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**Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH as a
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► **To cite this version:**

Arezou Fazli, Marcello Brigante, Alireza Khataee, Gilles Mailhot. Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH as a visible-light-responsive photocatalyst for the degradation of caffeine, bisphenol A, and simazine in pure water and real wastewater under photo-Fenton-like degradation process. *Chemosphere*, 2022, 291, pp.132920. 10.1016/j.chemosphere.2021.132920 . hal-03634868

HAL Id: hal-03634868

<https://hal.science/hal-03634868>

Submitted on 28 Nov 2022

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1 **Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH as a visible-light-responsive photocatalyst for**
2 **the degradation of Caffeine, Bisphenol A, and Simazine in pure water and**
3 **real wastewater under photo-Fenton-like degradation process**

4
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28 **Abstract**

29 This paper outlines the synthesis and application of a sustainable composite for the photo-
30 Fenton-like degradation of caffeine, bisphenol A, and simazine. The phase, morphology, optical
31 and magnetic properties of the samples were evaluated by different characterization techniques.
32 The composite of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$ and copper-chromium layered double hydroxide (CuCr-
33 LDH) was determined to be the most favorable photocatalyst in the photo-Fenton-like process
34 when compared with Fe_3O_4 , $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$, CuCr-LDH, and $\text{Fe}_3\text{O}_4/\text{CuCr-LDH}$ composite.
35 Studying the efficiency of the photo-Fenton-like degradation process in the presence of the
36 $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite revealed a degradation rate constant of caffeine twice
37 more than the sum of those obtained for the individual processes. This ascribes to the synergistic
38 effect by which the photo-generated electron-hole from the catalyst and the efficient reduction
39 of Fe^{3+} , Cu^{2+} , etc. during the photo-Fenton-like reaction is accelerated. Moreover, under the
40 optimal condition and after 120 min of heterogenous photo-Fenton-like process at natural pH,
41 > 90% of pollutants mixture was decomposed. The experiments fulfilled in near-real conditions
42 demonstrated I) the high stability and magnetically recoverability of the photocatalyst and II)
43 the proper degradation performance of the applied heterogenous photo-Fenton-process in the
44 removal of pollutant mixture in different water bodies and in the presence of chloride and
45 bicarbonate ions.

46

47 **Keywords:** Sustainable photocatalyst; CuCr-LDH; Doped magnetite; Mineralization;
48 Micropollutants mixture.

49

50

51 **1. Introduction**

52 Industrial toxic wastes like pharmaceuticals, pesticides, and phenols are present in water and
53 wastewater, which turned into a globally concerning issue. Caffeine (CAF) is a widely used
54 psychoactive medicine and it can be found in coffee seeds (0.43 to 0.82 mg/mL), tea leaves,
55 etc. (Chen et al., 2018). Some industrial raw materials such as bisphenol A (BPA) are being
56 used for the preparation of water bottles, food containers, and polycarbonates. Nevertheless,
57 according to the World Health Organization (WHO), a low concentration of BPA can result in
58 hypertension and cell disorders (Chen et al., 2020). Furthermore, different s-triazine herbicides
59 have been used in the agriculture to manage the broadleaf and grassy weeds (X. Yang et al.,
60 2020). Due to the excessive usage of the herbicides such as simazine (SIM), a different amount
61 of them has appeared in groundwater which leads to DNA replication and disorders in the
62 central nervous system (Nahim-Granados et al., 2020). Due to the entrance of the above-
63 mentioned compounds to the water bodies, researchers have recently focused on the
64 performance of various treatment processes for the degradation of an individual kind of
65 pollutant (Hieu et al., 2021). However, it is well-known that real wastewater comprises a
66 mixture of diverse kinds of pollutants which should be treated before their arrival into aquatic
67 ecosystems (Chavan and Fulekar, 2020).

68 As the representative AOPs, the Fenton processes can activate H_2O_2 (HP) by the Fenton
69 reagent Fe^{2+} to produce reactive $\cdot\text{OH}$ (Brillas, 2020). So far, different inherent shortcomings
70 such as higher efficiencies at acidic pHs and the rapid decay of the utilized catalyst confined
71 their usage for practical applications (Zhang et al., 2020). To overcome these restrictions, the
72 photo-Fenton processes in the presence of a photocatalyst is of great consideration. The photo-
73 generated electron and hole pairs in the photocatalysts promote the regeneration of Fenton
74 reagent Fe^{2+} which is favourable for the Fenton reactions (Sharma et al., 2020). In this context,
75 a big effort has been devoted to design the effective heterogeneous photocatalysts grounded on

76 the advantages such as high activity in different pH values and efficient recovery from the
77 reaction media (Sharma et al., 2020). Layered double hydroxides (LDHs) are a class of two-
78 dimensional (2D) synthetic compounds with a high specific structure and chemical stability
79 which make them suitable candidates for the varied catalytic degradation processes (Wu et al.,
80 2022). For instance, Bai et al. (Bai et al., 2017) and Li et al. (Li et al., 2020) used Co-Fe-LDH
81 and Zn-Al-LDH as Fenton and photo-Fenton catalysts to degraded different water pollutants,
82 respectively. Besides the higher photocatalytic activity, recoverability and reusability of the
83 nanoscale photocatalysts after degradation reactions are of great consideration for sustainable
84 process management (Fazli et al., 2021b). In order to recover LDHs from the reaction media by
85 a permanent magnet, different LDH heterojunctions with magnetic materials have been
86 synthesized and used in AOPs (Gonçalves et al., 2019).

87 In previous work, the activation of persulfate and HP in the presence of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$
88 nanoparticles to decompose a pharmaceutical water pollutant was studied. It was found out that
89 the nanoparticles were magnetically separable; however, under UVA illumination and the
90 solution pH of 8, the co-doped magnetite had lower efficiency for the activation of HP (Fazli et
91 al., 2021b). Therefore, it would be of great importance to add a highly active semiconductor to
92 co-doped magnetite to prepare a high-performance and environmentally friendly photocatalyst
93 for the photo-Fenton-like process. Considering the reaction rate constant of Fe (III) (10^{-3} – 10^{-2}
94 $\text{M}^{-1} \text{s}^{-1}$), Fe (II) ($76 \text{M}^{-1} \text{s}^{-1}$), Cu (I) ($10^4 \text{M}^{-1} \text{s}^{-1}$) and Cu (II) ($4.6 \times 10^2 \text{M}^{-1} \text{s}^{-1}$), copper can
95 react with HP faster (Xiao et al., 2020). Moreover, previous works have confirmed the high
96 impact of chromium on the further production of hydroxyl radicals in the UV/Fenton system
97 (Liang et al., 2012). Therefore, herein, we synthesized a CuCr-LDH as the proper
98 semiconductor and merged its merits with the magnetically separable $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$
99 nanoparticles to prepare an efficient visible-light-responsive photocatalyst for the photo-
100 Fenton-like degradation of 3 kinds of water contaminants. To the authors' knowledge, no

101 research was devoted to studying the effect of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite in the
102 photo-Fenton-like degradation of pollutant mixture in pure water and real wastewater.
103 Therefore, the proposed research study was undertaken with the following goals: a) to prepare
104 a visible-light responsive magnetic composite ($\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$); (b) investigate
105 the optical, magnetic, and physicochemical properties of the composite, (c) study the
106 performance of the so-synthesized photocatalysts for the photo-Fenton-like degradation of
107 water pollutants, (d) examine the stability and reusability of so-synthesized photocatalyst, (e)
108 investigate the effect of inorganic anions and radical scavengers, (f) assess the performance of
109 composite as the photo-Fenton-like photocatalyst for the effective degradation of pollutants
110 mixture in pure and tap water, as well as real wastewater matrix, and finally (g) examine the
111 efficiency of the photo-Fenton-like process for the mineralization of the pollutants mixture.

112

113 **2. Experimental**

114 **2.1. Materials**

115 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 97%, NaNO_3 99%, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 99%, $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$ 98%, HCl 38%, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$
116 90–100%, NaOH 99%, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ 99%, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 99%, H_2O_2 30%, KI 99.5%,
117 NaHCO_3 , 99.7%, NaCl , 99% and organic solvents (purity greater than 99%) were provided
118 from Sigma Aldrich France and used with no further purification.

119

120 **2.2. Preparation of the photocatalysts**

121 The required solutions were prepared with previously deoxygenated distilled water via argon
122 gas. The typical procedure to synthesize the $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite is
123 summarized in Fig. S1. As the first step, we synthesized Co and Zn co-doped Fe_3O_4
124 nanoparticles by applying the method explained in our previous work (Fazli et al., 2021c). In
125 this regard, a 100 mL solution comprised of FeCl_2 , H_2O , $\text{ZnCl}_2 \cdot 4\text{H}_2\text{O}$, and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and

126 10 mL of HCl (0.6 M) was prepared and added to the three-neck flask. The solution was stirred
127 at 500 rpm, and then 1 mL hydrazine was added to the solution to reach lower solution pH.
128 Afterward, the alkaline solution comprised of NaNO₃ (0.9 M) and NaOH (0.4 M), was added
129 drop by drop to the solution. After the addition of the alkaline solution with the speed of 3
130 drops/second, the mixture was stirred for 2 h at 95 °C. The resulted particles were magnetically
131 collected, washed three times with distilled water, and finally dried at 90 °C for 24 h.

