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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
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32

33 **Abstract**

34 Herein, a stable and S-scheme $\text{Fe}_3\text{O}_4@\text{CuCr-LDH}$ 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_3O_4 , and LDH, the $\text{Fe}_3\text{O}_4@\text{CuCr-LDH}$
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 $\text{Fe}_3\text{O}_4@\text{CuCr-LDH}$ 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^{-1} , 20 mg L^{-1} , 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 Fe₃O₄ [10] and CuO [11] were ascertained to possess high activity for PMS
83 activation. Among different metal oxides, Fe₃O₄ is of great importance due to its magnetic
84 property. Accordingly, Fe₃O₄ 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 $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M²⁺, M³⁺, and Aⁿ⁻ 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 MoS₂/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 Fe₃O₄ 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 Fe₃O₄ and CuCr-LDH nanoparticles to use in the photocatalytic activation
113 of PMS. For the first principle scope of the present work, the Fe₃O₄@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 Fe₃O₄, CuCr-LDH, and Fe₃O₄@CuCr-LDH**

131 Fe₃O₄ 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(NO₃)₂·3H₂O and Cr(NO₃)₃·9H₂O 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 Fe₃O₄@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 Fe₃O₄ 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(NO₃)₂·3H₂O and (0.25 M)
146 Cr(NO₃)₃·9H₂O 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⁻¹ 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⁻¹) 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 μ 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 μ 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⁻¹ 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 C₀
207 and C_t 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**

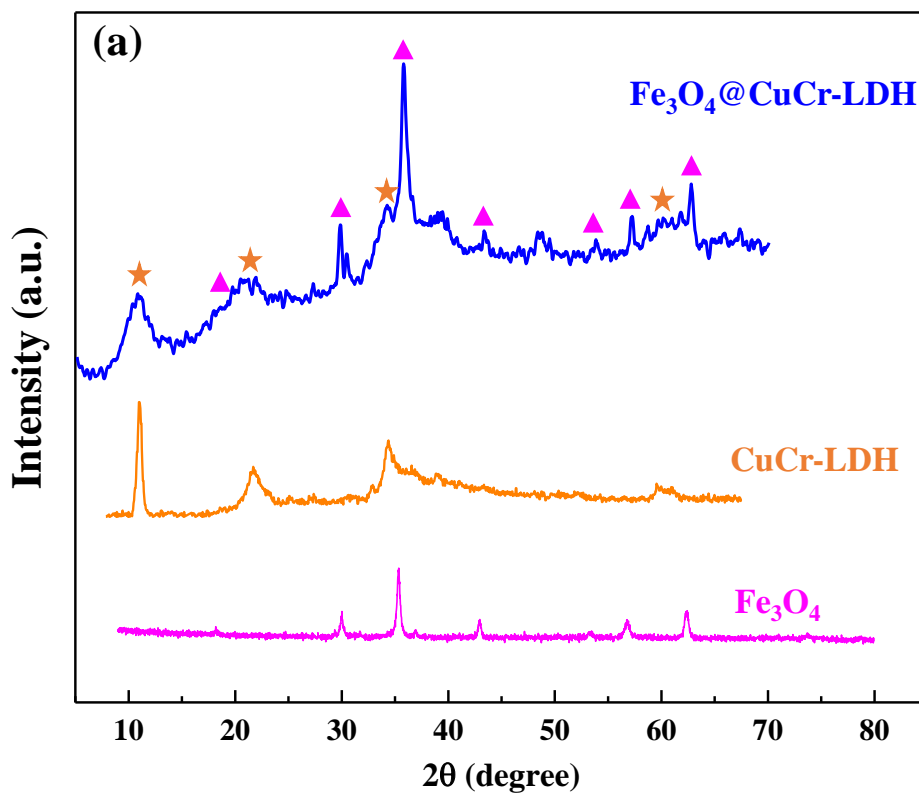
216 **3.1. Characterization**

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 Fe₃O₄@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

