1	Inactivation of harmful algal bloom by an environmentally friendly
2	photocatalyst under photo-Fenton-like degradation process
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23 Abstract

In the present work, the photo-Fenton-like process based on the use of the $Fe_{2.5}Co_{0.3}Zn_{0.2}O_4/$ 24 CuCr-LDH composite was applied for the removal of green algal cells. First, the biological 25 activity of the composite was proved with the antibacterial tests against the S. aureus; 26 27 thereafter, it was used for the removal of Scenedesmus quadricauda algal cells under the photo-Fenton-like process. Interestingly, compared with the individual processes, the photo-Fenton-28 29 like process displayed a synergistic effect in the deactivation of green algal cells. The effect of various parameters such as the initial concentration of the algal cells, concentration of the 30 31 hydrogen peroxide (HP), and the solution pH on the total algal. The maximuml was assessed. Maximum algal removal efficiency was obtained in the presence of the algal cell concentration 32 of 3.5×10^9 cells mL⁻¹, 0.1 g L⁻¹ composite, and HP concentration of 10 mM. Furthermore, the 33 34 microscopic and SEM images of the algal cells before and after the photo-Fenton-like process proved their appropriate destruction. The reduction of the chlorophyll content after 60 and 120 35 min of the process was observed revealing the destruction of the algal cell walls. Finally, the 36 disintegration of the macromolecules in the algal cell walls was proved by the GC-MS 37 technique. 38

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40 Keywords: Green algal removal; *Scenedesmus quadricauda*; Doped magnetite; Layered
41 double hydroxide; Antibacterial activity.

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44 **1. Introduction**

Harmful algal blooms (HABs) describe a natural phenomenon caused by the proliferation 45 of algal species in water bodies (X. He et al., 2021). Different factors such as sunlight, 46 temperature, climate variation, and the discharge of excessive amounts of nutrients such as 47 phosphorus and nitrogen can all have an impact on the photosynthesis and growth of the algal 48 cells, which consequently induces the appearance of algal blooms (Jin et al., 2022; Kislik et 49 50 al., 2018). Diatoms, dinoflagellates, cyanobacteria, and green algal cells like Scenedesmus *quadricauda* are the critical classes of organisms that produce algal blooms. Though diatoms 51 52 and dinoflagellates are commonly found in seawater blooms, cyanobacteria and green algal cells thrive in freshwater (Khataee et al., 2018a, 2018b; Paerl, 2009; Zou et al., 2020). 53

According to the literature review, the generated algal blooms result in the generation of the 54 unpleasant taste and odor in water and its turbidity (Glibert et al., 2014). In addition, some algal 55 blooms contain nocive toxins, which make water toxic and cause fish mortality (Fan et al., 56 2021). An effect on human health through the ingestion of infected seafood, skin touch, and 57 swallowing water during recreational activities has been proved (Hilborn and Beasley, 2015). 58 For instance, diatoms and dinoflagellates play a role in the development of toxins that cause 59 various poisonings in humans, focusing on the nervous and digestive systems (Ding et al., 60 2019). HABs are also responsible for economic losses, whether direct or indirect (Martino et 61 al., 2020). Direct effects comprise decreased income in the marine industry due to shellfish 62 63 closures, medical costs for human illness, removing algae from the water bodies, and investment costs in eliminating and tracking HABs. At the same time, indirect consequences 64 include a significant decline in tourism activity in the contaminated areas (Martino et al., 2020; 65 Shumway et al., 2018). 66

In order to overcome the challenges mentioned above aroused by algal proliferation,different treatment approaches have been presented (Chen et al., 2021). In this regard, different

69 techniques such as filtration (Sabiri et al., 2017), coagulation (Jiang and Kim, 2008), as well as biological methods have been applied (L. He et al., 2021). However, strategies mentioned 70 71 above can have unintended consequences such as secondary contamination and high cost (Sun et al., 2018). Advanced oxidation processes (AOPs) have sparked increased interest in 72 managing the algal bloom from contaminated water (Chae et al., 2019). Some researchers have 73 used AOPs as the pre-oxidation processes to coagulate HABs efficiently. For instance, Jia et 74 75 al. (Jia et al., 2018) studied the effect of the improved Fe (II) coagulation by the UV/H₂O₂ process to efficiently remove Microcystis aeruginosa. They reported that after 5 min of the pre-76 77 treatment process and the FeSO₄ coagulation, almost 94.7% of algae cells were removed.