132 In the following, the obtained nanoparticles were used to prepare the
133 Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composite. For this purpose, two separated solutions (I and II)
134 were prepared as follows: Solution I: 0.5 g of the so-synthesized co-doped magnetite was
135 dispersed in 150 mL of water for 30 min; after that, 150 mL of NaOH (2 M) was added drop
136 by drop. At the same time, the specific amount of Cr (NO₃)₃·9H₂O (0.25 M) and Cu
137 (NO₃)₂·3H₂O (0.5 M) were respectively dissolved in 50 and 100 mL of distilled water and
138 mixed with each other to prepare a solution of 150 mL as the salts solution (II). Thereafter,
139 solutions I and II were mixed drop by drop; while, the mixture was vigorously stirring and the
140 pH was being kept between 9.3 and 10. The final mixture was aged for 24 h. As the final step,
141 the particles of the composite were magnetically separated, rinsed three times with water, and
142 dried at 60 °C for 12 h. Pure CuCr-LDH was prepared with the same procedure without adding
143 co-doped Fe₃O₄.

144 **2.3. Characterization**

145 X-ray diffraction (XRD, D8 Advance, Bruker, Germany) and X-ray photoelectron
146 spectroscopy (XPS, OMICRON EA125, Germany) were utilized to investigate the structural
147 properties of the samples. SEM (Tescan Mira3, Czech Republic, equipped with a Zeiss Sigma
148 300) and TEM (H-7650, AMT40, Germany) were used to studying the surface morphology of
149 the samples. Also, a 3 Flex instrument (Micromeritics, USA) was used to determine the surface
150 area of the prepared nanomaterials based on the adsorption-desorption isotherms. UV–visible

151 diffuse reflectance spectrophotometry (UV-Vis DRS, S 250, Germany) and a vibrating sample
152 magnetometer (VSM, Lakeshore, 7400 Series) were used to study the optical and magnetic
153 aspects of the prepared nanoparticles.

154

155 **2.4. Photo-Fenton-like catalytic tests**

156 According to the picture inserted in Fig. S1, all the experiments were carried out in a 50 mL
157 Pyrex cylindrical photocatalytic reactor. Meanwhile, a solar simulator lamp (Ocean optics)
158 fitted with cut-off filters at $\lambda \geq 400$ nm was used to simulate the vis-light. Fig. S2 shows the
159 emission spectra related to the abovementioned lamp with and without using a filter. The light
160 source was placed at a 15 cm distance from the reactor. In order to control the temperature, a
161 water circulator system was embedded around the reactor. For each run, 50 mL of pollutants
162 solution with the concentration of 50 μM was prepared and after adding a certain amount of
163 catalyst the pH of the solution was adjusted to be 8. Prior to irradiation, the minimum time
164 needed for the maximum adsorption of organic pollutants on the surface of the catalyst was
165 studied by stirring the suspension in dark. It was found out that the maximum adsorption of
166 three target pollutants was reached approximately after 30 min of stirring. Therefore, after 30
167 min of stirring in dark, the predetermined amount of HP was added to the suspension and the
168 irradiation of the suspension was started. Several samples were collected after 15 min, filtered,
169 and passed to a vial with 20 μL of methanol to stop the possible reactions. A high-performance
170 liquid chromatography (Alliance, waters, USA) using a C18 column was applied for measuring
171 the concentration of remaining pollutants in the reaction media. UPLC condition: injection
172 volume of 10 μL , flow rate of 0.2 mL min^{-1} , and isocratic elution comprising of 40 %
173 acetonitrile and 60 % ultrapure water were used as the best method for the detection of
174 pollutants. The retention time for CAF, BPA, and SIM was found to be 1.4, 4.4, and 3 min,
175 respectively. The relative pollutant concentration (%) in the reaction was determined from the

176 decay of pollutants as $\frac{C_t}{C_0}$ during the reaction time where C_0 and C_t are the initial concentration
177 and remaining concentration at time t , respectively. The reusability of the composite was studied
178 by collecting it after each degradation run and reusing it for other runs. Moreover, a TOC
179 analyzer (Shimadzu, TOC-L, Japan) was used for monitoring the mineralization of pollutants.
180 The dissolved concentrations of Cu, Cr, Fe, Co, and Zn were measured by an inductively
181 coupled plasma emission spectroscopy (ICP-AES, Jobin-Yvon ULTIMA C, USA). The real
182 wastewater was obtained at the outlet of the treatment from the “3 rivières” urban STP,
183 Clermont-Ferrand, France in December 2019 and main physico-chemical parameters are
184 reported elsewhere (Fazli et al., 2021c).

185

186 **3. Results and discussion**

187 **3.1. Characterization**

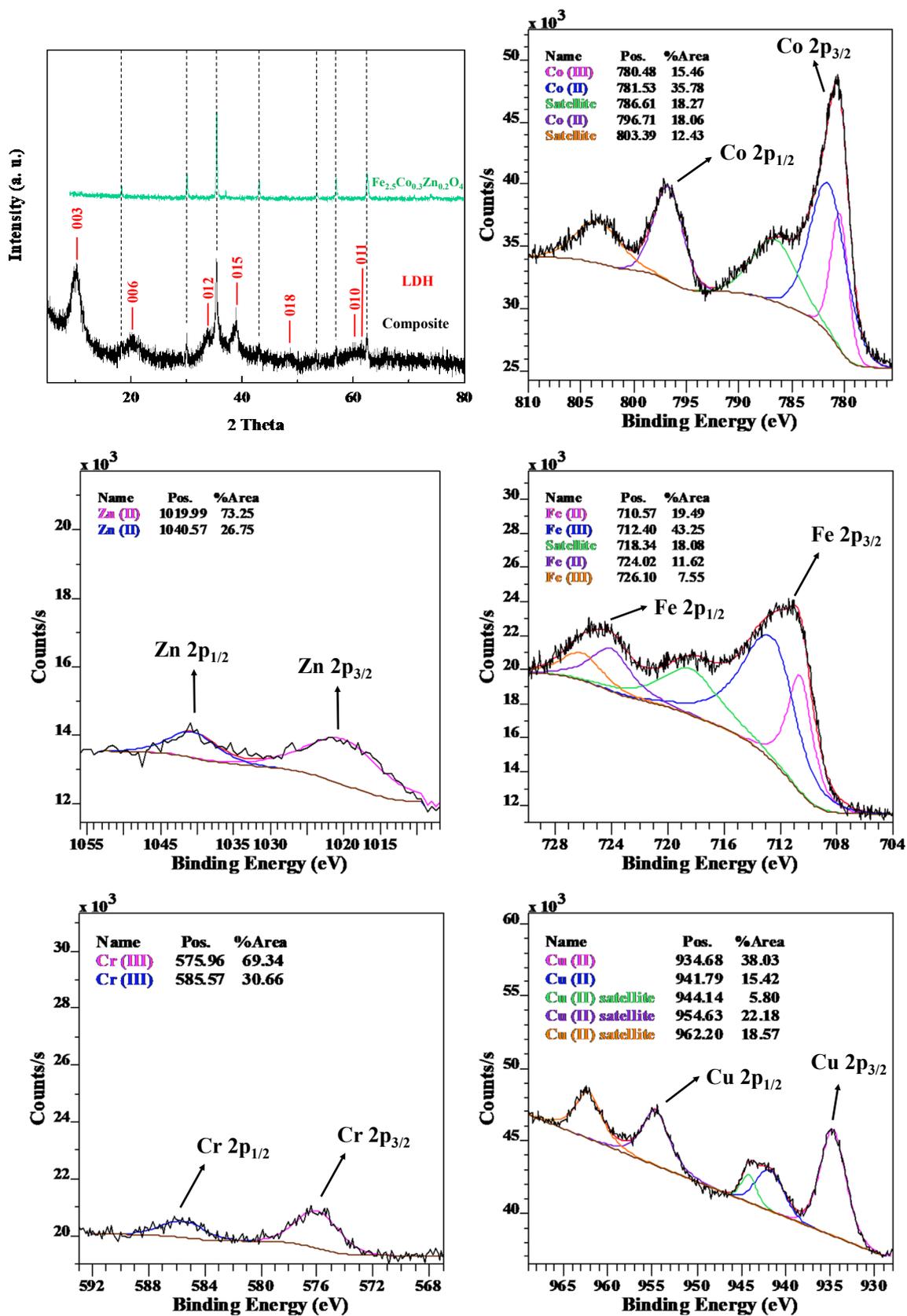
188 **3.1.1. Phase analysis: XRD and XPS**

189 The XRD patterns of the so-synthesized samples were plotted together for comparison in
190 Fig. 1. From the results, it is evident that the obtained positions of peaks for co-doped magnetite
191 are consistent with the standard diffraction data for magnetite (JCPDS file no. 01–089-0951)
192 (Fazli et al., 2021c). Furthermore, the XRD pattern related to the $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$
193 composite proved the existence of the specific peaks at the 2θ values of 18° , 30.05° , 35.9° ,
194 36.7° , 43.6° , 54.1° , 57.5° , and 62.5° relating to the co-doped magnetite and also the peaks at
195 10.66° , 21° , 35.1° , 38° , 47.05° , 60.05° , and 61.5° corresponding to CuCr-LDH (JCPDS file no.
196 00-035-0965) (Aghaziarati et al., 2020). The co-existence of the related peaks proved that the
197 phase of co-doped magnetite and LDH are well coupled with each other. In addition, no more
198 irrelevant peaks were observed in the XRD pattern of the composite, which revealed the purity
199 and crystallinity of the sample. However, in comparison with pure $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$

200 nanoparticles and LDH, the intensity of the related peaks in the XRD pattern of the composite
201 was mitigated. This phenomenon has been widely related to the weak crystallinity nature of the
202 composite arising from the formation of heterojunction between $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$ and co-doped
203 magnetite.

