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## **Mn<sub>3</sub>O<sub>4</sub>/ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> mixed oxide catalyst derived from Mn-doped Zn-(Al/Ce)-LDHs: efficient visible light photodegradation of clofibric acid in water**

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1 **Mn<sub>3</sub>O<sub>4</sub>/ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> mixed oxides catalyst derived from Mn doped Zn-(Al/Ce)-LDHs:**  
2 **Efficient visible light photodegradation of clofibric acid in water**

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14 **Abstract**

15 Mn<sub>3</sub>O<sub>4</sub>/ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst was synthesized through a solid-state process from 3% Mn-  
16 doped Zn-(Al/Ce) layered double hydroxide structure. Detailed structural and optical  
17 characterization using XRD, FTIR, UV-visible DRS and TEM was conducted. By investigating  
18 clofibric acid (CA) degradation in aqueous solution, Mn<sub>3</sub>O<sub>4</sub>/ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> photocatalytic  
19 activity was evaluated. The results show that the heterostructure mixed oxides catalyst has  
20 excellent CA photodegradation performance. Further, the characterization reveals that such  
21 photocatalytic efficiency can be attributed to two facts that are summarized in the optical properties  
22 and the synergic effect between Mn and Ce elements. The sample demonstrated a narrow band  
23 gap of 2.34 eV based on DRS. According to the experimental results of the photodegradation, after  
24 120 minutes of irradiation, the photocatalyst exhibited the highest photocatalytic activity, with a  
25 degradation efficiency of 93.6 %. Optimization outcomes indicated that maximum degradation  
26 efficiency was attained under the following optimum conditions: catalyst dose of 0.3 g/L, initial  
27 dye concentration of 20 mg/L, pH 3.86 and 120 min of reaction time. The quenching test  
28 demonstrates that photogenerated electrons and superoxide radicals are the most powerful reactive  
29 species. The catalyst could be useful in decreasing the photogenerated charges recombination,

30 which offers more redox cycles simultaneously during the catalytic process. The strong Ce-Mn  
31 interaction and the formation of their different oxidation states offer a high degradation efficiency  
32 by facilitating electron-hole transfer. The introduction of  $Mn_3O_4$  in the catalyst can effectively  
33 improve the visible absorption properties, which are beneficial in the photocatalytic process by  
34 reaching a high catalytic efficiency at a low cost.

35 **Keywords:** Mixed oxides; Ce-Mn synergic effect; Visible light photocatalysis; Clofibric acid.

## 36 1. Introduction

37 Emergent molecules like clofibric acid (CA) have been widely used in pharmaceutical  
38 formulations. CA is a lipid-lowering agent (Ajala et al. 2022) that reacts against excess cholesterol  
39 and reduces blood lipid levels (Aydın et al. 2022). However, CA has a potentially toxic effect on  
40 the aquatic environment. Its existence and prolonged accumulation in the ecosystem could pose a  
41 major threat to human health (Wu et al. 2022)(Korkmaz et al. 2022). CA is considered one of the  
42 most commonly detected emergent molecules in surface water (Ighalo et al. 2020). In 2019,  
43 research performed by Chafi et al. (Chafi et al. 2022) reported the presence of CA at about 500  
44 ng/L at rivers in Rabat, Morocco. The observation remains the same for the African water  
45 resources (Shehu et al. 2022). Indeed, Silori et al. (Silori et al. 2022) confirmed the presence of  
46 CA in these waters in their respective studies. Robelo et al. (Rebelo et al. 2020) indicated the  
47 presence of a high amount of CA in different wastewater areas.

48 Due to its robust structure and immunity to microbial deterioration, CA is challenging to  
49 the removal using traditional wastewater treatment (Wu et al. 2022)(Shi et al. 2022). As a  
50 consequence, CA has a very extended survival period in the environment possibly up to 21 years  
51 (Reza et al. 2014). Furthermore, CA polarity prevents it from being readily absorbed in significant  
52 quantities by soil, despite the fact that it easily reaches groundwater or surface waters (Beausse  
53 2004). In order to protect the public's health, more focus has been paid to the development of  
54 effective technologies for removing CA from the environment. Photocatalytic process is currently  
55 the most effective way to treat wastewater that is rich in contaminants similar to CA (Iqbal et al.  
56 2022). Photodegradation has recently become one of the most promising techniques because it  
57 may effectively decompose more kinds of contaminant while also employing a low-cost and  
58 efficient process owing to their high oxidation capacity, strong stability, low toxicity, high  
59 flexibility, and cost-effectiveness.

60 Despite its advantages, the recombination behavior of the photogenerated electron-hole pairs  
61 during the photocatalytic reaction remains the most hindrance of conventional catalysts (Akir et  
62 al. 2017),(Ma et al. 2024). As a result, potential and effective catalysts have been the most  
63 important materials for CA oxidation. Several research groups are interested in developing novel  
64 catalysts like mixed oxides with low cost and high photocatalytic activity. Mixed metal oxides  
65 derived from LDHs materials have been recognized as one of the most effective catalysts for  
66 emergent molecule degradation, owing to their higher thermal stability, optical properties, and  
67 reusability behavior (Taoufik et al. 2022). Early studies have verified their catalytic performance  
68 toward emergent molecules degradation by using bar or doped ZnO oxides such as Ca/ZnO,  
69 Mg/ZnO and M-ZnO/CeO<sub>2</sub> where M is Ag or Au (Elhalil et al. 2018a)(Elhalil et al. 2018b)(Liang  
70 et al. 2020). Catalysts based on ZnO demonstrated their efficacy against certain kinds of pollutants,  
71 like saturated fatty acids, dyes and heavy metals. Furthermore, studies confirmed that combining  
72 ZnO with other transition metal oxides can significantly improve its catalytic performance (Janani  
73 et al. 2022). In the meanwhile, a number of studies have looked into the use of combination  
74 catalysts, such as ZnO and CeO<sub>2</sub>, in the photo-degradation of organic contaminants. Due to the  
75 heterojunction between the two catalysts, which successfully reduced the recombination of  
76 photogenerated charges, these examples showed notable photocatalytic efficacies. Among these  
77 instances is the assessment of Cerrato et al. (Cerrato et al. 2022), which verified the excellent  
78 photocatalytic activity of CeO<sub>2</sub>-ZnO heterojunction impregnated with Cu<sub>2</sub>O for the oxidation of  
79 tolyltriazole. The improved performance was attributed to the reduced photo-excited electron  
80 recombination. Indeed, thanks to their easily achievable Ce<sup>4+</sup>/Ce<sup>3+</sup> redox couple (Seo et al. 2021),  
81 the recombination of photo-produced charges was reduced. For example, Lin et al. (Lin et al. 2021)  
82 reported excellent photocatalytic CA degradation by g-C<sub>3</sub>N<sub>4</sub>/CeO<sub>2</sub>. The obtained results due to the  
83 availability of transfer of charge carriers between the g-C<sub>3</sub>N<sub>4</sub> and CeO<sub>2</sub> heterojunction. Chaudhari  
84 et al. (Chaudhari et al. 2021) evaluated also the catalytic degradation of diclofenac by a catalyst  
85 based on CeO<sub>2</sub> and the result demonstrates better photocatalytic activity due to improved charge  
86 separation. Typical mixed metal oxides including, Ce-doped Zn/Al (Janani et al. 2021), Mn-Ce-  
87 Al-LDO (Zhao et al. 2019) etc., also being investigated for pollutant degradation by different  
88 researchers, on account of the high potential of these catalysts towards the contaminants.  
89 Additionally, the introduction of CeO<sub>2</sub> in LDHs structures demonstrates the improvement in  
90 catalytic performances toward several pollutants (Janani et al. 2021). In general, the advantage of

91 mixed metal oxides derived from LDHs structures would be their facile manipulation through low  
92 cost and eco-friendly approaches. Peculiar photocatalytic performances can be reached by efficient  
93 visible light absorption, which provides a performance with high quantum yields and low cost  
94 (Wang et al. 2024), (Cheng et al. 2023).

95 The combination of various redox cycles in the same catalyst has also received attention in  
96 order to prevent photogenerated pairs recombination. Wan et al. (Wan et al. 2022) demonstrated  
97 that the presence of  $Mn^{4+}/Mn^{3+}$  and  $Ce^{4+}/Ce^{3+}$  redox couples is beneficial for chlorobenzene  
98 oxidation because the simple interaction ( $Ce^{4+}/Ce^{3+} Mn^{4+}/Mn^{3+}$ ) generates oxygen vacancies on  
99 the semi-conductor surface. Therefore, a mixture of ZnO, CeO<sub>2</sub>, and MnO<sub>x</sub> mixed oxide  
100 optimization with appropriate morphology, absorption capacity, and different metal oxidation  
101 states would be an effective strategy to develop new catalysts. On the other hand, the correlations  
102 between structure design, optical properties, and photocatalytic efficiency also merit more  
103 attention. The Mn introduction into Zn-based LDHs greatly improves visible light absorption,  
104 avoids photogenerated charge recombination by band offset charge transfer (Binas et al. 2019).  
105 Together, the mentioned properties provide excellent photocatalytic performance. However, it has  
106 not been reported that Zn-Al-Ce-based LDHs loaded with Mn are used as catalysts in the  
107 photodegradation process.

108 In this work, a Mn<sub>3</sub>O<sub>4</sub>/ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst was synthesized. The produced catalysts  
109 were tested for their ability to degrade CA when exposed to visible light, and they were further  
110 examined by XRD, TEM, FTIR, and UV-visible diffuse reflectance technique analysis. The main  
111 scope of this study is: i) to obtain Mn<sub>3</sub>O<sub>4</sub>/ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst with satisfactory catalytic  
112 performance and alternatives for typical emergent molecular decomposition; ii) to display new  
113 insight regarding the possible influence of Mn incorporation on the structure and activity behavior  
114 correlations as well as optical properties improvement for CA photodegradation.

## 115 2. Material and methods

### 116 2.1. Materials

117 Analytical-grade chemicals were employed in this study; Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (purity ≥ 99),  
118 Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (≥ 98), Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (≥ 99%), Na<sub>2</sub>CO<sub>3</sub> (≥ 99%), Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (≥ 99.5%),  
119 NaOH (≥ 99%), HCl (≥ 37%), and CA (≥ 95%) have been provided by Sigma-Aldrich (Germany).  
120 Bidistilled water was used all over this study.