Feng et al. (Feng et al., 2022) used an ultrasonic cavitation process to remove Microcystis 78 aeruginosa. Yang et al. (Yang et al., 2022) developed an electrochemical degradation process 79 80 to remove cyanotoxins released from the cyanobacterial harmful algal blooms. Zheng et al. (Zheng et al., 2022) reported that 90 % of *Microcystis aeruginosa* was removed using a sulfate 81 radical-based process. In our previous works, we reported the use of martite nanoparticles for 82 the catalytic ozonation of the appeared green algal cells (Oocystis sp. and Cosmarium sp.) 83 (Khataee et al., 2018a), as well as diatoms (Nitzschia sp.) (Khataee et al., 2018b) in the surface 84 water. Moreover, as pioneer AOPs, photocatalytic degradation processes were also used to 85 deactivate algal bloom (Gu et al., 2016; Mohan et al., 2022). However, the production of 86 87 secondary pollution, the low stability of ozone, the high recombination rate of photo-induced 88 electron-hole of photocatalysts, and the complexity and high cost of the applied processes decline their efficiency in the deactivation of algal bloom. 89

Fenton and photo-Fenton degradation processes are the other potent AOPs in which iron reacts with H_2O_2 and produces reactive hydroxyl radicals (*OH). Nonetheless, the homogenous Fenton processes were reported to work at a lower pH and yield much ferric hydroxide sludge (Du et al., 2022). In contrast, heterogeneous photo- Fenton catalysts are the potent alternative believed to reduce the production of secondary pollution, provide a high surface area for the
occurrence of reactions, and finally enhance the efficiency of Fenton reactions in the wide pH
values (Oller and Malato, 2021). In this regard, magnetically recoverable photocatalysts were
widely applied as the iron-rich catalysts in photo-Fenton-like processes. This relates to their
easy isolation from the reaction mixture after treatment (He et al., 2016; Zanchettin et al.,
2021).

100 Various photo-Fenton catalysts have been synthesized and used to degrade various organic water contaminants (Oller and Malato, 2021). However, to the best of our knowledge, there is 101 102 no report on applying the photo-Fenton-like process in the presence of magnetically recoverable photocatalyst for the effective deactivation of algal cells such as Scenedesmus 103 quadricauda. In our previous study (Fazli et al., 2021a, 2022), we studied the photo-Fenton-104 105 like degradation efficiency of different types of water contaminants in the presence of Fe₃O₄, Fe_{2.5}Co_{0.3}Zn_{0.2}O₄, Fe₃O₄/CuCr-LDH and, Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composites. Moreover, 106 from the previous studies, we knew that the materials containing Zn^{2+} and Cr^{3+} have an 107 appropriate influence on the deactivation of microorganisms (Fan et al., 2018). Therefore, these 108 efficient photo-Fenton catalysts were used to deactivate green algal cells as the biological water 109 pollutants in the current work. The specific purposes of the present work lie in I) reporting the 110 biological activity of the so-synthesized photocatalysts by evaluating the antibacterial activity 111 against the most dangerous species of staphylococcal bacterial, II) studying the effect of 112 113 different photocatalysts on the removal of Scenedesmus quadricauda algal cells by the photo-Fenton-like degradation process, and III) evaluating the effect of different physicochemical 114 parameters (such as catalyst and oxidant concentrations, pH and initial algae concentration). 115

117 **2. Experimental**

118 **2.1.** Chemicals

All used chemicals were of analytical grade and were used without further purification.

120 Scenedesmus quadricauda algal cells were collected from the Nahand dam in East Azerbaijan,

- 121 Iran. Hydrogen peroxide (H₂O₂ 35%, Merck, Germany), Ethanol (C₂H₅OH 96%, Jahan Alcohol
- 122 Teb Arak Co, Iran), Acetone (C₃H₆O \geq 99.8%, Merck, Germany) were used in experiments.

123 Nutrient agar and nutrient broth were provided by Biomark Laboratories (India).

Fe₃O₄, Fe_{2.5}Co_{0.3}Zn_{0.2}O₄, Fe₃O₄/CuCr-LDH, and Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH samples were used as they were prepared in our previous paper. Any further information about the synthesis and characterization of the samples was given in our previous paper (Fazli et al., 2021a, 2022).

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129 **2.2. Green algal culturing**

Water samples containing *Scenedesmus quadricauda* algal cells were kept in a liquid BG-11 culture medium and cultivated according to the previously published method (Khataee et al., 2018a). In order to provide the required light for the growth of green algal cells, the algal samples were exposed to 200 lx of white fluorescence light with a 12:12 h light: dark cycle. The algal solutions were maintained at room temperature. During cultivation, the algal solutions were shaken twice daily to avoid the attachment of algal cells. Any changes in the algal cells during the cultivation method were controlled using a microscope (Olympus CH-2).