204 Furthermore, the high-resolution XPS (HRXPS) spectra of the so-synthesized
205 nanocomposite have been presented in Fig. 1. Considering the observed sub-peaks, the binding
206 energies of 710.57 and 724.02 eV ascertain the existence of Fe (II), while the related peaks for
207 Fe (III) are located in the 712.40 and 726.10 eV (Fazli et al., 2021c). The observed satellite
208 (shoulder) peaks are in coherence with the reported results of the other researchers (Rad et al.,
209 2018; Yamashita and Hayes, 2008) and affirm the presence of Fe (II). Moreover, the spectrum
210 corresponding to Co 2p_{1/2}, Co 2p_{3/2} revealed the presence of Co (II) (781.53 eV and 796.71 eV)
211 and Co (III) (780.6 eV) on the surface of the composite (Chen et al., 2014). The existence of
212 Zn 2p_{3/2} and Zn 2p_{1/2} were affirmed with the binding energies at 1019.99 eV and 1040.57 eV
213 (Nguyen et al., 2021), respectively. Furthermore, considering the HRXPS peak related to Cu
214 2p, the signals of Cu (II) was observed at 954.63 eV (Liu et al., 2016; Wu et al., 2006). An other
215 peak at 934.68 eV also confirmed the presence of Cu (II) (Liu et al., 2016; Wu et al., 2006). It
216 is worth noting that the satellite peaks characterize the materials which possess a d⁹
217 configuration in the ground state (Wu et al., 2006). Concerning this fact, the appeared peaks at
218 941.79 eV, 944.14 eV, and 962.20 eV relate to the 3d⁹ shell of Cu (II) (Liu et al., 2016). Finally,
219 Cr (III) has been recognized by the peaks positioned at the emerged peaks at 575.96 eV and
220 585.57 eV for Cr 2p.

221



222

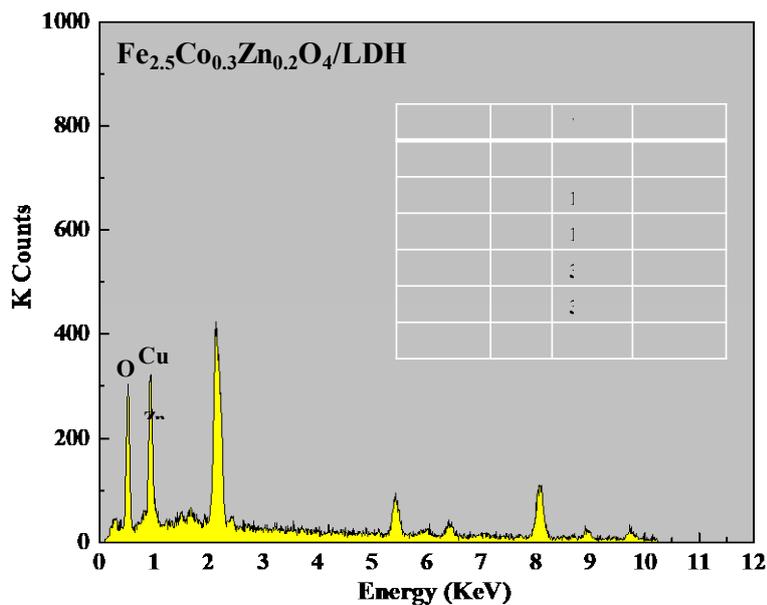
223 Fig. 1. XRD 2θ scans for the so-synthesized photocatalysts and high-resolution XPS spectra

224 of Fe 2p, Zn 2p, Co 2p, Cu 2p, and Cr 2p of Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composite.

225 **3.1.2. Morphological analysis**

226 Fig. S3 (a-c) shows the SEM images of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$, CuCr-LDH, and
227 $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite. The cubic and lamellar structures were observed for
228 the co-doped magnetite and pure LDH, whereas, the SEM image corresponding to the
229 composite revealed the coverage of co-doped magnetite nanoparticles with the LDH layers.
230 This was further proved by the TEM images (Fig. S3 (d-e)) and SEM elemental mapping.
231 According to the magnified TEM image of the composite, the composite consists of the cubic
232 co-doped magnetite and layers of Cu-Cr-LDH. Notably, Fig. 2 depicts the EDX spectra with
233 the relative weight and atomic percentage of the elements.

234



235

236 **Fig. 2.** The EDX spectrum of the $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite.

237

238 Moreover, based on Fig. 3 which present the SEM elemental mapping it can be deduced that
239 the composite contains the elements such as Co, Cr, Cu, Zn, and Fe which have been uniformly
240 distributed on the surface.

241

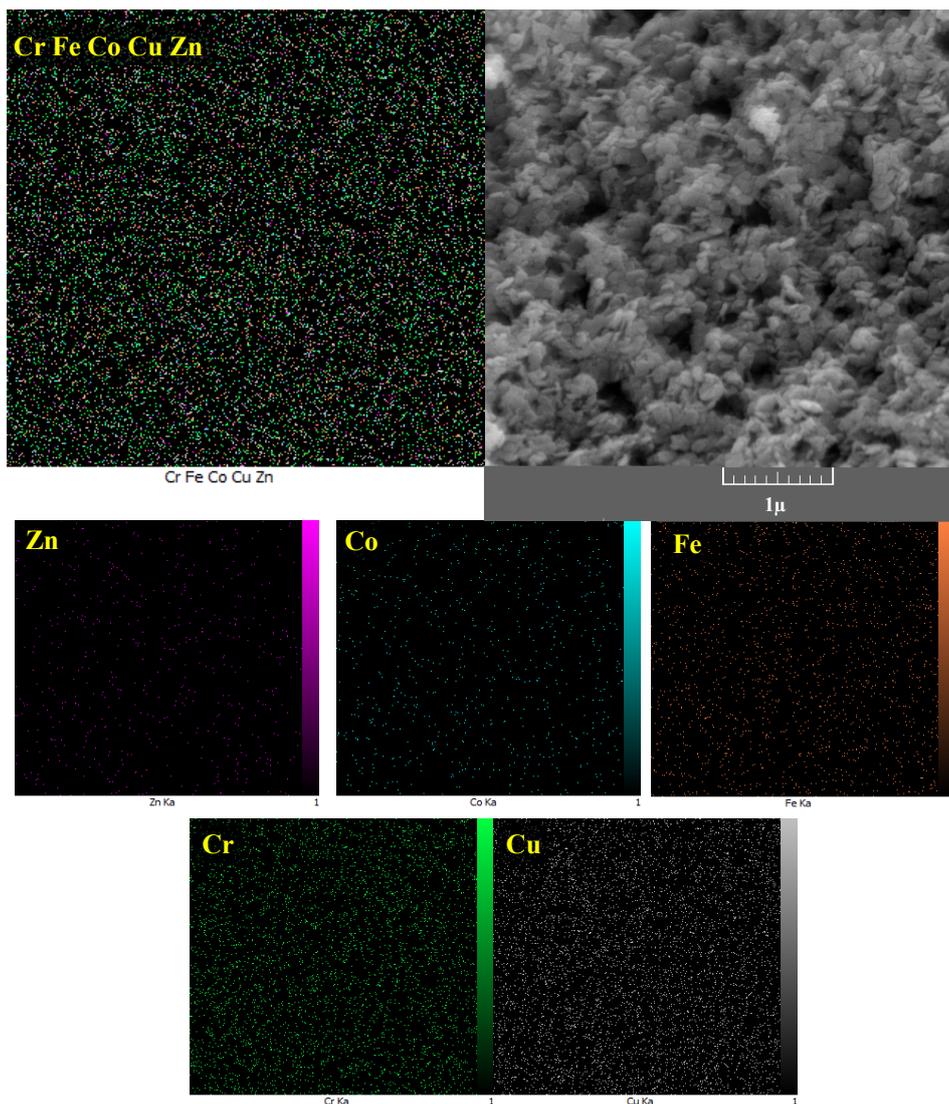


Fig. 3. SEM elemental mapping of the $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$.

242

243

244

245 Furthermore, the surface area, the volume of gas adsorbed (V_m) at standard temperature and

246 pressure, and pore volume extracted from the BET plot are inserted in Table 1. Accordingly,

247 the specific surface area of the composite was the largest, which in turn results in the higher

248 contribution of its surface in the photocatalytic degradation reactions. On the other hand, V_m

249 was increased in the order of co-doped < LDH < composite, depicting the higher porosity of

250 the sample. Moreover, it should be noted that the obtained pore volume of the

251 $\text{Fe}_{2.5}\text{Co}_{0.2}\text{Zn}_{0.3}\text{O}_4/\text{CuCr-LDH}$ composite is relatively higher than those reported for other

252 composites such as NiFe-LDH/rGO (Khataee et al., 2019) and magnetic Mg-Fe/LDH

253 intercalated activated carbon (Alagha et al., 2020), which acknowledges the mesoporous
254 characterization of the so-synthesized composite (Alagha et al., 2020).