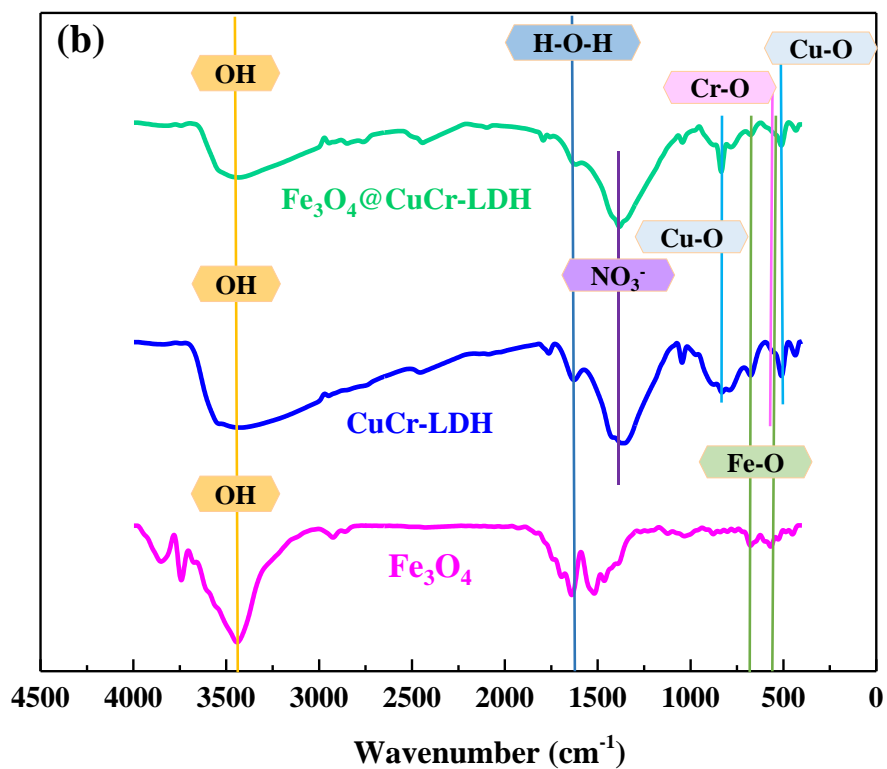
229 layered double hydroxide [25].

230 The main functional group of the so-synthesized nanomaterials was ascertained by applying
231 the FTIR analysis. The attained FT-IR spectrums of Fe_3O_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 cm^{-1}
233 revealed the M-O-H bindings and M-O vibrations mainly Cu-O at 524 , and 831 cm^{-1} , Fe-O at
234 568 and 678 cm^{-1} , and eventually Cr-O at 610 cm^{-1} [26–28]. The absorption band that
235 appeared at 1382 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 NO_3^- anions [29]. Moreover, the peaks at
237 3451 and 1650 cm^{-1} correlate to the O-H stretching vibration of the layered double hydroxide
238 and the interlayer water molecules, respectively [30].