## 121 2.2. Catalysts preparation

### 122 2.2.1. Synthesis of LDHs and their derived material

123 The pristine LDHs sample was synthesized through a simple co-precipitation approach  
124 (Janani et al. 2021). In 200 mL of deionized water, corresponding amounts of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  
125  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were dissolved using a Zn/Al molar ratio of 3. Following that, 50 mL of sodium  
126 carbonate solution was added to the metal ions solution. The pH of the mixture was then fixed to  
127 8.5 using a NaOH solution. The combined mixture was stirred continuously for 4 hours before  
128 being put into a stainless autoclave for 16 hours hydrothermal treatment at 75 °C. The white  
129 precipitate was then purified until it achieved a neutral pH solution, and it was then dried for 24  
130 hours at 100°C. The generated substance was finely powdered and kept in test bottles for further  
131 use. In a tube furnace, the formed product was calcined at 500°C for 6 hours.

### 132 2.2.2. Synthesis of $\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$ and $\text{Mn}_3\text{O}_4/\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$

133 The substituted sample was synthesized through the same approach and at the same  
134 condition by substituting 10% of Al with Ce, and then the yellow precipitate was calcined at  
135 500°C. The obtained samples were labeled  $\text{ZnO-Al}_2\text{O}_3$  and  $\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$ .

136 The doped catalyst was prepared by solid-state impregnation of pristine Zn-(Al/Ce) with  
137 3% of Mn. The preparation of the sample was performed as follows: Appropriate amounts of the  
138 prepared pristine LDHs (Zn-Al/Ce-LDHs) and  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were finely grounded. Then, the  
139 obtained mixture was calcined in the same condition of the pristine LDHs samples. The obtained  
140 product was labeled  $\text{Mn}_3\text{O}_4/\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$ .

## 141 2.3. Characterization of the prepared catalysts

142 Using a Malvern Panalytical Empyrean with CuK radiation, X-ray diffraction patterns of  
143 the samples from 7 to 70 were recorded. Highscore software was used to examine the phase  
144 indexation. The FullProf program was employed to determine the cell parameters, and Scherrer's  
145 equation was used to estimate the size of the crystallite [42]. Transmission electron microscope  
146 (TECNAIG2 12 TWIN) operating at an accelerating voltage of 120 kV was used to study the  
147 morphology of the materials. A Perkin Elmer FTIR2000 spectrophotometer was used to collect  
148 Fourier transform infrared spectra. Room temperature UV-visible diffuse reflectance spectra of  
149 the materials were obtained using a Lambda 1050 UV/Vis/NIR spectrometer with a 150 mm

150 integrating sphere. The spectra were used to calculate the photocatalysts' band gap energy.  
151 Drawing lines tangent to the Kubelka-Munk function plots of the resulting spectra, assuming the  
152 permitted direct transition, was then conducted to derive the band gap ( $E_g$ ) value (Dias et al. 2020).  
153 The following equations were used to calculate the valence band energy EVB and the conduction  
154 band energy ECB (Abdi et al. 2020)(Shan et al. 2021):

$$155 \quad E_{CB} = \chi - E_e - 0.5E_g \quad (1)$$

$$156 \quad E_{VB} = E_{CB} + E_g \quad (2)$$

157 where  $\chi$  denotes the catalyst's absolute electronegativity and  $E_e$  represents the free electron energy  
158 vs. hydrogen, which rounds out to 4.5.

#### 159 **2.4. Photocatalytic degradation experiment**

160 A 250 W Halide lamp ( $\lambda$  from 350 to 700 nm) that emit visible light was used to evaluated  
161 the catalysts' photocatalytic performance. In order to prevent the lamp from overheating, water  
162 circulation in a quartz double jacket was used to maintain the ambient temperature of the using  
163 solution constant. In each experiment, 800 mL of CA aqueous solution and 20 mg/L of catalyst  
164 powder were combined in the catalytic reactor. The mixture was magnetically stirred for 60 min  
165 in the dark to reach adsorption/desorption equilibrium prior to the photocatalytic reaction. After  
166 that, the irradiation was started, and the mixture was irradiated on the top and was stirred under  
167 continuous oxygen flow for 180 min. In order to confirm the reached photocatalytic performances  
168 of the used catalyst, the photocatalytic activity of the prepared catalyst was compared to  
169 commercial P25 TiO<sub>2</sub>, which it was irradiated under UV irradiation (UV mercury lamp: 400w)  
170 and at the identical conditions ( $m=50\text{mg}$ ,  $C_0=20\text{mg/L}$  and  $\text{pH}=3.86$ ). A METASH UV-vis  
171 spectrophotometer operating at a wavelength of 278 nm was used to measure the concentration of  
172 CA at predetermined time intervals.

173 The adsorbed amount  $Q_{\text{ads}}$  (mg/g) and the degradation efficiency (D.E.%) were calculated  
174 according to the following equations:

$$175 \quad Q_{\text{ads}} = (C_0 - C_t) * (V/m) \quad (3)$$

$$176 \quad \text{D.E.}\% = 100 * (C_0 - C_t) / C_0 \quad (4)$$

177 where  $C_0$  and  $C_t$  signify the CA concentrations before and after adsorption (mg/L) and  $R$  (g/L)  
178 refers to the mass of the  $Mn_3O_4/ZnO-Al_2O_3-CeO_2$  catalyst per liter of aqueous solution.

179 Using the pseudo-first-order kinetics model, the photocatalytic degradation was expressed  
180 and the kinetic constant was assessed. The equation for the model can be explained as follows:

$$181 \quad \ln(C_0/C_t) = k_{ap} t \quad (5)$$

182 where the  $k_{ap}$  is the apparent rate constant ( $\text{min}^{-1}$ ).

183 Furthermore, the operation parameters were modified to evaluate the catalytic performances  
184 under different conditions. The solution's initial pH was ranged from 3.86 to 9.5 at  $C_0=50\text{mg/L}$  and  
185  $m=20\text{mg/L}$ , and the starting CA concentration was ranged from 25 to 50 mg/L at pH of 3.86 and  
186  $m=20\text{mg/L}$ . The scavenging test was performed to identify the reactive species responsible for the  
187 CA photodegradation by adding  $AgNO_3$  (1 mM), EDTA (1 mM), ethanol (1 mM), or ascorbic acid  
188 (10 mM) as trapping agents for  $\bar{e}$ ,  $h^+$ ,  $\cdot OH$ , and  $O_2^{\cdot -}$ , respectively. This test was explored at the optimal  
189 condition by using 50mg/L of CA, pH 3.86 and catalyst dose of 20 mg/L. The photostability and  
190 reusability of the used catalyst were established after 3 cycles of photocatalytic degradation testing  
191 under identical conditions. After each experiment, the catalyst powder was dried at  $100^\circ\text{C}$  and was  
192 then reused in another CA aqueous solution degradation reaction.

### 193 3. Results and discussion

#### 194 3.1. Catalysts characterization

##### 195 3.1.1. X-ray diffraction

196 Figure 1 depicts the various XRD patterns obtained from the different samples. According  
197 to the result, the pristine Zn-Al and pristine Zn-(Al/Ce) exhibit characteristic patterns of lamellar  
198 structures. The main reflection corresponds to a hydrotalcite like structure for both samples, and it  
199 is clearly seen that the sample substituted by Ce conserves its lamellar structure with the presence  
200 of an additional peak at the  $2\theta$  value between  $27^\circ$  and  $30^\circ$  assigned to the  $CeO_2/Ce_2O_3$  impurities  
201 (JCPDS No. 81-0792) (Hussain et al. 2016)(Nagendran et al. 2018). The characteristic peaks of  
202 the pristine Zn-Al sample are located at  $2\theta$  related to (003), (006), (012), (015), (018), (1010),  
203 (0111), (110), and (113) planes of layered double hydroxide structure (JCPDS No. 38-0486) (Olf  
204 et al. 2009). Using FullProf software, the reflection peaks were fitted to a hexagonal phase with  
205 rhombohedral 3R symmetry and space group P6/mmm. The cell parameters, volume, and



206 interlayer distance for the prepared pristine LDHs are calculated. The cell parameters and volume  
 207 cell are proportionally dependent on the ionic radii. A slight increase in these cell parameters and  
 208 a remarkable change in peak location result from Al being substituted with Ce, whose ionic radius  
 209 is larger than Al (1.01 and 0.54 Å, respectively). With an increase in metal radius, which is directly  
 210 related to the angle  $2\theta$ , the d value rises (7.55 Å and 9.3 Å for pristines Zn-Al and Zn-(Al/Ce),  
 211 respectively). As a result,  $\theta$  values decrease as the interlayer distance increases, according to the  
 212 Bragg equation:  $2d\sin\theta = n\lambda$ . This is consistent with the peak position shifting to the lower 2  
 213 degrees.

