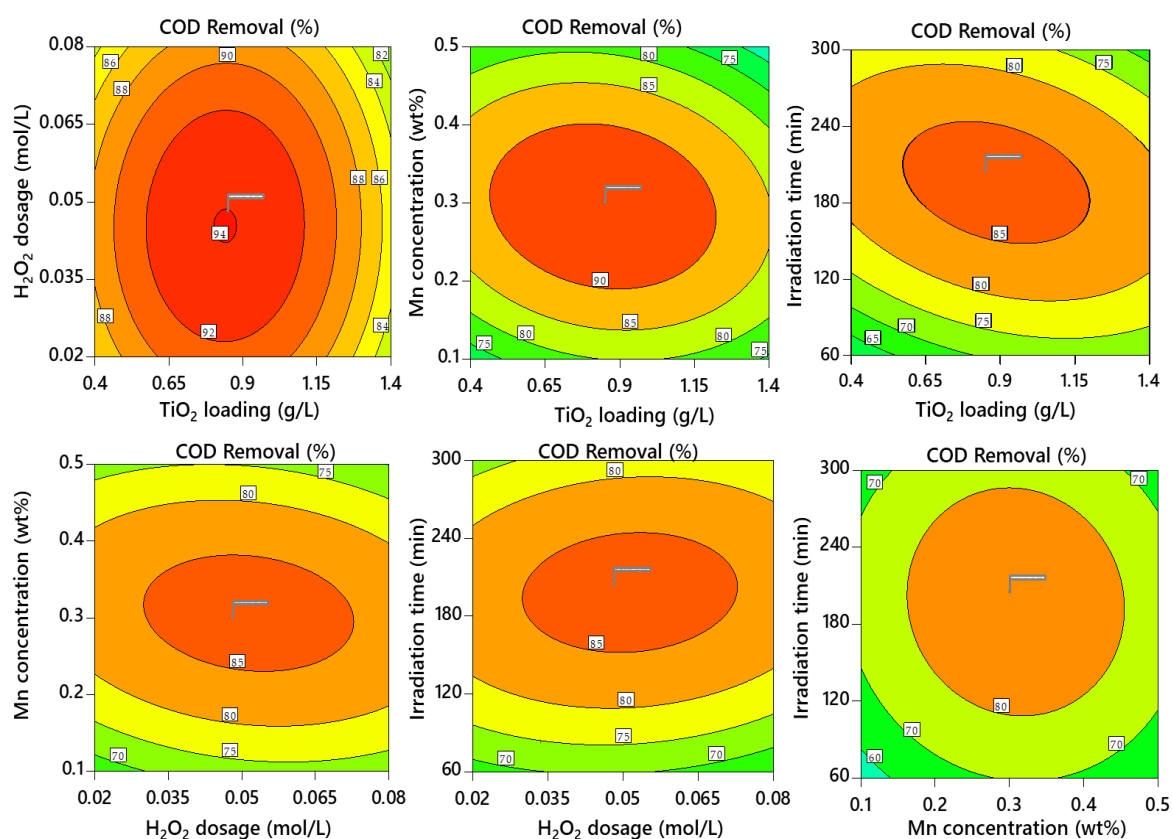


Fig. 15. Contour plots for COD (GAE) removal.

The ranges of the chosen independent factors can also be determined using the contour plot in order to achieve the same level of PCs and COD removal (responses, Y_1 and Y_2). For instance, the contour plots shown in Figs. 14 and 15 demonstrate that it is statistically possible to achieve the same level of PCs and COD removal for the same colour in the plot. For instance, the level of PCs and COD removal (80–90%) shown by the middle dark oval region of the

contour plot in Fig. 14 and 15 can be attained with TiO_2 loadings between 0.7 and 1.12 g/L, H_2O_2 dosages between 0.03 and 0.065 mol/L, Mn dosage 0.25 and 0.36wt%, and irradiation time between 140 and 260 min.

3.4.3 Perturbation plots

The effects of the chosen independent variables on PCs and COD removal were assessed using perturbation plots. By default, the Design Expert chose the independent variables' midpoint levels as the reference point. The perturbation plots in Fig. 16 were constructed to test the response variables' sensitivity to changes in the input variables. In order to identify a set of variables that meet the requirements set for each of them, the response is mapped by changing just one variable over its range while holding the others constant.