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138 2.3. Photo-Fenton-like degradation of algal cells

The prepared algal solutions were added to a big container to obtain a homogeneous solution of the algal cells for any experimental use. In order to study the algal adsorption on the surface of the catalysts, and the algal removal by the photo-Fenton-like reaction, an appropriate volume of algal stock solution was used, and the total algal concentration was measured to be 3.5×10^9 cells mL⁻¹. Then, it was mixed with the pre-determined concentration of composite into a reactor of 50 mL. This reactor was placed at 20 cm of a LED lamp (50 W) as the visible light source and equipped with a stirrer. It is worth noting that before adding hydrogen peroxide (H₂O₂) and starting irradiation, the adsorption of the algal cells on the surface of the catalysts was also studied. After starting the reaction, 2 mL of the algal solution was withdrawn from the reactor, and the number of the live cells was counted immediately.

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150 **2.4. Counting the viable algal cells**

A hemocytometer and a microscope were used to count the number of viable algal cells. 151 According to the literature review, a hemocytometer is a typical counting cell that has been 152 used to count algal cells under a microscope (Karlson et al., 2010). A hemocytometer slide 153 with nine big squares, from which the middle square with 400 grids is considered for counting 154 the algal cells (Sui et al., 2014a). First, the surface of the hemocytometer was disinfected, and 155 then ten µL of the algal solution was added to the hemocytometer according to the method 156 described by Sui et al. (Sui et al., 2014a). The number of viable cells in the squares defined as 157 1, 2, 3, 4, and 5 was counted, respectively. Consequently, Eq. (1) was used to calculate the 158 algal density. 159

160
$$\rho = \frac{V}{80} \times 400 \times 10^4 \times f \tag{1}$$

where ρ represents the algal density (cells mL⁻¹), V is the counted viable algal cells in 80 counting grids (1, 2, 3, 4, and 5), and 400 is the whole number of grids within the central square, and f is the dilution factor. Moreover, each of the large squares has a volume of 100 nL; therefore, 10⁴ is the conversion factor to count the number of cells per mL (Sui et al., 2014b). 166 **2.5.** Preparing samples for Scanning Electron Microscopy (SEM)

167 A pre-determined volume of the sample was removed from the reactor before and after the 168 photo-Fenton-like process. According to the method described in the previously published 169 article (Khataee et al., 2018a), the algal cells were separated from their suspension by using a 170 filter paper (with a pore size of 2 μ m). The collected algal cells were then hydrated with a pre-171 determined amount of acetone, kept at 4 °C for one night, and dried in a vacuum. In order to 172 observe any morphological alteration in the algal cells, a scanning electron microscope (Mira3, 173 Tescan, Czech Republic) was applied.

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175 **2.6. Measuring chlorophyll-a content**

In order to determine the chlorophyll-a content, the following method was applied: 10 mL of algal samples were withdrawn from the reaction media at 0, 30, 60, 90, and 120 min of the Photo-Fenton-like degradation process. After filtering the samples, they were mixed with 10 mL of acetone (\geq 99.8%). After shaking the mixture vigorously, the chlorophyll-a content was analyzed using a spectrophotometer (Lightwave S2000, England) at the λ_{max} of 661.6 and 644.8 nm. Consequently, the equations proposed by Wellburn and Lichtenthaler (El-Shenody et al., 2019) were used to calculate the chlorophyll-a concentration.

183 Chlorophyll-a concentration =
$$(11.75 A_{661.6} - 2.35 A_{644.8})$$
 (2)

184

185 2.7. GC-MS analysis

The produced by-products during the degradation process were studied by GC-MS analysis.
To this end, two samples were collected from the solution before and after 120 min of the
reaction. The resulted organic compounds from the algal cell destruction were extracted by
two-times addition of diethyl ether (30 mL). When the solvent was evaporated, 100 µL of N,
O-bis-(trimetylsilyl)-acetamide was added and followed by vigorously stirring for 15 min in a

water bath at 60 °C. Afterward, the sample was injected into an Agilent 6890 gas chromatograph with a HP-5MS capillary column (30 m in length - 0.25 mm of diameter) equipped with an Agilent 5973 mass spectrometer (Agilent, Palo Alto, Canada). The temperature program was as follows: 50°C for 40 min, and the temperature was raised to 300°C at the rate of 8 °C. It was kept at this temperature for 4 min. Moreover, the temperature related to the inlet, transfer, and detector were 250, 250, and 300 °C, respectively. The resulted chromatogram was compared with the Wiley7Nist05.L database.