239



240



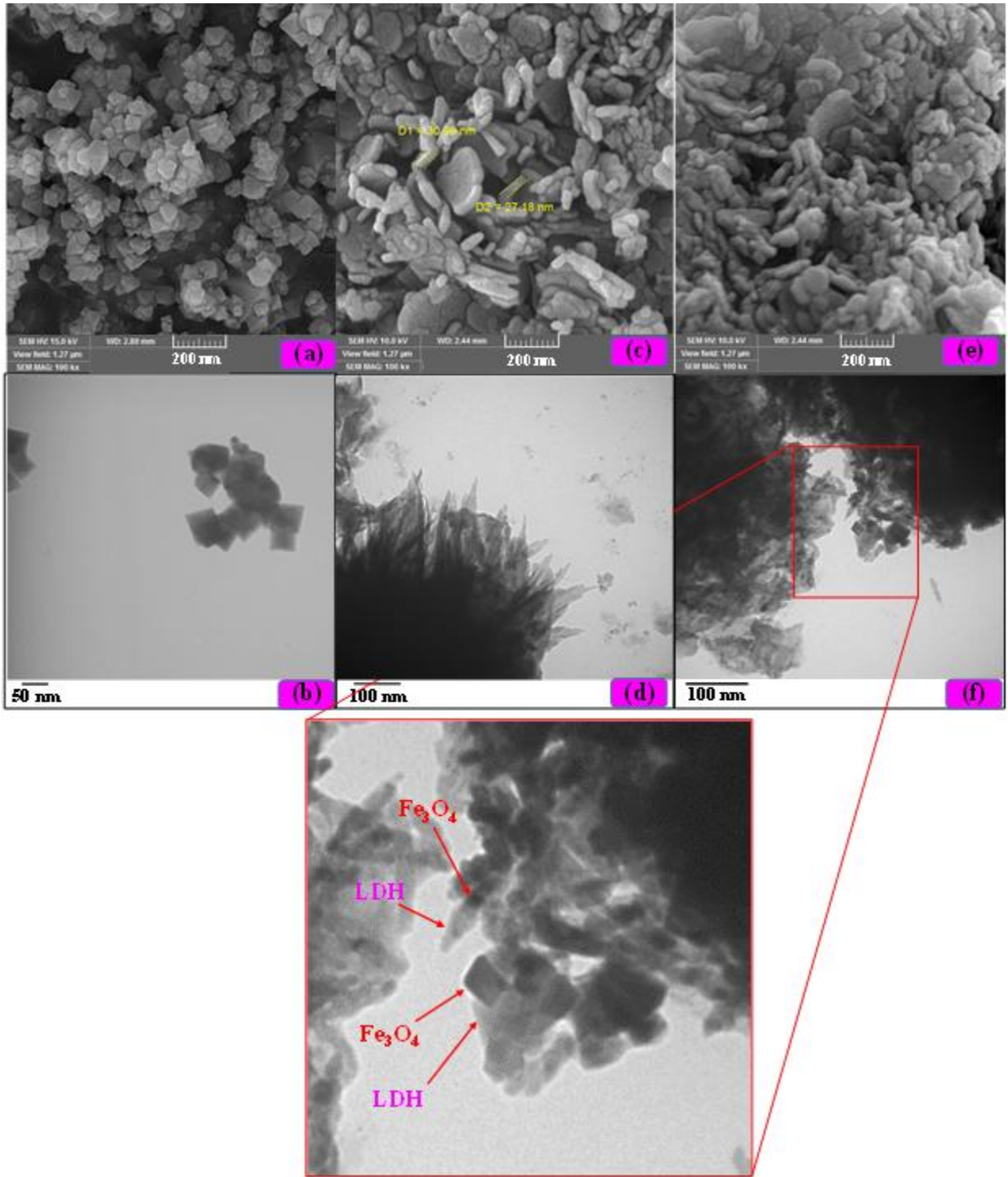
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Fig. 1. (a) XRD pattern (b) FT-IR spectrum of the so-synthesized nanomaterials.

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Fig. 2. The SEM and TEM images of (a and b) pure Fe₃O₄, (c and d) CuCr-LDH, and finally (e and f) Fe₃O₄@CuCr-LDH nanocomposite.

The SEM images of the so-synthesized Fe₃O₄, CuCr-LDH, and Fe₃O₄@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 Fe₃O₄@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 Fe₃O₄@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 Fe₃O₄@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 Fe₃O₄@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 Fe₃O₄@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 Fe₃O₄, CuCr-LDH, and Fe₃O₄@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 N₂ 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 cm² g⁻¹, 0.32 cm³ g⁻¹).

