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# Synthesis of a magnetically separable LDH-based S-scheme nano-heterojunction for the activation of peroxymonosulfate towards the efficient visible-light photodegradation of diethyl phthalate

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1           **Synthesis of a magnetically separable LDH-based S-scheme nano-**  
2 **heterojunction for the activation of peroxydisulfate towards the efficient**  
3 **visible-light photodegradation of diethyl phthalate**

4  
5           **Arezou Fazli<sup>a, b</sup>, Marcello Brigante<sup>a</sup>, Alireza Khataee<sup>b, c\*</sup>, Gilles Mailhot<sup>a\*</sup>**

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32

33 **Abstract**

34 Herein, a stable and S-scheme Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite was synthesized and used  
35 for the photocatalytic degradation of diethyl phthalate (DEP) through the activation of  
36 peroxymonosulfate (PMS). In comparison with pure Fe<sub>3</sub>O<sub>4</sub>, and LDH, the Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH  
37 nanocomposite demonstrated significantly enhanced photocatalytic activity due to its S-  
38 scheme charge-carrier migration mechanism. The prepared composite was also magnetically  
39 recoverable from the treated water which is favorable to avoid the production of secondary  
40 pollution. The integration of the composite and visible light showed the presence of a synergy  
41 factor of 14 for the degradation of diethyl phthalate. However, the photocatalytic  
42 performance of Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH was dependent on the different physicochemical  
43 parameters; wherein, the higher degradation efficiency was achieved using the solution pH of  
44 8, the catalyst, DEP, and PMS concentrations of 1 g L<sup>-1</sup>, 20 mg L<sup>-1</sup>, and 8 mM, respectively.  
45 The high photocatalytic activity of the catalyst was maintained after 5 consecutive reaction  
46 runs and the stability of the material was proved by the XPS. Moreover, the ICP-AES analysis  
47 proved that the leaching of Fe, Cr, and Cu is lower than the standard concentration in the  
48 drinking water. Finally, the mineralization ability and the decreased toxicity of the treated  
49 solution of DEP were assessed.

50

51 **Keywords:** Visible light photocatalysis; Peroxymonosulfate; S-scheme; Layered double  
52 hydroxide; Diethyl phthalate.

53

## 54 **1. Introduction**

55 The wide-ranging usage of phthalates in the different industrial products such as paints,  
56 medical devices, lubricants, adhesives, and packing products resulted in the occurrence of  
57 these compounds in the wastewater [1]. According to the literature review [2], the United  
58 States Environmental Agency, as well as, the European Union, have classified the phthalates  
59 as the main pollutants which have arisen the great concern. As the phthalates are ubiquitous in  
60 the environment, the human being has been environmentally exposed to the various kinds of  
61 them. However, these toxic and carcinogenic compounds have been widely declared to be the  
62 disrupting agents for the normal endocrine system which can subsequently damage the body  
63 organs and influence the metabolic, cardiovascular, and immune systems in people [1].  
64 Hence, various potential adverse health risks of phthalate wastewater have garnered the  
65 attention of different researchers from all over the world [3]. It has been acknowledged that  
66 the traditional wastewater treatment methods are insufficient for the thorough removal of  
67 these compounds from the water bodies [4]. The presently available sulfate radical-based  
68 advanced oxidation processes (SR-AOPs) relying on the generation of the reactive sulfate  
69 radicals ( $\text{SO}_4^{\bullet-}$ ) with the high oxidation potential and a half-life time ( $E_0 = 2.5\text{--}3.1\text{ V}$  and  
70  $t_{1/2} = 30\text{--}40\ \mu\text{s}$ , respectively) have been considered for the degradation of a wide range of  
71 phthalates [5]. Persulfate (PS) and peroxymonosulfate (PMS) have been applied as the main  
72 sources for the generation of sulfate radicals. PMS has a higher reactivity due to its  
73 asymmetric structure; in consequence, it has been widely used as the oxidant for the  
74 degradation of diverse kinds of water pollutants through the AOPs [6]. Furthermore, it has  
75 been already affirmed that PMS can be activated by heat, UV light, and transition metals [7].  
76 Nonetheless, Ruobai and et al. [8] have previously reported that the integration of light and  
77 metal ions can be an accelerated activating approach for the decomposition of PMS by the  
78 occurrence of redox cycling of metal ions during the irradiation [8]. To date, different metal

79 ions such as Co, Fe, and Mn have been used to efficiently activate PMS [9]. To avoid the  
80 metal ion-leaching to the water, the researchers have worked on the numerous heterogeneous  
81 photocatalysts comprising the transition metals to activate the PS and PMS. To this end, metal  
82 oxides such as Fe<sub>3</sub>O<sub>4</sub> [10] and CuO [11] were ascertained to possess high activity for PMS  
83 activation. Among different metal oxides, Fe<sub>3</sub>O<sub>4</sub> is of great importance due to its magnetic  
84 property. Accordingly, Fe<sub>3</sub>O<sub>4</sub> and its incorporated form with another nanomaterial could be  
85 recycled from the reactor by applying an external magnetic field [12]. On the other hand, by  
86 possessing a special structure, extensive surface area, low cost, and narrow bandgap  
87 semiconductor properties, 2D structured layered double hydroxides (LDHs) have been  
88 categorized as promising photocatalysts in water treatment applications [13]. LDHs have the  
89 specific formula of [M<sub>1-x</sub><sup>2+</sup>M<sub>x</sub><sup>3+</sup>(OH)<sub>2</sub>]<sup>x+</sup>(A<sup>n-</sup>)<sub>x/n</sub>·mH<sub>2</sub>O, where M<sup>2+</sup>, M<sup>3+</sup>, and A<sup>n-</sup> represent the  
90 divalent, and trivalent metal ions, as well as an anion, respectively [14]. Despite the  
91 remarkable advantages of the pristine LDHs and metal oxides, their high energy cost demand,  
92 the low recoverability, and the fast electron-hole recombination confined their usage in the  
93 wastewater treatment methods [15]. Therefore, different researchers have combined the  
94 advantages of each photocatalyst by synthesizing different heterojunctions [16]. According to  
95 the literature review [17,18], the heterojunctions composed of a semiconductor (SC) with  
96 higher CB and VB position than those in other SC, can result in the type II heterojunction. It  
97 is widely believed that in the type II heterojunctions the photogenerated electrons of SC (I)  
98 can be accumulated on the CB of SC (II), and also the photogenerated holes can be gathered  
99 on SC (I) [19]. On the other hand, recently the step-scheme (S-scheme) heterojunctions have  
100 been nominated to possess a similar band structure with the type (II) heterojunction, but  
101 completely different photogenerated carrier transfer pathway [20]. In such kinds of  
102 heterojunctions, the useless photogenerated charge carriers recombine and the strong  
103 photogenerated electrons and holes remain in the CB of the reduction photocatalyst and VB of

104 the oxidation semiconductor, respectively. For instance, Tao et. al. [21] have synthesized a S-  
105 scheme heterojunction of MoS<sub>2</sub>/CoAl LDH which was able to induce more charge transfer  
106 and consequently high photodegradation performance.

107 So far, LDHs containing Cu or Cr have shown efficient catalytic activates due to providing  
108 specific structure. Considering the low recyclability, as well as the fast electron-hole  
109 recombination of the sole LDH, we decided to integrate the merits of Fe<sub>3</sub>O<sub>4</sub> and CuCr-LDH to  
110 synthesize a novel magnetically separable nanocomposite which can be activated under  
111 visible-light irradiation. To the best of our knowledge, there is no report for the synthesis of a  
112 heterojunction of Fe<sub>3</sub>O<sub>4</sub> and CuCr-LDH nanoparticles to use in the photocatalytic activation  
113 of PMS. For the first principle scope of the present work, the Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH  
114 nanocomposite was synthesized and characterized. Thereafter, the activation of PMS was  
115 assessed in the presence of so-synthesized nanocomposite for the effective degradation of  
116 diethyl phthalate (DEP). The impact of main physicochemical parameters such as the catalyst  
117 concentration, the solution pH, different light sources, and different concentrations of PMS  
118 was also studied. As the next step, the synergy factor of the Vis-light/composite/PMS process  
119 was investigated through the DEP and TOC removal. For further evaluation of the proposed  
120 degradation process in decreasing the toxicity of the target pollutant, some ecotoxicological  
121 tests were fulfilled using *Lemna minor* species. Finally, the S-scheme mechanism was  
122 thoroughly studied to give a deeper understanding of the high-performance S-scheme  
123 heterojunction photocatalyst.

124

## 125 **2. Experiments**

### 126 **2.1. Chemicals**

127 All the used chemicals were purchased from Sigma-Aldrich and used in the experiments  
128 without any further purification.

129

## 130 **2.2. Synthesis of Fe<sub>3</sub>O<sub>4</sub>, CuCr-LDH, and Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH**

131 Fe<sub>3</sub>O<sub>4</sub> was synthesized with a method as described in the previously reported work [12].  
132 Moreover, a facile co-precipitation method was used to prepare pure CuCr-LDH. To this end,  
133 Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with the Cu/Cr molar ratio of 2:1 were dissolved in 80  
134 mL of deionized water to prepare Solution A. Afterward, NaOH (2 M) was provided in 20 mL  
135 of the deionized water as solution B. As the next step, solution A was titrated slowly by  
136 solution B under vigorously stirring until the solution pH closed to 9.5. Then, the achieved  
137 mixture was stirred continuously for 24 h. The gained precipitation was collected after  
138 centrifuge, washed with water and ethanol, and finally transferred to the oven to be dried for  
139 12 h under 60°C.

140 Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite was also prepared with a co-precipitation method. In this  
141 context, three specific solutions were prepared as follows. Typically, 0.5 g of the so-  
142 synthesized Fe<sub>3</sub>O<sub>4</sub> was dispersed in 150 mL of the water/methanol mixture ( $V_{\text{water}}/V_{\text{methanol}} =$   
143 1) for 15 min (solution A), followed by the dropwise addition of the same volume of NaOH (2  
144 M) prepared in the water/methanol mixture ( $V_{\text{water}}/V_{\text{methanol}} = 1$ ) as solution B. Thereafter,  
145 solution C was prepared with the addition of (0.5 M) Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and (0.25 M)  
146 Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 100 and 50 mL of water/methanol mixture ( $V_{\text{water}}/V_{\text{methanol}} = 1$ ),  
147 respectively. As the final step, solution C was dropped by drop added to the prepared mixture  
148 of solution A and B within 40 min and the solution was stirred for 24 h under continuous  
149 stirring at 60°C. The obtained mixture was centrifuged and the resulted precipitation was  
150 washed and dried as like pure CuCr-LDH. It worth noting that all the solutions were prepared  
151 with the incorporation of Argon gas.

152

## 153 **2.2. Characterization of the catalysts**

154 The crystal phases of the synthesized nanomaterials were determined by X-ray diffraction  
155 (D8 Advance, Bruker, Germany) conducting at 45 kV and 40 mA, with an X-ray source of Cu  
156  $K\alpha$  radiation ( $\lambda = 0.15406$  nm). The Fourier-transform infrared (FT-IR) analysis was carried  
157 out for the detection of the possible functional groups using a Tensor 27 spectrophotometer  
158 (Bruker, Germany) and a KBr disk method. The Brunauer-Emmett Teller (BET) method with  
159 a 3 Flex instrument (Micromeritics, USA) was applied to evaluate the surface area and the  
160 pore volume, from the recorded nitrogen absorption-desorption isotherms. Besides, the  
161 surface morphology, as well as the elemental mappings, were appraised using a scanning  
162 electron microscope (SEM, Tescan Mira3, Czech Republic) equipped with a Zeiss Sigma 300.  
163 A Hitachi H-7650 microscope operating at 80 kV, as well as a Hamamatsu AMT40 camera  
164 placed in a side position, was used to take the TEM images of the samples. Furthermore, an  
165 inductively coupled plasma emission spectroscopy (ICP-AES) using a Jobin-Yvon ULTIMA  
166 C instrument (USA) was applied for measuring the leaching concentrations of chromium,  
167 iron, and copper. Surface binding energy was measured by adopting X-ray photoelectron  
168 spectroscopy (XPS) analysis which was carried out with a hemispherical electron energy  
169 analyzer OMICRON EA125, Germany. All the recorded XPS spectrums were analyzed with  
170 an XPSPEAK software, Version 4.1. The Ultraviolet-visible diffuse reflectance  
171 spectrophotometry (UV-Vis DRS) with an Analytik Jena spectrophotometer (S 250,  
172 Germany) was used for measuring the bandgap of the as-prepared photocatalysts. The  
173 magnetic characterization of the synthesized samples was studied by a typical vibrating  
174 sample magnetometer (VSM, Lakeshore, 7400 Series). Furthermore, the produced hydroxyl  
175 radicals were detected by using a simple method using terephthalic acid (TA) as a probe [17].  
176 Considering this method, nonfluorescence TA can react with  $\cdot\text{OH}$  to produce 2-  
177 hydroxyterephthalic acid which produces an emission peak at around 425 nm (under the  
178 excitation of 310 nm). Therefore, in this work, 50 mL of TA solution (0.5 mM) was prepared



179 in the presence of NaOH (2mM). Afterward, 1 g L<sup>-1</sup> of the prepared catalysts were added to  
180 the solution, and then it was exposed to the visible-light irradiation under continuous stirring.  
181 Finally, at the predetermined time intervals, the samples were withdrawn and the  
182 concentration of 2-hydroxyterphthalic was tracked by a fluorescence spectrophotometer  
183 (Varian Cary Eclipse, USA).

