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Degradation of tetracycline antibiotic utilizing light driven-activated oxone in the presence of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH binary heterojunction nanocomposite

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### Author contributions

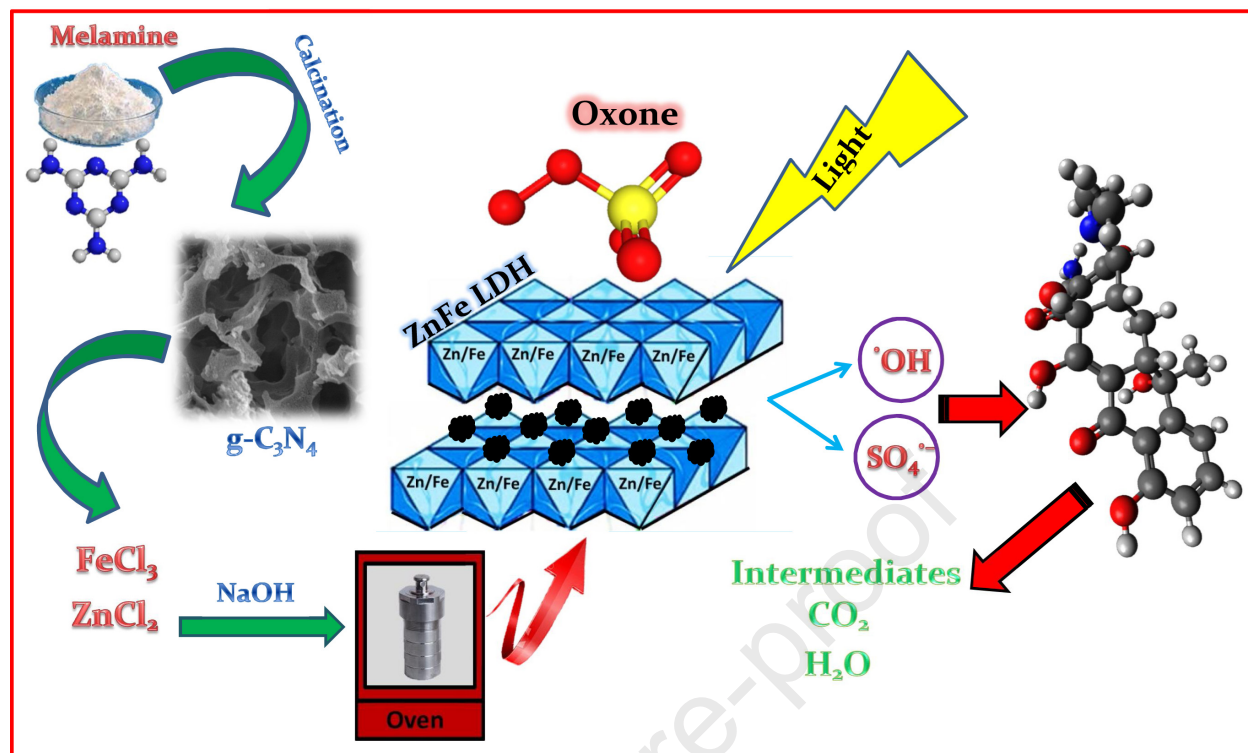
**Reza Darvishi Cheshmeh Soltani:** Writing-original draft, Methodology, Conceptualization.

**Elham Abolhasani:** Formal analysis, Investigation. **Masoumeh Mashayekhi:** Formal analysis,

Investigation. **Najla Jorfi:** Formal analysis, Investigation. **Grzegorz Boczkaj:** Writing-review &

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1 **Degradation of tetracycline antibiotic utilizing light driven-activated Oxone in the presence**  
2 **of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH binary heterojunction nanocomposite**