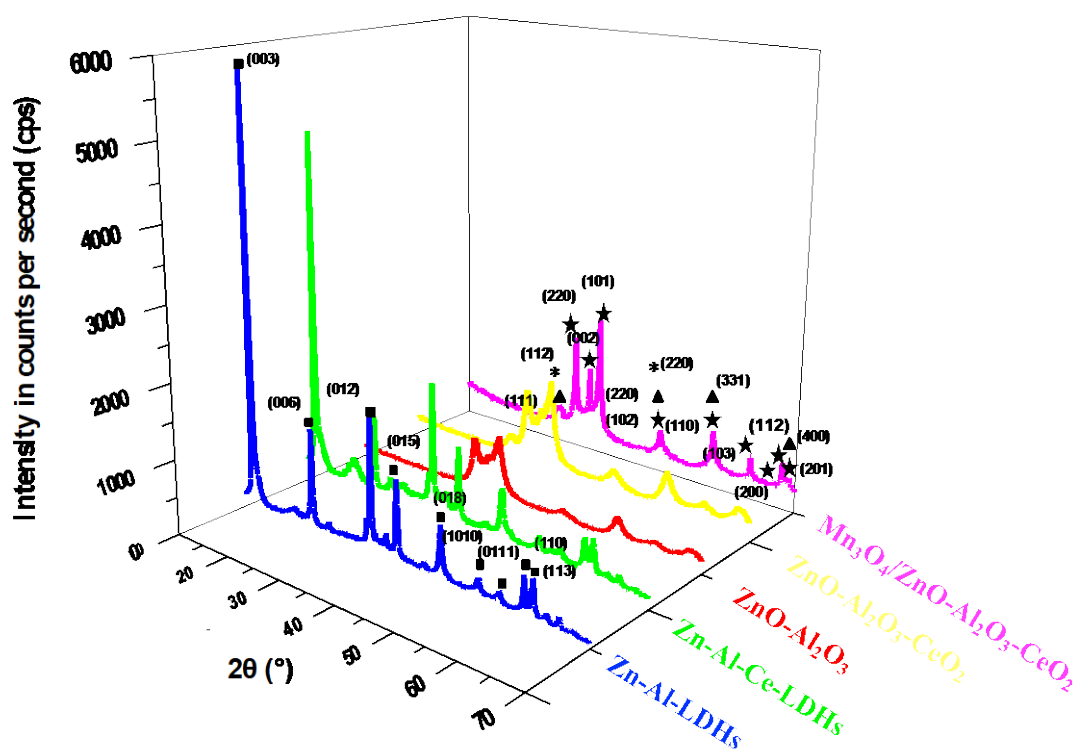
214 Table 1 indicates a slightly difference in parameters a, c, and volume cell with  
 215 incorporation of Ce in the LDHs matrix. The interplanar spacing increased steadily with increasing  
 216 average radii of metallic cations, which depends directly on the angle  $q$  in accordance with Bragg's  
 217 equation. A considerable decrease of parameter c was observed with increase in Ce content; this  
 218 is due to the low affinity of intercalation of carbonate. The same tendency was observed in the  
 219 crystallite size, which were significantly dependent on the unit cell.

220 **Table 1:** Calculated unit cell parameters, crystal sizes and volume cell of the calcined LDHs  
 221 materials.

Catalyst	Lattice parameters (Å°)		Cell volume (Å <sup>3</sup> )	Crystallite size (Å°)
	a	c		
Zn-Al-CO <sub>3</sub>	3.069	22.613	184.451	185.12
Zn-Al-Ce5%-CO <sub>3</sub>	3.071	22.723	185.7	223.4
Zn-Al-Ce10%-CO <sub>3</sub>	7.568	22.572	1119.73	170.2

222 The patterns clearly show that the lamellar structure has been completely distorted  
 223 following calcination. The diffraction peaks correspond to ZnO were observed in calcined  
 224 samples. Some additional peaks for the substituted matrix, corresponding to the CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub>  
 225 cubic fluorite structures with coincident primary reflections to the planes (111), were also observed  
 226 (220) (Yang et al. 2014)(Nagendran et al. 2018)(Hussain et al. 2016). No further characteristic  
 227 reflections correspond to Al<sub>2</sub>O<sub>3</sub>, confirming the amorphous structure of this oxide (ZHANG et al.  
 228 2016). The characteristic peaks attributed to ZnO were indexed at (100), (002), (101), (102), (110),

229 (103), (200), (112) and (201) planes, corresponding to  $2\theta$  of  $31.74^\circ$ ,  $34.4^\circ$ ,  $36.22^\circ$ ,  $47.51^\circ$ ,  $56.59^\circ$ ,  
 230  $62.85^\circ$ ,  $66.35^\circ$ ,  $67.93^\circ$  and  $69.09^\circ$ , respectively (JCPDS Card No.00-001-1127) (Sahoo et al.  
 231 2015). For the Mn doped catalyst, remarkable reflection peaks appeared at  $2\theta$  of  $28.42^\circ$  and  $47.6^\circ$   
 232 indexed to the (112) and (220) planes, and it is seen that the diffraction peaks have shifted to the  
 233 lower  $2\theta$ . These peaks correspond to the formation of  $Mn_3O_4$  in the sample with relatively weak  
 234 peak intensities, suggesting that the  $Mn_3O_4$  oxide is well dispersed in the  $ZnO-Al_2O_3-CeO_2$  matrix  
 235 surface (Velu et al. 1999). The presence of  $Mn_3O_4$  was confirmed by the peak's intensity rising  
 236 after catalyst doping, which means that the Mn metal was successfully introduced into the lattice.  
 237 In the doped catalyst, it is worthy to mention that the crystallite size of the heterostructure was  
 238 systematically increased by Mn doping, which has a value of 28.7 nm, 3.016 nm, and 2.19 nm for  
 239  $Mn_3O_4/ZnO-Al_2O_3-CeO_2$ ,  $ZnO-Al_2O_3$  and  $ZnO-Al_2O_3-CeO_2$ , respectively, indicating that a small  
 240 Mn content affects the crystallite size of the sample.

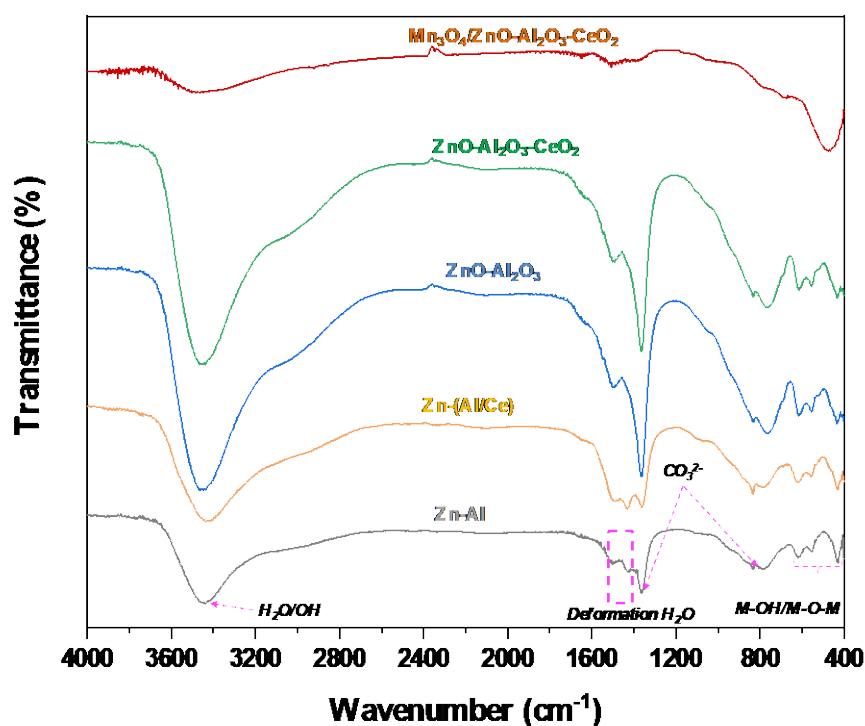


241  
 242 **Fig.1.** XRD patterns of different samples (■pristine LDHs; \* ZnO; ▲CeO<sub>2</sub>/Ce<sub>2</sub>O<sub>3</sub>; \*Mn<sub>3</sub>O<sub>4</sub>).

243 **3.1.2. Fourier transform infrared spectra**

244 Fig.2 presents the FTIR spectra of the materials between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$ . The spectra  
 245 of pristine Zn-Al and Zn-(Al/Ce) show a large absorption band between  $3500$  and  $3200\text{ cm}^{-1}$ . This

246 band can be linked to the hydroxyl group stretching vibration present in the brucitic sheets as well  
247 as in the H<sub>2</sub>O molecules mainly intercalated in the lamellar space or adsorbed on the material  
248 surface. The angular deformation vibration of the intercalated water molecules (H<sub>2</sub>O) can be  
249 observed at 1600 cm<sup>-1</sup>. The interlamellar carbonate ions are marked by the asymmetric stretching  
250 vibration around 1350-1380 cm<sup>-1</sup>, outside-plane deformation at 850-880 cm<sup>-1</sup> and in-plane bending  
251 vibration at 670-690 cm<sup>-1</sup>. Among the characteristic vibrational bands of the pristine LDHs that  
252 cover the region between 1000 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. The observed bands at around 430 cm<sup>-1</sup>  
253 correspond to O-M-O strain, and the bending vibrations between 670 cm<sup>-1</sup> and 590 cm<sup>-1</sup> are linked  
254 to M-O elongation vibrations. Even after calcination of pristine LDHs structure, some H<sub>2</sub>O  
255 molecules from the air were reversibly absorbed on the oxide surfaces during the powder storage.  
256 Compared with the synthesized pristine LDHs structure, there was a slight decrease of the metal-  
257 oxygen intensity bands. This could be due to the charge distribution in the lamellar medium as a  
258 result of the calcination process, as well as the subsequent organization of cations within the sheet.