287

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

| Samples | Surface area (m ² g ⁻¹) 1) | Pore volume (cm ³ g ⁻¹) |
|--|--|--|
| Fe ₃ O ₄ | 7.85 | 0.12 |
| CuCr-LDH | 50.69 | 0.20 |
| Fe ₃ O ₄ @CuCr- LDH | 80.60 | 0.32 |

290

291 Given the magnetic properties of the photocatalysts in which were Fe₃O₄, these materials
292 have attracted the attention of scientists. Herein, the magnetic behavior of the Fe₃O₄ was
293 evaluated after its composition with the CuCr-LDH nanosheets. Therefore, the magnetic
294 measurement of the fresh Fe₃O₄ and the Fe₃O₄@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 $Fe_3O_4@CuCr-LDH$.

| Samples | 1M_s (emu g ⁻¹) | SQR ($^2M_r/M_s$) | 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_{1/2} and Cu 2p_{3/2} 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_{3/2} state; whereas, the Cr 2p_{1/2} 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, Fe₃O₄, and
321 Fe₃O₄@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 Fe₃O₄@CuCr-
324 LDH > CuCr-LDH > Fe₃O₄. However, among them, the degradation performance of the
325 Fe₃O₄@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 Fe₃O₄ boosted their photocatalytic activity by increasing the visible light absorption of the
328 composite. Consequently, the Fe₃O₄@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 TiO₂, as well as tungsten oxide doped TiO₂.
332 According to their results, loading WO₃ onto the pristine TiO₂ 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⁻¹ 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⁻¹
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⁻¹ to 2 g L⁻¹
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⁻¹. 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⁻¹ 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 pH_{pzc} for the Fe₃O₄@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 pK_a of PMS which is reported to be 9.4, HSO₅⁻ is
363 a more stable ion than the ionic form (SO₅²⁻). Owing to the occurrence of the hydrogen bonds
364 between the O-O group of HSO₅⁻ and the available H⁺ in the acidic solution [40], the
365 attachment of the H⁺ to the HSO₅⁻ species can inhibit its approach to the positively charged
366 surface of Fe₃O₄@CuCr-LDH. Therefore, the declined DEP degradation efficiency in the

367 lower pH value can be attributed to the descended participation of 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 SO_5^{2-} [42]. Further reaction of PMS with the produced 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 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 Fe₃O₄@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.