184

### 185 **2.3. Photocatalytic experiments**

186 The degradation experiments were fulfilled in a 50 mL Pyrex cylindrical photocatalytic  
187 reactor using a solar simulator lamp (Ocean optics) as the source of the light for irradiation.  
188 To select the visible light irradiation, a cut-off filter ( $\lambda \geq 420$  nm) was located before the  
189 reactor. The emission spectrum of the above-mentioned lamp was presented in Supplementary  
190 information (Fig S1). Water circulation was embedded around the reactor to maintain a  
191 constant temperature of around 293±2 K. A predetermined amount of PMS and DEP (20 mg  
192 L<sup>-1</sup>) were added to a 50 mL reaction solution containing a certain concentration of catalysts.  
193 After adjusting the solution pH around 8, it was transferred to the reactor. Before starting the  
194 photocatalytic degradation, the adsorption of DEP on the catalyst was assessed by stirring its  
195 solution in the dark for 2 hours. However, after 30 min of stirring no more adsorption of DEP  
196 was observed. Therefore, for each run, the solution was stirred for 30 min to reach the  
197 equilibrium of adsorption/desorption between the photocatalyst and DEP molecules. This  
198 stage was followed by 120 min of irradiation under continuous stirring. In each 15 min  
199 intervals, 3 mL of the suspension were regularly withdrawn from the reaction media, filtered  
200 by a syringe with a filter of 0.2  $\mu$ m (Macherey-Nagel, Germany), and finally transferred to a  
201 vial containing 1 mL of radical quencher (methanol). The residual DEP was analyzed by  
202 high-performance liquid chromatography (Alliance, waters, USA), using a C18 column  
203 (2.1×100 mm and particle size of 1.7  $\mu$ m). An isocratic mode with a mobile phase consisted

204 of 30 % ultrapure water and 70 % methanol at a flow rate of 0.8 mL min<sup>-1</sup> was adopted for  
205 appropriate detection of DEP with a retention time of 8 min. The corresponding degradation  
206 efficiency (DE) of DEP was calculated by considering the equation  $\frac{C_0 - C_t}{C_0} \times 100$  where C<sub>0</sub>  
207 and C<sub>t</sub> are the initial and t (min) of DEP concentrations, respectively. Lastly, the Error bars  
208 representing ± one standard deviation was reported from the mean of two measurements. The  
209 TOC analysis as well as the ecotoxicological assessment method have been precisely  
210 explained in the supplementary data. For the ecotoxicological studies, the *Lemna minor*  
211 species were collected from the Anzali Wetland in the North of Iran and cultivated by the  
212 described method in our previously published paper [22]. Also, the chlorophyll content was  
213 measured by the previously explained procedure [23].

214

### 215 **3. Results and discussion**

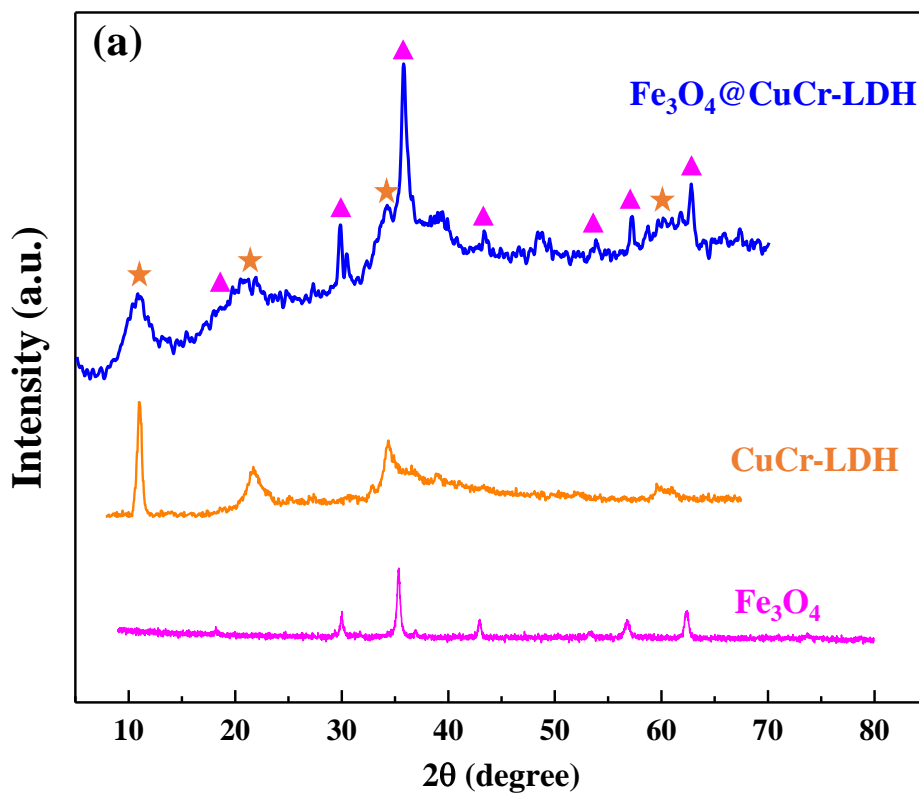
#### 216 **3.1. Characterization**

217 The X-ray diffraction (XRD) method was used to study the crystal structure of the obtained  
218 nanocomposite, as presented in Fig. 1 (a). The results verified the existence of pure magnetite  
219 nanoparticles according to JCPDS card no. 01-089-0951. It is worth noting that the XRD  
220 pattern of the Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite showed the corresponding peaks of both  
221 magnetite and CuCr-LDH nanoparticles. The main XRD peaks of the CuCr-LDH  
222 nanoparticles obtained at 2θ values of 10.9, 22, 34, and 60.5 indexing to the (003), (006),  
223 (012), and (110) reflections (JCPDS file no. 00-035-0965) indicate the layered structure with  
224 the hexagonal unit cells and the rhombohedral symmetry (space group R-3m) [24].  
225 Consequently, the results are good evidence for the existence of layered double hydroxide and  
226 magnetite in the final composite [24]. Although the intensity of the related peaks of CuO is  
227 lower than the specific peaks of LDH, the main reason for the appearing impurity phases can  
228 be the outcome of poor controlling of pH and temperature in the course of the synthesis of

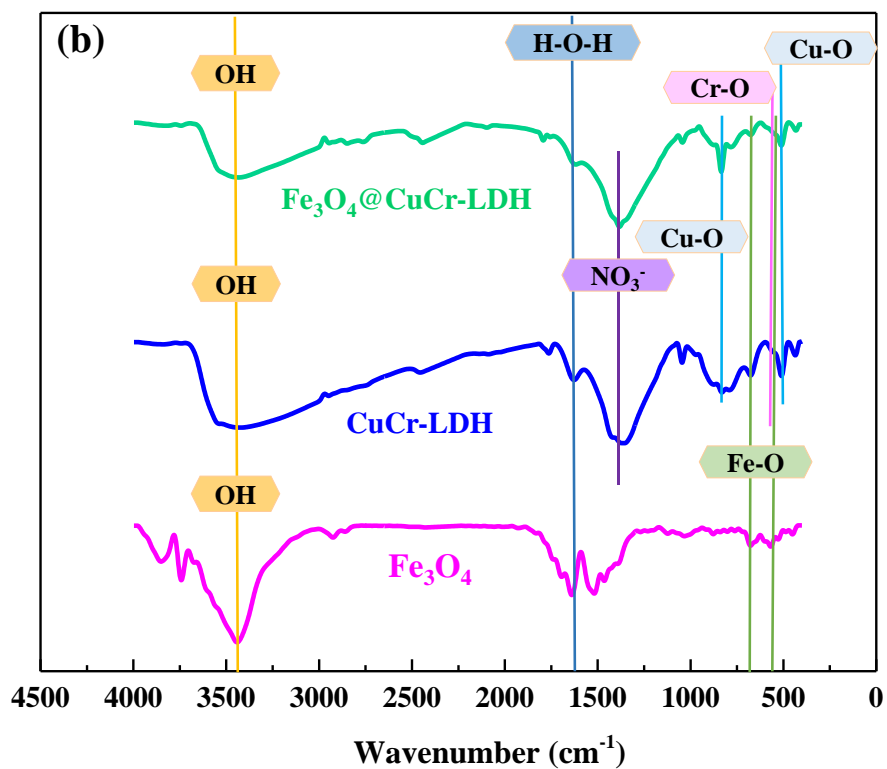
229 layered double hydroxide [25].

230 The main functional group of the so-synthesized nanomaterials was ascertained by applying  
231 the FTIR analysis. The attained FT-IR spectrums of  $\text{Fe}_3\text{O}_4$ , CuCr-LDH, and  $\text{Fe}_3\text{O}_4@$ CuCr-  
232 LDH nanocomposite are presented in Fig. 1 (b). The observed peaks below the  $1000\text{ cm}^{-1}$   
233 revealed the M-O-H bindings and M-O vibrations mainly Cu-O at  $524$ , and  $831\text{ cm}^{-1}$ , Fe-O at  
234  $568$  and  $678\text{ cm}^{-1}$ , and eventually Cr-O at  $610\text{ cm}^{-1}$  [26–28]. The absorption band that  
235 appeared at  $1382\text{ cm}^{-1}$  in the FT-IR spectrums of the pure CuCr-LDH and  $\text{Fe}_3\text{O}_4@$ CuCr-LDH  
236 composite deduced the existence of intercalated  $\text{NO}_3^-$  anions [29]. Moreover, the peaks at  
237  $3451$  and  $1650\text{ cm}^{-1}$  correlate to the O-H stretching vibration of the layered double hydroxide  
238 and the interlayer water molecules, respectively [30].

239



240



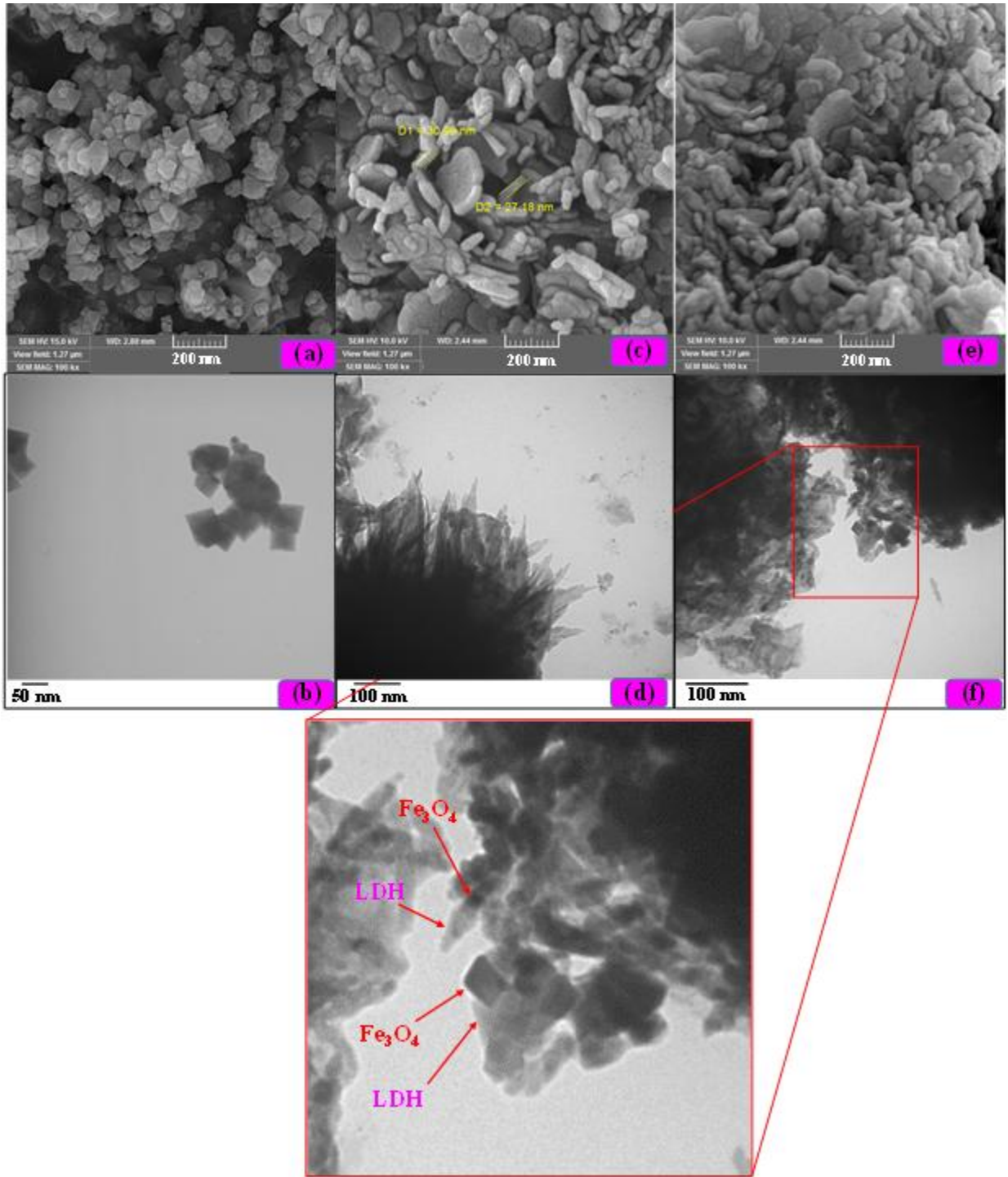
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**Fig. 1.** (a) XRD pattern (b) FT-IR spectrum of the so-synthesized nanomaterials.