255

256 **Table 1.** Textural properties of the so-synthesized samples extracted from the BET plot.

| Samples | S_{BET} ($\text{m}^2 \text{g}^{-1}$) | V_{m} ($\text{cm}^3 \text{(STP)} \text{g}^{-1}$) | V_{P} ($\text{cm}^3 \text{g}^{-1}$) |
|---|---|---|--|
| $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$ | 19.98 | 4.6 | 0.32 |
| Pure CuCr-LDH | 43.21 | 9.64 | 0.28 |
| $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ | 74.21 | 17.21 | 0.39 |

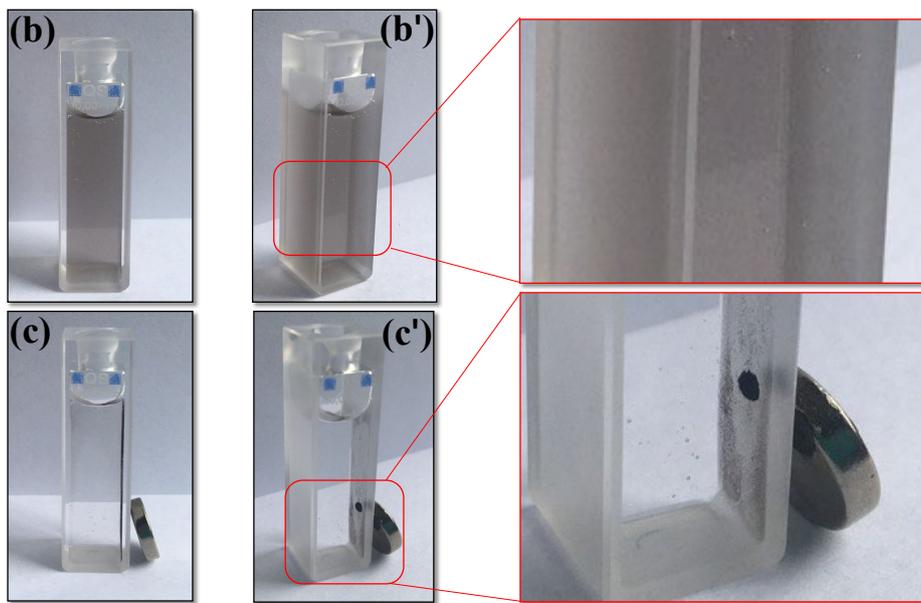
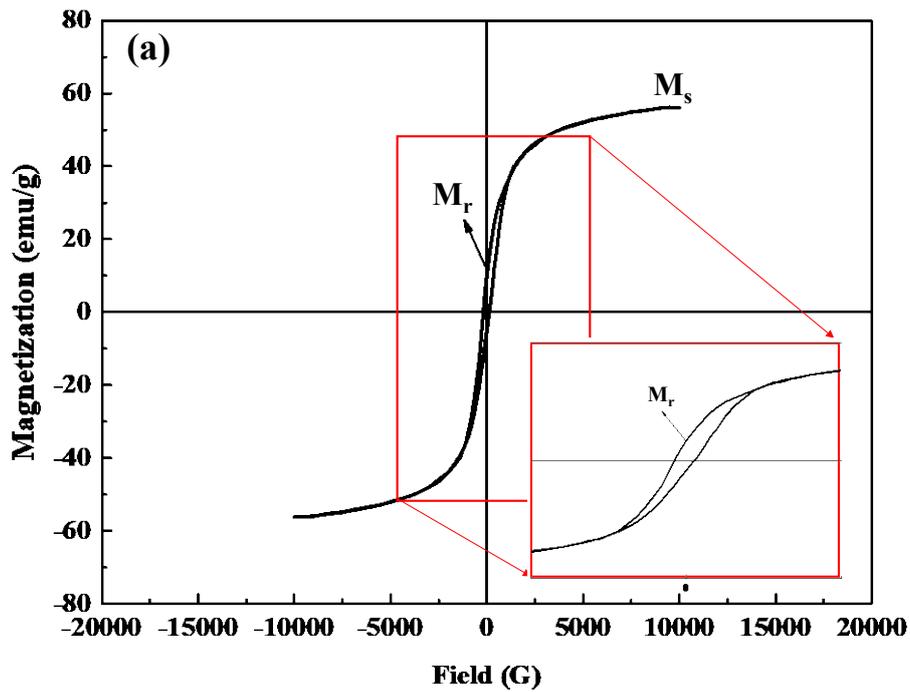
257

258 3.1.3. Optical and magnetic properties

259 To investigate the light response of the so-synthesized nanomaterials the UV–vis DRS
260 analysis was applied. It was proved that the doped elements such as Co and Zn could modify
261 the redox properties of the pure magnetite by preparing the oxygen vacancies in the magnetite
262 structure which favors the electron capture (Fazli et al., 2021c). However, the prepared
263 photocatalyst was not active under visible light irradiation. Considering Fig. S4, the composite
264 of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$ nanoparticles with the CuCr-LDH enhanced the visible light absorption
265 capacity. In conclusion, the effective light-absorbing capability of the composite could be
266 aroused from two main facts: (I) the promoted photocatalytic efficiency of magnetite by doping
267 Zn and Co metal ions to its structure, and (II) the inherent visible light absorption ability of
268 CuCr-LDH compared to the magnetite nanoparticles could narrow the bandgap and raise the
269 optical response of the final composite (Nguyen et al., 2021). The bandgap energies were
270 estimated using the Kubelka-Monk formula and Tauc's plot (Rad et al., 2018). The $(\alpha h\nu)^2$ - $h\nu$
271 curves of the samples were displayed in Fig. S4. Using tangent line to the curves shown in Fig.
272 S4, the bandgap of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$ nanoparticles, CuCr-LDH, and $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-}$
273 LDH composite was found to be 2.78, 2.69, and 1.66, respectively. The results confirmed the
274 existence of a redshift in the absorbance spectrum of the composite which could be the main

275 role in its greater excitation under the visible light irradiation to generate reactive electron-hole.
276 In our previous work (Fazli et al., 2021a), we realized that the combination of pure magnetite
277 and layered double hydroxide results in the effective electron transfer on the surface of the
278 composite leading to the lower recombination rate of the electron and holes. Consequently, the
279 low bandgap as well as the efficient electron transfer on the surface of the
280 $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite results in the increased production and availability of
281 the electrons on its surface.

282 In our previous work, we observed that Fe_3O_4 preserved its magnetic properties even after
283 co-doping of Zn and Co in its structure (Fazli et al., 2021c). In addition, the magnetic properties
284 of the prepared composite were evaluated by applying a systematic magnetization measuring
285 as a function of the used field. Fig. 4 shows that the appraised value for the magnetization
286 saturation (M_s) of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite was 56.14 emu g^{-1} , indicating that
287 the so-synthesized nanomaterial is a ferromagnetic phase (Kiziltaş et al., 2020). Hence, this
288 magnetic behavior allowed the composite to be separated from the reaction media by applying
289 an external magnetic field (inserted photo in Fig. 4).



290

291 **Fig.4.** (a) The VSM plot of the so-synthesized $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite, the
 292 front and side images of a spectrophotometer cell containing the suspension of
 293 $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite before (b-b') and after (c-c') applying an external
 294 magnetic field.

295

296 **3.2. Impact of different oxidation processes**

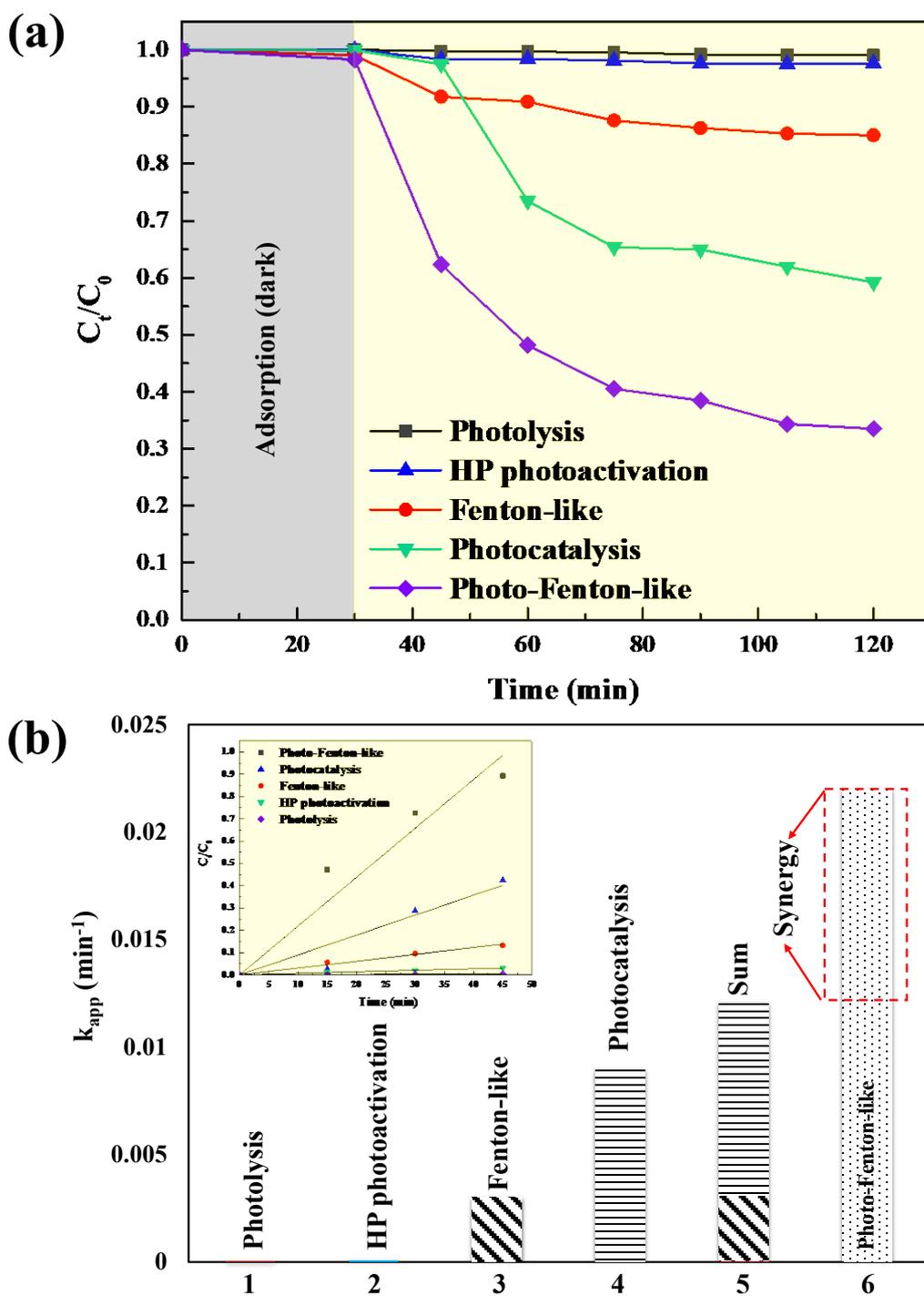
297 CAF was used as a model pollutant for evaluating the photo-Fenton-like degradation
298 performance using $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$, CuCr-LDH, and $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite
299 under visible-light irradiation. Moreover, for better evaluation of their photocatalytic activity,
300 the previously synthesized and characterized pure magnetite (Fazli et al., 2021c) and its
301 composite with CuCr-LDH (Fazli et al., 2021a) was also used (Fig. S5). Before starting the
302 photo-Fenton-like reactions, the adsorption trend of 50 μM of CAF on the surface of the
303 samples was studied. When the prepared solutions were stirred for 2 hours in the dark, the
304 adsorption/desorption of CAF was equilibrated after 30 min (the results of 2 hours have not
305 been reported). Therefore, in the case of stirring the solutions for 2h in the dark, the CAF
306 adsorption percentage of 0.15, 2.46, 9.11, 0.05, and 2.7 % were achieved in the presence of
307 Fe_3O_4 , $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$, CuCr-LDH, $\text{Fe}_3\text{O}_4/\text{CuCr-LDH}$, and $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$
308 composite, respectively. According to the results presented in Fig. S5, pure and co-doped
309 magnetite have almost no response under the visible light irradiation for the CAF degradation.
310 Also, the pure layered double hydroxide has shown more adsorption of CAF rather than its
311 degradation. Considering the results obtained from the BET analysis, the main reason for high
312 adsorption in the presence of the layered double hydroxide can be related to its higher surface
313 area. However, combined adsorption and photo-Fenton-like processes reduced C_t/C_0 of CAF,
314 where the degradation efficiency was to be 41.6, and 66.4 % for $\text{Fe}_3\text{O}_4/\text{CuCr-LDH}$, and
315 $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$, respectively. The higher degradation efficiency of CAF in the
316 presence of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite is in line with the obtained results from the
317 DRS analysis. The Low bandgap of the composite (1.66 eV), as well as, the presence of
318 structural defects and metal-semiconductor interface (Schottky interface) in co-doped
319 magnetite/LDH resulted in the higher production and better transference of electrons. This
320 phenomenon led to the production of more hydroxyl radicals in the presence of HP (Cao et al.,
321 2021). Our results followed the similar sequence obtained by the other researchers. For instance,