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199 2.8. Antibacterial activity test for the photocatalysts

Staphylococcus aureus (S. aureus, ATCC 25993), as a Gram-positive bacteria, was cultured 200 at 37 °C overnight to investigate the antibacterial activities of the so-synthesized 201 202 photocatalysts. According to the schematic figure (Fig. 1), the antibacterial test consists of three steps (Sadeghi Rad et al., 2021): (1) 100 µL of nutrient broth was injected into the entire 203 column. (2) Then, 100 μ L of catalyst suspension (400 μ g mL⁻¹) was transferred to the well of 204 the first column. Afterward, the suspension was shaken, gotten homogenized, and then 100 μ L 205 of column 1 was added to the well of the second column. After shaking suspension and 206 homogenizing, 100 µL of this column was added to the third column. This procedure was 207 repeated up to column 11. Finally, (3) S. aureus (10⁵ CFU mL⁻¹) was injected into all wells of 208 12 columns. Then the samples were kept at 37 °C for 24 hours. The transparent wells were then 209 210 cultivated in the nutrient agar plates to study the MIC (minimum inhibitory concentration) and MBC (minimum bactericidal concentration). 211





Fig. 1. Schematic figure of the antibacterial activity test for the so-synthesized
 photocatalysts.

217 **3. Results and discussion**

218 **3.1.** The antibacterial evaluations of so-synthesized photocatalysts

Before evaluating the removal of algal cells under the photo-Fenton-like degradation 219 process, the biological activity of the so-synthesized photocatalysts was studied. In this context, 220 221 the antibacterial activity of photocatalysts was assessed against the Staphylococcus aureus (S. aureus). The results are presented in Tables 2 and 3 and Fig. 2. MIC demonstrates the 222 concentrations with no turbidity after the first incubation; however, the apparent microbial 223 growth can be observed in the second incubation. On the other hand, MBC defines the sample 224 concentration for which, after the first and second incubations, no turbidity or bacterial growth 225 226 can be recognized (Thuc et al., 2016).

In Fig. 2 and Table 1, it was recognized that there is no turbidity in the existence of 200, 100, and 50 μ g mL⁻¹ of LDH, Fe₃O₄, and composite. The transparent content of chambers was cultivated in the agar plate. All samples with a concentration of 50 μ g mL⁻¹ illustrated no

230 growth of bacteria on the agar plate (Table 2, and the inserted photo on the right side of Fig. 2). Based on the literature review, the structure of the LDH-based catalysts plays an essential 231 role in antibacterial activity (Awassa et al., 2022). In addition, the interposed transition metals 232 such as Cr, Cu, Fe, Zn, and Co can promote antibacterial activity (Camacho-González et al., 233 2019). Sadeghi Rad et al. (Sadeghi Rad et al., 2022) reported the exact amounts of MIC and 234 MBC for antibacterial evaluation of zinc chromium layered double hydroxide/rGO. In their 235 other work (Sadeghi Rad et al., 2021), the MIC/MBCs was identified at the same range while 236 exposing Fe₃O₄/Cr/Ce/rGO to S. aureus bacteria strain. They also reported that the chambers 237 238 containing the as-synthesized proved no turbidity and no bacterial growth on the agar plate.

Composite concentration	Turb	idity ii	1 bro	th							
$(400 \ \mu g \ mL^{-1})$	200	100	50	25	12.5	6.25	3.12	1.56	0.78	0.39	0.195
S. aureus	×	Х	×	\checkmark							
co-doped Fe ₃ O ₄	Turb	idity ii	n bro	th							
concentration	200	100	50	25	12.5	6.25	3.12	1.56	0.78	0.39	0.195
$(400 \ \mu g \ mL^{-1})$											
S. aureus	×	Х	×	\checkmark							
CuCr-LDH	Turb	idity iı	1 bro	th							
concentration	200	100	50	25	12.5	6.25	3.12	1.56	0.78	0.39	0.195
(400 μg mL ⁻¹)											
S. aureus	×	X	×	\checkmark							

Table 1. Effect of the synthesized samples in the deactivaton of S. aureus.

 \checkmark = Turbidity; \times = without turbidity.



Fig. 2. MIC and MBC of A: composite, B: co-doped Fe₃O₄, and C: CuCr-LDH with *S. aureus*.

Table 2. Growth of S. aureus using different concentrations of the samples.

Composite concentration	Growth on agar			
$(400 \ \mu g \ mL^{-1})$	200	100	50	
S. aureus	×	×	×	

co-doped Fe ₃ O ₄	Growth on agar		
concentration	200	100	50
$(400 \ \mu g \ mL^{-1})$	200	100	50
S. aureus	×	Х	×
CuCr-LDH concentration	Gro	wth on a	gar
$(400 \ \mu g \ mL^{-1})$	200	100	50
S. aureus	×	×	×

 \checkmark = Growth; \times = Without Growth.

248

249 **3.2. Algal removal under photo-Fenton-like process**

The so-synthesized photocatalysts were then examined for the removal of *Scenedesmus quadricauda* algal cells by the photo-Fenton-like degradation process. Considering the results obtained in our previous work (Fazli et al., 2022), the $Fe_{2.5}Co_{0.3}Zn_{0.2}O_4/CuCr$ -LDH composite is more active in the degradation of different industrial pollutants under a photo-Fenton-like process. Therefore, the $Fe_{2.5}Co_{0.3}Zn_{0.2}O_4/CuCr$ -LDH composite was selected to evaluate its photocatalytic efficiency for removing the algal cells under the photo-Fenton-like process.