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**Fig. 2.** The SEM and TEM images of (a and b) pure  $\text{Fe}_3\text{O}_4$ , (c and d) CuCr-LDH, and finally (e and f)  $\text{Fe}_3\text{O}_4$ @CuCr-LDH nanocomposite.

The SEM images of the so-synthesized  $\text{Fe}_3\text{O}_4$ , CuCr-LDH, and  $\text{Fe}_3\text{O}_4$ @CuCr-LDH nanocomposite were displayed in Fig. 2. As indicated in Fig. 2 (a) the pristine magnetite nanoparticles possess a cubic morphology. However, the SEM image of the pure CuCr-LDH

252 depicts a lamellar structure that accords with the reported morphology for the other layered  
253 double hydroxides [31]. Fig. 2 (e) illustrates that CuCr-LDH nanosheets with an average  
254 thickness of 28-29 nm were uniformly distributed over the cubic magnetite nanoparticles,  
255 giving rise to the Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite. Besides, the attained TEM images had  
256 further confirmed the loading of lamellar CuCr-LDH on the cubic magnetite nanoparticles.  
257 The TEM image of Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH composite which has been presented in Fig. 2 (f)  
258 proves the co-existence of magnetite nanoparticles with CuCr-LDH nanosheets. Moreover,  
259 the Energy Dispersive X-ray (EDX) analysis was accomplished to a precise study of the semi-  
260 quantitative elemental composition of pure magnetite, CuCr-LDH, and the resulted  
261 Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite. Fig. S2 shows that Cu, Cr, Fe, and O elements were  
262 detected for the final nanocomposite, demonstrating the successful synthesis of Fe<sub>3</sub>O<sub>4</sub>@CuCr-  
263 LDH nanocomposite. Nonetheless, the pure magnetite comprised of Fe, and O; whereas, the  
264 bare CuCr-LDH demonstrated the existence of Cu, Cr, O, elements. Furthermore, sought to  
265 other analyses, the SEM mapping was carried out to demonstrate the elemental distribution of  
266 the elements on the surface of the nanocomposite, and the results were documented in Fig. S3.  
267 The results are good evidence for an appropriate and homogeneous distribution of the Cu, Cr,  
268 Fe, and O elements throughout the whole structure of Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite.

269 The bandgap energy of the prepared nanomaterials plays a remarkable role in their  
270 photocatalytic performance. Therefore, the bandgaps of as-synthesized nanomaterials were  
271 estimated by using Tauc's equation [22,28] . To this end, the  $(\alpha h\nu)^2$  graph for photon energy  
272 was drawn and the bandgap values were reported by the tangent extrapolation with the  $(\alpha h\nu)^2$   
273 = 0 (Fig. S4). Therefore, the calculated bandgap values were 3.25 eV, 2.85 eV, and 1.72 eV,  
274 for Fe<sub>3</sub>O<sub>4</sub>, CuCr-LDH, and Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH, respectively. Consequently, in comparison  
275 with the pure magnetite and CuCr-LDH, their composite has a smaller bandgap, which in turn  
276 results in its appropriate excitation under the visible light irradiation to form more electron-

277 hole pairs and improve the photocatalytic activity under visible light [32].

278 To further explore the photocatalytic activity of the so-synthesized nanomaterials, their  
279 specific surface area and porosity were analyzed by applying the Brunauer-Emmett-Teller  
280 (BET) analysis. For this perspective, the N<sub>2</sub> adsorption/desorption isotherms of the  
281 nanocatalysts at 77 K were recorded and summarized in Fig. S5. Taking into consideration the  
282 types of isotherms defined by the IUPAC classification, the samples manifested a type IV  
283 isotherm as the characterization of the mesoporous material [33]. Moreover, the total pore  
284 volume, the specific surface area of the pure magnetite, LDH, and the composite were  
285 tabulated (Table. 1). Accordingly, the acquired BET surface area, and the total pore volume  
286 were raised for the composite (80.6 cm<sup>2</sup> g<sup>-1</sup>, 0.32 cm<sup>3</sup> g<sup>-1</sup>).

287

288 **Table 1.** The Brunauer-Emmett-Teller surface areas and pore-volume were gained from the  
289 BET analysis.

Samples	Surface area (m <sup>2</sup> g <sup>-1</sup> ) 1)	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
Fe <sub>3</sub> O <sub>4</sub>	7.85	0.12
CuCr-LDH	50.69	0.20
Fe <sub>3</sub> O <sub>4</sub> @CuCr- LDH	80.60	0.32

290

291 Given the magnetic properties of the photocatalysts in which were Fe<sub>3</sub>O<sub>4</sub>, these materials  
292 have attracted the attention of scientists. Herein, the magnetic behavior of the Fe<sub>3</sub>O<sub>4</sub> was  
293 evaluated after its composition with the CuCr-LDH nanosheets. Therefore, the magnetic  
294 measurement of the fresh Fe<sub>3</sub>O<sub>4</sub> and the Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH composite was carried out by the  
295 VSM analysis. According to Fig. S6 and the results reported in Table 2 the magnetization

296 saturation values ( $M_s$ ) of  $Fe_3O_4$  and  $Fe_3O_4@CuCr-LDH$  composite were 77 and 59,  
 297 respectively. Therefore, the results evidenced the high magnetic property of the prepared  
 298 samples which was further confirmed by placing a magnet near the solution of the solution  
 299 containing composite (Fig. S6 (b)). As it is clear, the placed magnet attracted the particles  
 300 toward itself after a few seconds, depicting the magnetic properties of the composite.

301

302

**Table 2.** Magnetic characterization of  $Fe_3O_4$  and  $Fe_3O_4@CuCr-LDH$ .

<b>Samples</b>	$^1M_s$ (emu g <sup>-1</sup> )	<b>SQR</b> ( $^2M_r/M_s$ )	$^3H_c$ (G)
$Fe_3O_4$	77	0.22	191
$Fe_3O_4@CuCr-$ LDH	59	0.16	195

303

304

$M_s$  (saturation magnetization),  $M_r$  (remnant magnetization),  $H_c$  (coercivity)

305 XPS analysis was performed for the determination of the chemical state, and the elemental  
 306 composition of the sample surface and the achieved spectra were presented in Fig.S7. The full  
 307 survey XPS spectrum of  $Fe_3O_4@CuCr-LDH$  displayed in Fig. S7 proves the existence of all  
 308 constituent elements such as Cu, Cr, Fe, and O in the ultimate  $Fe_3O_4@CuCr-LDH$   
 309 nanocomposite. Likewise, the deconvoluted peaks at Cu 2p were also presented in Fig. S6.  
 310 Given that,  $Cu^{2+}$  was recognized by the emergence of the distinct peaks at the binding  
 311 energies of 960.59, 951.9, 941.36, and 933 eV. In this context, the peaks at 951.9 eV and 933  
 312 eV verify the Cu 2p<sub>1/2</sub> and Cu 2p<sub>3/2</sub> signals, respectively [34–36]. On the other hand, the  
 313 attendance of  $Cr^{3+}$  was studied through the ascribed fine spectra Cr 2p. The peaks settled at  
 314 577.38 affirmed Cr 2P<sub>3/2</sub> state; whereas, the Cr 2p<sub>1/2</sub> state was confirmed with the appeared  
 315 peak at 587.1 eV [36,37]. Lastly, the recorded high-resolution Fe 2p spectrum implied the  
 316 presence of  $Fe^{2+}$  and  $Fe^{3+}$  on the surface of the sample by observing two main peaks with their



317 satellite peaks located at the binding energy of 705-735 [38].

318

### 319 **3.2. Photocatalytic activity of prepared nanomaterials**

320 In Fig. S8, the photocatalytic activity of the synthesized pristine CuCr-LDH, Fe<sub>3</sub>O<sub>4</sub>, and  
321 Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite was appraised for the degradation of DEP in the presence  
322 of visible light irradiation. According to the results, the adsorption and the degradation  
323 efficiency (DE) of DEP upon the visible light irradiation ascent in the series of Fe<sub>3</sub>O<sub>4</sub>@CuCr-  
324 LDH > CuCr-LDH > Fe<sub>3</sub>O<sub>4</sub>. However, among them, the degradation performance of the  
325 Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite was higher compared with its adsorption ability.  
326 According to the results gained from the DRS results (Fig. S3), the integration of CuCr-LDH  
327 and Fe<sub>3</sub>O<sub>4</sub> boosted their photocatalytic activity by increasing the visible light absorption of the  
328 composite. Consequently, the Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH composite was adopted as an appropriate  
329 photocatalyst for further experiments. It worth noting that our results are in good agreement  
330 with the results obtained by Sea Jin et. al. [39]. They have tried to study the degradation  
331 efficiency of DEP by using a widely used TiO<sub>2</sub>, as well as tungsten oxide doped TiO<sub>2</sub>.  
332 According to their results, loading WO<sub>3</sub> onto the pristine TiO<sub>2</sub> has improved the degradation  
333 efficiency of DEP under visible light.

334

### 335 **3.3. Influence of operational parameters**

#### 336 **3.3.1. Impact of photocatalyst concentration**

337 Fig. 3 illustrates the impact of the catalyst concentration of 0.5-2 g L<sup>-1</sup> on the effective  
338 degradation of DEP with respect to the degradation efficiency (DE) at different intervals of  
339 time. The results suggest that the increase in the photocatalyst concentration from 0.5 to 1 g L<sup>-1</sup>  
340 has a positive effect on achieving the higher degradation efficiency, wherein, the DE of DEP  
341 enhances from 40% to 70%. Indeed, compared with the lower catalyst concentration, the

342 increase in the catalyst dose could compensate for the impoverished amount of active sites  
343 and surface area [22]. Nevertheless, the increasing catalyst concentration from 1 g L<sup>-1</sup> to 2 g L<sup>-1</sup>  
344 resulted in the reverse effect and showed a drop in the DE of DEP during 150 min of  
345 irradiation. On the other hand, during 30 min of the process and in the absence of light the  
346 DEP removal was gradually increased by the increment of the catalyst concentration up to 2 g  
347 L<sup>-1</sup>. These results provide appropriate evidence that the higher amount of catalyst displayed  
348 the principal effect on the degradation of DEP under the visible light irradiation, and the main  
349 reason for this phenomenon can be interpreted to the lower penetration of the visible light due  
350 to the higher turbidity in the solution [22]. Finally, considering all the aspects, the catalyst  
351 concentration of 1 g L<sup>-1</sup> was reported as the optimum value for the other experiments.

352

### 353 **3.3.2. The effect of initial pH**

354 It is well-known that the initial pH can influence the performance of different advanced  
355 oxidation processes [5]. Therefore, a set of experiments were fulfilled in this regard and the  
356 results were exhibited in Fig. 3. As clear from the figure, under the visible light irradiation, a  
357 clear alteration of DE was observed. The activity of the Vis-light/Composite/PMS process for  
358 the degradation of DEP was enhanced by increasing the solution pH from 3 to 8 and finally  
359 followed with an obvious drop for the pH value of 10 and 12.

360 Furthermore, the obtained  $\text{pH}_{\text{pzc}}$  for the Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite was found to  
361 be 8.9, which reveals that the surface of the composite possesses a positive charge in the  
362 acidic and neutral solution. Considering the  $\text{pK}_a$  of PMS which is reported to be 9.4, HSO<sub>5</sub><sup>-</sup> is  
363 a more stable ion than the ionic form (SO<sub>5</sub><sup>2-</sup>). Owing to the occurrence of the hydrogen bonds  
364 between the O-O group of HSO<sub>5</sub><sup>-</sup> and the available H<sup>+</sup> in the acidic solution [40], the  
365 attachment of the H<sup>+</sup> to the HSO<sub>5</sub><sup>-</sup> species can inhibit its approach to the positively charged  
366 surface of Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH. Therefore, the declined DEP degradation efficiency in the

367 lower pH value can be attributed to the descended participation of  $\text{HSO}_5^-$  in the activation  
368 process which can result in the reduced yield of reactive  $\text{SO}_4^{\bullet-}$  [41]. On the other hand, in  
369 the case of higher pH values, the drop in the DE of DEP relates to the PMS tendency to be  
370 decomposed to  $\text{SO}_5^{2-}$  [42]. Further reaction of PMS with the produced  $\text{SO}_5^{2-}$  can result in the  
371 production of singlet oxygen. However, from the reactivity point of view, the singlet oxygen  
372 has a lower oxidizing potential in comparison with hydroxyl and sulfate radicals [43].