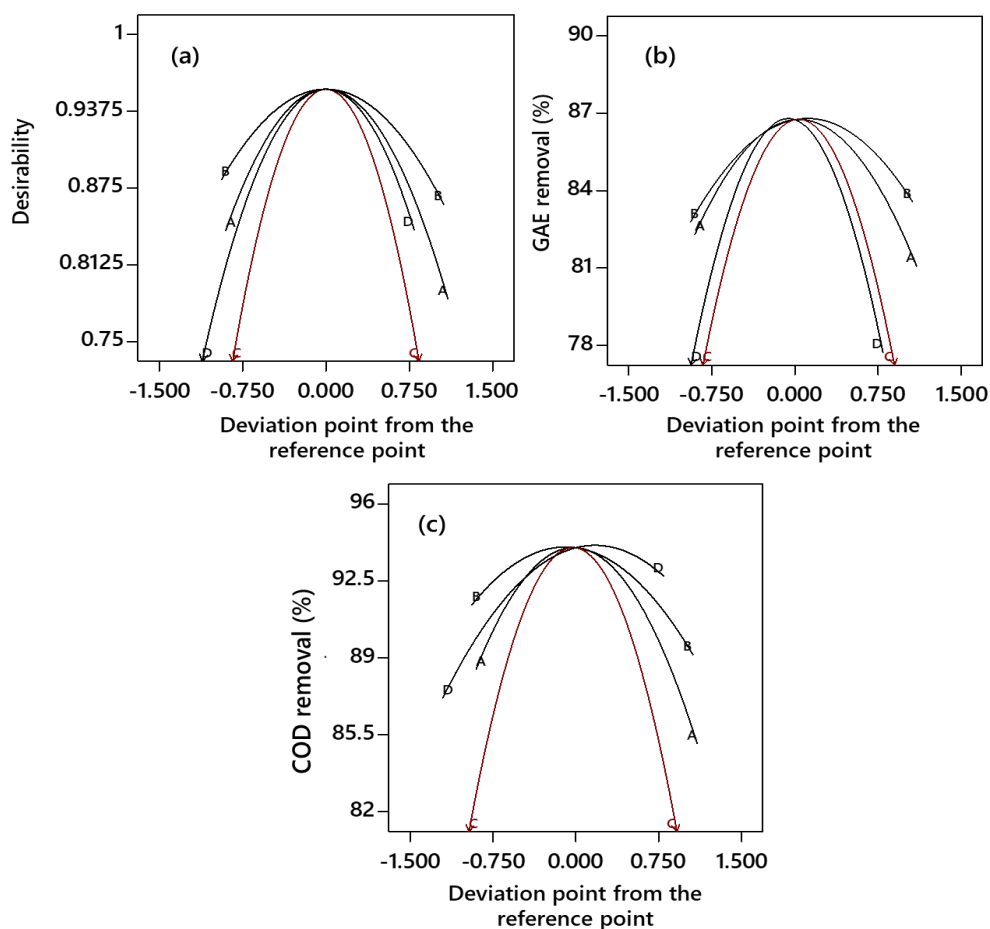


Fig. 16. Perturbation plots for (a) desirability, (a) PCs as GAE removal, and (c) COD removal.

As evidenced by a steeper curvature in the independent variables, both of the responses, PCs and COD removal, were sensitive to the change in selected independent variables (Morero et al., 2017). However, PCs removal responded differently to the independent variables than COD removal as shown in Fig.16(b). The change in TiO₂ loading, Mn concentration, and H₂O₂ dosage were found to affect the removal of COD more than they did the removal of PCs, which was more sensitive to Mn concentration and irradiation time. Perturbation plots with two analogous lines made it easy to explain the interaction between two-variables where the effects of one depend on the levels of the other variable. The removal of PCs and COD both increase as a result of the interaction, which is consistent with the 3D view response surface plots displayed in Fig. 13 and 14, respectively.

3.4.4 Experimental validation and numerical optimization

The 100% desirability function was chosen in numerical optimization to find the optimal set of parameters for the maximum photocatalytic removal of PCs and COD from TPOME. The goals for numerical optimization are listed in Table S5. The range of precise numbers was determined using the desirability values that were the closest to 1. By creating the best overlay plots, it was possible to visualise these simulated figures with multiple responses and the impact of independent variables on the responses (PCs as GAE and COD removal).