3  
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**20 Abstract**

21 In the present study, a binary heterojunction nanocomposite composed of graphitic carbon nitride  
22 (g-C<sub>3</sub>N<sub>4</sub>) and Zn/Fe-contained layered double hydroxide (ZnFe LDH) was employed as  
23 heterogeneous catalyst for the decomposition of tetracycline (TC) antibiotic utilizing Oxone and  
24 UV light irradiation. The sole use of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH as adsorbent led to the negligible  
25 elimination of TC. In addition, the sole use of Oxone or UV (photolysis) and even their  
26 combination were not effective enough to degrade the target pollutant, while the combined  
27 process of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis revealed significantly enhanced (synergistic)  
28 degradation of TC (92.4% within 30 min). Indirect detection tests for the identification of free  
29 radical species indicated the major role of both hydroxyl (<sup>•</sup>OH) and sulfate (SO<sub>4</sub><sup>•-</sup>) radicals in the  
30 degradation of TC by the g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis system. The elimination of TC  
31 followed a pseudo-first order kinetic model. The complete degradation of TC (degradation  
32 efficiency of 100%) was achieved within the reaction time of 25 min when ultrasound (US) was  
33 applied as enhancing agent. Furthermore, the results of total organic carbon (TOC) analysis were  
34 used to exhibit progress in the mineralization of the pollutant. The bioassay results indicated the  
35 decreased toxicity of the process effluent toward microbial population of *Escherichia coli* after  
36 the treatment.

37

38 **Keywords:** Tetracycline; Peroxymonosulfate; Graphitic carbon nitride; Layered double  
39 hydroxides; Heterojunction catalyst; Advanced oxidation processes (AOPs).

40

41



## 42 **1. Introduction**

43 Water contamination is proposed as one of the greatest health and environmental concerns of  
44 many developing societies (Darvishi Cheshmeh Soltani et al., 2014; Abazari et al., 2019). Due to  
45 the wide adverse effects of emerging pollutants including antibiotics, endocrine disrupting  
46 compounds, pesticides, veterinary medications and personal care products on ecosystems and  
47 human body, these compounds are nominated as target pollutants to be eliminated via various  
48 preventive and treatment strategies. Among the wide range of emerging pollutants in water, the  
49 existence of pharmaceutical compounds especially antibiotics has been considered as a global  
50 concern because of their hazards for the ecosystem and human health. The worldwide  
51 consumption of antibiotics is between 100,000 and 200,000 tons per year (Chen et al., 2019).

52 As a widely used antibiotic, tetracycline (TC) is commonly prescribed to treat various infections  
53 of intestines, urinary tract, skin, lymph nodes, respiratory tract and genitals because of its low  
54 price and good effectiveness (Ao et al., 2019; Chen et al., 2021b). This antibiotic compound is  
55 discharged as metabolized and unmetabolized forms into aquatic environments. As a result, it is  
56 detected and measured in the activated sludge process effluent of municipal wastewater  
57 treatment plants because of its low bio-degradability (Soltani et al., 2018). Significantly, the  
58 emergence of resistant genes and antibiotic resistant bacteria is the main problem owing to the  
59 release of antibiotic compounds into the water resources (Soltani et al., 2018; Karim and  
60 Shriwastav, 2021).

61 Conclusively, the degradation of TC antibiotic in water and wastewater is of great challenge  
62 considering both health and environmental aspects. Different treatment technologies have been  
63 developed and utilized for the removal of antibiotics from the aquatic phase including adsorption



64 process (Gao et al., 2012), electrochemical processes (Wu et al., 2012), membrane technologies  
65 (Sharma et al., 2017), conventional and advanced chemical oxidation (Anjali and Shanthakumar,  
66 2019; Wang et al., 2019). Advanced oxidation processes (AOPs) based on the formation of free  
67 oxidizing radicals such as hydroxyl radical ( $\cdot\text{OH}$ ) and sulfate radical ( $\text{SO}_4^{\cdot-}$ ) is attracted much  
68 more attention for the removal of antibiotics from water resources, converting the target pollutant  
69 to low-hazardous or even non-hazardous intermediates and final products (Li et al., 2022).