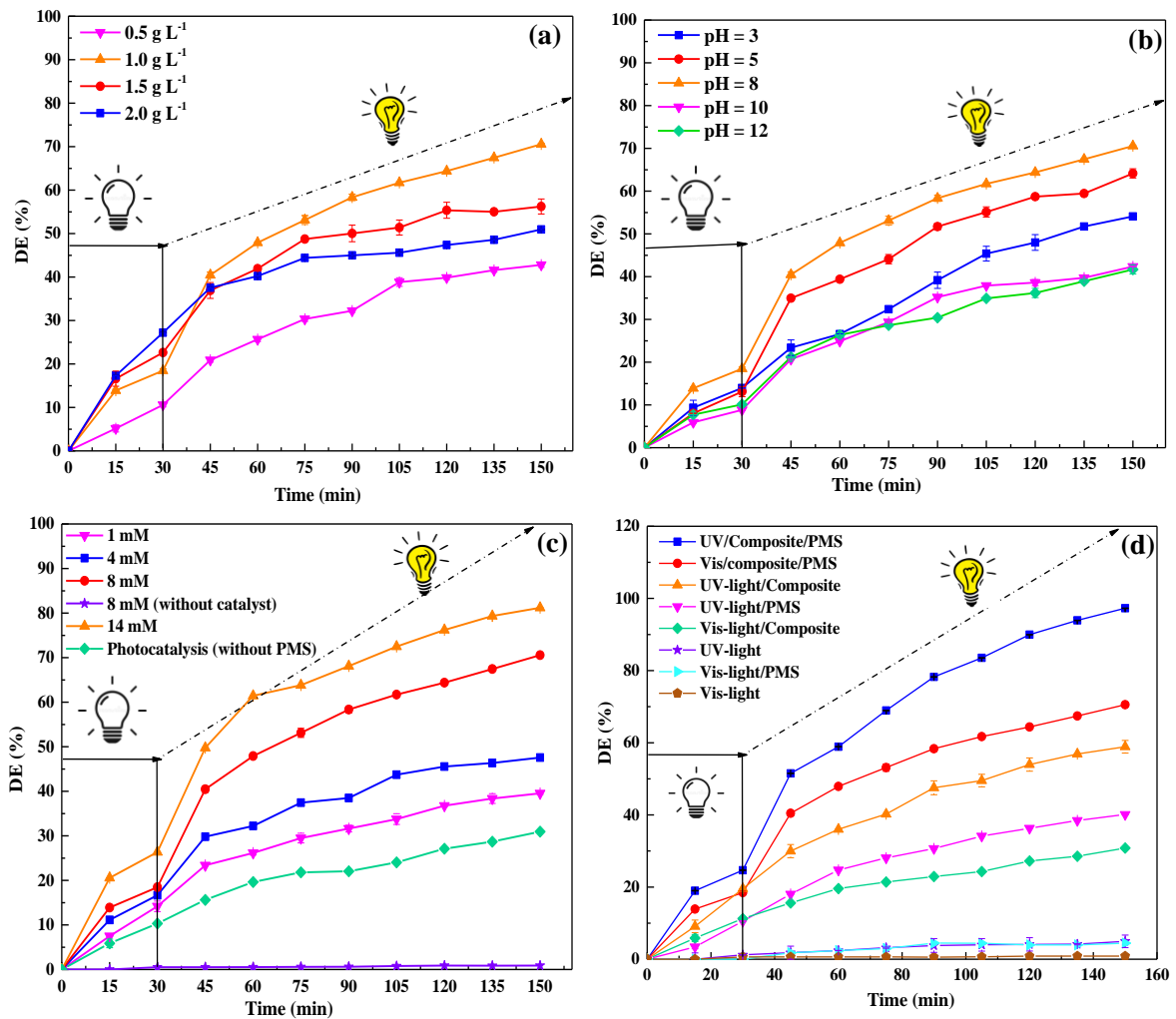




421

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,

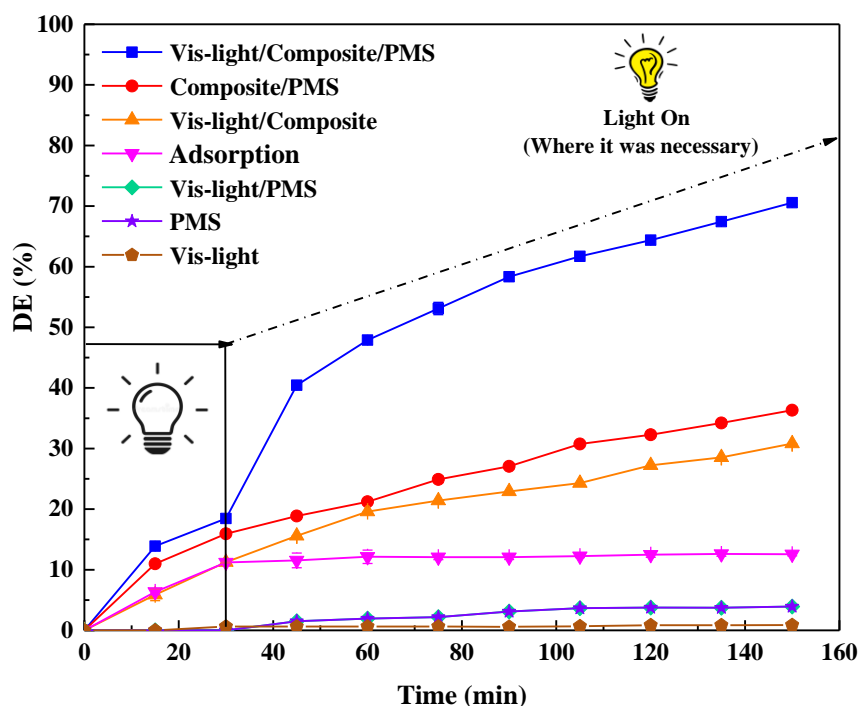
428 and different light conditions on the DE of the DEP. Experimental conditions: [DEP] = 20 mg
429 L⁻¹, catalyst concentration of 1 g L⁻¹, [PMS] = 8 mM, and pH = 8.