373 To avoid the formation of metal hydrated and hydroxide species in acidic and basic  
374 condition [44], respectively, and not to use the chemicals for adjusting the pH of the solution,  
375 a pH value of 8 with the higher DE of DEP was selected to be as the optimum value for the  
376 further reactions.

377  
378

### 379 **3.3.3. Impact of PMS concentration**

380 The main dependency of the DEP degradation to the PMS concentration was investigated  
381 and the results were presented in Fig. 3. Overall, the attained results for the Vis-  
382 light/Composite/PMS process affirm that the DE of DEP enhances by the synchronic rising in  
383 the PMS concentration from 1 to 14 mM. The principal reason for the obtained results can be  
384 attributed to the promoted degradation of DEP due to the formation of a higher amount of  
385 reactive  $\text{SO}_4^{\bullet-}$  species in the presence of more PMS. Notwithstanding, a slight difference in  
386 DE of DEP was observed in the presence of 8 and 14 mM of PMS. As these results well  
387 accord with the obtained results in the previous studies [45], by enhancing the PMS  
388 concentration to 14 mM, the restrained amount of  $\text{F}_3\text{O}_4@\text{CuCr-LDH}$  for the activation of  
389 PMS and the self-quenching reaction aroused between the extra amount of  $\text{HSO}_5^-$  and the  
390 available  $\text{SO}_4^{\bullet-}$  can decline the DE [46,47]. For further investigation, the obtained results  
391 were compared with the direct oxidation of the DEP by 8 mM of PMS as well as the sole

392 photocatalytic degradation in the absence of PMS as the control reactions. Consequently, only  
393 8 mM of the PMS or the sole photocatalytic degradation is insufficient for the effective  
394 degradation of DEP; whereas, their integration led to the proper activation of PMS and finally  
395 higher degradation of DEP.

396

#### 397 **3.3.4. Impact of the light source**

398 According to the photoactivity of PMS and the prepared photocatalyst, the effect of different  
399 light sources was evaluated for different processes such as photolysis (just light),  
400 photocatalytic (light/composite), and activated PMS with just light (light/ PMS) or both the  
401 composite and PMS with light (light/composite/PMS) (Fig. 3). From the figure, it can be  
402 concluded that photolysis resulted in negligible DEP degradation efficiency even in the case  
403 of using UVA-light. However, in comparison with Vis-light, UVA-light illustrated an  
404 efficient PMS activation performance to result in the enhanced DEP degradation efficiency  
405 [48]. Considering the DRS analysis, it was found that Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH was a visible light-  
406 responsive photocatalyst; in consequence, its activity was assessed under different light  
407 conditions and in the absence of PMS. Despite obtaining 59% of the DEP degradation  
408 efficiency in the presence of UVA-light, the so-synthesized catalyst resulted in 28% of  
409 degradation efficiency for DEP under the visible light irradiation. On the other hand, it was  
410 found out that with the combination of so-synthesized nanocomposite and PMS, a further  
411 amount of DEP was degraded under all light conditions. Taking account of the reactions (1) to  
412 (6) [46,49,50], these findings can mainly be related to the photocatalytic activity of the so-  
413 synthesized composite which in turn can enhance the activation of PMS to produce different  
414 radical species and subsequently attack the DEP molecules.

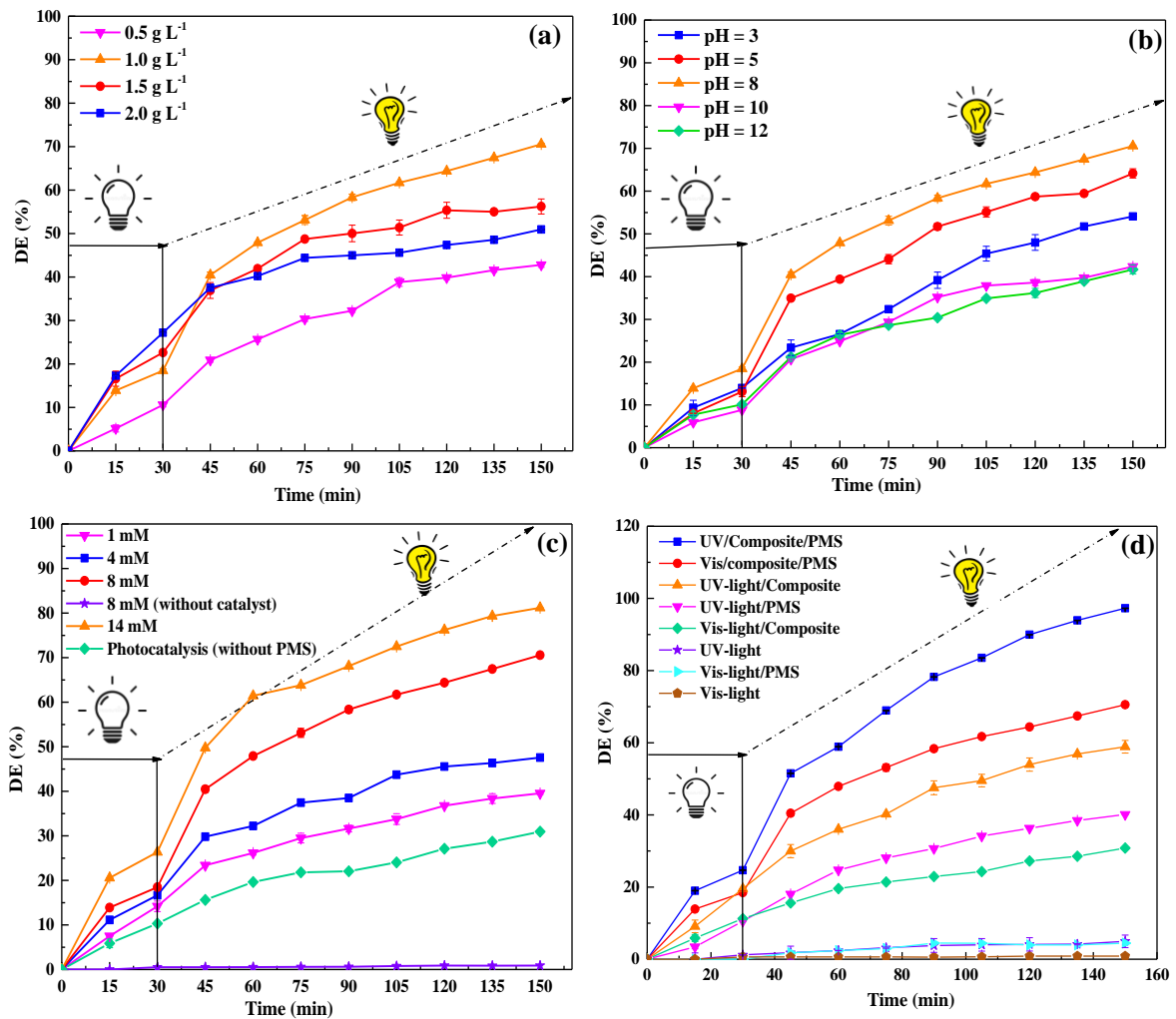




421

422 As the degradation efficiency for DEP was still high (70%) in the case of using Vis-  
 423 light/Composite/PMS, the degradation process has occurred under the visible light source ( $\lambda \geq$   
 424 420 nm) was adopted for further DEP degradation study.

425



426

427 **Fig. 3.** Impact of the (a) photocatalyst concentration, (b) initial pH, (c) PMS concentration,

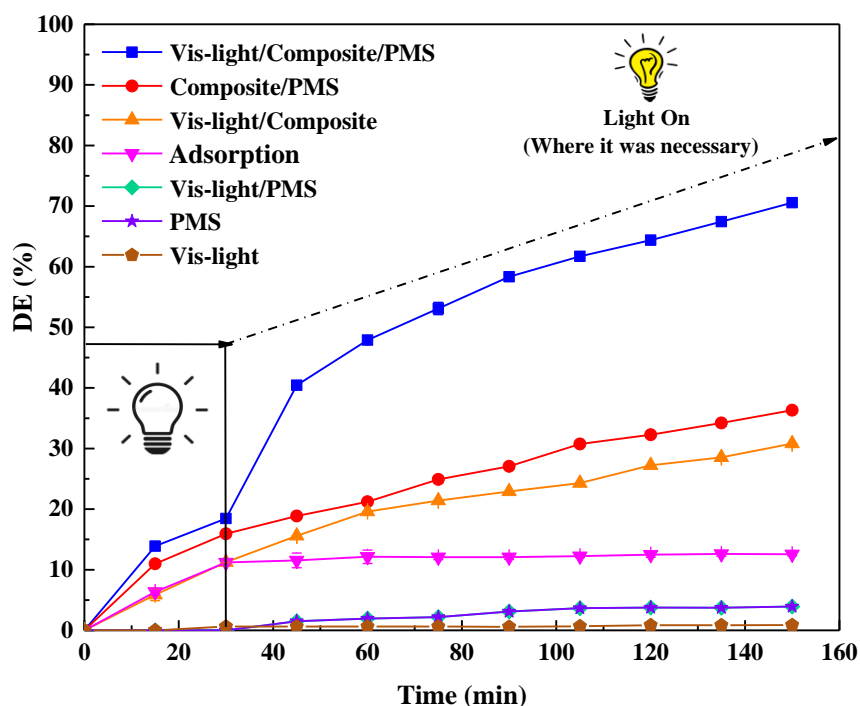
428 and different light conditions on the DE of the DEP. Experimental conditions: [DEP] = 20 mg  
429 L<sup>-1</sup>, catalyst concentration of 1 g L<sup>-1</sup>, [PMS] = 8 mM, and pH = 8.

430

### 431 **3.4. Synergistic effect of the optimum process**

432 Diverse processes such as photolysis, adsorption, direct oxidation, photocatalytic  
433 degradation, and activated PMS by visible-light, sole composite, and visible-light/composite  
434 were evaluated for the removal of DEP and the results were reported in Fig. 4. It is evident  
435 from the results that direct photolysis and oxidation processes showed negligible degradation  
436 efficiency of DEP. On the other hand, according to the literature review, PMS cannot be  
437 activated by visible light irradiation [50]; therefore, its performance in the proper degradation  
438 of DEP was negligible. According to Fig. 4, 10 % of DEP was adsorbed on the Fe<sub>3</sub>O<sub>4</sub>@CuCr-  
439 LDH and it was preserved until 120 min of the reaction time. However, the direct  
440 photocatalytic degradation of DEP under visible light irradiation resulted in approximately  
441 30% of DE. Finally, it can be concluded from Fig. 4 that the activation of PMS in the  
442 presence of Vis-light and composite was the effective process for the degradation of DEP.

443



444

445 **Fig. 4.** The effect of different processes on the degradation of DEP. Experimental conditions:

446 catalyst concentration of  $1 \text{ g L}^{-1}$ ,  $[\text{DEP}] = 20 \text{ mg L}^{-1}$ ,  $[\text{PMS}] = 8 \text{ mM}$  and  $\text{pH} = 8$ .

447

448 Herein, the synergistic effect of the optimal process was evaluated to clarify the efficient

449 impact of integrating the Vis-light and composite for the activation of PMS. To this end, the

450 pseudo-first-order kinetic model [35] was used and the corresponding rate constants ( $k_{\text{app}}$ )

451 were reported for each of the processes. The  $k_{\text{app}}$  as well as the correlation coefficient were

452 inserted in Fig. S9. As it is clear from Fig. 4, the sole Vis-light and PMS showed negligible

453 effect on the degradation of DEP. Moreover, during 30 min of dark condition the adsorption

454 was equilibrated and no more adsorption was observed after 30 min. Therefore, the obtained

455  $K_{\text{app}}$  for the sole PMS ( $K_{\text{PMS}} = 0.0003 \text{ M}^{-1} \text{ min}^{-1}$ ,  $R^2 = 0.95$ ), Vis-light ( $K_{\text{Vis-light}} = 0.0001 \text{ M}^{-1}$

456  $\text{min}^{-1}$ ,  $R^2=0.96$ ) and adsorption ( $K_{\text{composite}} = 0.0001 \text{ M}^{-1} \text{ min}^{-1}$ ,  $R^2=0.95$ ) was negligible and

457 they were not inserted in Fig. S9. The results revealed that the correlation coefficient ( $R^2$ )

458 values for the pseudo-first-order model were higher than 0.95. Therefore, it can be deduced

459 that the degradation rates related to all the applied processes followed the pseudo-first-order

460 kinetic.