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257 **3.2.1. Impact of influential factors on the algal removal**

The catalyst concentration represents a significant parameter affecting the algal removal efficiency (Khataee et al., 2018a). In this regard, the catalyst concentrations of 0.02, 0.04, 0.1, 0.2, and 0.3 g L⁻¹ were used to study the influence of Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composite on the algal removal. Before starting the photo-Fenton-like process, the adsorption of the algal cells was evaluated. The results demonstrated no adsorption of algal cells on the surface of the composite. Moreover, 0.02 g L⁻¹ of the catalyst showed almost no increasing effect on the algal removal efficiency. Therefore, the result of this concentration was not displayed in the figure.

Considering the results presented in Fig. 3 (a), as the concentration of the composite increases 265 from 0.04 to 0.1 g L^{-1} , the algal removal enhances. This increase can relate to the availability 266 of more composite surfaces leading to the formation of more amount of •OH via the photo-267 Fenton-like reaction, which in turn destroys the algal cells. Any further increase in catalyst 268 concentration (from 0.1 g L⁻¹ to 0.3 g L⁻¹) led to a decrease in algal removal efficiency. This 269 phenomenon ascribes to two factors as follows: 1) a higher concentration of composite results 270 271 in the accumulation of nanoparticles, which declines the contribution of the composite surface on the Fenton-like or photo-Fenton-like reactions; moreover, 2) the high concentration of the 272 273 composite avoids the penetration of visible light inside the solution (Fazli et al., 2022). The lower light contribution reduces the photocatalytic efficiency of the composite in the 274 degradation process, which confirms the critical importance of applied visible light and 275 276 composite in algal removal. Since a maximum algal removal efficiency was achieved with 0.1 $g L^{-1}$, this amount of composite was set as the optimal concentration for the other experiments. 277 The concentration of HP is another essential factor in the performance of the photo-Fenton-278 like degradation process. Therefore, further experiments were carried out to investigate the 279 effect of different hydrogen peroxide concentrations (such as 2.5, 5, 10, 15, and 20 mM) on the 280 algal removal efficiency, as depicted in Fig. 3 (b). As the degradation efficiency was too low 281 in the case of using 2.5 mM, this concentration was not reported in Fig. 3 (b). On the other 282 hand, the results revealed that the photo-Fenton-like process in the presence of 5mM of HP 283 284 resulted in 39 % of algal removal efficiency after 2 hours, whereas increasing the concentration of HP from 5 mM to 10 mM brought about the algal removal efficiency almost 2.5 times more. 285 In the presence of a high concentration of HP, more reactive radical species (ROSs) such as 286 •OH can be produced under the photo-Fenton-like process. The higher amount of generated 287 ROSs directly correlates to the algae removal efficiency. In contrast, a high concentration of 288

HP (15 and 20 mM) noticeably reduced the algal removal, which can be due to the H_2O_2 scavenging effect of $^{\bullet}OH$.

Previously it has been confirmed that the pH of the solution directly affects the performance 291 of the photo-Fenton-like degradation processes (Xu et al., 2021) by impacting the activity of 292 HP and the surface activity of the composite. The initial algal solution pH was found to be 293 around 8. However, any change in the pH value of the solution resulted in the attachment of 294 295 the Scenedesmus quadricauda algal cells to each other, making their counting almost impossible. Therefore, all the experiments were performed at their initial pH of 8. Moreover, 296 297 the effect of the initial algal cell concentration on removal performance was assessed. Fig. 3 (c) depicts the algal removal efficiency in the presence of an initial concentration of 2.5×10^9 . 298 3.5×10^9 , 4.25×10^9 , and 6.0×10^9 cells mL⁻¹, while all the other effecting parameters are kept at 299 the obtained optimal values (the catalyst concentration of 0.1 g L⁻¹, HP concentration of 10 300 mM, and the initial pH value of 8). Fig. 3 (C) is clear evidence that the higher concentration of 301 the algal cells resulted in the lower removal efficiency. This phenomenon can be justified in 302 the way that the concentration of generated ROS in the reaction media was constant, while it 303 was not sufficient for the deactivation of more cells in the presence of higher algal cell 304 concentration, and consequently, the algal removal efficiency was declined (Khataee et al., 305 2018a). 306