An important component of the RSM analysis was the adjustment in the desirability region when the variables varied within the selected ranges. This kind of research is helpful in determining the best operating parameters in light of the analysis's original conditions as well as the desired removal efficiency for PCs as GAE and COD removal from TPOME. By overlapping critical response, the overlay plot in Fig. 17 displays areas of desired response. In one optimum layered plot, the surface contours of the two responses were overlaid to create the simulated figures. The reasonable level constraints were chosen to be fairly similar to the acquired maximum removal efficiencies in order to obtain a moderately precise optimum zone

(Whitcomb and Anderson, 2004). According to the overlay plot, effective PCs and COD removal occurs at the optimal zone indicated by the yellow color shaded area. The optimum values for TiO₂ loading, H₂O₂ dosage, Mn concentration, and irradiation time are shown in Table 6 and were found to be 0.85 g/L, 0.048 mol/L, 0.301 wt.%, and 204 min, respectively.

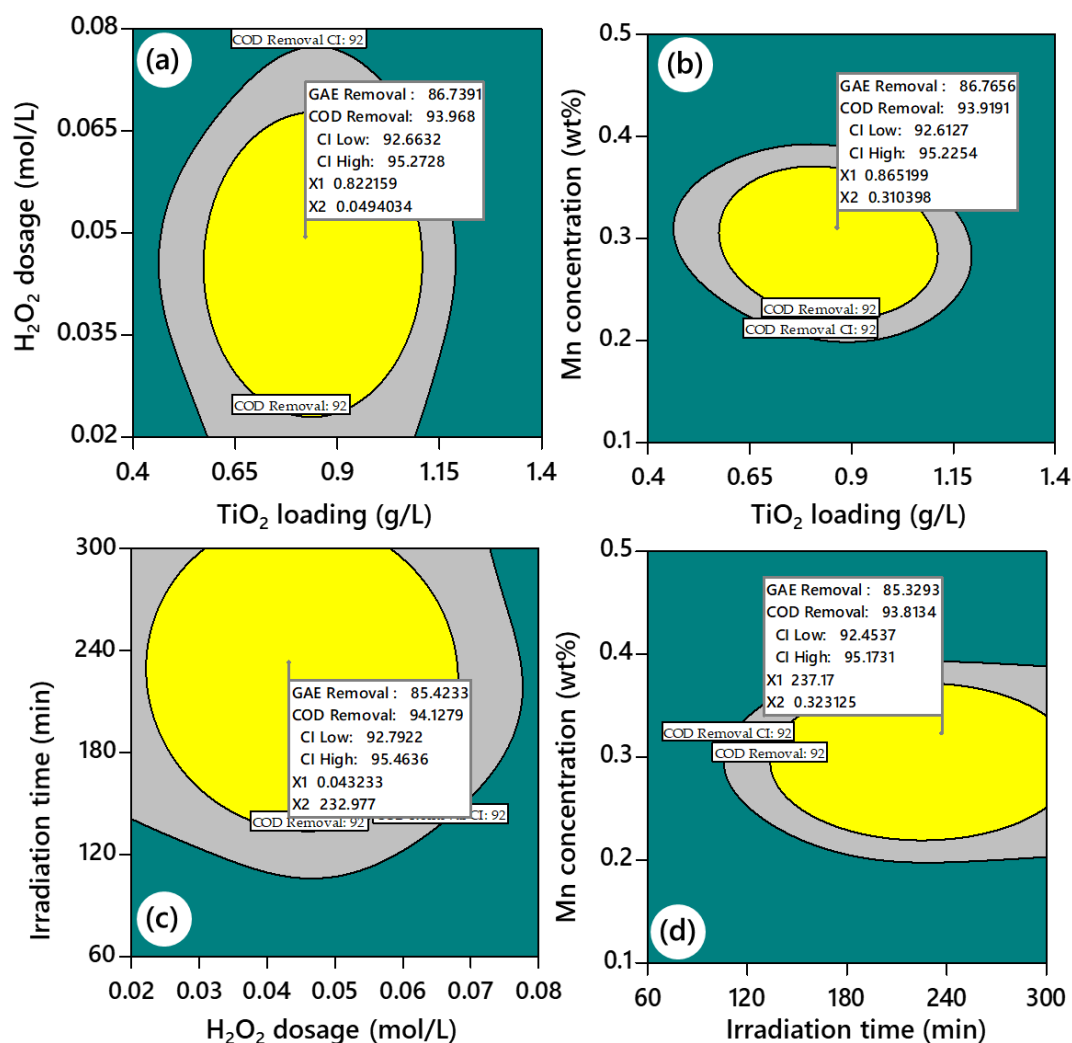


Fig. 17. Optimum overlay plot for (PCs as GAE) and COD removal.