322 Cao et al (Cao et al., 2021). reported that the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\alpha\text{-Fe}_2\text{O}_3$ composite possesses the
323 best photocatalytic behavior in comparison with the pure $\alpha\text{-Fe}_2\text{O}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. Xiao et
324 al (Xiao et al., 2020) also reported that the composite of Cu doping magnetite with Cu/C showed
325 higher degradation efficiency for Rhodamine-B in comparison with the sole components.

326 As the $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite resulted in high photo-Fenton-like oxidation
327 of CAF, it was selected as the photocatalyst for evaluating CAF degradation under different
328 degradation processes (Fig. 5) such as photolysis (just vis-light), HP photoactivation (HP/vis-
329 light), Fenton-like (HP/composite), photocatalysis (vis-light/composite), photo-Fenton-like
330 (HP/composite/vis-light). It is worth noting that CAF removal under dark conditions
331 (adsorption) was lower than 2.7 %, therefore the related results have not been reported in Fig.
332 5. No direct activation of HP under visible light irradiation was observed as expected, while the
333 photocatalytic and Fenton-like processes raised the degradation rate of CAF to 40.8 and 14.9
334 %, respectively. The results also confirmed that the presence of visible light resulted in the
335 degradation efficiency of 3 times more than those for the sole Fenton-like process.

336 The enhanced degradation efficiency in the presence of the visible light source relates to the
337 acceleration of $\equiv\text{M(III)}/\equiv\text{M(II)}$ and $\equiv\text{M(II)}/\equiv\text{M(I)}$ cycles by the contribution of photogenerated
338 electrons coming from the excitation of the prepared semiconductor under visible light
339 irradiation (Wu et al., 2020). This enhances the Fenton-like reactions for the production of $\cdot\text{OH}$
340 in the presence of HP. Palanivel et al, (Palanivel et al., 2019) proved that the nanocomposite of
341 ZnFe_2O_4 and $\text{g-C}_3\text{N}_4$ showed the existence of a synergistic effect for the appropriate degradation
342 of Methylene blue in the presence of HP and under visible light irradiation. According to the
343 authors, the high-performance photo-Fenton-like process had been resulted from the efficient
344 separation of charge carriers and consequently more involvement of electrons in the
345 $\equiv\text{Fe(III)}/\equiv\text{Fe(II)}$ cycle.

346



347

348 **Fig. 5.** Degradation of caffeine under different processes (a). Studying the synergistic effect

349 of photo-Fenton-like process using $Fe_{2.5}Co_{0.3}Zn_{0.2}O_4/CuCr-LDH$ composite (b). Experimental

350 conditions: composite concentration of 0.5 g L^{-1} , $[caffeine] = 50 \mu\text{M}$, $[H_2O_2 (HP)] = 5 \text{ mM}$

351 and $\text{pH} = 8$.

352

353 In the context of water pollutant degradation processes, the existence of a synergy factor is
 354 essential (Fazli et al., 2021c). The synergy factor can be defined for those mixed degradation
 355 processes which lead to a better degradation efficiency in comparison with the sum of individual
 356 processes (Bansal and Verma, 2017). For this purpose, we studied the kinetics of CAF
 357 degradation by applying the pseudo-first-order model ($\ln \frac{C_0}{C_t} = k_{app} t$). The obtained correlation
 358 coefficient values ($R^2 > 0.9$) for all the processes reveal that the above-mentioned model fits
 359 well for the degradation of CAF under the applied photo-Fenton-like process. The rate constants
 360 (k_{app}) for different processes have been reported in Table 2.

361

362 **Table 2.** The impact of various processes on the pseudo-first-order rate constants of caffeine
 363 degradation.

| Processes | k_{app} (min⁻¹) | Correlation coefficient (R²) |
|------------------------------|--|--|
| Photolysis | 4.1×10^{-5} | 0.99 |
| Photoactivation of HP | 5.7×10^{-5} | 0.99 |
| Fenton-like | 0.003 | 0.99 |
| Photocatalysis | 0.008 | 0.95 |
| Photo-Fenton-like | 0.022 | 0.97 |

364

365 For studying in detail, a synergy factor (equation 1) was defined to determine the extent of
 366 the synergy effect of the photo-Fenton-like process compared with the photolysis,
 367 photoactivation of HP, Fenton-like, and photocatalytic processes. As a consequence, the
 368 calculated synergy factor values for the photo-Fenton-like process were calculated to be 2.2,
 369 verifying the enhancing performance in the integrated processes. In our previous work (Fazli et

370 al., 2021c), we also reported the synergistic effect of persulfate and HP activation using co-
371 doped magnetite.

$$372 \quad R = \frac{k_{\text{app}}(\text{photo-Fenton-like})}{k_{\text{app}}(\text{photolysis}) + k_{\text{app}}(\text{HPphotoactivation}) + k_{\text{app}}(\text{Fenton-like}) + k_{\text{app}}(\text{photocatalysis})} \quad (1)$$

373

374 **3.3. Investigating the influential factors on CAF degradation**

375 Various factors such as the amount of composite, pH, HP concentration, and light source are
376 known to have a significant effect on the Fenton-like and photo-Fenton-like processes (Fazli et
377 al., 2021c). The composite concentration can have a positive or even reverse effect on the
378 performance of different photocatalytic degradation processes (J. E. Yang et al., 2020).
379 Therefore, the relationship between the composite concentration and CAF degradation was
380 evaluated and the results were inserted in Fig. 6 (a). The increased composite concentration
381 from 0.1 g L⁻¹ to 0.5 g L⁻¹ was accompanied by the enhanced degradation efficiency for CAF.
382 It is assumed that the abundance of the active sites (J. E. Yang et al., 2020), as well as the
383 generation of different reactive free radicals (Fazli et al., 2021a; Rad et al., 2018) in the reaction
384 media, can be the major reason for the degradation of CAF. Nevertheless, beyond the observed
385 increasing trend, the composite concentration of 0.75 g L⁻¹ and 1 g L⁻¹ displayed an obvious
386 decline for the CAF degradation. In other terms, a higher increase in the amount of composite
387 inhibited the performance of the photo-Fenton-like process. The results obtained by the other
388 researchers are in good agreement with those of ours. Ghasemipour et al. (Ghasemipour et al.,
389 2020) reported that in the case of using 0.7 g L⁻¹ of the RGO10%/ZnO20%/MoS₂ composite,
390 the penetration of the utilized light to the surface of the composite decreased which was due to
391 the fact that the reaction media had become opaque.

392 Since the solution pH is one of the crucial operating parameters affecting the Fenton-like
393 and photo-Fenton-like reactions at the surface of the composite, we evaluated the effect of

394 different solution pHs on the degradation efficiency of CAF (Fig. 6 (b)). The results revealed
395 that both strong acidic or basic solutions led to lower CAF degradation efficiency. Commonly,
396 the Fenton-like reactions are more likely to occur in the lower pH values (Ye et al., 2021).
397 However, the CAF degradation efficiency was observed to be low in very acidic conditions.
398 Different researchers have also reported a lower performance of the photo-Fenton-like process
399 in strong acidic conditions (Li et al., 2021; Xiaoliang Fan et al., 2021). Moreover, for basic
400 solution, the lower degradation efficiency can be interpreted to I) the formation of less active
401 structures such as $\text{Fe}(\text{OH})_n$, and II) the decomposition of HP to O_2 and H_2O (Behrouzeh et al.,
402 2020; Morshed et al., 2020). For basic solutions, This phenomenon restricts the production of
403 different reactive species for the degradation of CAF reduces.