Moreover, the visible light absorption via the green algal cells can reduce the penetration of photons and leads to a screening effect. This phenomenon produces a lower amount of reactive radical species, which reduces algal removal efficiency. Hence, the subsequent experimental studies were conducted in the presence of 3.5×10^9 cells mL⁻¹. The same behavior was observed for the removal performance of diatom *Nitzschia sp.* cells in the catalytic ozonation process (Khataee et al., 2018b). Accordingly, when the diatom concentration was enhanced from

100 100 (a) (b) 0.10 g L⁻¹ 10 mM 0.20 g L⁻¹ 15 mM 0.04 g L⁻¹ 20 mM80 80 0.30 g L⁻¹ $5 \, \mathrm{mM}$ 60 60 DE (%) DE (%) 40 40 20 20 0 k 0 <mark>4</mark> 0 20 40 40 60 100 60 80 100 120 20 80 120 Time (min) Time (min) 100 (c) 2.50×10⁹ cell mL⁻¹ 3.50×10⁹ cell mL⁻¹ 4.25×10⁹ cell mL⁻¹ 80 6.00×10⁹ cell mL⁻¹ 60 DE (%) 40 20 0 0 20 40 60 80 100 120 Time (min)

313 2.0×10^5 to 4.6×10^5 cells mL⁻¹, the removal efficiency decreased from 100 % to 36.8% within 314 20 min.

315



Fig. 3. Effect of the composite concentration (a), HP concentration (b), and algal cells concentration (c) on the algal cell removal efficiency (DE (%)). Apart from the studied parameter, the other parameters were kept the same. Experimental conditions: composite concentration of 0.1 g L⁻¹, [HP] = 10 mM, algal cell concentration of 3.5×10^9 cells mL⁻¹, and pH = 8.

323 3.3. Performance of different processes on the algal removal

After assessing the effect of different factors on the photo-Fenton-like process of the algal cells, some control experiments were conducted to study and compare the performance of the individual processes (Fig. 4 (a)). Fig. 4 (b) presents the pseudo-first-order kinetic rate constants (k_{app}) calculated using $\ln \frac{C_0}{C_t} = k_{app}t$ equation.

According to the results, the algal adsorption on the surface of the catalyst was almost zero; 328 this can be related to the interaction between the surface of the catalyst and the algal cell walls. 329 The algal cell walls contain different amino acids sensitive to the pH of the environment (Li et 330 331 al., 2018). Therefore, according to the pKa of amino acids, a pH close to 8 can deprotonate (Li et al., 2018). On the other hand, the pH_{pzc} of the composite was found to be 5.9 in our previous 332 work (Fazli et al., 2021a). Consequently, in the solution pH value of 8, the repulsion force of 333 334 the composite's negatively charged surface and amino acids could result in low adsorption (Khataee et al., 2018a). 335

The sole photolysis (under visible light) has shown no adverse effect on the viability of the 336 algal cells, resulting in no algal removal efficiency. It is worth noting that in all the experiments, 337 the solution was mixed with a magnetic bar, and the rate of the stirring was kept the same in 338 339 all the experiments. However, there is no removal efficiency in the adsorption and photolysis processes in which the photo-Fenton-like reactions do not occur. This suggests that the 340 agitation does not affect the destruction of the algal cells. Moreover, before starting different 341 photo-Fenton processes, the direct disinfecting effect of HP was also studied on the algal 342 removal. It was observed that in the addition of just HP almost 9% of the algal removal 343 efficiency was achieved, which can be due to the chemical disinfection (oxidation) of the algal 344 345 cells with HP (Flores et al., 2012). The photoactivation of HP (HP/visible light), as well as the Fenton-like (HP/composite), processes resulted in approximately the same level of degradation 346 efficiency in 120 min of the processes (around 10%). Therefore, the above processes do not 347

348 play an essential role in the alga removal efficiency. Moreover, although the photocatalytic 349 process individually raised the algal removal to 20%, the photo-Fenton-like process was the 350 most effective process for deactivating algal cells.

Synergy is one of the variables to assess the practical effect of integrating different processes rather than the algebraic sum of the processes. In this regard, the obtained rate constants for the individual processes presented in Fig. 4 (b) were used in the following equation to calculate the amount of synergy factor for the photo-Fenton-like process. It is worth noting that the rate constant for the adsorption and direct photolysis was found to be zero; therefore, they were not considered in the figure and the following equation.