259

260

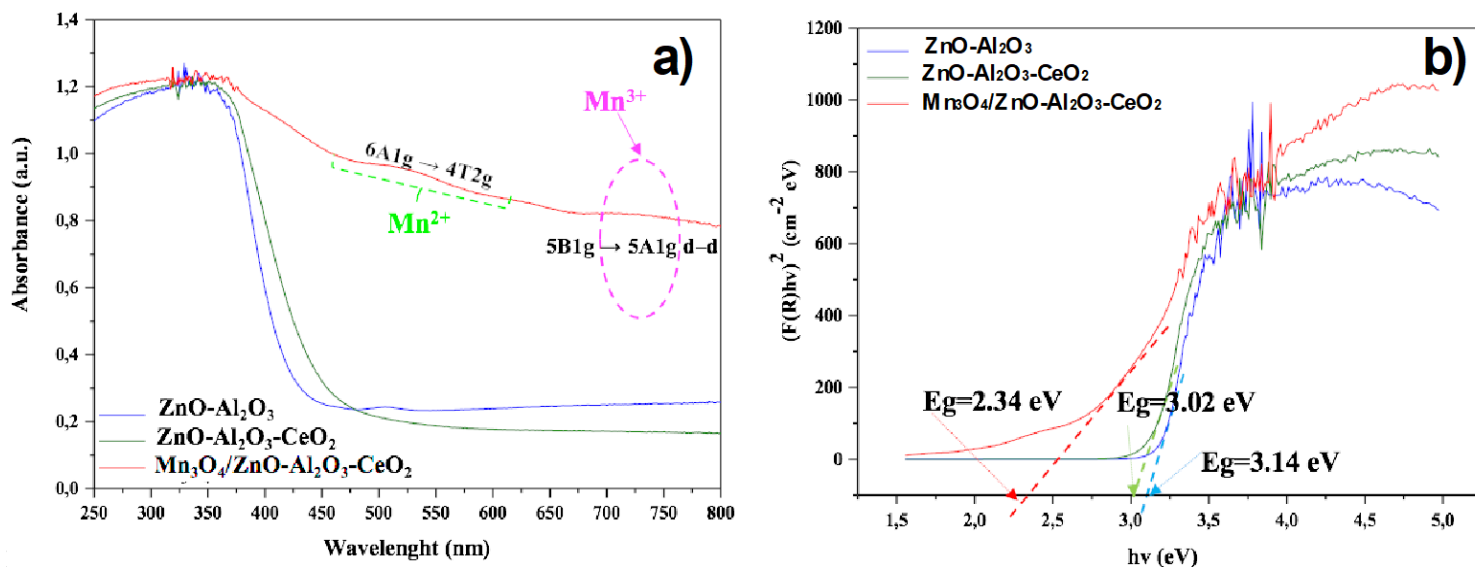
Fig.2. FTIR spectrum of different materials.

261

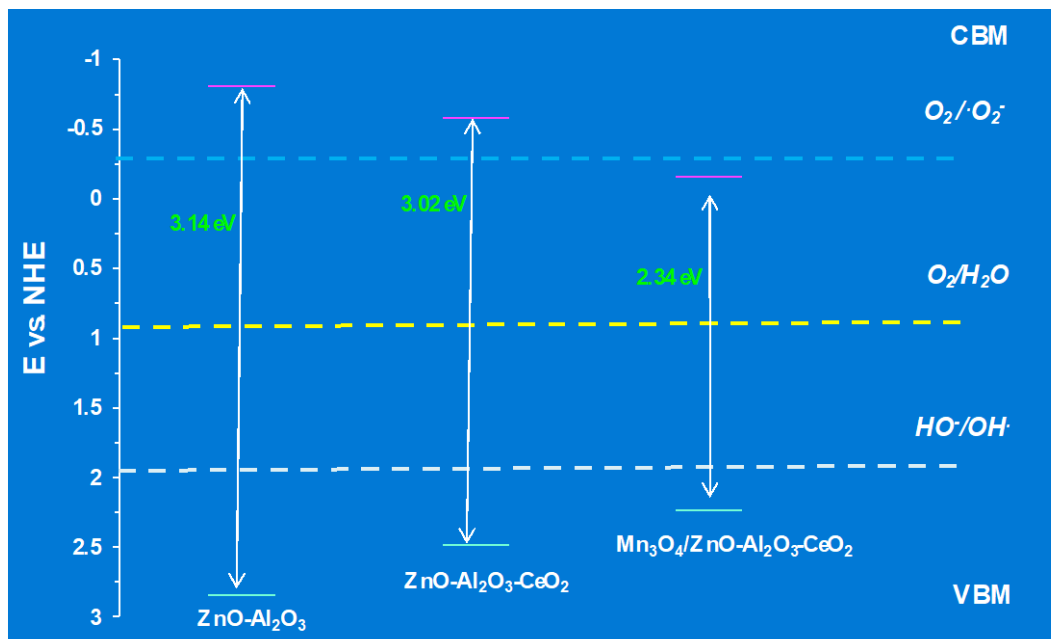
### 3.1.3. Optoelectronic properties

262 The optical characteristics of catalysts are the key criterion of their photocatalytic activity.  
263 The UV-vis diffuse spectra of such mixed metal oxides are depicted in Figure 3. As shown in the  
264 spectra, all the catalysts exhibit an intense absorption band in the UV region, dedicated to a charge  
265 transfer of M-O. Interestingly, the absorption band intensity underwent a significant change, for  
266 which an increased absorption intensity can be clearly observed in the visible region for  
267  $\text{Mn}_3\text{O}_4/\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$ . Near to 350 nm is the optimal energy absorbed by all samples (UV  
268 area). The incorporation of Mn proved to have culminated in a greater capacity for absorption.  
269 This highest absorption band intensity of the semi-conductor material is primarily attributed to the  
270 synergistic effect between  $\text{Mn}_3\text{O}_4$  and the  $\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$  system. It is worthy of mention that  
271 UV-vis spectra provide more information related to electron transitions and the oxidation states of  
272 the used catalyst (Velu et al. 1999). Thought, the d-d transition in  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  can be used to  
273 explain visible absorption bands. Weak bands intensity in the 400–600 nm range are ascribed to  
274 the  $\text{Mn}^{2+}$  specie, which is spin- and orbital-forbidden (Velu et al. 1999). The bands detected at the  
275 two wavelengths of 500 nm and 610 nm are assigned to the electron transition of  $6A1g \rightarrow 4T2g$   
276 crystal field transitions of  $\text{Mn}^{2+}$  (Velu et al. 1999)(Pratt and Coelho 1959)(Kijlstra et al. 1997).  
277 Moreover, the observed absorption band at 755 nm corresponds to  $5B1g \rightarrow 5A1g$  d–d transitions  
278 in  $\text{Mn}^{3+}$ . Since  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  can also be present but overlap with the above-described transition,  
279 it could be argued that manganese is present based on the absorption bands in the 500–800 nm  
280 area (Pratt and Coelho 1959)(Kijlstra et al. 1997). Owing to the presence of these absorption bands,  
281 it is expected that the Mn is available in  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  oxidation states. Independently of the  
282 valence states of Mn, it was obviously assigned the absorption band expansion in the visible area  
283 to the Mn incorporation, which presents a band gap of 2.34 eV smaller than those of  $\text{ZnO-Al}_2\text{O}_3$   
284 and  $\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$  of 3.14 eV and 3.02 eV, respectively (see Fig.4). As a matter of fact, it is  
285 liable to be assumed that the board absorption band of  $\text{Mn}_3\text{O}_4/\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$ , along with the  
286 band capacity stretching to the visible region, could mainly enhance photon absorption and be a  
287 viable candidate for boosting the photocatalytic degradation pathway. A remarkable shift was  
288 clarified from the results shown in the spectra, after the formation of  $\text{Mn}_3\text{O}_4/\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$ , the  
289 valence band moved up and the conduction band moved down, which is mostly responsible for the  
290 band gap reduction. The conduction band of  $\text{Mn}_3\text{O}_4/\text{Zn-(Al/Ce)-MMO}$  is located in a more  
291 positive position, reaching a value of -0.16 eV (ECB= -0.16 Vs NHE) than that of  $\text{ZnO-Al}_2\text{O}_3$   
292 (ECB = -0.59 Vs NHE) and  $\text{ZnO-Al}_2\text{O}_3\text{-CeO}_2$  (ECB = -0.52 Vs NHE). For the valance band, it is

293 also shifted to a smaller value (EVB = 2.18 eV) than those obtained for ZnO-Al<sub>2</sub>O<sub>3</sub> (EVB = 2.55  
 294 eV) and Zn-(Al/Ce)-MMO (EVB = 2.5 eV).



296 **Fig.3.** UV-vis DRS for ZnO-Al<sub>2</sub>O<sub>3</sub>, ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub>/ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>.



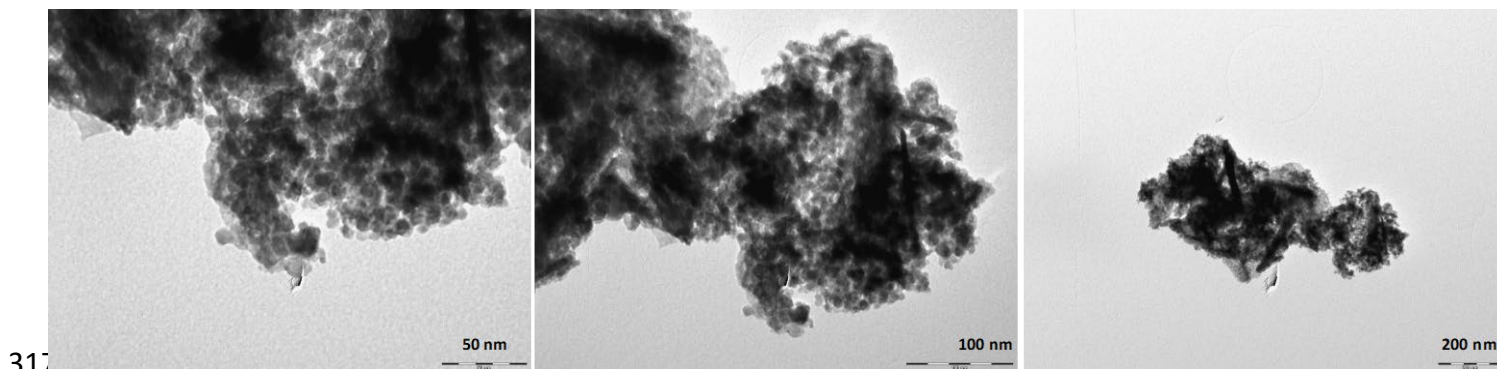
297  
 298 **Fig.4.** Representation of the band gap edges for ZnO-Al<sub>2</sub>O<sub>3</sub>; ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub>/ZnO-  
 299 Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>.

300

301

#### 3.1.4. TEM analysis

Fig.5 shows TEM graphs of the surface morphology of the  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$  catalyst at various magnifications. The figure shows the formation of a dense heterostructure with agglomerated, indistinct grains on the catalyst surface. A disordered structure and the irregular and unshaped forms of the sample were observed, indicating the evolution of mixed oxides with various morphologies. The 'darker diapars' remarked can be linked to the formation of manganese oxide on the sample surface, due to the distribution of segregated Mn particles as oxide on the sample surface. The images also show the formation of a rolled-sheet-like structure. According to reported studies, the  $\text{CeO}_2$  nucleation is mainly affected by the presence of Mn like oxides (Wan et al. 2022)(Wu et al. 2011)(Mohan et al. 2012). Manganese oxide excess can also result in rolled morphology that is individually sandwiched (Morales-mendoza et al. 2015). So, the finding suggests that the introduction of the Mn oxides into the system avoids the homogenous distribution of the constituent elements of the system, leading to the formation of rolled-like morphologies. The obtained heterostructure morphology of the mixed metal oxides seems extremely favorable for improving photocatalytic application.