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 Fe₃O₄@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 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_{app})

451 were reported for each of the processes. The k_{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_{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 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.

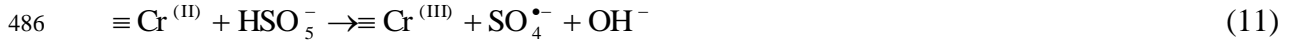
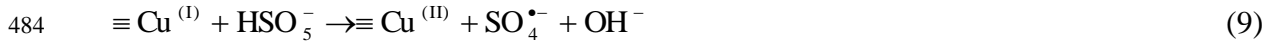
$$467 \quad \text{Synergy factor}_{\text{PMS/Vis-light}} = \frac{K_{\text{PMS/Vis-light}}}{K_{\text{PMS}} + K_{\text{Vis-light}}} \quad (1)$$

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

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

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 TiO_2 and CuFe_2O_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

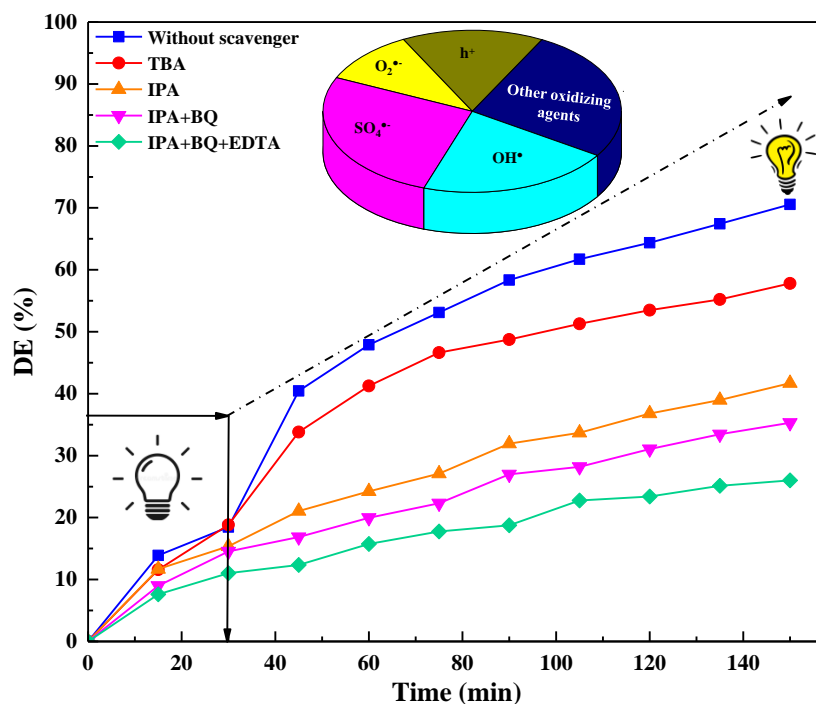
507 system for the breaking the DEP molecules to the less or nontoxic compounds. It worth noting
508 that our results are in good accordance with the literature reports [23].