357

358 Synergy factor =
$$\frac{k_{app (photo-Fenton-like)}}{k_{app (disinfection with HP)^{+}k_{app (HP photoactivation)^{+}k_{app (Fenton-like)^{+}k_{app (photocatalysis)}}}$$
(3)

359

Accordingly, the synergy factor was calculated to be 4.4, revealing the effective 360 361 performance of the degradation process in the production of active radical species (Fig. 4 (c)). Therefore, this resulted in a higher algal removal performance than the sole processes (Xu et 362 al., 2021). The existence of the synergy factor can be related to the 1) the production of useful 363 photogenerated charge carriers (Wang et al., 2021), 2) the contribution of the produced 364 electrons in the regeneration of \equiv M (II) and \equiv M (I) of the composite (Ahmadi et al., 2017), and 365 3) the formation of further •OH by the Fenton-like reactions in the presence of Fenton reagents 366 $(\equiv M (II), \equiv M (I), and HP)$ (Xie et al., 2020). 367

Different scavengers were used to evaluate the contribution of different ROS in the degradation of algal cells. In this context, the inhibiting compounds such as tert-butanol (TBA), benzoquinone (BQ), and potassium iodide (KI) were used to scavenge the produced respectively 'OH, 'O₂, and h⁺ (Fazli et al., 2021b). Based on the results presented in Fig. 4(d), the degradation efficiency is diminished from 93 % to 32 % by utilizing TBA. This reduction

could be attributed to the interaction of TBA with •OH, which reduces algal removal. 373 Additionally, as a famous 'O₂ scavenger, BQ was used to study the effect of superoxide radicals 374 on the algal removal efficiency. Moreover, to remove the possible contribution of •OH in 375 studying 'O₂ contribution, TBA and BQ were added simultaneously. Therefore, with both TBA 376 as potent 'OH scavenger, the contribution of BQ in inhibiting 'OH radicals can be neglected. 377 Therefore, the rest of the reduction in removal efficiency can be ascribed to the existence of 378 379 'O₂. 26 % degradation efficiency decline was observed in the presence of TBA and BQ, revealing the existence and contribution of 'O₂ radicals. Furthermore, as a photo-Fenton-like 380 381 degradation process, it was supposed that h⁺ could contribute to the destruction of algal cells. Accordingly, 9% more inhibition was obtained in the presence of KI, verifying the direct effect 382 of h⁺ in the destruction of algal cells. 383

In addition, ICP analysis was conducted for the treated samples to evaluate further the 384 contribution of the heterogeneous photo-Fenton-like process in the destruction of algal cells. 385 According, at a solution pH of 8, the dissolved Cu, Cr, Fe, Zn, and Co were found to be 1.5 µg 386 L^{-1} , 1.3 µg L^{-1} , 1.9 µg L^{-1} , 1.2 µg L^{-1} , and 1.8 µg L^{-1} , respectively. The obtained results were 387 lower than the standard values reported by the World Health Organization. The dissolved 388 elements after the treatment were low compared with the applied catalyst concentration (0.1 389 g/L) in each experiment. Therefore, the heterogeneous reactions are supposed to significantly 390 contribute to the deactivation of algal cells. 391



392

Fig. 4. (a) The performance of different processes in algal removal efficiency, (b and c) assessing the synergistic effect of photo-Fenton-like process, and (d) the effect of different scavengers on the algal removal efficiency. Experimental conditions: composite concentration of 0.1 g L⁻¹, [HP] = 10 mM, algal cell concentration of 3.5×10^9 cells mL⁻¹, and pH = 8.

399 **3.4.** Studying the algal cell variation during the photo-Fenton-like process

400 Microscopic and SEM images were taken during the photo-Fenton-like process to evaluate 401 the surface cellular morphology alteration. The images of the algal cells before the photo402 Fenton-like process were presented in Fig. 5 (a) and (a'). Accordingly, the algal cells are alive, consisting of four grouped flagellate capsules. Moreover, the images prove the existence of 403 chlorophyll in viable cells. However, after 60 min of the reaction (Figs. 3(b) and 3(b')), not 404 only were the capsules isolated, showing deformation of cells morphology, but also the 405 reduction in the chlorophyll content of the algal cells was observed. In Figs. 3 (c) and (c'), the 406 images clarify that in the case of exposing the algal cells to the photo-Fenton-like process for 407 two hours, the algal cells destruct and shrink. The visible chlorophyll content reduction after 408 60 and 120 min of the photo-Fenton-like process can be ascribed to the destruction of the algal 409 410 cell walls, leading to the release of chlorophyll in the media. Xu et al. (Xu et al., 2020) have also used the SEM images to study the morphological alteration of the Scenedesmus 411 quadricauda in the presence of acrylamide. They observed that after 96 h of exposing the algal 412 413 cells to acrylamide (50 mg L^{-1}), the algal cells were disintegrated and shrank.



415

416 Fig. 5. The SEM and microscopic images of the algal cells before (a-a'), after 60 min (b-b'), 417 and 120 min (c-c') of the photo-Fenton-like process. (d) The removal efficiency of 418 chlorophyll-a for the algal cells. Experimental conditions: composite concentration of 0.1 g L⁻ 419 ¹, [HP] = 10 mM, algal cell concentration of 3.5×10^9 cells mL⁻¹, and pH = 8.