404 To better interpret the obtained results, the point of zero charges (pH_{pzc}) was measured for
405 the surface of the $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite which is expressed in section (3-6-
406 1) in details (Fig. S8). Based on the obtained results for pH_{pzc} and considering the protonated
407 form of CAF in the lower pHs ($\text{pH} < 10.4$) (Li et al., 2005a), the optimum degradation efficiency
408 of CAF occurred at pH 8. Indeed, the repulsion force in $\text{pH} < 6$ decreased the occurrence of
409 degradation reactions on the surface of the composite. It is worth noting that in contrast to the
410 homogenous photo-Fenton-like process, our proposed process showed higher performance for
411 the degradation of CAF in the solution pH value of 8; hence, this pH value was selected as the
412 optimum value for the subsequent test.

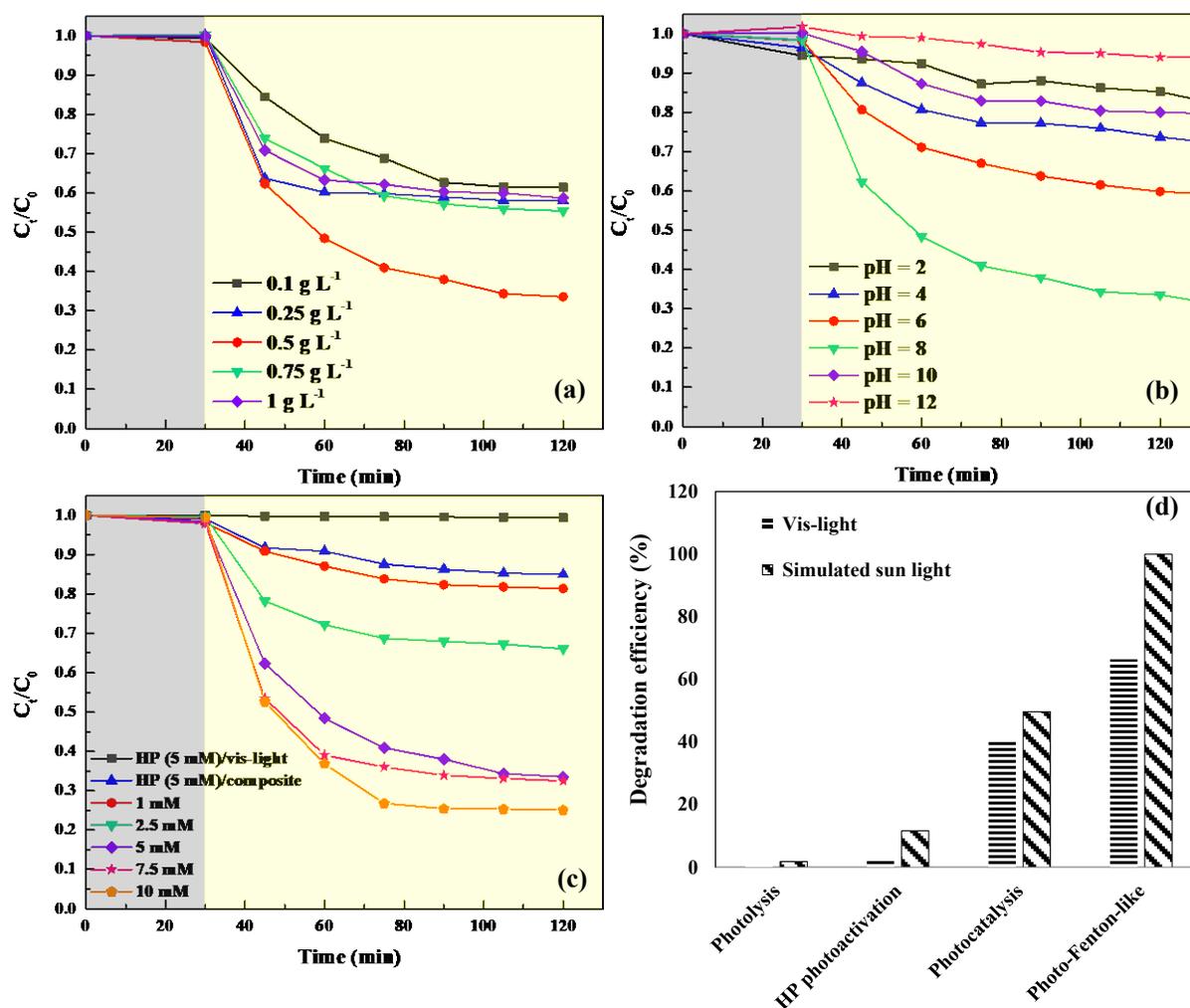
413 The impact of different HP concentrations on the degradation efficiency in the photo-Fenton-
414 like process was also studied and the results were presented in Fig. 6 (c). From the results, it
415 can be inferred that when more HP was introduced to the photo-Fenton-like process the
416 degradation of CAF was accelerated. The increased degradation performance of the photo-
417 Fenton-like process can be related to the fact that the composite was able to activate more
418 amount of HP to generate reactive hydroxyl radicals for the degradation of the target pollutants.

419 However, further increase of HP concentration up to 7.5 and 10 mM didn't show a significant
420 effect to accelerate the degradation efficiency of CAF under the optimal condition. Indeed,
421 when the concentration of HP reaches its critical point, the performance of $\cdot\text{OH}$ can be
422 restricted by its reaction with the excessive amount of HP. The results obtained by Yang et al.
423 (Yang et al., 2015) are in accordance with our results illustrated in Fig. 6 (c). They reported that
424 the decomposition of methylene blue was enhanced by increasing the HP concentration from
425 0.009 M to 0.176 M, whereas, further increasing it to 0.22 M demonstrated an adverse trend for
426 the removal efficiency of methylene blue. To identify that the composite has the major effect
427 on the degradation efficiency of CAF, 5 mM of HP was used for the degradation of CAF in the
428 absence of photocatalyst and presence of the visible light. The results imply that the sole HP is
429 not capable of CAF degradation, while the presence of composite and 5 mM of HP without vis-
430 light brought about 15% of CAF degradation efficiency. Considering the factors mentioned
431 above, we selected the HP concentration of 5 mM as the optimal concentration for the other
432 tests.

433 Moreover, a set of experiments were fulfilled to assess the effect and contribution of different
434 irradiating lights on the degradation efficiency of CAF during different processes. In this
435 context, a simulated solar light was provided using a Xenon lamp with or without UV-cut-off
436 filter ($\lambda > 400$ nm). As it is clear from Fig. 6 (d), photolysis of CAF has not occurred in the
437 presence of both light sources. Nonetheless, the presence of additional UV light in the simulated
438 solar light enhanced the degradation efficiency of CAF from 2.2, 41.2, and 66.5 % (in the
439 presence of vis-light) to 11.6, 50.1, and 100% for the HP photoactivation, photocatalysis, and
440 photo-Fenton-like degradation processes, respectively. The principal reason for the enhanced
441 degradation efficiency can be ascribed to the presence of UV fraction of the solar light (Li et
442 al., 2018). Taking account of this fact, the so-synthesized photocatalyst can absorb available
443 UV light, which in turn results in the generation of more electron-hole and subsequently more

444 reactive radical species. Therefore, the more reactive radical species produced in the reaction
 445 media, the more CAF degradation achieved. Furthermore, not only can UV light activate HP to
 446 produce more amount of $\cdot\text{OH}$ (Gabet et al., 2021), it accelerates the reduction of Fe (III) into
 447 Fe (II) (iron photolysis) as the essential agent for the Fenton-like reaction (Wu et al., 2020). Wu
 448 et al. (Wu et al., 2020) compared the effect of visible and simulated solar light for the Fenton-
 449 like degradation of tetracycline hydrochloride. Accordingly, they claimed that the existence of
 450 UV light in the simulated solar light boosted the degradation efficiency of the target pollutant
 451 from 34.5% to 78.3 %.

452



453
 454 **Fig. 6.** The effect of (a) composite concentration, (b) initial pH, and (c) H₂O₂ (HP)
 455 concentration on the degradation efficiency of caffeine under photo-Fenton-like degradation

456 process. (d) The effect of different light sources on the performance of various processes.
457 Experimental condition: composite concentration of 0.5 g L⁻¹, [caffeine] = 50 μM, [H₂O₂] = 5
458 mM and pH = 8.

459

460 **3.4. The stability and reusability of the photocatalyst**

461 The high photocatalytic activity, as well as a long-term stability of the composite, are the
462 vital factors in the practical applications; hence, the reusability potential of the
463 Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composite was tested in 5 cycles of recycling experiments for
464 CAF degradation. According to the results depicted in Fig. S6 (inserted figure), the degradation
465 efficiency of CAF from the first to 5th run decreased from 66.5 to 58.6%. Therefore, comparing
466 with the first cycle, around a 10 % decrease in the CAF degradation efficiency was gained,
467 revealing the persistence of composite stability. Our results in previous work (Fazli et al.,
468 2021c) demonstrated that 5 cycles of the UVA/Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/HP process resulted in a 10 %
469 decrease in Sulfalene degradation efficiency. Yang et al. (Yang et al., 2015) reported that 99%
470 of methylene blue was degraded in the cycle of the degradation process; however after six times
471 of using the removal efficiency of the composite reduced to almost 90%.