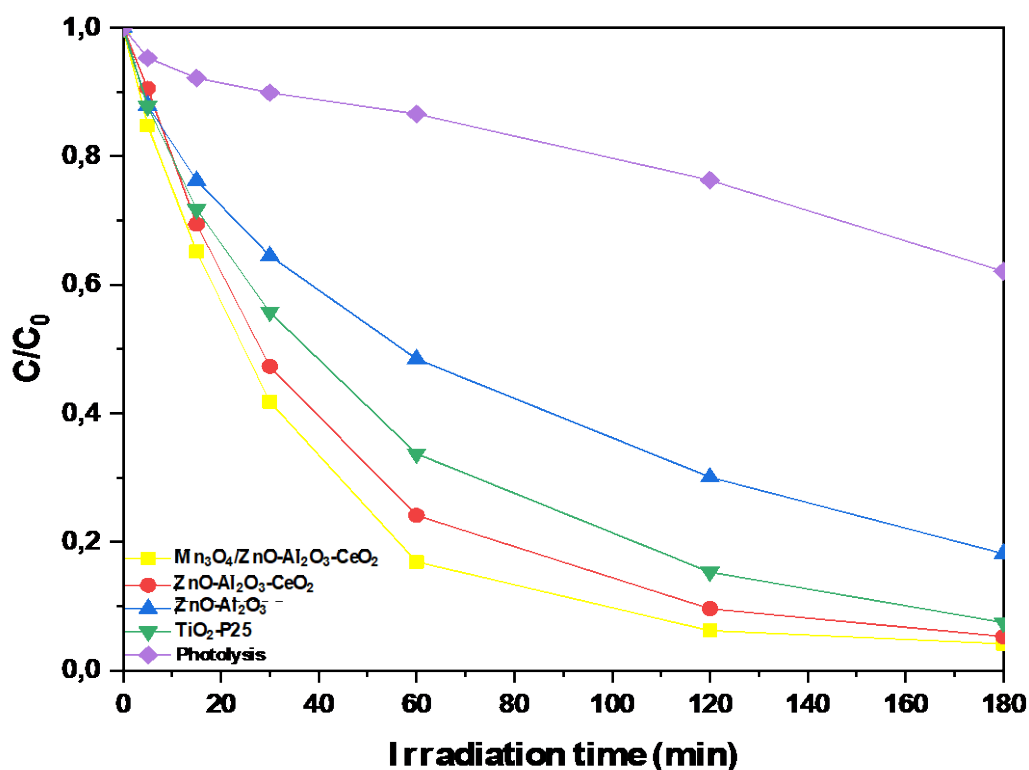


**Fig. 5.** TEM images of  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$  catalyst.

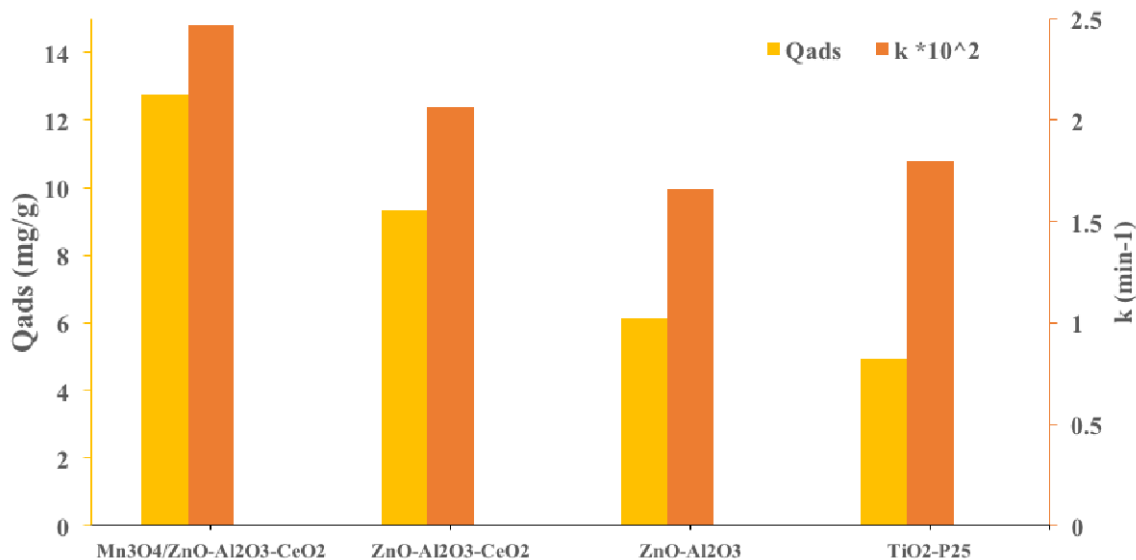
#### 3.2. Adsorption/Photocatalytic performances

The photocatalytic degradation of CA through the catalysts expressed in term of  $C/C_0$  us function of time is reported in Fig.6. As shown, from the photolysis test, about 20% of CA degradation efficiency was achieved after 120 min, which was negligible compared to that reached in the presence of each used catalyst The  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$  heterostructure shows the highest photocatalytic efficiency compared to  $\text{ZnO}-\text{Al}_2\text{O}_3$ ,  $\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$  and commercial  $\text{TiO}_2$  catalysts under the conditions. The majority of CA was degraded within 120 min by using

326  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$ , which exhibits 93.6 % degradation efficiency under visible light  
 327 irradiation with a constant rate of  $2.47 \cdot 10^{-2} \text{ min}^{-1}$ . While  $\text{ZnO}-\text{Al}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$   
 328 and  $\text{TiO}_2$  achieve only 69.91 %;  $1.66 \cdot 10^{-2} \text{ min}^{-1}$ , 90.36 %;  $2.06 \cdot 10^{-2} \text{ min}^{-1}$  and 84.68 %;  $1.8 \cdot 10^{-2}$   
 329  $\text{min}^{-1}$ , respectively. On the other hand, the photocatalytic performance considerably depends on  
 330 the adsorption behavior of the catalysts. As demonstrated in Fig. 7, there is a high correlation  
 331 between the adsorbed amounts and the kinetic rate constant of photodegradation. During the  
 332 photodegradation process, the adsorption behavior is crucial, which will accelerate the  
 333 photocatalytic reaction. Therefore, based on the UV-vis DRS data that were obtained and the  
 334 calculated experimental parameters, the highest photocatalytic activity of  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-$   
 335  $\text{CeO}_2$  is primarily due to the significant adsorption ability of CA onto the surface of catalyst, to the  
 336 surface morphology, and to the optical characteristics.



337  
 338 **Fig.6.** Kinetics of CA photodegradation over catalysts ( $C_0= 50 \text{ mg/L}$ ;  $m= 20 \text{ mg/L}$ ; pH of  
 339 solution  $\sim 3.86$ )



340

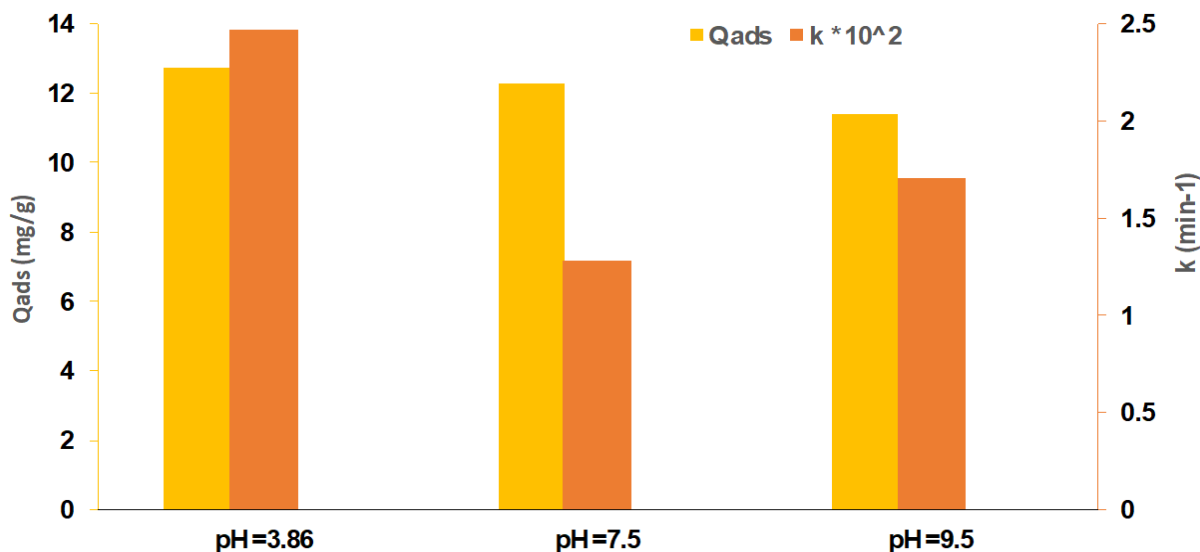
341 **Fig.7.** Correlation between degradation rate and adsorbed amounts of CA by different  
 342 photocatalysts (m= 20 mg/L; C<sub>0</sub>= 50 mg/L; pH of the solution ~3.86).