461 The higher  $k_{app}$  of the Vis-light/composite/PMS system from those of the others revealed the  
462 efficient activation of PMS with the assistance of composite and visible light. For further  
463 studying, we used the attained  $k_{app}$  for the calculation of the synergy factor for different  
464 methods of PMS activation. Accordingly, by applying the following equations [22,51] the  
465 synergy factors of PMS/Vis-light, PMS/composite, and PMS/Vis-light/composite processes  
466 were determined to be 0.1, 8, and 14, respectively.

$$467 \quad \text{Synergy factor}_{\text{PMS/Vis-light}} = \frac{K_{\text{PMS/Vis-light}}}{K_{\text{PMS}} + K_{\text{Vis-light}}} \quad (1)$$

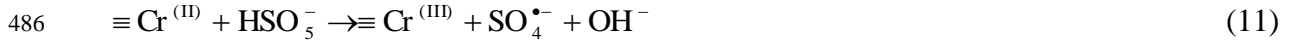
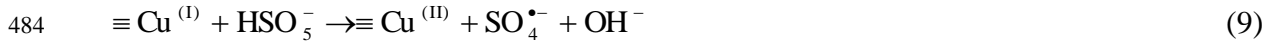
$$468 \quad \text{Synergy factor}_{\text{PMS/composite}} = \frac{K_{\text{PMS/composite}}}{K_{\text{PMS}} + K_{\text{composite}}} \quad (2)$$

$$469 \quad \text{Synergy factor}_{\text{PMS/composite/Vis-light}} = \frac{K_{\text{PMS/composite/Vis-Light}}}{K_{\text{PMS}} + K_{\text{composite}} + K_{\text{Vis-light}}} \quad (3)$$

470 Different researches have been done for the activation of PMS in the presence of light  
471 irradiation and heterogeneous catalysts. For instance, Golshan et.al. [52] studied the effect of  
472 a widely used  $\text{TiO}_2$  and  $\text{CuFe}_2\text{O}_4$  and their composite for the activation of PMS. According to  
473 their results, the integration of UV and  $\text{TiO}_2@ \text{CuFe}_2\text{O}_4$  composite enhanced the activation of  
474 PMS. Therefore, the degradation performance of the UV/ $\text{TiO}_2@ \text{CuFe}_2\text{O}_4$ /PMS process has  
475 been enhanced two times more in comparison with the individual  $\text{TiO}_2@ \text{CuFe}_2\text{O}_4$ /PMS and  
476 UV/PMS processes. However, in our work the synergy factor of 14 of PMS/Vis-  
477 light/composite demonstrated the efficient activation of PMS in the presence of visible light  
478 and composite. The principal reason can be associated with the effectual activation of PMS in  
479 the presence of the photocatalyst under the visible light irradiation [46] (reactions (1) to (6)).  
480 It worth noting that according to the reactions (7) to (13), the presence of transition metals in  
481 the so-synthesized photocatalysts can accelerate the PMS activation to the  $\text{SO}_4^{\bullet-}$  [41,53].







489

### 490 **3.5. Toxicity assessment and TOC removal**

491 According to the literature review [22], in the course of photocatalytic degradation, the target  
 492 pollutants can be broken into smaller products which have been reported to be more toxic than  
 493 the parent compounds [54]. Therefore, the ecotoxicological tests were fulfilled to under the  
 494 optimum operational parameters to assess the biological responses of the living organisms to  
 495 the photocatalytically treated or untreated DEP solution using the Vis-light/composite/PMS  
 496 process. *Lemna minor* species as the aquatic plants are sensitive to a wide range of water  
 497 pollutants; therefore, they were used for the toxicity assessment of the target pollutant and the  
 498 produced by-products. After exposing the *Lemna minor* fronds were exposed with the control  
 499 solution of untreated DEP and treated DEP solution for 60 and 120 min the visual changes of  
 500 the fronds were monitored and reported in Fig. S10. The images which have been taken after  
 501 8 days showed that the toxicity of the DEP solution was decreased with increasing the  
 502 degradation time up to 120 min. Moreover, the fronds of *Lemna minor* species kept their  
 503 growth rate after 120 min of the degradation process. Furthermore, the total chlorophyll  
 504 content of the fronds exposed to 60 and 120 min of degradation process has been presented in  
 505 Fig. S10. It is obvious that the chlorophyll content increased after 60 min and 120 min of  
 506 process. These findings can be interpreted as the ability of the proposed optimum degradation

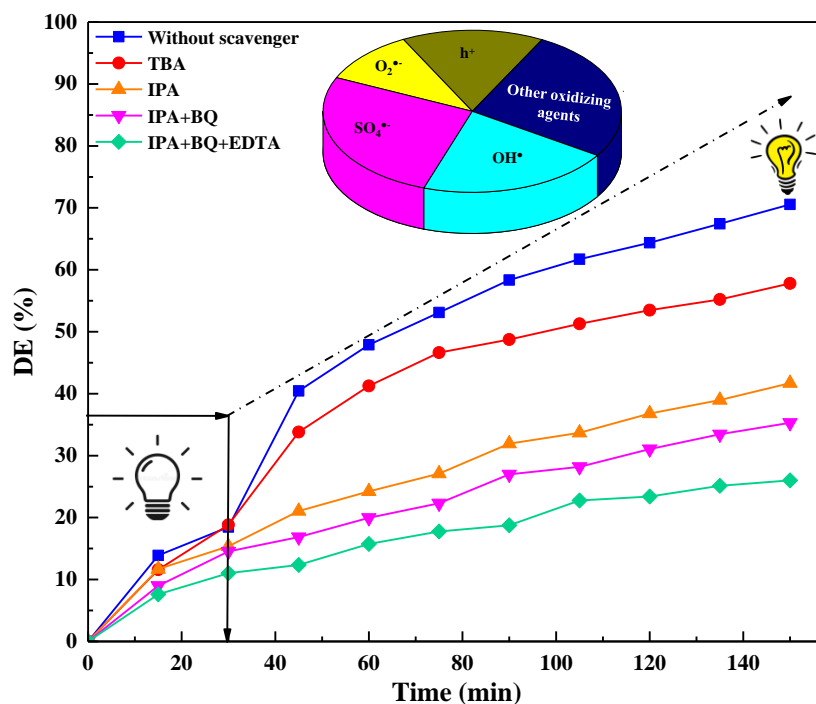
507 system for the breaking the DEP molecules to the less or nontoxic compounds. It worth noting  
508 that our results are in good accordance with the literature reports [23].

509 Moreover, the mineralization of DEP was evaluated under applying diverse degradation  
510 processes such as Vis-light/composite/PMS, UV-light/composite/PMS, and sole UV or Vis-  
511 light. Fig. S11 shows the TOC decrease as a function of irradiation time in the presence of the  
512 so-synthesized composite while holding all other operational parameters the same. The results  
513 were good evidence that the sole photolysis with the UVA or Vis-light did not affect the TOC  
514 decrease (the results were not shown). However, it can be observed that after 45 h of UV  
515 irradiation, Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH composite had an overall TOC removal of 74%; whereas, it  
516 was found to be 50% under the Vis-light irradiation. This can be interpreted by the higher  
517 activation of PMS under UVA irradiation [48].

518

### 519 **3.6. Photocatalytic mechanism**

520 To probe the contribution of principle ROS accounting for the effective degradation of  
521 DEP, some quenching tests were done. In this context, different radical scavengers such as  
522 tert-butyl alcohol (TBA) [22], isopropyl alcohol (IPA) [53], Benzoquinone (BQ) [22], and  
523 EDTA [55] were used as the appropriate inhibitors of  $\cdot\text{OH}$ ,  $\text{SO}_4^{\cdot-}$ ,  $\text{O}_2^{\cdot-}$ , and  $\text{h}^+$ , respectively.  
524 According to the results presented in Fig. 5, under the optimal conditions, and in the absence  
525 of the scavengers, 70% of the DEP was degraded. However, the influence of the radical  
526 scavenging agents on the performance of the DEP degradation followed the order of  
527 IPA>TBA>EDTA>BQ affirming the predominant contribution of  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  (22.8 % and  
528 18.1 % respectively). According to the inserted figure in Fig. 5, the contribution of  $\text{h}^+$  and  
529  $\text{O}_2^{\cdot-}$  was also confirmed by adding EDTA and BQ. Therefore, the results prove that the  
530 photogenerated  $\text{e}^-$  and  $\text{h}^+$  on the prepared composite have an adequate reduction and oxidation  
531 potential for generating  $\text{O}_2^{\cdot-}$  and  $\cdot\text{OH}$ .



533

534 **Fig. 5.** The effect of different scavengers on the DEP degradation. Experimental  
 535 conditions: catalyst concentration of  $1 \text{ g L}^{-1}$ ,  $[\text{DEP}] = 20 \text{ mg L}^{-1}$ ,  $[\text{PMS}] = 8 \text{ mM}$ ,  $\text{pH} = 8$  and  
 536 molar ratio of scavenger vs. DEP = 10:1.

537

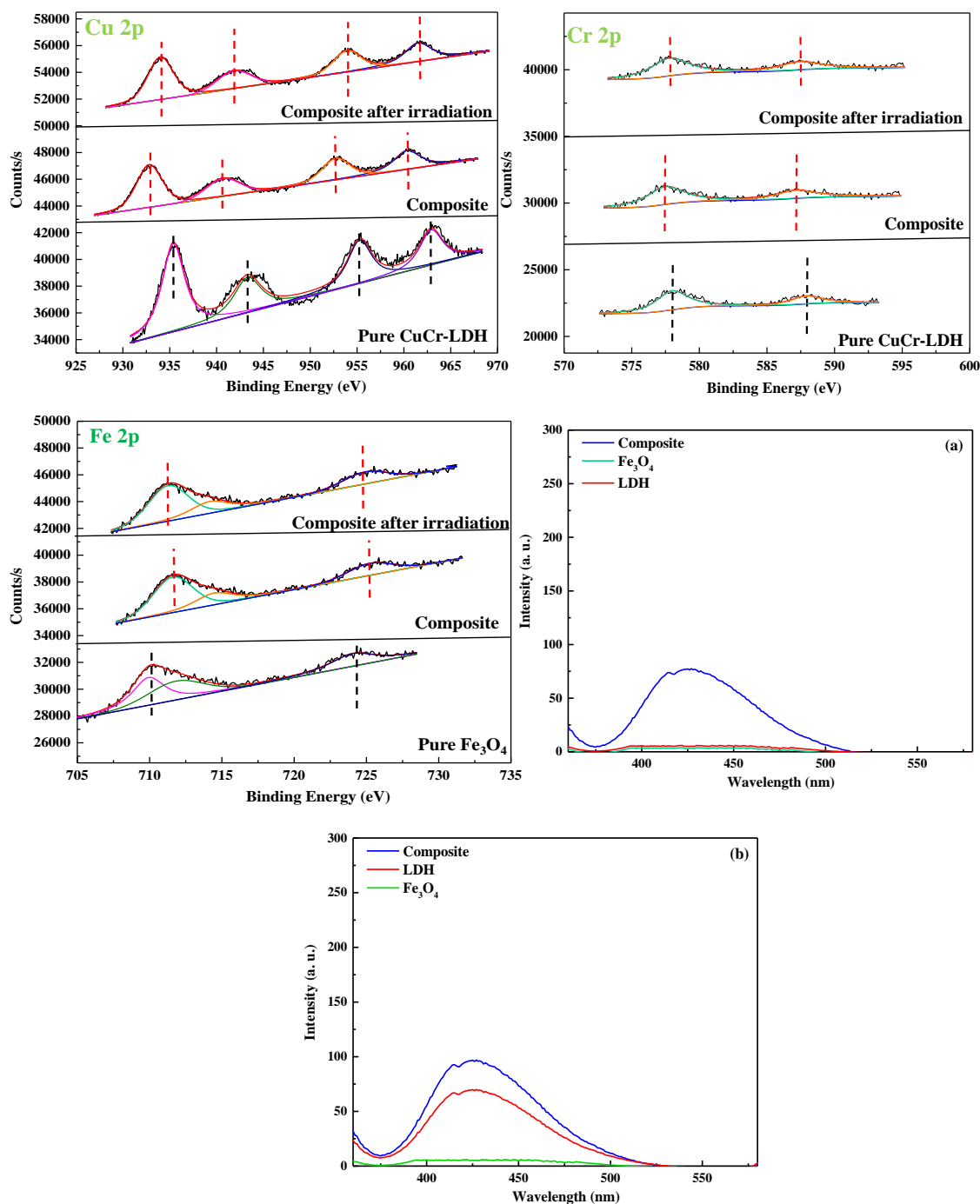
538 A set of experiments were done to deeply investigate the type of the prepared  
 539 heterojunction and define the separation and transfer pathway of the charge carriers between  
 540 the semiconductors. In this regard, the CB and VB of the semiconductors were determined by  
 541 using XPS valance band spectra [17]. Therefore, the XPS valance spectra of the materials  
 542 presented in Fig. S12 (a and b) revealed that the VB edge potentials of the so-synthesized  
 543 LDH and  $\text{Fe}_3\text{O}_4$  were ascertained to be 4.1 and 3.2 eV, respectively. Taking account of the  
 544 obtained band gap energy from the DRS results, the conduction band (CB) of each compound  
 545 was calculated using Eq. 1.

$$546 \quad E(\text{VB}) = E(\text{CB}) - E_g \quad (1)$$

547 Consequently, the CB of  $\text{Fe}_3\text{O}_4$  and LDH was calculated to be 1.35 and -0.15 eV. The  
548 achieved results have good accordance with the previously reported results in the published  
549 paper [56]. Considering the optical results presented in Fig. S3, although pure magnetite is not  
550 visible-light-responsive, its heterojunction with the LDH possessing narrower bandgap,  
551 resulted in a significant red-shift in the bandgap of the composite. The decreased bandgap and  
552 high ability of the composite in absorbing visible light are in favor of producing more  
553 photogenerated charges. This phenomenon facilitates the photocatalytic performance in the  
554 degradation of pollutants which was thoroughly confirmed in section 3.2.