70 As sulfate radical-based chemical treatment systems, Oxone (peroxymonosulfate) activated by  
71 various agents such as light irradiation (Ao et al., 2018), ultrasonic radiation (Yin et al., 2018;  
72 Fedorov et al., 2021), heat (Ahn et al., 2021), carbonaceous materials (Shahzad et al., 2020;  
73 Soltani et al., 2020; Yang et al., 2021) and metal ions (Darvishi Cheshmeh Soltani et al., 2021;  
74 Guo et al., 2021) are extensively applied for the decomposition of emerging pollutants due to the  
75 production of free oxidizing species in the contaminated water. Graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ )  
76 with high light absorption potential, narrow band gap, high thermal stability, large surface area  
77 and simplicity of the synthesis procedure is proposed for not only photocatalytic treatment  
78 systems (Di et al., 2019; He et al., 2021b) but also for the activation of Oxone (Feng et al., 2018;  
79 Alnaggar et al., 2021).

80 The combination of  $\text{g-C}_3\text{N}_4$  with other catalysts forming heterojunction is a novel method to  
81 improve the photo-induced catalytic activity due to the efficient separation of as-generated  $\text{e}^-/\text{h}^+$   
82 pairs (Lestari et al., 2021). As a promising and innovative technique, hydrotalcite-like structures  
83 of layered double hydroxides (LDHs) have been also used in several areas such as photocatalysis  
84 and electrochemical processes (Liu et al., 2018; Motlagh et al., 2020; He et al., 2021b). Actually,  
85 LDHs are inorganic layered materials containing divalent and trivalent metal ions, along with an  
86 n-valent anion to balance the positively charged layers (Zhao et al., 2018; Rad et al., 2022).



87 LDHs have attracted remarkable attention as catalyst for the advanced oxidation processes  
88 (AOPs) because of their exceptional structure. Regarding the need to synthesize and use  
89 innovative and effective heterogeneous catalysts, in the present investigation, both g-C<sub>3</sub>N<sub>4</sub> and  
90 ZnFe LDH compounds were synthesized and applied as binary heterojunction nanocomposite for  
91 the synergistic activation of Oxone in the presence of UV light irradiation. Furthermore, the  
92 combination of g-C<sub>3</sub>N<sub>4</sub> and ZnFe LDH could be acted as an excellent photocatalyst under UV  
93 light irradiation (Song et al., 2019).

94 Briefly, in the present study, batch flow-mode experimental reactors containing the binary  
95 heterojunction of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH were applied to activate Oxone for the efficient removal  
96 and degradation of TC antibiotic in water. The UV light irradiation was also employed to  
97 synergistically degrade the target pollutant. Moreover, the influence of main operating  
98 parameters on the process performance was examined to assess the process capability under  
99 variable operating conditions. Finally, a bioassay was performed on the process effluent using  
100 the reference microorganism of *Escherichia coli* relying on antimicrobial effects of the  
101 undecomposed TC and its intermediates generated during the treatment process.

## 102 **2. Materials and methods**

### 103 *2.1. Materials*

104 Analytical grade powder of TC (molecular formula: C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>8</sub>; molecular weight: 444.43  
105 g/mol) and melamine (molecular formula: C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>; molecular weight: 126.12 g/mol; purity of  
106 99%) were obtained from Sigma-Aldrich, USA. Oxone (potassium peroxydisulfate) with  
107 molecular weight of 152.2 g/mol was supplied from Merck, Germany. Other reagents and





108 chemicals such as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{NaOH}$ ,  $\text{C}_2\text{H}_5\text{OH}$  (EtOH),  $\text{CH}_3\text{OH}$  (MeOH),  $\text{C}_4\text{H}_{10}\text{O}$  (tert-  
109 Butyl alcohol, TBA) and  $\text{HCl}$  were also obtained from Merck, Germany.