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, Fe₃O₄@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 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 h^+ and
529 $\text{O}_2^{\cdot-}$ was also confirmed by adding EDTA and BQ. Therefore, the results prove that the
530 photogenerated e^- and 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 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

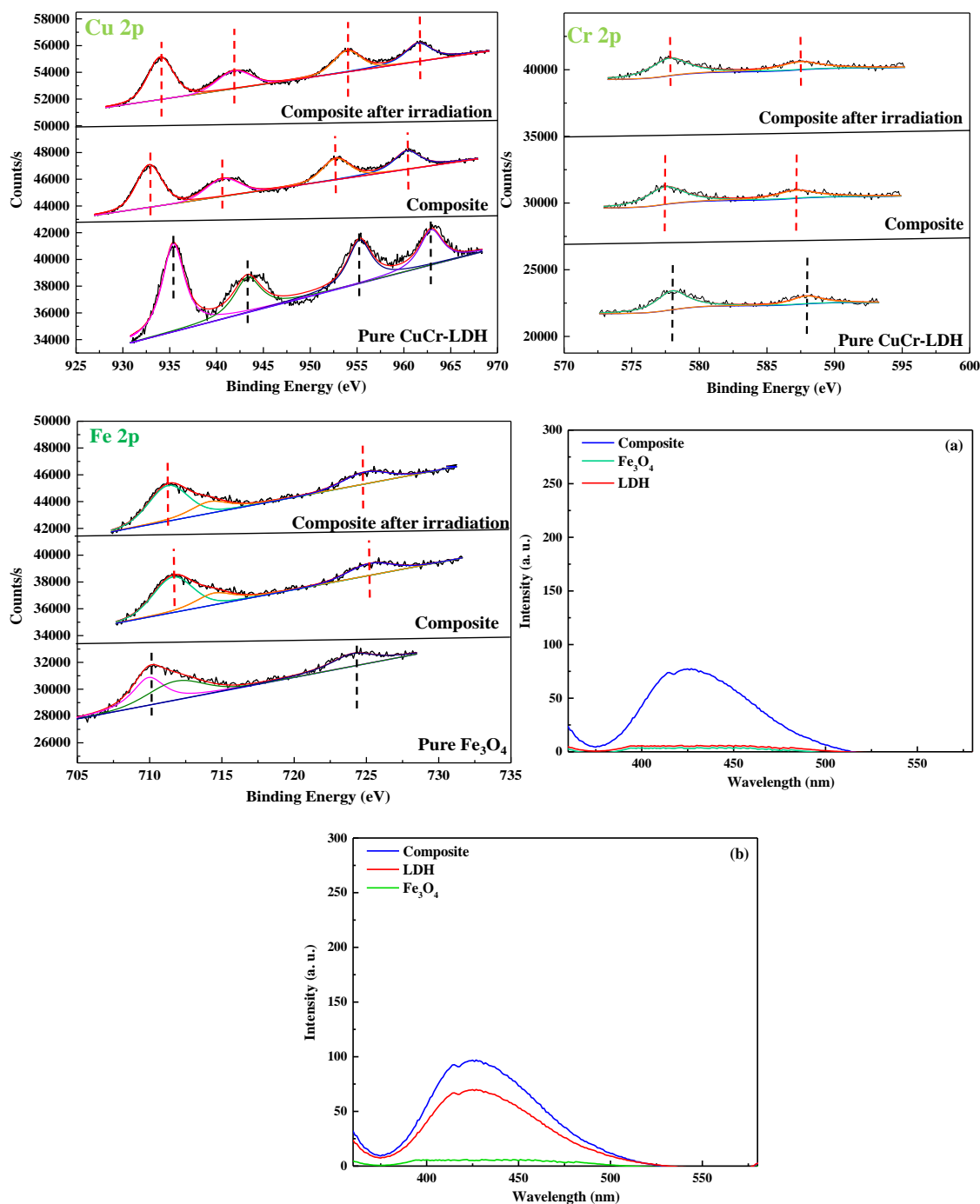
538 A set of experiments were done to deeply investigate the type of the prepared
 539 heterojunction and define the separation and transfer pathway of the charge carriers between
 540 the semiconductors. In this regard, the CB and VB of the semiconductors were determined by
 541 using XPS valance band 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 Fe_3O_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 Fe_3O_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 Fe_3O_4 , CuCr-LDH, Fe_3O_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 Fe_3O_4 . Considering the literature review, the
561 appeared opposite shifts of the binding energies are good evidence for the appropriate
562 interfacial contact of Fe_3O_4 to the LDH which leads to the flow of electrons from Fe_3O_4 to
563 LDH and equilibrium the Fermi levels [16]. Hence, an internal electric field pointing from
564 Fe_3O_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 Fe_3O_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 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 Fe_3O_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 Fe_3O_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 Fe_3O_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 O_2 , the pure CuCrLDH composite
585 was capable of generating $\cdot\text{OH}$ revealing the presence of photogenerated h^+ with sufficient
586 oxidation potential. On the contrary, according to the results, the presence of EDTA as the h^+
587 inhibitor brought about no fluorescent peak for the pristine LDH due to its lower CB position
588 for the reduction of 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 O_2 , respectively.