421 According to the literature, the destruction of the algal cell walls can result in the release of422 chlorophyll pigment into the reaction media. The algal solution was withdrawn after 0, 30, 60,

90, and 120 min of the process to evaluate the chlorophyll-a content. Hence, the chlorophyll-a
was extracted using the described method in section (2.6). The results presented in Fig. 5 (d)
demonstrate that the degradation efficiency of chlorophyll was boosted during 120 min. This
variation ascribes to the degradation of chlorophyll-a pigment in the presence of ROSs
produced during the photo-Fenton-like process.

428

429 **3.5. GC-MS analysis**

According to the literature review (Gao et al., 2020), algal cells contain different 430 431 macromolecules such as protein, carbohydrates, polypeptides, amino acids, chlorophyll a, DNA, and RNA are supposed to have a complex structure. Therefore, any destruction of the 432 algal cells can lead to the degradation of these macromolecules into leaner and small 433 434 compounds. To study the production of by-products in the course of the photo-Fenton-like process, GC-MS analysis was fulfilled. Table 3 displays the structure, the main fragments, and 435 the retention time of the peaks for nine determined compounds. Results identify the existence 436 of simple structures which ascribes to the broken down of macromolecules by active radicals. 437 Therefore, the applied photo-Fenton-like process in the existence of the so-synthesized 438 composite was an appropriate system for effective algal removal. 439

440

Table 3. Identified by-products (with Wiley7Nist05.L database) produced during the443photo-Fenton-like process of the algal cells. Experimental conditions: composite444concentration of 0.1 g L⁻¹, [HP] = 10 mM, algal cell concentration of 3.5×10^9 cells mL⁻¹, and

	N .		R.T	Main fragments after derivation
NO	Name	Name Structure		(m / z)
				141.10 (100.00%), 75.00 (95.31%),
1	1,3-pentadiene	Н	2.407	73.10 (32.64%), 99.10 (24.77%),
		H H		147.10 (19.25%)
		0		75.10 (100.00%), 116.10 (100.00%),
2	Acetic acid		2.618	73.10 (16.83%), 117.10 (15.49%),
		ОН		76.10 (11.89%)
	Ethonicaidie	N, 0,		147.10 (100.00%), 73.10 (73.23%),
3	ecid		2.995	203.10 (46.87%), 148.10 (4317%),
	aciu	I		188.10 (25.45%)
	Bis	l		72 10 (100 000/) 147 10 (42 420/)
	(trimethylsilyl)	methylsilyl)	<i>,</i> 0,	/5.10 (100.00%), 147.10 (45.42%),
4	trifluoroacetami		3.605	188.10 (24.26%), 192.10 (19.47%),
	1	OF ₃		75.00 (19.44%)
_	de			
	Butanoic acid	0		75.00 (100.00%), 73.10 (53.54%),
5		\sim	3.616	130.00 (38.98%), 147.00 (38.41%),
		и сон		116.00 (20.18)
	L-alanine	NH ₂		75.10 (100.00%), 116.10 (84.81%),
6			5.503	147.10 (21.81%), 73.10
				(17.35%),117.10 (10.21%)



447 **4.** Conclusion

Briefly, the performance of the photo-Fenton-like process in the existence of 448 Fe_{2.5}Co_{0.3}Zn_{0.2}O₄/CuCr-LDH composite was assessed as a novel and promising process on the 449 removal performance of the *Scenedesmus quadricauda* algal cells. The effects of pH, algal cell 450 451 concentration, and the concentration of HP on the total algal removal were studied. The maximum deactivation efficiency reached its maximum level with 0.1 g L⁻¹ composite, HP 452 concentration of 10 mM, and the algal cell concentration of 3.5×10^9 cells mL⁻¹. The results 453 454 revealed the synergistic effect of the photo-Fenton-like process compared with the sole processes such as adsorption, photolysis, disinfection with HP, HP photoactivation, Fenton-455 like, and photocatalysis. The microscopic and SEM images of the algal cells and the 456 chlorophyll-a measurement depicted the destruction of the algal cell walls and the chlorophyll 457 degradation. Finally, based on the results obtained from the GC-MS technique, the produced 458 459 reactive radical species during the photo-Fenton-like process led to the destruction of the macromolecules of the algal cells into small and linear compounds. Furthermore, the as-460 prepared catalysts displayed an admissible antibacterial activity against S. aureus. In 461

462	conclusion, the system involving the Fe _{2.5} Co _{0.3} Zn _{0.2} O ₄ /CuCr-LDH composite and visible light
463	demonstrated a strong effect as antialgal agents. This kind of process, which has several aspects
464	in terms of sustainability, can be one of the other promising methods for water disinfection.
465	

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