The average of the four experimental runs at the optimal conditions for PCs and COD removal efficiency was 88.87 and 86.04%, respectively. These values fall within the ranges of 85.35–88.13 and 87.41–95.60 with a 95% confidence interval, demonstrating an excellent correlation with the predicted data. The values obtained should fall within the range predicted by the model with a 95% confidence interval for accurate results. The minimal difference

between predicted values and experimental results from laboratory tests for verification demonstrates the value of CCD/RSM as a tool for achieving best operating conditions for photocatalytic processes for PCs and COD removal from TPOME. The reliability of the results obtained is evidently demonstrated by the validation and verification. Table S7 is referred to for thorough numerical optimization statistics of PCs and COD removal.

Table 8 compares the photocatalysis used in this study with the previously researched technologies for remediating TPOME. Under the optimal conditions, the color removal efficiency was 62.76%, which is better than reported in the earlier studies. For instance, Tan et al. [57] investigated the photocatalytic process for removing color from TPOME using the photocatalyst Degussa P-25. However, even under UVB irradiation, they could only remove 50% of the color from TPOME in 240 minutes. Surprisingly, in the current study, COD removal efficiency (88.87%) outperformed previously reported values for the sono-Fenton process of 80% (Taha and Ibrahim, 2014), 56% for photocatalysis using calcium ferrite as photocatalyst (Charles and Cheng, 2019), 16% for silver doped TiO₂ (Cheng et al., 2016), and 10% for platinum loaded TiO₂ (Cheng et al., 2015). The efficiency of PCs removal (86.04%) is much higher than that of earlier studies' findings and much quicker than the biological treatments under investigation so far. As shown in Table S8, the anaerobic digestion process could only remove 60–64% from initial 33 and 112 mg/L PCs in TPOME.

Table 6.
Optimum experimental conditions and their laboratory verification.

Independent variable	Symbol	Coded value	Unit	Removal (%)		Run	Removal (%)	
				PCs	COD		PCs	COD
TiO ₂ loading	A	X ₁	g/L	0.85	0.86	1	86.04	88.73
H ₂ O ₂ dosage	B	X ₂	mol/L	0.048	0.048	2	84.83	88.62
Mn concentration	C	X ₃	wt.%	0.301	0.30	3	87.12	87.93
Irradiation time	D	X ₄	min	204	202	4	86.17	90.22
Mean							86.04	88.87
σ							1.82	0.83

Monitoring the TOC removal allows to gauge the level of mineralization. Since the TOC concentration of the TPOME decreased by 84.66%, it is possible that PCs have been mineralized to some extent without the production of persistent intermediates. The efficiency of the TOC removal was a little lower than that of the PCs and COD removal, indicating that the organic removal might not be preferential to those two processes. The fact that TPOME had almost 62.81% of its color removed is significant because it shows that no extra intermediates or byproducts were created during the photocatalytic degradation process. The solution's yellow color is a common indicator of the presence of by-products from PC degradation and intermediate formation (Ayodhya et al., 2018). But in the present study, the final solution was clear and colorless, showing that the PCs had fully mineralized.

According to the findings, a highly effective and quick method for TPOME remediation that simultaneously reduces several pollution parameters, including phenolic compounds, COD, color, and TOC, is an improved photocatalytic method based on black TiO₂ that has had 0.3 weight percent Mn added. The aforementioned method holds great promise for the effective treatment of wastewater coming from the global palm oil industry's agricultural sector as well as other industries with high phenolic compound concentrations.