### 343 3.2.1. Effect of the initial solution pH

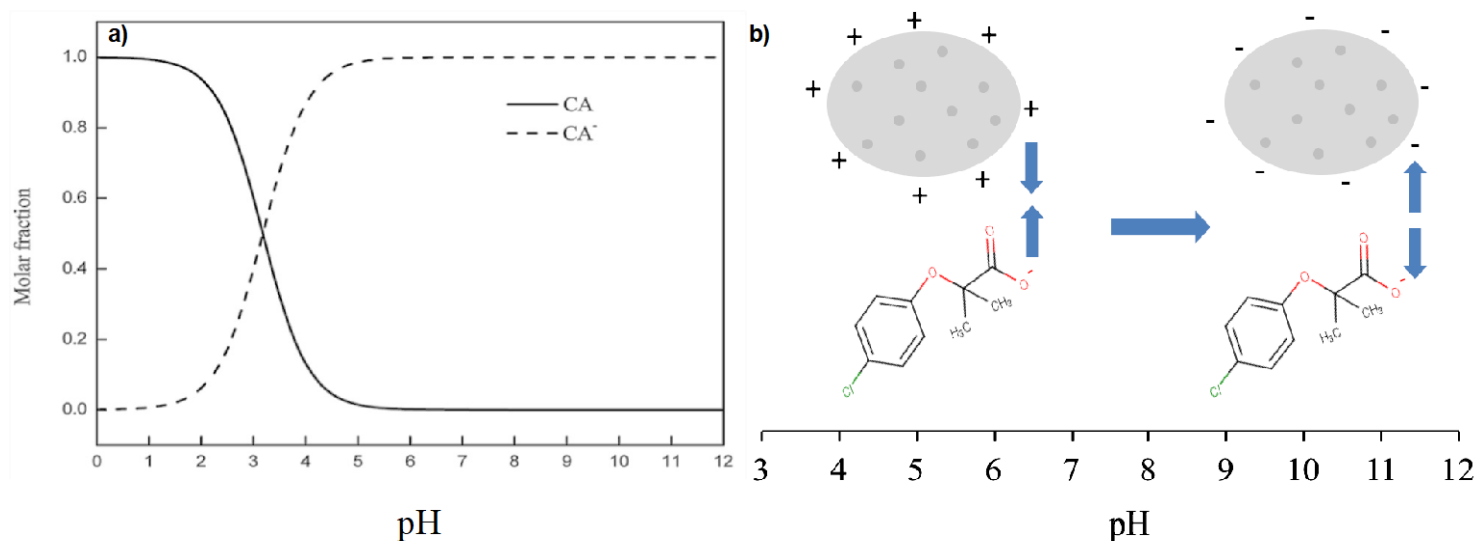
344 In the photocatalytic process, the pH of the solution is crucial. Fig.8 illustrates the change  
 345 observed in degradation efficiency of CA by Mn<sub>3</sub>O<sub>4</sub>/ZnO-Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> with the change of initial  
 346 solution pH. As illustrated in Fig. 9, the photocatalytic activity increased at a natural solution pH  
 347 of 3.86, dropped when the pH was raised to 7.5, and then slightly increased at pH 9.5. The catalyst  
 348 exhibits a maximum degradation efficiency in acidic medium achieving 93.6% of efficiency.  
 349 While 77.01 and 86.06 % for neutral and basic solution, respectively. The apparent rate constant  
 350 of CA photodegradation at pH of 3.86 is over faster than those at pH 7.5 and 9.5. As known, the  
 351 catalyst surface is significantly affected by the solution pH, it can be protonated or deprotonated  
 352 depending on its pH<sub>PZC</sub>. The catalyst exhibits a pH<sub>PZC</sub> of 8, which indicates that its surface is  
 353 positively charged below of this value, and negatively charged above of it. Furthermore, Fig.9 (a)  
 354 shows the species distribution of CA and its pK<sub>a</sub> value, which is around 3.18. By increasing pH  
 355 from 0 to 12, it can be seen that the molecular form fraction reduced while the anionic form fraction  
 356 increased. According to the experimental data, the higher adsorbed amount was observed at a low  
 357 pH value and then decreased by increasing the pH of the solution. This outcome might be assigned  
 358 to the electrostatic interactions between the CA anions and the catalysts protonated surface.  
 359 Similarly, increasing the pH of CA reduces its adsorption capacity primarily due to repulsion



360 interactions between the negative surface charge and the anionic form fraction of CA in the basic  
 361 medium (Fig. 9(b)). At a high pH value, more  $\cdot\text{OH}$  could be generated through  $^-\text{OH}$  groups, which  
 362 are the powerful oxidants in the photocatalytic process.



363  
 364 **Fig.8.** Effect of initial solution pH of CA on its adsorption and degradation efficiency by  
 365  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$ .



367  
 368 **Fig.9.** Distribution of dissociation species of CA (a) and the predicted electrostatic interaction  
 369 between CA and  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$  surface depending  $\text{pH}_{\text{pzc}}$  (b).

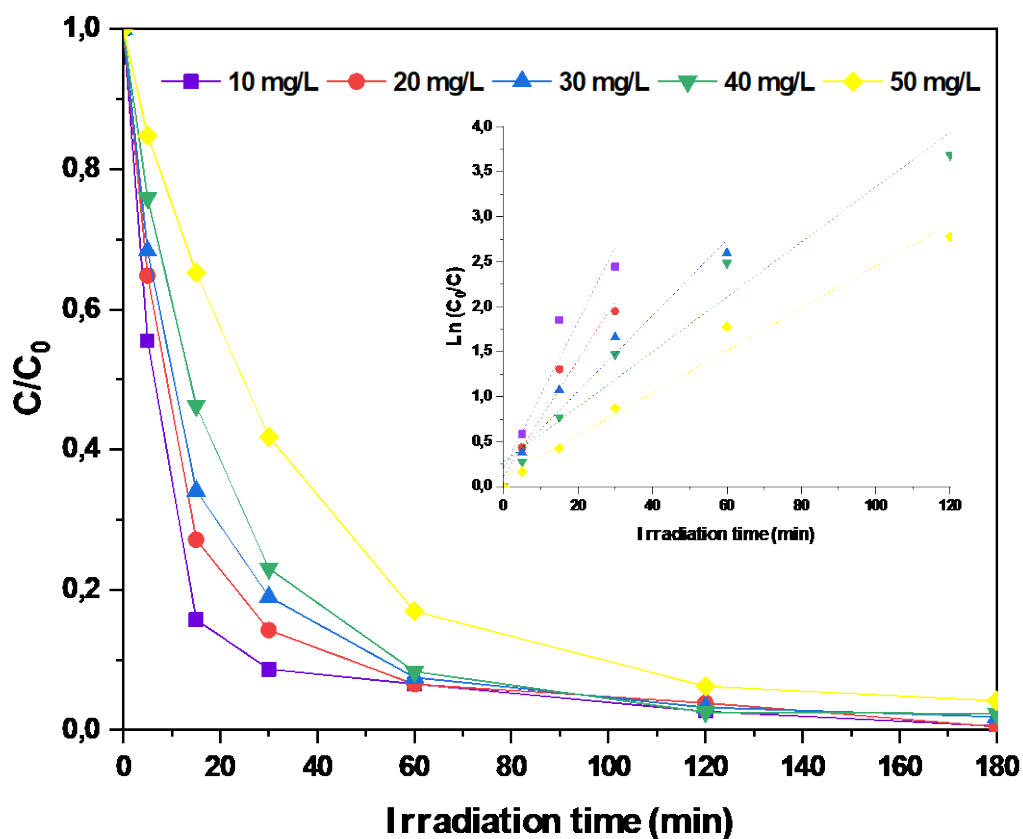
### 3.2.2. Effect of the initial concentration of CAF

Fig.10 shows the kinetics of CA photocatalytic oxidation at varied starting concentrations. The insert of the figure also displays the  $\ln(C_0/C)$  against time plot. The data reveals that the initial CA concentration affects the kinetics of degradation. At low concentration, the photodegradation process was very faster in a short time. These results indicated that a significant number of active sites were available at the start of the reaction, increasing the photodegradation rate. The degradation kinetics at different concentration fits considerably the pseudo-first order kinetic model. By increasing starting concentration, the efficiency of CA degradation tends to decline. Therefore, a lower initial CA concentration could increase the performance of CA removal This could be explained by the fact that, as the starting pollutant content rises, more molecules were deposited on the photocatalyst surface. The adsorption of  $O_2$  and  $\cdot OH$  on the catalyst surface reduced as more active sites were filled by the CA molecules, which reduced the amount of radical production. Furthermore, a decline in photon adsorption by the catalyst due to a photon penetration inhibition on its surface leads to a decrease in the generation of reactive species. Thus, the important degradation of a high concentration of CA requires a very efficient catalyst. As a consequence, the synthesized  $Mn_3O_4/ZnO-Al_2O_3-CeO_2$  leads to excellent CA degradation efficiency at high initial concentrations.

In order to make a comparison with other catalysts, Table 1 reports information about several studies regarding the CA degradation in aqueous solutions carried out with different operating conditions. It is necessary to underline that the literature about the degradation of CA by photocatalytic processes using  $Mn_3O_4/ZnO-Al_2O_3-CeO_2$  is not reported. From the Table 1, it is possible to observe that,  $Mn_3O_4/ZnO-Al_2O_3-CeO_2$  employed in our study provide higher performances in CA also after several reuse cycles. A direct comparison between the commercial  $TiO_2-P25$  and our system is applicable to show the efficient performance of the used material.

A low dose of the proposed material exhibits excellent photodegradation in a shorter time and for a high concentrations of CA.

The existence of mixed metal oxides based on Mn, Ce, and Zn, which are confirmed for prospective use in the photocatalytic test, may be the reason for the findings. The main properties of the presented catalyst would make the photocatalytic process economically feasible. In addition, none of the analyzed papers reports data about the synthesis, application, stability and reusability of the tested material.



401  
 402 **Fig.10.** Effect of initial CA concentration on its photocatalytic degradation over  $\text{Mn}_3\text{O}_4/\text{ZnO}-$   
 403  $\text{Al}_2\text{O}_3-\text{CeO}_2$  ( $m=20$  mg/L; pH of solution  $\sim 3,86$ ).