590

591 **Fig. 6.** Comparison of Cu 2p, Cr 2p, and Fe 2p XPS spectra for the pure Fe₃O₄, CuCr-LDH,

592 and Fe₃O₄@CuCr-LDH in the dark and after the visible light irradiation. Fluorescence spectra

593 of Fe₃O₄@CuCr-LDH, CuCr-LDH, Fe₃O₄ in the presence of EDTA (a) and in the absence of

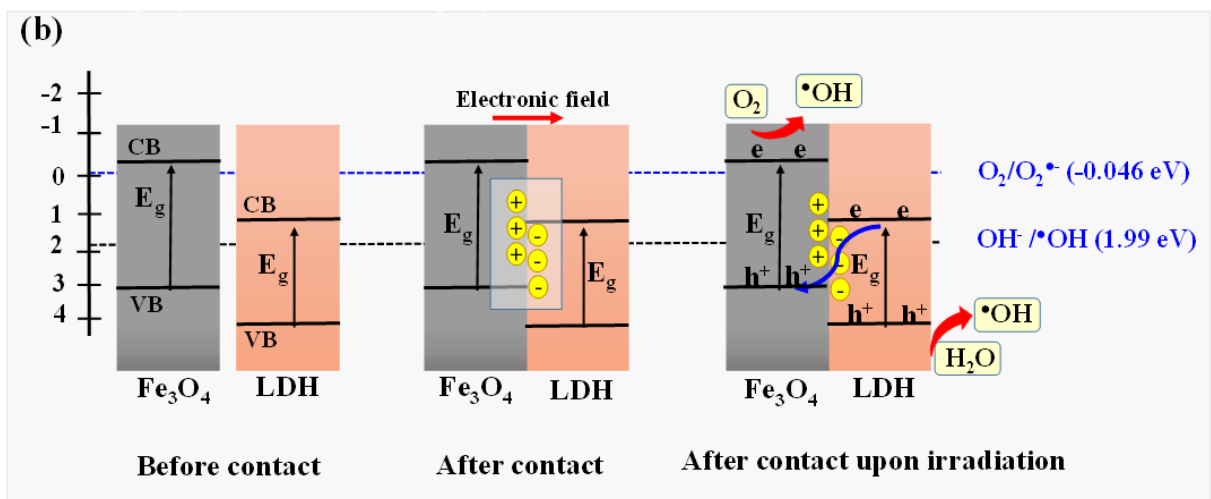
594

oxygen (b).

595

596 Based on the above results, in our system Fe_3O_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 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 Fe_3O_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 Fe_3O_4 @CuCrLDH heterojunction.

610

611 3.7. The reusability and stability of Fe_3O_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 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 Fe₃O₄@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 SO₄^{•-} and [•]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

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