3.5 Recyclability of the M/BTiO₂ photocatalysts

Nanomaterial-containing treated effluents that are released into the environment may be toxic and harmful to biological systems (Clément et al., 2013). It is therefore necessary to recover them from the photoreactor to prevent environmental problems. Furthermore, their recovery is crucial because it determines how well the designed photocatalyst can be applied repeatedly in wastewater remediation and future applications. To assess the recyclability of our synthetic Mn/BTiO₂ photocatalyst, we used it for five consecutive cycles. The used Mn/BTiO₂ photocatalyst was removed from the TPOME suspension using centrifugation. After being thoroughly cleaned with water several times, this catalyst was dried for 24 hours at 60 °C before

being re-used to test its efficiency for PCs and COD removal in subsequent runs. The results for recyclability are shown in Fig. 18, which demonstrates a slight decline in the removal efficiency of PCs as GAE and COD from 86.04% and 88.87% to 78.38% and 79.92%, respectively, after the fifth repeated cycle. After the fifth cycle, the removal efficiency of COD and phenolic compounds, respectively, had standard deviations of 3.65% and 3.18%. PCs and COD removal efficiency decreased by 7.66% and 8.83%, respectively.

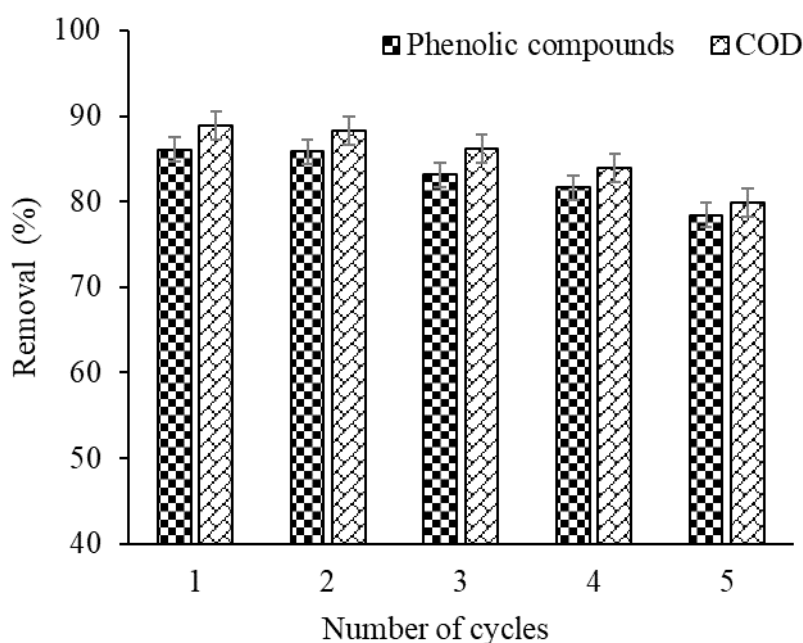


Fig. 18. Removal efficiency of PCs and COD by Mn/BTiO₂ photocatalyst at five consecutive cycles of 204 min.

The COD removal efficiency by CaFe₂O₄ (Charles and Cheng, 2019) and ZnO (Ng et al., 2017) decreased by 7% and 8.14% after the third repeated cycle, respectively, when the results are compared to those from earlier studies. It is therefore possible to draw the conclusion that the synthesized Mn/BTiO₂ used in the current study demonstrates extremely high performance and stability and can be used for the remediation of TPOME.

4. Conclusions

The current study assessed the efficacy of visible-light driven photocatalysis based on manganese modified black TiO₂ photocatalyst and addressed some significant process

limitations for remediating TPOME, particularly the removal of phenolic compounds and chemical oxygen demand. The black TiO₂ was produced in glycerol and calcination at 300°C for one hour to give it improved physicochemical and semiconducting properties as well performance for the removal of phenolic compounds (48%). With additional Mn modification, the black TiO₂ that was performing the best under non-optimized conditions, phenolic compound removal was further increased to 60.12%. The removal of phenolic compounds along with COD was improved by optimizing the independent factor to 86.04% and 88.87%, respectively. High reliability in the estimation of phenolic compound and COD removal was indicated by the statistical analysis, which showed high R² and lower MSE, RMSE, and MAPE for both the response variables, phenolic compounds. Additionally, the optimized process was successful in removing 62.76% color and 84.66% TOC from TPOME. The results of this study confirm that the improved photocatalytic process, which uses Mn modified black TiO₂ that responds to visible light, is an effective method for polishing TPOME, particularly for removing phenolic compounds and chemical oxygen demand. The lower TOC value following the treatment shows that the aforementioned process also ensures complete mineralization of phenolic compounds with minimal intermediate formation.

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Author credit statement



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