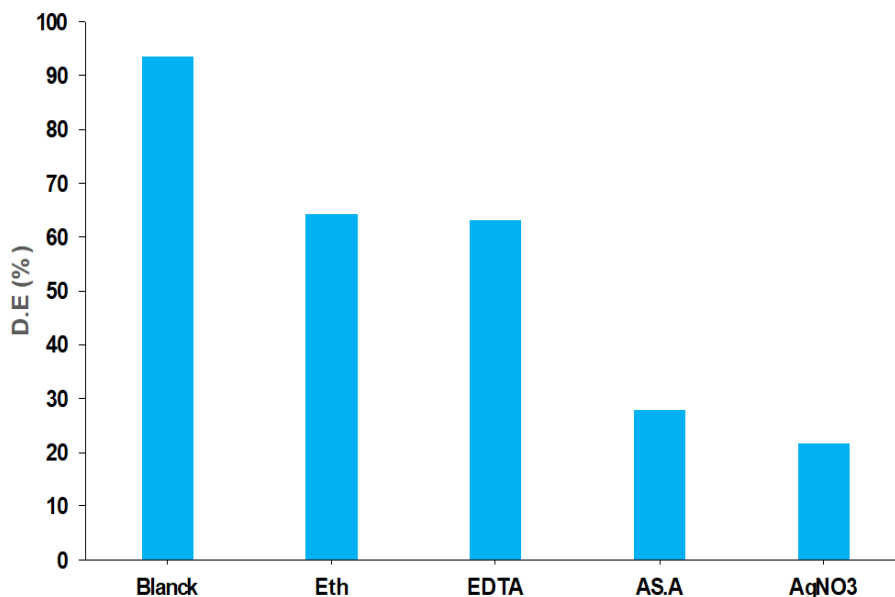
404 **Table 1.** Comparison of the effectiveness of  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$  for CA degradation with  
 405 published data.

Catalyst	Concentration (mg/L)	Catalyst dose (mg/L)	Ratio (m/C)	pH	Light source	Time (min)	$k_{app}$ ( $\text{min}^{-1}$ ) and D.E (%)	Ref.
$g\text{-C}_3\text{N}_4/\text{P25}$	2.0	25	12.5	5.3	Sunlight	30	0.039, 85.4	(Chen et al. 2017)
$\text{TiO}_2$	1.5	1000	666.6	5.9	2 UVA lamps	130	0.077, 85	(Favier et al. 2019)
Zn-La mixed oxide	20	500	25	Natural	UV light	90	97	(Sescu et al. 2020)
$g\text{-C}_3\text{N}_4/\text{CeO}_2$	21.5	500	23.25	4.5	Visible light	60	98.5	(Lin et al. 2021)
$\text{Mn}_3\text{O}_4/\text{Zn}-(\text{Al}/\text{Ce})\text{-MMO}$	50	20	0.4	3.86	Visible light	120	0.0247, 93.6	This work

406

### 407 3.2.3. Discussion of photocatalytic mechanism

408 From the previously discussed results, we assumed that the main reason for the excellent  
409 photocatalytic performances toward the degradation of CA can be assigned to two facts: the  
410 incorporation of Mn in the system, which extends the absorption intensity to the visible area and  
411 enhances the optical characteristics of the produced samples owing to the existence of the two  
412 oxidation states of Mn ( $Mn^{2+}$  and  $Mn^{3+}$ ). This is confirmed by UV-vis spectra and the synergic  
413 effect between  $CeO_2$  and  $Mn_3O_4$  as reported in the literature (Wan et al. 2022)(Binas et al.  
414 2019)(Morales-mendoza et al. 2015). The presence of mixed oxides promotes CA degradation via  
415 a strong synergy between  $CeO_2$  and  $Mn_3O_4$ , which promotes ( $Ce^{4+}/Ce^{3+}$   $Mn^{4+}/Mn^{3+}$ ) redox  
416 couples. A brief discussion about the enhanced photocatalytic performance of the  $Mn_3O_4/ZnO-$   
417  $Al_2O_3-CeO_2$  heterostructure is suggested to be as follows: Firstly, it is widely acknowledged that  
418 the presence of intermediate photogenerated active species such as electron ( $\bar{e}$ ), holes ( $h^+$ ),  
419 superoxide radicals ( $O_2\cdot^-$ ) and hydroxyl radicals ( $\cdot OH$ ) on the exposed surface catalyst is primarily  
420 responsible for the photocatalytic reaction (Shang et al. 2019). Fundamentally, electron-hole pairs  
421 effectively contribute to the degradation process in the photocatalytic process; the holes ( $h^+$ )  
422 directly reacted with the organic molecules deposited on the catalyst surface or with the  $OH^-$  anion  
423 present in an aqueous solution to produce  $\cdot OH$  radicals. The photo-induced electrons ( $\bar{e}$ ) are  
424 captured through adsorbed  $O_2$  forming  $O_2\cdot^-$  radicals, which participate in the generation of  $OH\cdot$  by  
425 a simple reaction with  $H_2O$  molecules. The fast rate of photogenerated charges recombination,  
426 which prevents the degradation reaction of organic compounds, is the process's fundamental flaw.  
427 So, the presence of redox cycles in the catalytic system can significantly improve the carrier's  
428 charge separation by avoiding their recombination rate, promoting the favorite migration of  
429 electrons to the CB, and producing more holes in the CB. To explore the photocatalytic degradation  
430 of the CA mechanism, quenching tests were performed. Fig.11 demonstrates that the  
431 photodegradation efficiency decreased from 93.6 % to 64.23, 63.10, 27.9 and 21.7 % after the  
432 addition of ethanol, EDTA, ascorbic acid, and  $AgNO_3$ , respectively. So, based on the obtained  
433 date, the photogenerated electrons and superoxide radicals are the most responsible in the  
434 photocatalytic degradation reaction of CA. Additionally, the hydroxyl radicals and holes provide  
435 a reasonable contribution to the photodegradation of CA.