555 This phenomenon was more supported with the high resolution XPS spectra of Cu 2p, Cr  
556 2p, and Fe 2p in the samples of  $\text{Fe}_3\text{O}_4$ , CuCr-LDH,  $\text{Fe}_3\text{O}_4$ @CuCr-LDH composite (Fig. 6).  
557 According to the results, the binding energy of Cu 2p and Cr 2p were high for the pure LDH;  
558 however, in the composite, it shifted towards the lower binding energies. Moreover, the  
559 detected peaks in the high-resolution XPS spectra of Fe 2p for the composite shifted to the  
560 higher binding energies relative to that of pure  $\text{Fe}_3\text{O}_4$ . Considering the literature review, the  
561 appeared opposite shifts of the binding energies are good evidence for the appropriate  
562 interfacial contact of  $\text{Fe}_3\text{O}_4$  to the LDH which leads to the flow of electrons from  $\text{Fe}_3\text{O}_4$  to  
563 LDH and equilibrium the Fermi levels [16]. Hence, an internal electric field pointing from  
564  $\text{Fe}_3\text{O}_4$  to LDH would form at the interface of the catalyst which can result in the upward and  
565 downward bending of the band edges for  $\text{Fe}_3\text{O}_4$  and CuCr-LDH, respectively. Also, Meng and  
566 et al. [57] reported the opposite shift of binding energies for Ti 2p, O 1s, Cd 3d, and S 2p.  
567 This was reported to be ascribed to the effective electron transference from CdS to  $\text{TiO}_2$ .  
568 Moreover, considering the results displayed in Fig. 6, after the visible light irradiation of  
569 composite, the related binding energies of Cu 2p and Cr 2p changed to the higher binding  
570 energies and the corresponding peaks of Fe 2p were found to appear in the lower binding  
571 energies. As a result, the formation of an internal electric field restricted the transference of

572 photogenerated electrons from the CB of  $\text{Fe}_3\text{O}_4$  to the CB of LDH. Therefore; the  
573 photogenerated electrons went through a different pathway which left the photogenerated  
574 electrons and holes in the CB of  $\text{Fe}_3\text{O}_4$  and VB of LDH, respectively. Different methods such  
575 as ESR, or photoluminescence (PL) spectroscopy in the presence of different radical  
576 scavengers have been used for the confirmation of the charge carrier transference mechanism  
577 of the photocatalysts [58,59]. Therefore, in order to further confirm the S-scheme mechanism,  
578 we used the  $\cdot\text{OH}$  trapping method in which non-fluorescence terephthalic acid (TA) can be  
579 used as the probe agent [17]. In the course of the reaction between generated  $\cdot\text{OH}$  with TA, a  
580 fluorescent 2-hydroxyterephthalic acid (HTA) can be produced which can be followed by the  
581 fluorescence spectroscopy. Fig. 6 (a and b) demonstrates the fluorescence spectra of HTA for  
582  $\text{Fe}_3\text{O}_4$ , CuCrLDH, and  $\text{Fe}_3\text{O}_4@\text{CuCrLDH}$  in the absence of oxygen and the presence of  
583 EDTA as the hole scavenger. As discussed before the pure magnetite showed no production  
584 of  $\cdot\text{OH}$  under the visible light irradiation. In the absence of  $\text{O}_2$ , the pure CuCrLDH composite  
585 was capable of generating  $\cdot\text{OH}$  revealing the presence of photogenerated  $\text{h}^+$  with sufficient  
586 oxidation potential. On the contrary, according to the results, the presence of EDTA as the  $\text{h}^+$   
587 inhibitor brought about no fluorescent peak for the pristine LDH due to its lower CB position  
588 for the reduction of  $\text{O}_2$  ( $E_{\text{O}_2/\text{O}_2\cdot^-} = -0.046 \text{ eV}$ ) (Fig. 6 (b)). Also, the synthesized composite  
589 showed the fluorescent peak in the presence and absence of EDTA and  $\text{O}_2$ , respectively.



590

591 **Fig. 6.** Comparison of Cu 2p, Cr 2p, and Fe 2p XPS spectra for the pure Fe<sub>3</sub>O<sub>4</sub>, CuCr-LDH,

592 and Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH in the dark and after the visible light irradiation. Fluorescence spectra

593 of Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH, CuCr-LDH, Fe<sub>3</sub>O<sub>4</sub> in the presence of EDTA (a) and in the absence of

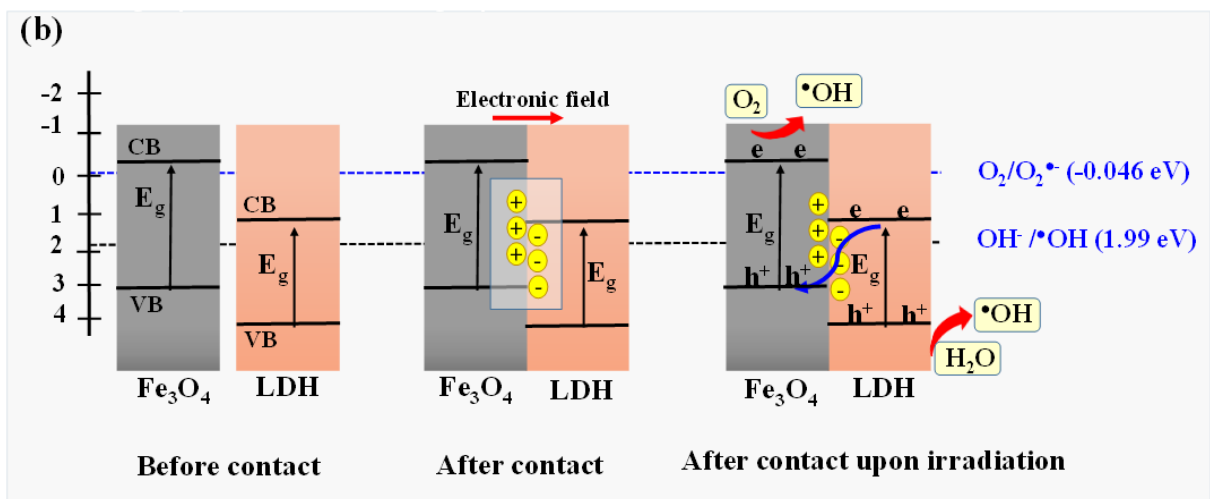
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oxygen (b).

595

596 Based on the above results, in our system  $\text{Fe}_3\text{O}_4$  with higher CB acts as the reduction  
 597 photocatalyst (SC (I)) and CuCr-LDH forms the oxidation photocatalyst (SC (II)). The  
 598 composition of magnetite and CuCr-LDH results in the type (II) heterojunction. However, in  
 599 the case of being a type (II) heterojunction, the photogenerated electrons should have been  
 600 gathered on the CB of CuCr-LDH and were able to reduce  $\text{O}_2$ . With respect to the results  
 601 obtained from the XPS spectra as well as the produced hydroxyl radicals, the S-scheme  
 602 charge-carrier migration mechanism was proposed for the photocatalyst (Fig. 7). Accordingly,  
 603 the useless photogenerated holes and electrons from  $\text{Fe}_3\text{O}_4$  and CuCr-LDH combine  
 604 introducing a strong redox potential

605



606

607

608 **Fig. 7.** The proposed S-scheme schematic mechanism for the charge-carrier migration on  
 609 the  $\text{Fe}_3\text{O}_4$ @CuCrLDH heterojunction.

610

### 611 3.7. The reusability and stability of $\text{Fe}_3\text{O}_4$ @CuCr-LDH

612 One of the essential criteria for the practical application of the so-synthesized  
 613 nanomaterials is their reusability and stability under the degradation processes [17,22,60]. In  
 614 this regard, under the same operational conditions, the activity of the prepared composite was

615 evaluated over five consecutive cycles. To this end, the spent photocatalyst was collected after  
616 each of the cycles and dried to be reused in the other cycle of the degradation process. The  
617 degradation efficiency of DEP calculated after each reaction run was demonstrated in Fig.  
618 S13 (a). Taking consideration of the obtained results, the photocatalytic efficiency of  
619  $\text{Fe}_3\text{O}_4@\text{CuCr-LDH}$  was maintained after five consecutive reactions preserving the  
620 degradation efficiency of DEP over 65%. Not only do the robustness and reusability of the  
621 composite were affirmed by consecutive reaction runs, but also the metal leaching of either  
622 Cu, Cr, and Fe was determined by the ICP analysis. Using ICP-AES, no more leaching of Cu,  
623 Cr, and Fe was observed which were found to be lower than  $1.5 \mu\text{g L}^{-1}$ . Nevertheless, the  
624 World Health Organization (WHO) has reported the iron, chromium, and copper standard  
625 concentration in the drinking water as lower than  $0.1 \text{ mg L}^{-1}$ ,  $2 \mu\text{g L}^{-1}$ , and  $5 \mu\text{g L}^{-1}$ ,  
626 respectively [61].

627 Moreover, as reported in the Supplementary section, the XPS survey spectrum of the post-  
628 utilized composite was recorded and compared with the fresh samples. Thus, Fig. S13 (b)  
629 evidences a few changes in the overall spectrum indicating the high stability of the so-  
630 synthesized nanocomposite.

631

#### 632 **4. Conclusion**

633 In summary, we have proved that  $\text{Fe}_3\text{O}_4@\text{CuCr-LDH}$  nanocomposite acts as a promising  
634 S-scheme nano-heterojunction for the efficient activation of peroxymonosulfate. Moreover, it  
635 was affirmed that under visible light irradiation, the photocatalytic activity of the so-  
636 synthesized photocatalysts was in the order of  $\text{Fe}_3\text{O}_4@\text{CuCr-LDH} > \text{CuCr-LDH} > \text{Fe}_3\text{O}_4$ .  
637 Under the determined optimal conditions, the Vis-light/ $\text{Fe}_3\text{O}_4@\text{CuCr-LDH}$ /PMS process  
638 showed a proper synergistic effect for increasing the degradation efficiency of DEP. The  
639 appropriate degradation efficiency of DEP in the presence of composite, relies on the



640 construction of the S-scheme electron transport mechanism which in turn results in the higher  
641 separation of electron-hole as well as retaining of the redox ability. At the same time, the  
642 Fe<sub>3</sub>O<sub>4</sub>@CuCr-LDH nanocomposite preserved its structure and photocatalytic properties after  
643 5 cycles of the photocatalytic degradation processes, promising the outstanding performance  
644 of the so-synthesized nanocomposite for its application in the other degradation processes.  
645 Importantly, the radical trapping tests illustrated the more contribution of SO<sub>4</sub><sup>•-</sup> and <sup>•</sup>OH in  
646 the degradation of DEP. We hopefully expect that our current study will provide a new  
647 perspective in the synthesis and application of magnetically separable S-scheme  
648 photocatalysts for the activation of peroxymonosulfate and degradation of different newly  
649 emerged water contaminants. Finally, the easy recovery of the catalyst, its stability, the pH  
650 range close to neutral, and the use of visible light make this system very favorable in the  
651 approach of sustainable development for water treatment.

652  
653

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660

#### 661 **References**

- 662 [1] C.-D. Dong, C.-W. Chen, T.-B. Nguyen, C.P. Huang, C.-M. Hung, Degradation of  
663 phthalate esters in marine sediments by persulfate over Fe–Ce/biochar composites,  
664 Chem. Eng. J. 384 (2020) 123301. <https://doi.org/10.1016/j.cej.2019.123301>.
- 665 [2] E. Ahmadi, S. Yousefzadeh, M. Ansari, H.R. Ghaffari, A. Azari, M. Miri, A.  
666 Mesdaghinia, R. Nabizadeh, B. Kakavandi, P. Ahmadi, M.Y. Badi, M. Gholami, K.