## 110 2.2. Preparation of heterojunction nanocomposite

111 For the synthesis of g- $\text{C}_3\text{N}_4$ /ZnFe LDH heterojunction nanocomposite, firstly, 2 g melamine was  
112 added to 50 mL distilled water and then heated on a hot plate at  $60^\circ\text{C}$  under gentle mechanical  
113 stirring. The resulting sample was dried in an oven at  $80^\circ\text{C}$ . Finally, it was calcined in an electric  
114 furnace for 2 h at  $550^\circ\text{C}$  to attain g- $\text{C}_3\text{N}_4$  sample. In the next step, as-synthesized g- $\text{C}_3\text{N}_4$   
115 nanostructures (weight percent of 0.5%), together with 2 mM  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 6 mM  $\text{ZnCl}_2$ ,  
116 were dissolved in 100 mL distilled water. Then it was homogenized using mechanical stirrer for  
117 20 min. Afterwards, 1 N sodium hydroxide was gradually added to the above solution under  
118 mechanical stirring and argon gas at  $60^\circ\text{C}$  until pH reached around 9.0. The resulting precipitate  
119 was poured into a hydrothermal vessel and heated in an oven at  $120^\circ\text{C}$  for 24 h. After that, the  
120 sample was washed several times on the filter using distilled water and ethanol to reach neutral  
121 pH of 7.0. Ultimately, the obtained g- $\text{C}_3\text{N}_4$ /ZnFe LDH heterojunction nanocomposite was dried  
122 in an oven at  $90^\circ\text{C}$  until reaching a constant weight. It was stored in a desiccator until use.

## 123 2.3. Experimental protocols

124 Batch flow-mode reactors were used to remove TC antibiotic from water samples. One 6-W  
125 UVC lamp was utilized to irradiate the reactor containing TH (photolysis process). An Elma  
126 ultrasonic bath made by Italy with an input power of 320 W and working frequency of 80 kHz  
127 was applied to enhance the process effectiveness using ultrasound (US). Firstly, the role of  
128 adsorption of TC onto g- $\text{C}_3\text{N}_4$ , ZnFe LDH and g- $\text{C}_3\text{N}_4$ /ZnFe LDH nanocomposite in the removal  
129 of TC was investigated. Then, the efficiency of different processes involved in the removal of



130 TC was determined under the same operating conditions. One-factor-at-a-time statistical  
131 approach was applied for the experimental design due to its simplicity. According to the results,  
132 the most efficient process for the decomposition and removal of the pollutant was selected for  
133 conducting the rest of experiments. Oxidizing agents involved in the decomposition of TC  
134 pollutant were indirectly identified using TBA and EtOH alcohols. The effect of important  
135 operating variables such as initial pH (natural, neutral and basic pH), the amount of g-C<sub>3</sub>N<sub>4</sub>/ZnFe  
136 LDH nanocomposite (0.05–0.3 g/L), the pollutant concentration (10–55 µM) and the Oxone  
137 concentration (0.1–0.5 mM) on the reactor performance in terms of TC removal was examined.  
138 Finally, bio-toxicity test was performed on the process effluent under selective operating  
139 conditions.

#### 140 *2.4. Analysis of TC and characterization*

141 To determine the efficiency of the treatment process, the residual concentration of TC in the  
142 process effluent was measured using high-performance liquid chromatography (HPLC)  
143 technique utilizing UV detector of 360 nm wavelength. A mixture of methanol, oxalic acid and  
144 acetonitrile was prepared as mobile phase of the HPLC device. In this regard, 2-ml samples were  
145 withdrawn from the batch flow-mode reactor at regular time intervals based on the experimental  
146 design. They were centrifuged and filtered before the HPLC analysis. Progress in the  
147 mineralization of TC was checked by the total organic carbon (TOC) analyzer (Skalar, the  
148 Netherlands). Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX)  
149 spectroscopy were performed to exhibit morphological characteristics of the samples (TESCAN  
150 microscope, model: Mira3, Czech Republic). In addition, elemental mapping was carried out to  
151 show elemental distribution of the synthesized compounds. Fourier transform infrared (FTIR)  
152 spectroscopy (Bruker Co., Germany) was used to identify surface functional groups and crystal