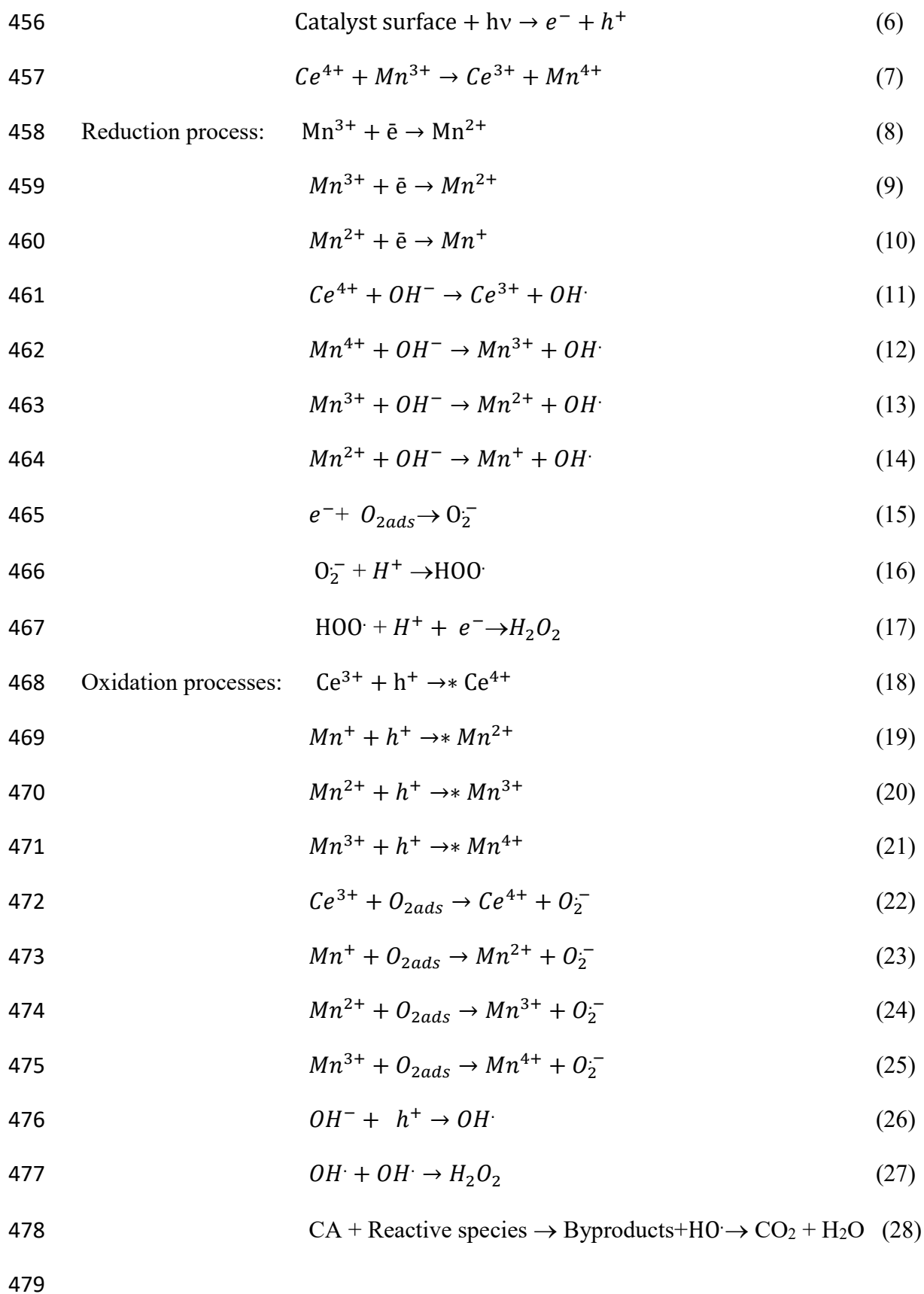


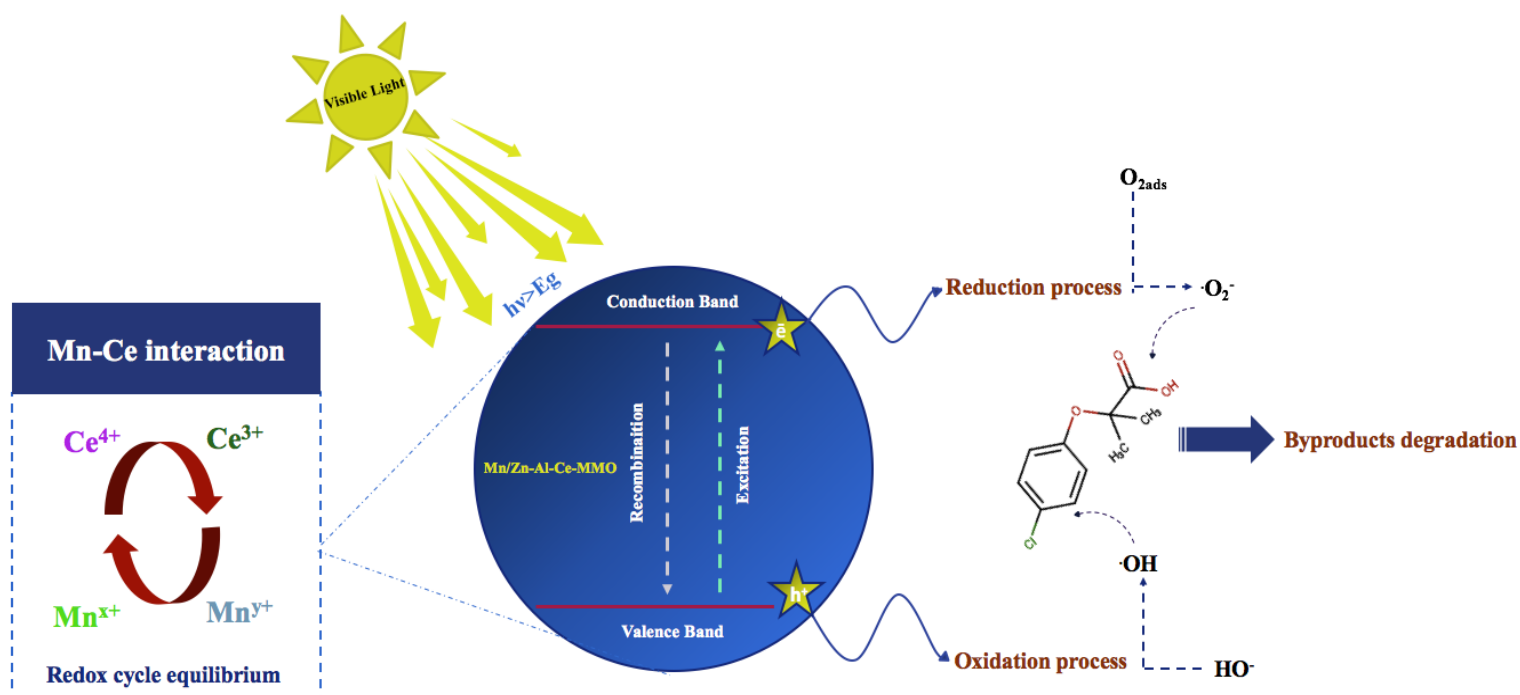
**Fig.11:** Scavenger reactive species.

436

437

438 In this case, we can propose that the most responsible and powerful active species are  
 439 photogenerated electrons and that the Mn can exist in a variety of oxidation states ( $Mn^+$ ,  $Mn^{2+}$ ,  
 440  $Mn^{3+}$  and  $Mn^{4+}$ ) owing to the production of  $\bar{e}-h^+$  charges under irradiation. The excitation of the  
 441 catalyst surface by visible light provides for the transfer of electrons ( $\bar{e}$ ) to the CB, producing  
 442 deficiency charges like holes ( $h^+$ ) in the VB (Eq 6), which could oxidize the present species in  
 443 aqueous solution. According to the band edge position of the catalyst, the creation of  $OH\cdot$  species  
 444 is induced by the holes (Eq 26). Similarly, the generated electrons reduced the  $Mn^{x+}$ ,  $Ce^{x+}$ , leading  
 445 to the formation of elements with different valences (Eqts 8,9,10,18,19,20 and 21). In addition, the  
 446 lifetime of these generated pairs was increased owing to the presence of different couple redox,  
 447 which provide a high photogenerated charges separation and enhance significantly the catalytic  
 448 performance of the photocatalyst. The high degradation efficiency could be assigned to the  
 449 photogenerated  $\bar{e}$  capture through  $Ce^{4+}$  in 4f level of cerium ion,  $Mn^{2+}$ ,  $Mn^{3+}$  and  $Mn^{4+}$  forming  
 450  $Ce^{3+}$ ,  $Mn^+$ ,  $Mn^{2+}$  and  $Mn^{3+}$ , respectively. These couple redox leads to formation of the intermediate  
 451 reactive species mainly including  $OH\cdot$  (Eqts 11,12,13 and 14),  $O_2^{\cdot-}$  (Eqts 15, 22,23,24 and 25),  
 452  $HOO\cdot$  (Eq 16) and  $H_2O_2$  (Eq 17 and 27). According to the band position spectra (Fig.5), all of the  
 453 mentioned reactive species could be produces. As a consequent, the high interaction between Ce  
 454 and Mn species contribute to reaching a potential photocatalytic efficiency. The proposed reactions  
 455 pathway is examined as following:

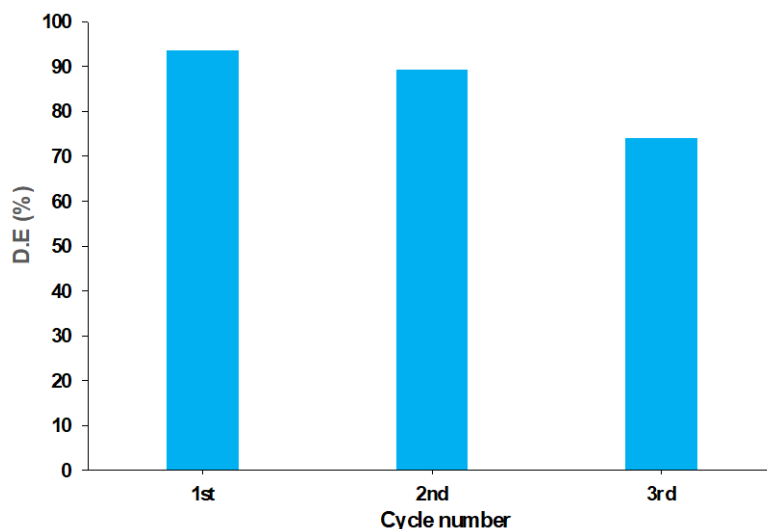




481 **Fig.12.** Schematic illustration of the photocatalyst surface under light irradiation.

#### 482 3.2.4. Photostability and reusability of catalyst

483 The stability and the recyclability application of the used catalyst are shown in Fig.12. The  
 484 result depicted that the photocatalytic activity of  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$  catalyst remained  
 485 almost stable even at 3 cycles with a low reduction of degradation efficiency from 93 to 74%,  
 486 which can be due to the mass loss of the catalyst. The present study demonstrates that  $\text{Mn}_3\text{O}_4/\text{ZnO}-$   
 487  $\text{Al}_2\text{O}_3-\text{CeO}_2$  present an excellent stability and photocatalytic activity and can be used like  
 488 promising catalyst for several time for the degradation of emergent pollutant. The obtained results  
 489 indicate that this efficient and stable system could be considered as a potential catalyst and presents  
 490 a trend practical application in photocatalytic degradation process of emergent molecules.



491

492

**Fig.12.** Reusability and photostability of  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$ .

493 **Conclusion**

494 In the present study, a well-shaped heterostructure was obtained by doping pristine Zn-  
 495 (Al/Ce)-LDHs with Mn in reasonable content of 3% and calcination treatment at  $500^\circ\text{C}$ . A  
 496 thorough optoelectronic properties analysis suggests that the high visible absorption capacity of  
 497 the catalyst is linked to the presence of  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  in the catalyst system.  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-$   
 498  $\text{CeO}_2$  mixed oxides obtained with abundance particles size less than 30 nm and with an efficient  
 499 absorption capacity in both ultraviolet and visible regions, which shows a small band gap (2.34  
 500 eV). The corresponding catalyst outperforms the others with regard of photocatalytic performance  
 501 activity when under visible light. This catalyst exhibits an excellent photocatalytic performance  
 502 toward CA under visible light irradiation, which achieved 93.6 % for 50 mg/L of CA by using a  
 503 low catalyst dose of 20 mg/L. In conclusion, charge transfer between  $\text{Mn}^{x+}$ ,  $\text{Ce}^{3+}$ , and  $\text{Ce}^{4+}$  is the  
 504 main reason for the significant separation between the photogenerated electrons and holes. So, the  
 505 ability to produce Mn and Ce in different oxidation states with strong interaction and synergy  
 506 between Ce and Mn redox couples improves photocatalytic performance under combined and  
 507 simultaneous action. According to the reusability tests, the catalyst is much more  
 508 photostable under visible light irradiation. This study could offer a straightforward method for the  
 509 synthesis of a cost-effective photocatalyst based on mixed oxides of  $\text{Mn}_3\text{O}_4/\text{ZnO}-\text{Al}_2\text{O}_3-\text{CeO}_2$   
 510 derived from LDHs structure thus enable their application in environmental pollution control  
 511 issues.



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517 **Declarations**

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519 Researchers Supporting Project number (RSPD2024R768), King Saud University, Riyadh, Saudi  
520 Arabia

521 **Competing interests**

522 The authors have no relevant financial or non-financial interests to disclose

523 **Author Contributions**

524 **Fatima Zahra Janani:** Performed the experiments; Analyzed and interpreted the data, Writing:  
525 original draft. **Habiba Khiar:** Performed the experiments; Analyzed and interpreted the data.  
526 **Nawal Taoufik:** Analyzed and interpreted the data; Data curation. **Mhamed Sadiq:** Analyzed  
527 and interpreted the data; Data curation. **Lidia Favier:** Analyzed and interpreted the data;  
528 Writing: review and editing, Data curation. **Abdelrahman Osama Ezzat:** Writing: review and  
529 editing. **Alaâeddine Elhalil:** Analyzed and interpreted the data; Writing: review and editing.  
530 **Noureddine Barka:** Conceived and designed the experiments; Analyzed and interpreted the  
531 data; Writing: review and editing, Supervision.

532 **Ethics approval and consent to participate**

533 Not applicable.

534 **Consent for publication**

535 Not applicable

536 **Availability of data and materials**

537 The datasets used and/or analyzed during this study are available from the corresponding author  
538 on reasonable request.

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