472 The stability of the Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composite was further proved by
473 comparing the XRD patterns of the freshly provided composite and the composite recycled after
474 5 times of the degradation process (Fig. S6). The XRD patterns illustrated that the so-
475 synthesized composite did not undergo significant structural variation even after five times of
476 usage. This fact was further verified by ICP analysis, which was applied to determine the
477 concentration of dissolved metal ions from the utilized composite in solution pH of 8.
478 Interestingly, the released concentration of Fe, Co, Zn, Cu, and Cr was attained to be 1.8 μg L⁻¹,
479 2.1 μg L⁻¹, 1.5 μg L⁻¹, 1.7 μg L⁻¹, and 1.2 μg L⁻¹, respectively. The achieved results were
480 found to be lower than the standard value reported by the World Health Organization (WHO)

481 (Fazli et al., 2021c, 2021a), indicating the excellent stability of the Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-
482 LDH composite during the applied degradation process. Therefore, our findings affirmed that
483 the Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composite is a stable photocatalyst, which can be used
484 continually in extended environmental applications.

485

486 **3.5. The effect of inorganic anions and radical scavengers**

487 The existence of different inorganic ions in natural water and wastewater can interfere with
488 the oxidation process of various water contaminants. In this context, different concentrations of
489 chloride and bicarbonate were used to identify their inhibitory impact on the photo-Fenton-like
490 degradation of CAF. As it is clear from Fig. S7 (a), in the case of using 5 and 10 mM of Cl⁻ a
491 slight decrease (4% and 9%, respectively) in the degradation efficiency of CAF was observed.
492 This effect can be explained considering the complex reaction system starting from the reaction
493 between [•]OH and Cl⁻ (reactions 1 to 3). In fact, the formation of less oxidant species such as
494 dichloride radical anion Cl₂^{•-} is only favored under acidic conditions (reaction 2) (Huang et al.,
495 2018a; Khataee et al., 2018).



499 HCO₃⁻ is one of the other effective radical scavengers that can convert the highly active
500 hydroxyl radicals to carbonate radicals (CO₃^{•-}) (reaction 4).

501



503 In fact, when we used different concentrations of HCO₃⁻ ions in the photo-Fenton-like the
504 CAF degradation efficiency was reduced from 66.5% to 58.9% and 52.8% using 5 and 10 mM

505 of HCO_3^- , respectively. Moreover, our results elucidated that in comparison with chloride the
506 HCO_3^- ions have a slightly stronger inhibiting effect on the degradation of CAF. Liu et al. (Liu
507 et al., 2020) studied the effect of 10 mM of chloride and bicarbonate in the photo-Fenton-like
508 degradation of nitrobenzene in the presence of 8 mM of HP and UV light. They also reported
509 that in comparison with the Cl^- ions, 10 mM of HCO_3^- showed a more inhibiting effect on the
510 degradation of nitrobenzene. Wu et al. (Wu et al., 2017) studied the effect of bicarbonate in the
511 degradation of 4-tert-butylphenol in the course of persulfate activation by Fe (III) species at the
512 solution pH of 8. According to their results, the presence of 2 and 10 mM of bicarbonate resulted
513 in the complete inhibition of 4-tert-butylphenol degradation. Moreover, Tao et al. (Tao et al.,
514 2021) studied the degradation of phenantrene by using UVB activation of hydrogen peroxide.
515 They have also studied the effect of bicarbonate on the phenantrene degradation. According to
516 their results, in the presence of 50 mM of bicarbonate, phenantrene concentration of 10 mg L^{-1} ,
517 and at pH of 8, the degradation efficiency of phenantrene was decreased from 33% to almost
518 16%, indicating a great inhibiting effect of bicarbonate in the presence of homogenous
519 activation of hydrogen peroxide. Heung et al. (Huang et al., 2018b) reported a 50% inhibition
520 of bisphenol A in the presence of 5mM of carbonates and UV- H_2O_2 process. Therefore, it is
521 evident that bicarbonate showed a lower inhibiting effect on CAF during our applied photo-
522 Fenton-like process.

523 Different scientists such as He et al. reported that $\bullet\text{OH}$, superoxide anion radical ($\text{O}_2^{\bullet-}$), and
524 photo-generated electron-hole are the primary active species that are responsible for the
525 degradation of organic pollutants through the photo-Fenton-like process. In this regard,
526 isopropanol alcohol (IPA), 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (Tempol),
527 chloroform, and KI have been widely used as the appropriate radical scavenger for $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$,
528 and photogenerated electron and holes, respectively (Fazli et al., 2021c; Jing et al., 2021;
529 Shyamala and Gomathi Devi, 2020). The degradation efficiency of CAF was evaluated in the

530 absence and presence of the abovementioned radical inhibitors and the results were
531 demonstrated in Fig. S7 (b). Owing to the obtained results, an obvious reduction of CAF
532 degradation efficiency was observed in the presence of IPA, which reveals the participation of
533 reactive $\cdot\text{OH}$ in the CAF decomposition. Also, to avoid the probable reaction of $\cdot\text{OH}$ with
534 other radical scavengers, IPA with its much higher second-order reaction rate constant ($k_{\cdot\text{OH}}$
535 $= 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Jin et al., 2018) were used in all the following experiments. Therefore, the
536 presence of IPA and tempol brought about an additional 13.5% inhibition in the CAF
537 degradation, which can be effectively ascribed to the contribution of $\text{O}_2^{\bullet-}$. On the other hand,
538 chloroform has been reported to react with both $\text{O}_2^{\bullet-}$ and photogenerated electrons ($k_{\text{O}_2^{\bullet-}}$
539 $= 2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{e^-} = 3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) (Guo et al., 2021). The holes were capture by the
540 available iodide ion and resulted in decreased degradation extent. However, to remove the
541 possible reaction between chloroform and superoxide or hydroxyl radicals, this experiment has
542 been fulfilled in the presence of tempol and IPA. The reduction was found to be approximately
543 10.6 %. Chloroform was used to study the participation of photogenerated electrons in the
544 degradation efficiency of CAF. The results showed less contribution of the photogenerated
545 electrons in the decomposition of CAF. Consequently, the active impact of the reactive species
546 can be denoted in the following raising order: $\cdot\text{OH} > \text{O}_2^{\bullet-} > \text{h}^+ > \text{e}^-$. The obtained results were
547 similar to the research conducted by Abdelhaleem (Abdelhaleem and Chu, 2020) et al., which
548 used a Fe^{III} impregnated N-TiO₂/HP/visible LED process for the degradation of a pesticide
549 (Carbofuran) from water. They also found out that the photo-Fenton-like degradation process
550 in the presence of Fe (III) impregnated N-TiO₂ resulted in more production and contribution of
551 $\cdot\text{OH}$ in the Carbofuran degradation.

552

553 **3.6. Simultaneous degradation of different water pollutants**

554 The effectiveness of the degradation process for the decomposition of different kinds of
555 organic pollutants is of great importance for different scientists (Chavan and Fulekar, 2020;
556 Rimoldi et al., 2017a). Therefore, we studied the photo-Fenton-like degradation of pollutants
557 mixture. With respect to the literature review, BPA and SIM have been classified as water
558 contaminants that are able to create health disorders (Jiang et al., 2020; Sahu et al., 2021).
559 Therefore, besides caffeine as the pharmaceutical water pollution, BPA and SIM were also used
560 as industry and herbicide contaminants. The detailed information of the compounds was given
561 in Table S1.

562

563 **3.6.1. Degradation and mineralization of pollutants mixture**

564 The dark adsorption curves of three target pollutants at the pre-irradiated composite surface
565 illustrated that adsorption/desorption equilibrium was reached less than 5% in 30 min (results
566 were not shown in Fig. 7). Besides, Fig. 7 (a) demonstrates the degradation of pollutants mixture
567 under the photo-Fenton-like degradation process. The results depicted that, the degradation
568 efficiencies of three organic pollutants (SIM, CAF, and BPA) with the total concentration of 25
569 μM were found to be almost 52, 48, and 37 %, respectively. Therefore, the utilized process was
570 found to be more effective for the degradation of SIM and CAF in comparison with BPA. The
571 reason can be ascribed to the reactions which take place on the surface of the composite. With
572 respect to the obtained $\text{pH}_{\text{pzc}} = 5.9$ for the composite (Fig. S8), in the case of a greater pH value
573 of the solution ($\text{pH} > \text{pH}_{\text{pzc}}$), the surface would be saturated with the negative charge, while in
574 the acidic solution ($\text{pH} < \text{pH}_{\text{pzc}}$) the surface of the composite would be stuffed with the positive
575 charges (Fazli et al., 2021c). Besides, the dissociation constant (pK_{a}) of CAF, BPA, and SIM
576 (Lee et al., 2020, p. 4; Li et al., 2005b) have been presented in Fig. S8. Thus, for the solution
577 pH of 8, the surface of the composite is negative which can attract the protonated CAF and the
578 least soluble SIM (6.2 mg L^{-1}) toward the surface of the composite. In the research study
579 belonging to Rimoldi et al. (Rimoldi et al., 2017b), similar results were achieved. They studied

580 the photocatalytic degradation of the mixture containing tetracycline, caffeine, paracetamol,
581 and atenolol in the presence of TiO₂. They reported that among the available pollutants poorly
582 soluble tetracycline showed a higher rate of photocatalytic degradation.

583 The effect of the photo-Fenton-like process on the mineralization of pollutants mixture was
584 investigated with the aim to study the fate of the produced intermediates in the treated water.
585 In this context, an experiment was conducted in the predetermined optimum condition and the
586 TOC removal was reported. The efficiency of the photo-Fenton-like degradation process in
587 terms of the TOC removal for the pollutants mixture was found to be ~ 68% after 4 h of process,
588 respectively. Therefore, the photo-Fenton-like process in the presence of the
589 Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composite can be determined as the reliable process for the
590 degradation and long-term mineralization of the pollutants mixture in the solution pH close to
591 the real wastewater. Ghasemipour et al. in their study on the photocatalytic degradation of
592 Aniline reported that at pH solution of 4, and the RGO10%/ZnO20%/MoS₂ concentration of
593 0.7 g L⁻¹, the TOC removal of 40% over the time of 120 min (Ghasemipour et al., 2020). They
594 also reported that more TOC removal of the pollutants mixture was obtained during the longer
595 photocatalytic degradation process.