153 structure of the samples via a non-destructive route. X-ray diffraction analysis (XRD) was  
154 utilized to specify the crystallographic composition of the samples (Tongda, model: TD-3700,  
155 China). Differential reflectance spectroscopy (DRS) analysis (S250, Analytik Jena Co.,  
156 Germany) using wavelength range of 400–1000 nm was employed to study the spectral  
157 properties of the solid samples on the basis of not only surface reflected light but also internally  
158 reflected light. Moreover, band gap energy of the synthesized catalysts could be determined via  
159 the DRS analysis. Contribution of the adsorption process to the elimination of TC was  
160 determined via the adsorption equation (Soltani et al., 2015; Durrani et al., 2022). Bio-toxicity of  
161 the process effluent containing undecomposed TC molecule and its byproducts was examined  
162 using plate count method using *Escherichia coli* (*E. coli*) as the reference microorganism.  
163 Briefly, 0.1 mL microbial suspension along with 0.5 mL effluent sample was dispersed on the  
164 agar plate surface. The plate was incubated at 37°C for 24 h. The abovementioned procedure was  
165 used for the treated and untreated samples under the same conditions.

### 166 **3. Results and discussion**

#### 167 *3.1. Characterization (SEM-EDX-Map, XRD, FTIR, DRS)*

168 Surface structure of the samples was examined by conducting SEM analysis. The SEM images  
169 and corresponding EDX-mapping graphs are represented in Fig. 1. Fig. 1a shows surface  
170 structure of the g-C<sub>3</sub>N<sub>4</sub> containing nanostructures with irregular shapes and high porosity. This  
171 construction gives a good potential to enhance the catalytic conversion of TC via increasing  
172 reaction sites. The EDX analysis was performed as a rapid, efficient and precise technique to  
173 specify elemental composition of the sample using electron microscope through a non-  
174 destructive approach. The corresponding EDX micrograph of the g-C<sub>3</sub>N<sub>4</sub> exhibits the existence



175 of C and N elements in the composition (Fig. 1b). Using SEM and EDX, elemental mapping of  
176 the g-C<sub>3</sub>N<sub>4</sub> on the basis of gathering highly particular elemental composition details upon  
177 specific area of the sample represents uniform distribution of the elements in the g-C<sub>3</sub>N<sub>4</sub>  
178 structure. An example of SEM images of the ZnFe LDH is shown in Fig. 1c. As displayed,  
179 nanostructures of the ZnFe LDH are well-distributed in the sample promoting reactivity of the  
180 catalyst to generate more oxidizing species in the solution due to the fine size and consequently  
181 large surface area. Based on the EDX micrograph (Fig. 1d), the ZnFe LDH is mainly composed  
182 of Zn and Fe with specified peaks in the graph. The distribution of as-mentioned elements is  
183 exhibited via an elemental mapping placed on the graph. The surface structure of as-synthesized  
184 binary heterojunction of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH is displayed via Fig. 1e. As can be seen, after the  
185 combination of g-C<sub>3</sub>N<sub>4</sub> with ZnFe LDH, the g-C<sub>3</sub>N<sub>4</sub> nanostructures are covered on the ZnFe  
186 LDH composite, revealing circular particles with some cracks on the surface. As shown in the  
187 EDX micrograph (Fig. 1f), this binary heterojunction is comprised of C, N, Zn and Fe elements  
188 which can be found in the structure of composing components. Distribution of the elements is  
189 also depicted.

190 XRD patterns of the samples are illustrated in Fig. 2a. The g-C<sub>3</sub>N<sub>4</sub> pattern shows two  
191 representative peaks placed at 12.7 and 27.8° corresponding to (100) and (002) planes of the  
192 crystalline structure, indicating the stacking of conjugated aromatic compounds in the interlayers  
193 and constructional pattern of the composition, respectively (Zeng et al., 2020; Lestari et al.,  
194 2021; Yu et al., 2021). The first peak had lower intensity than the later peak, exhibiting  
195 insignificant stacking of conjugated aromatic compounds in the interlayers of the binary  
196 heterojunction due to the calcination. In the case of ZnFe LDH, the peaks placed at 31.9, 34.5,  
197 36.4, 47.5, 56.7 and 62.8 corresponding to (101), (009), (015), (012), (110) and (113) planes

198 were the routine LDH characteristic peaks, respectively (Wang et al., 2020). The binary  
199 heterojunction pattern exhibits the presence of both LDH and g-C<sub>3</sub>N<sub>4</sub> characteristic peaks with  
200 lower intensity of the LDH peaks compared with that of g-C<sub>3</sub>N<sub>4</sub> because of the lower amounts of  
201 LDH in the binary heterojunction.