- 667 Sharafi, M. Karimaei, M. Ghoochani, M.B. Brahmand, S.M. Mohseni, M. Sarkhosh, S.  
668 Rezaei, H. Asgharnia, E. Dehghanifard, B. Jafari, A. Morteza pour, V.K. Moghaddam,  
669 M.M. Mahmoudi, N. Taghipour, Performance, kinetic, and biodegradation pathway  
670 evaluation of anaerobic fixed film fixed bed reactor in removing phthalic acid esters  
671 from wastewater, *Sci. Rep.* 7 (2017) 1–14. <https://doi.org/10.1038/srep41020>.
- 672 [3] C. Ebenau-Jehle, M. Mergelsberg, S. Fischer, T. Bröls, N. Jehmlich, M. von Bergen, M.  
673 Boll, An unusual strategy for the anoxic biodegradation of phthalate, *ISME J.* 11 (2017)  
674 224–236. <https://doi.org/10.1038/ismej.2016.91>.
- 675 [4] B. Wang, Y. Chen, X. Wang, J. Ramkumar, X. Zhang, B. Yu, D. Yang, M.  
676 Karpuraranjith, W. Zhang, rGO wrapped trimetallic sulfide nanowires as an efficient  
677 bifunctional catalyst for electrocatalytic oxygen evolution and photocatalytic organic  
678 degradation, *J. Mater. Chem. A.* 8 (2020) 13558–13571.  
679 <https://doi.org/10.1039/D0TA04383D>.
- 680 [5] X. Lin, Y. Ma, J. Wan, Y. Wang, Y. Li, Co<sub>0.59</sub>Fe<sub>0.41</sub>P nanocubes derived from  
681 nanoscale metal–organic frameworks for removal of diethyl phthalate by activation of  
682 peroxymonosulfate, *Appl. Catal. Gen.* 589 (2020) 117307.  
683 <https://doi.org/10.1016/j.apcata.2019.117307>.
- 684 [6] C. Jin, J. Kang, Z. Li, M. Wang, Z. Wu, Y. Xie, Enhanced visible light photocatalytic  
685 degradation of tetracycline by MoS<sub>2</sub>/Ag/g-C<sub>3</sub>N<sub>4</sub> Z-scheme composites with  
686 peroxymonosulfate, *Appl. Surf. Sci.* 514 (2020) 146076.  
687 <https://doi.org/10.1016/j.apsusc.2020.146076>.
- 688 [7] R. Feizi, M. Ahmad, S. Jorfi, F. Ghanbari, Sunset yellow degradation by  
689 ultrasound/peroxymonosulfate/CuFe<sub>2</sub>O<sub>4</sub>: Influential factors and degradation processes,  
690 *Korean J. Chem. Eng.* 36 (2019) 886–893. <https://doi.org/10.1007/s11814-019-0268-0>.
- 691 [8] R. Li, J. Huang, M. Cai, J. Huang, Z. Xie, Q. Zhang, Y. Liu, H. Liu, W. Lv, G. Liu,

- 692       Activation of peroxymonosulfate by Fe doped g-C<sub>3</sub>N<sub>4</sub>/graphene under visible light  
693       irradiation for Trimethoprim degradation, *J. Hazard. Mater.* 384 (2020) 121435.  
694       <https://doi.org/10.1016/j.jhazmat.2019.121435>.
- 695 [9] X. Zhao, C. Niu, L. Zhang, H. Guo, X. Wen, C. Liang, G. Zeng, Co-Mn layered double  
696       hydroxide as an effective heterogeneous catalyst for degradation of organic dyes by  
697       activation of peroxymonosulfate, *Chemosphere.* 204 (2018) 11–21.  
698       <https://doi.org/10.1016/j.chemosphere.2018.04.023>.
- 699 [10] Y. Ding, C. Pan, X. Peng, Q. Mao, Y. Xiao, L. Fu, J. Huang, Deep mineralization of  
700       bisphenol A by catalytic peroxymonosulfate activation with nano CuO/Fe<sub>3</sub>O<sub>4</sub> with  
701       strong Cu-Fe interaction, *Chem. Eng. J.* 384 (2020) 123378.  
702       <https://doi.org/10.1016/j.cej.2019.123378>.
- 703 [11] J. Li, P. Ye, J. Fang, M. Wang, D. Wu, A. Xu, X. Li, Peroxymonosulfate activation and  
704       pollutants degradation over highly dispersed CuO in manganese oxide octahedral  
705       molecular sieve, *Appl. Surf. Sci.* 422 (2017) 754–762.  
706       <https://doi.org/10.1016/j.apsusc.2017.06.118>.
- 707 [12] T.S. Rad, A. Khataee, S. Rahim Pouran, Synergistic enhancement in photocatalytic  
708       performance of Ce (IV) and Cr (III) co-substituted magnetite nanoparticles loaded on  
709       reduced graphene oxide sheets, *J. Colloid Interface Sci.* 528 (2018) 248–262.  
710       <https://doi.org/10.1016/j.jcis.2018.05.087>.
- 711 [13] D.N. Ahmed, L.A. Najji, A.A.H. Faisal, N. Al-Ansari, M. Naushad, Waste foundry  
712       sand/MgFe-layered double hydroxides composite material for efficient removal of  
713       Congo red dye from aqueous solution, *Sci. Rep.* 10 (2020) 1–12.  
714       <https://doi.org/10.1038/s41598-020-58866-y>.
- 715 [14] G.Y.A. El-Reesh, A.A. Farghali, M. Taha, R.K. Mahmoud, Novel synthesis of Ni/Fe  
716       layered double hydroxides using urea and glycerol and their enhanced adsorption

- 717 behavior for Cr(VI) removal, *Sci. Rep.* 10 (2020) 1–20. <https://doi.org/10.1038/s41598->  
718 020-57519-4.
- 719 [15] H. Zhang, L. Nengzi, Z. Wang, X. Zhang, B. Li, X. Cheng, Construction of  
720 Bi<sub>2</sub>O<sub>3</sub>/CuNiFe LDHs composite and its enhanced photocatalytic degradation of  
721 lomefloxacin with persulfate under simulated sunlight, *J. Hazard. Mater.* 383 (2020)  
722 121236. <https://doi.org/10.1016/j.jhazmat.2019.121236>.
- 723 [16] F. He, B. Zhu, B. Cheng, J. Yu, W. Ho, W. Macyk, 2D/2D/0D TiO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub>/Ti<sub>3</sub>C<sub>2</sub> MXene  
724 composite S-scheme photocatalyst with enhanced CO<sub>2</sub> reduction activity, *Appl. Catal. B*  
725 *Environ.* 272 (2020) 119006. <https://doi.org/10.1016/j.apcatb.2020.119006>.
- 726 [17] A. Khataee, A. Fazli, F. Zakeri, S.W. Joo, Synthesis of a high-performance Z-scheme  
727 2D/2D WO<sub>3</sub>@CoFe-LDH nanocomposite for the synchronic degradation of the mixture  
728 azo dyes by sonocatalytic ozonation process, *J. Ind. Eng. Chem.* 89 (2020) 301–315.  
729 <https://doi.org/10.1016/j.jiec.2020.05.026>.
- 730 [18] M. Zhang, J. Yao, M. Arif, B. Qiu, H. Yin, X. Liu, S. Chen, 0D/2D CeO<sub>2</sub>/ZnIn<sub>2</sub>S<sub>4</sub> Z-  
731 scheme heterojunction for visible-light-driven photocatalytic H<sub>2</sub> evolution, *Appl. Surf.*  
732 *Sci.* 526 (2020) 145749. <https://doi.org/10.1016/j.apsusc.2020.145749>.
- 733 [19] Y. Wang, C. Zhu, G. Zuo, Y. Guo, W. Xiao, Y. Dai, J. Kong, X. Xu, Y. Zhou, A. Xie, C.  
734 Sun, Q. Xian, 0D/2D Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> Z-Scheme heterojunction for boosted photocatalytic  
735 degradation and mechanism investigation, *Appl. Catal. B Environ.* 278 (2020) 119298.  
736 <https://doi.org/10.1016/j.apcatb.2020.119298>.
- 737 [20] J. Mu, F. Teng, H. Miao, Y. Wang, X. Hu, In-situ oxidation fabrication of 0D/2D  
738 SnO<sub>2</sub>/SnS<sub>2</sub> novel Step-scheme heterojunctions with enhanced photoelectrochemical  
739 activity for water splitting, *Appl. Surf. Sci.* 501 (2020) 143974.  
740 <https://doi.org/10.1016/j.apsusc.2019.143974>.
- 741 [21] J. Tao, X. Yu, Q. Liu, G. Liu, H. Tang, Internal electric field induced S-scheme

- 742 heterojunction MoS<sub>2</sub>/CoAl LDH for enhanced photocatalytic hydrogen evolution, J.  
743 Colloid Interface Sci. (2020). <https://doi.org/10.1016/j.jcis.2020.10.028>.
- 744 [22] A. Fazli, A. Khataee, M. Brigante, G. Mailhot, Cubic cobalt and zinc co-doped  
745 magnetite nanoparticles for persulfate and hydrogen peroxide activation towards the  
746 effective photodegradation of Sulfalene, Chem. Eng. J. 404 (2021) 126391.  
747 <https://doi.org/10.1016/j.cej.2020.126391>.
- 748 [23] A. Khataee, T.S. Rad, M. Fathinia, The role of clinoptilolite nanosheets in catalytic  
749 ozonation process: Insights into the degradation mechanism, kinetics and the toxicity, J.  
750 Taiwan Inst. Chem. Eng. 77 (2017) 205–215. <https://doi.org/10.1016/j.jtice.2017.05.004>.
- 751 [24] M. Aghaziarati, Y. Yamini, M. Shamsayei, An electrodeposited terephthalic acid-layered  
752 double hydroxide (Cu-Cr) nanosheet coating for in-tube solid-phase microextraction of  
753 phthalate esters, Microchim. Acta. 187 (2020) 118. <https://doi.org/10.1007/s00604-019-4102-5>.
- 754
- 755 [25] J.-Y. Lee, G.-H. Gwak, H.-M. Kim, T. Kim, G.J. Lee, J.-M. Oh, Synthesis of  
756 hydrotalcite type layered double hydroxide with various Mg/Al ratio and surface charge  
757 under controlled reaction condition, Appl. Clay Sci. 134 (2016) 44–49.  
758 <https://doi.org/10.1016/j.clay.2016.03.029>.
- 759 [26] H. Zhang, B. Xia, P. Wang, Y. Wang, Z. Li, Y. Wang, L. Feng, X. Li, S. Du, From  
760 waste to waste treatment: Mesoporous magnetic NiFe<sub>2</sub>O<sub>4</sub>/ZnCuCr-layered double  
761 hydroxide composite for wastewater treatment, J. Alloys Compd. 819 (2020) 153053.  
762 <https://doi.org/10.1016/j.jallcom.2019.153053>.
- 763 [27] Z. Zhang, L. Sun, Z. Wu, Y. Liu, S. Li, Facile hydrothermal synthesis of CuO–Cu<sub>2</sub>O/GO  
764 nanocomposites for the photocatalytic degradation of organic dye and tetracycline  
765 pollutants, New J. Chem. 44 (2020) 6420–6427. <https://doi.org/10.1039/D0NJ00577K>.
- 766 [28] T.S. Rad, A. Khataee, S. Rahim Pouran, Synergistic enhancement in photocatalytic

- 767 performance of Ce (IV) and Cr (III) co-substituted magnetite nanoparticles loaded on  
768 reduced graphene oxide sheets, *J. Colloid Interface Sci.* 528 (2018) 248–262.  
769 <https://doi.org/10.1016/j.jcis.2018.05.087>.
- 770 [29] A.S. Patil, J.L. Gunjakar, C.D. Lokhande, U.M. Patil, S.V. Sadavar, N.S. Padalkar, R.B.  
771 Shinde, M.M. Wagh, J.S. Bagi, Nanocrystalline copper-chromium-layered double  
772 hydroxide with tunable interlayer anions for electrochemical capacitor application,  
773 *Synth. Met.* 264 (2020) 116371. <https://doi.org/10.1016/j.synthmet.2020.116371>.
- 774 [30] A. Pastor, F. Rodriguez-Rivas, G. de Miguel, M. Cruz-Yusta, F. Martin, I. Pavlovic, L.  
775 Sánchez, Effects of Fe<sup>3+</sup> substitution on Zn-Al layered double hydroxides for enhanced  
776 NO photochemical abatement, *Chem. Eng. J.* 387 (2020) 124110.  
777 <https://doi.org/10.1016/j.cej.2020.124110>.
- 778 [31] Y. Meng, T. Dai, X. Zhou, G. Pan, S. Xia, Photodegradation of volatile organic  
779 compounds catalyzed by MCr-LDHs and hybrid MO@MCr-LDHs (M = Co, Ni, Cu,  
780 Zn): the comparison of activity, kinetics and photocatalytic mechanism, *Catal. Sci.*  
781 *Technol.* 10 (2020) 424–439. <https://doi.org/10.1039/C9CY02098E>.
- 782 [32] W. Wang, J. Zhang, T. Chen, J. Sun, X. Ma, Y. Wang, J. Wang, Z. Xie, Preparation of  
783 TiO<sub>2</sub>-modified Biochar and its Characteristics of Photo-catalysis Degradation for  
784 Enrofloxacin, *Sci. Rep.* 10 (2020) 1–12. <https://doi.org/10.1038/s41598-020-62791-5>.
- 785 [33] A. Maleki, Z. Hajizadeh, P. Salehi, Mesoporous halloysite nanotubes modified by  
786 CuFe<sub>2</sub>O<sub>4</sub> spinel ferrite nanoparticles and study of its application as a novel and efficient  
787 heterogeneous catalyst in the synthesis of pyrazolopyridine derivatives, *Sci. Rep.* 9  
788 (2019) 1–8. <https://doi.org/10.1038/s41598-019-42126-9>.
- 789 [34] Y. Liu, Y. Liu, H. Shi, M. Wang, S.H.-S. Cheng, H. Bian, M. Kamruzzaman, L. Cao,  
790 C.Y. Chung, Z. Lu, Cobalt-copper layered double hydroxide nanosheets as high  
791 performance bifunctional catalysts for rechargeable lithium-air batteries, *J. Alloys*