596

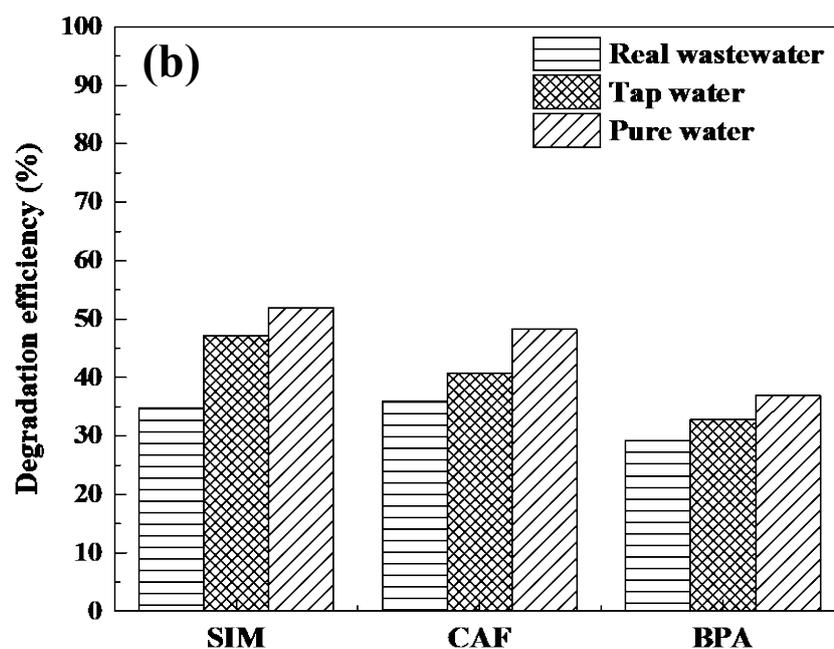
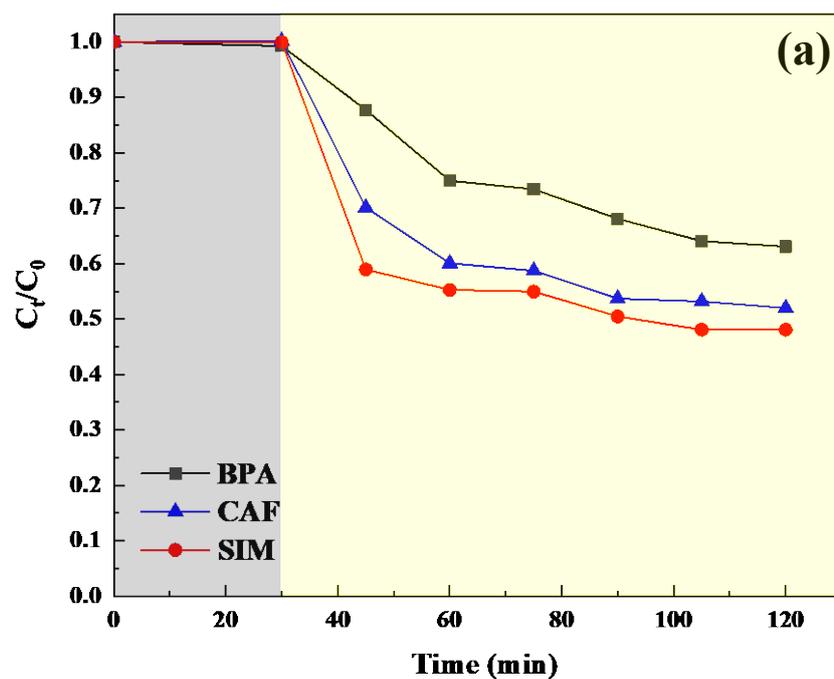
597 **3.6.2. Degradation of pollutants mixture in different water bodies**

598 In order to study whether the applied photo-Fenton-like process is suitable for practical
599 purposes, the degradation of the pollutant was assessed in different water types. In this regard,
600 we prepared the pollutants mixture solutions in the ultra-pure water, tap water from the
601 University Clermont Auvergne, and real wastewater obtained from the municipal wastewater
602 treatment plant of the Metropole of Clermont-Ferrand, France. The results presented in Fig. 7
603 (b) show that various water matrix resulted in quite different degradation efficiency. A decline
604 in the degradation efficiency of the pollutants in tap water can be related to the inhibition of

605 produced $\cdot\text{OH}$ by HCO_3^- (2.35 mM) that are present in this kind of water. Not only can the
606 hydrogenocarbonate anions occupy the active sites of the photocatalysts to reduce the
607 production of ROS, but also they react with the produced hydroxyl radicals and convert them
608 to the lower oxidative species (reaction 4).

609 Moreover, Fig. 7 (b) exhibits the accurate comparison for the effect of wastewater matrix on
610 the degradation of three target pollutants. Over 120 min of the process and in the real
611 wastewater, the degradation efficiencies of 34.8%, 36.0%, and 29.2% were respectively found
612 for each of SIM, CAF, and BPA from their mixture solution. The reason for lower efficiency
613 in comparison with those obtained in tap and ultra-pure water mainly depends on the presence
614 of organic matter and inorganic compounds in the real wastewater, which can compete with the
615 available reactive oxygen species such as hydroxyl radical, superoxide radical anion, and photo-
616 generated electron and hole. However, the results undoubtedly show that in the real wastewater,
617 the photo-Fenton-like process in the presence of $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite can
618 degrade more than 30 % of each three water contaminants from their mixture solution, which
619 is good evidence for the efficiency of the proposed performance for the degradation of a wide
620 range of pollutants in the wastewater. Ouyang et al. (Ouyang et al., 2020) declared the same
621 consequence in their research work. They reported that the existence of diverse inorganic and
622 organic substances in the acrylonitrile wastewater reduced the activity of the composite and the
623 generated reactive species during photocatalytic degradation.

624



625
 626 **Fig. 7.** (a) The adsorption and degradation of simazine (SIM), caffeine (CAF), and bisphenol
 627 A (BPA) from their mixture solution in pure water, (b) the effect of different water types on
 628 the degradation efficiency of pollutants in their mixture after 120 min of the process.
 629 Experimental condition: composite concentration of 0.5 g L^{-1} , total pollutant concentration of
 630 $25 \text{ } \mu\text{M}$, $[\text{H}_2\text{O}_2] = 5 \text{ mM}$, and $\text{pH} = 8$.

631

632 **Conclusion**

633 In this research, a $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4/\text{CuCr-LDH}$ composite with a well-defined structure was
634 synthesized with a co-precipitation method and its photocatalytic activity was compared with
635 those for Fe_3O_4 , CuCr-LDH, $\text{Fe}_{2.5}\text{Co}_{0.3}\text{Zn}_{0.2}\text{O}_4$, $\text{Fe}_3\text{O}_4/\text{CuCr-LDH}$ photocatalysts. Thereafter,
636 the synergistic effect of the photo-Fenton-like process for the degradation of an individual
637 pollutant (CAF) was assessed. Furthermore, a set of experiments were fulfilled to study the
638 effect of different composite concentrations, initial pH, HP concentration, and light sources
639 were evaluated. Accordingly, almost 67% of CAF was degraded in the presence of 0.5 g L^{-1}
640 composite concentration, HP (5mM), and at initial solution pH of 8. It was also observed that
641 the used composite preserved its structure and stability even after 5 cycles of successive
642 reactions and it was possible to separate it from the reaction media by applying an external
643 magnetic field. Moreover, in the presence of a simulated solar light without a UV cut-off filter,
644 the degradation efficiency was raised to be 100%. Comparing our results with those published
645 on homogenous photo-Fenton processes, chloride and bicarbonate showed lower inhibiting
646 effects on the degradation of CAF, which is an encouraging result for the future application.
647 Given the results obtained in the presence of different radical scavengers $\cdot\text{OH}$ was found to
648 contribute more to the photo-Fenton-like degradation of CAF. In addition, the mixture of CAF,
649 SIM, and BPA was subjected to the photo-Fenton-like degradation process to study their
650 removal efficiency. The TOC removal test depicted the existence of 68% TOC removal of
651 pollutants mixture after 4h of the photo-Fenton-like degradation process. This confirms the
652 complete conversion of the compounds to harmless compounds. Finally, the degradation of a
653 mixture of three contaminates was also investigated in the tap and real wastewater. Although
654 the probable impurities existing in the tap and wastewater reduced the degradation efficiency
655 of the pollutants, more than 30% removal efficiency was achieved for each of the pollutants (>
656 90 % for total pollutants mixture). In a conclusion, this work shows the feasibility of developing

657 new visible-light-responsive photocatalysts which reduces the limitation of AOPs such as their
658 pH-dependence, high cost, and generation of secondary pollution with the catalysts.

659

660 **Acknowledgments**

661 We acknowledge the French Embassy in Iran, the project I-Site CAP 20-25, the program
662 PAUSE of collège de France, and PAI (Pack Ambition Recherche internationale) SOLDE from
663 the Region Auvergne Rhône Alpes for the financial support of Arezou Fazli in this project.
664 Moreover, we would like to thank the Scientific and Technical Research Council of Turkey
665 (TUBITAK, Project Number: 120Y350) for the financial support of the research project. The
666 authors are thankful to Mhammed Banbakkar for conducting the ICP analysis and Dr.
667 Guillaume Monier for accomplishing the XPS analysis.

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672 **References**

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