- 792           Compd. 688 (2016) 380–387. <https://doi.org/10.1016/j.jallcom.2016.07.224>.
- 793 [35] P. Gholami, L. Dinpazhoh, A. Khataee, A. Hassani, A. Bhatnagar, Facile hydrothermal  
794           synthesis of novel Fe-Cu layered double hydroxide/biochar nanocomposite with  
795           enhanced sonocatalytic activity for degradation of cefazolin sodium, *J. Hazard. Mater.*  
796           381 (2020) 120742. <https://doi.org/10.1016/j.jhazmat.2019.120742>.
- 797 [36] S. Sarkar, R. Akshaya, S. Ghosh, Nitrogen doped graphene/CuCr<sub>2</sub>O<sub>4</sub> nanocomposites for  
798           supercapacitors application: Effect of nitrogen doping on coulombic efficiency,  
799           *Electrochimica Acta.* 332 (2020) 135368.  
800           <https://doi.org/10.1016/j.electacta.2019.135368>.
- 801 [37] C. Dong, X. Zhang, J. Xu, R. Si, J. Sheng, J. Luo, S. Zhang, W. Dong, G. Li, W. Wang,  
802           F. Huang, Ruthenium-Doped Cobalt–Chromium Layered Double Hydroxides for  
803           Enhancing Oxygen Evolution through Regulating Charge Transfer, *Small.* 16 (2020)  
804           1905328. <https://doi.org/10.1002/sml.201905328>.
- 805 [38] C.M. Navarathna, N.B. Dewage, A.G. Karunanayake, E.L. Farmer, F. Perez, E.B.  
806           Hassan, T.E. Mlsna, C.U. Pittman, Rhodamine B Adsorptive Removal and  
807           Photocatalytic Degradation on MIL-53-Fe MOF/Magnetic Magnetite/Biochar  
808           Composites, *J. Inorg. Organomet. Polym. Mater.* 30 (2020) 214–229.  
809           <https://doi.org/10.1007/s10904-019-01322-w>.
- 810 [39] S.J. Ki, Y.-K. Park, J.-S. Kim, W.-J. Lee, H. Lee, S.-C. Jung, Facile preparation of  
811           tungsten oxide doped TiO<sub>2</sub> photocatalysts using liquid phase plasma process for  
812           enhanced degradation of diethyl phthalate, *Chem. Eng. J.* 377 (2019) 120087.  
813           <https://doi.org/10.1016/j.cej.2018.10.024>.
- 814 [40] R. Yu, J. Zhao, Z. Zhao, F. Cui, Copper substituted zinc ferrite with abundant oxygen  
815           vacancies for enhanced ciprofloxacin degradation via peroxymonosulfate activation, *J.*  
816           *Hazard. Mater.* 390 (2020) 121998. <https://doi.org/10.1016/j.jhazmat.2019.121998>.

- 817 [41] Z. Li, D. Liu, Y. Zhao, S. Li, X. Wei, F. Meng, W. Huang, Z. Lei, Singlet oxygen  
818 dominated peroxymonosulfate activation by CuO-CeO<sub>2</sub> for organic pollutants  
819 degradation: Performance and mechanism, *Chemosphere*. 233 (2019) 549–558.  
820 <https://doi.org/10.1016/j.chemosphere.2019.05.291>.
- 821 [42] C. Liu, L. Liu, X. Tian, Y. Wang, R. Li, Y. Zhang, Z. Song, B. Xu, W. Chu, F. Qi, A.  
822 Ikhlaiq, Coupling metal–organic frameworks and g-C<sub>3</sub>N<sub>4</sub> to derive Fe@N-doped  
823 graphene-like carbon for peroxymonosulfate activation: Upgrading framework stability  
824 and performance, *Appl. Catal. B Environ.* 255 (2019) 117763.  
825 <https://doi.org/10.1016/j.apcatb.2019.117763>.
- 826 [43] S. Wang, J. Wang, Activation of peroxymonosulfate by sludge-derived biochar for the  
827 degradation of triclosan in water and wastewater, *Chem. Eng. J.* 356 (2019) 350–358.  
828 <https://doi.org/10.1016/j.cej.2018.09.062>.
- 829 [44] X. Duan, S. Yang, S. Waclawek, G. Fang, R. Xiao, D.D. Dionysiou, Limitations and  
830 prospects of sulfate-radical based advanced oxidation processes, *J. Environ. Chem. Eng.*  
831 8 (2020) 103849. <https://doi.org/10.1016/j.jece.2020.103849>.
- 832 [45] W. Sang, Z. Li, M. Huang, X. Wu, D. Li, L. Mei, J. Cui, Enhanced transition metal  
833 oxide based peroxymonosulfate activation by hydroxylamine for the degradation of  
834 sulfamethoxazole, *Chem. Eng. J.* 383 (2020) 123057.  
835 <https://doi.org/10.1016/j.cej.2019.123057>.
- 836 [46] Z. Yin, M. Han, Z. Hu, L. Feng, Y. Liu, Z. Du, L. Zhang, Peroxymonosulfate enhancing  
837 visible light photocatalytic degradation of bezafibrate by Pd/g-C<sub>3</sub>N<sub>4</sub> catalysts: The role  
838 of sulfate radicals and hydroxyl radicals, *Chem. Eng. J.* 390 (2020) 124532.  
839 <https://doi.org/10.1016/j.cej.2020.124532>.
- 840 [47] C. Cai, H. Zhang, X. Zhong, L. Hou, Ultrasound enhanced heterogeneous activation of  
841 peroxymonosulfate by a bimetallic Fe–Co/SBA-15 catalyst for the degradation of



- 842 Orange II in water, *J. Hazard. Mater.* 283 (2015) 70–79.  
843 <https://doi.org/10.1016/j.jhazmat.2014.08.053>.
- 844 [48] F. Ghanbari, J. Wu, M. Khatebasreh, D. Ding, K.-Y.A. Lin, Efficient treatment for  
845 landfill leachate through sequential electrocoagulation, electrooxidation and  
846 PMS/UV/CuFe<sub>2</sub>O<sub>4</sub> process, *Sep. Purif. Technol.* 242 (2020) 116828.  
847 <https://doi.org/10.1016/j.seppur.2020.116828>.
- 848 [49] Y. Tao, Q. Ni, M. Wei, D. Xia, X. Li, A. Xu, Metal-free activation of  
849 peroxymonosulfate by g-C<sub>3</sub>N<sub>4</sub> under visible light irradiation for the degradation of  
850 organic dyes, *RSC Adv.* 5 (2015) 44128–44136. <https://doi.org/10.1039/C5RA06223C>.
- 851 [50] N.S. Shah, J.A. Khan, M. Sayed, Z.U.H. Khan, A.D. Rizwan, N. Muhammad, G.  
852 Boczka, B. Murtaza, M. Imran, H.M. Khan, G. Zaman, Solar light driven degradation of  
853 norfloxacin using as-synthesized Bi<sup>3+</sup> and Fe<sup>2+</sup> co-doped ZnO with the addition of  
854 HSO<sub>5</sub><sup>-</sup>: Toxicities and degradation pathways investigation, *Chem. Eng. J.* 351 (2018)  
855 841–855. <https://doi.org/10.1016/j.cej.2018.06.111>.
- 856 [51] A. Khataee, A. Fazli, M. Fathinia, F. Vafaei, Preparation of martite nanoparticles  
857 through high-energy planetary ball milling and its application toward simultaneous  
858 catalytic ozonation of two green algae, *J. Taiwan Inst. Chem. Eng.* 82 (2018) 80–91.  
859 <https://doi.org/10.1016/j.jtice.2017.10.016>.
- 860 [52] M. Golshan, B. Kakavandi, M. Ahmadi, M. Azizi, Photocatalytic activation of  
861 peroxymonosulfate by TiO<sub>2</sub> anchored on copper ferrite (TiO<sub>2</sub>@CuFe<sub>2</sub>O<sub>4</sub>) into 2,4-D  
862 degradation: Process feasibility, mechanism and pathway, *J. Hazard. Mater.* 359 (2018)  
863 325–337. <https://doi.org/10.1016/j.jhazmat.2018.06.069>.
- 864 [53] Y. Zhong, Z.-F. Chen, S.-C. Yan, W.-W. Wei, Q. Zhang, G. Liu, Z. Cai, L. Yu,  
865 Photocatalytic transformation of climbazole and 4-chlorophenol formation using a floral  
866 array of chromium-substituted magnetite nanoparticles activated with

867 peroxymonosulfate, Environ. Sci. Nano. 6 (2019) 2986–2999.  
868 <https://doi.org/10.1039/C9EN00673G>.

869 [54] J. Lin, Y. Hu, L. Wang, D. Liang, X. Ruan, S. Shao, M88/PS/Vis system for degradation  
870 of bisphenol A: Environmental factors, degradation pathways, and toxicity evaluation,  
871 Chem. Eng. J. 382 (2020) 122931. <https://doi.org/10.1016/j.cej.2019.122931>.

872 [55] T. Cai, W. Zeng, Y. Liu, L. Wang, W. Dong, H. Chen, X. Xia, A promising inorganic-  
873 organic Z-scheme photocatalyst Ag<sub>3</sub>PO<sub>4</sub>/PDI supermolecule with enhanced  
874 photoactivity and photostability for environmental remediation, Appl. Catal. B Environ.  
875 263 (2020) 118327. <https://doi.org/10.1016/j.apcatb.2019.118327>.

876 [56] Z. Yang, C. Zhang, G. Zeng, X. Tan, H. Wang, D. Huang, K. Yang, J. Wei, C. Ma, K.  
877 Nie, Design and engineering of layered double hydroxide based catalysts for water  
878 depollution by advanced oxidation processes: a review, J. Mater. Chem. A. 8 (2020)  
879 4141–4173. <https://doi.org/10.1039/C9TA13522G>.

880 [57] A. Meng, B. Zhu, B. Zhong, L. Zhang, B. Cheng, Direct Z-scheme TiO<sub>2</sub>/CdS  
881 hierarchical photocatalyst for enhanced photocatalytic H<sub>2</sub>-production activity, Appl.  
882 Surf. Sci. 422 (2017) 518–527. <https://doi.org/10.1016/j.apsusc.2017.06.028>.

883 [58] A. Kumar, M. Khan, J. He, I.M.C. Lo, Visible–light–driven magnetically recyclable  
884 terephthalic acid functionalized g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> heterojunction nanophotocatalyst for  
885 enhanced degradation of PPCPs, Appl. Catal. B Environ. 270 (2020) 118898.  
886 <https://doi.org/10.1016/j.apcatb.2020.118898>.

887 [59] B. Palanivel, A. Mani, Conversion of a Type-II to a Z-Scheme Heterojunction by  
888 Intercalation of a 0D Electron Mediator between the Integrative NiFe<sub>2</sub>O<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub>  
889 Composite Nanoparticles: Boosting the Radical Production for Photo-Fenton  
890 Degradation, ACS Omega. 5 (2020) 19747–19759.  
891 <https://doi.org/10.1021/acsomega.0c02477>.

- 892 [60] F. Ghanbari, J. Wu, M. Khatebasreh, D. Ding, K.-Y.A. Lin, Efficient treatment for  
893 landfill leachate through sequential electrocoagulation, electrooxidation and  
894 PMS/UV/CuFe<sub>2</sub>O<sub>4</sub> process, *Sep. Purif. Technol.* 242 (2020) 116828.  
895 <https://doi.org/10.1016/j.seppur.2020.116828>.
- 896 [61] M. Kumar, A. Puri, A review of permissible limits of drinking water, *Indian J. Occup.*  
897 *Environ. Med.* 16 (2012) 40–44. <https://doi.org/10.4103/0019-5278.99696>.
- 898