202 Surface functional groups of the samples were determined through the FTIR analysis (Fig. 2b).  
203 Accordingly, FTIR spectrum of the g-C<sub>3</sub>N<sub>4</sub> exhibits the stretching vibration peak of N–H bond  
204 centered at wavenumber of 3200 cm<sup>-1</sup> (Di et al., 2019; Lestari et al., 2021). The peaks in the  
205 wavenumber range of 1250–1470 cm<sup>-1</sup> and 1480–1660 cm<sup>-1</sup> can be attributed to the stretching  
206 oscillation of C=N and C–N bonds, respectively (Di et al., 2019). The vibrating peak located at  
207 813 cm<sup>-1</sup> is associated with s-triazine rings of the g-C<sub>3</sub>N<sub>4</sub> (Yu et al., 2021). FTIR spectrum of the  
208 ZnFe LDH sample reveals a sharp peak centered at wavenumber of 3450 cm<sup>-1</sup> as a result of the  
209 existence of O–H stretching bond of the interlayer water molecules and layered hydroxyl groups  
210 of the sample (Qin et al., 2019). In addition, the sharp peak placed around 600 cm<sup>-1</sup> is related to  
211 the stretching vibration of M–O or M–OH bonds (M describes Fe and Zn) (Di et al., 2019;  
212 Naderi and Darvishi Cheshmeh Soltani, 2021). As can be clearly seen in Fig. 2b, FTIR spectrum  
213 of the binary heterojunction of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH nanocomposite is similar to the pure g-C<sub>3</sub>N<sub>4</sub>.  
214 This indicated no influence of the ZnFe LDH on the chemical structure of the g-C<sub>3</sub>N<sub>4</sub>. On the  
215 other hand, the structure of g-C<sub>3</sub>N<sub>4</sub> in the binary heterojunction nanocomposite was not  
216 destroyed during the fabrication process.

217 The DRS spectroscopy with the wavelength ranging from 200 to 800 nm was utilized to examine  
218 optical characteristics of the fabricated samples (Fig. 3). In the case of g-C<sub>3</sub>N<sub>4</sub>, as displayed in  
219 Fig. 3a, four distinct absorption peaks in the UV wavelength region (225, 265, 290 and 340 nm)  
220 were observed exhibiting its UV-light absorption properties. The ZnFe LDH compound shows



221 four main absorption peaks where the two were appeared in the UV light wavelength region (230  
222 and 395 nm) assigning to the charge transfer of metal-ligand in the layered compound, and the  
223 other two absorption peaks located in the visible light region wavelength range (485 and 570 nm)  
224 are attributed to metal ions transitions in the layered structure (Fig. 3b). In the UV light  
225 wavelength region, the optical absorption peaks of ZnFe LDH and g-C<sub>3</sub>N<sub>4</sub> were also observed in  
226 the case of the heterojunction nanocomposite of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH (Fig. 3c), thereby indicating  
227 the presence of ZnFe LDH and g-C<sub>3</sub>N<sub>4</sub> in the nanocomposite structure (Jo and Tonda, 2019).  
228 Furthermore, overlapping the absorption peaks intimated the effective interaction between the  
229 components in the structure of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH heterojunction. The enhanced optical  
230 absorption in the UV light wavelength range makes the heterojunction nanocomposite an  
231 efficient catalyst under UV light irradiation. According to the obtained DRS spectra, the band  
232 gap energy ( $E_g$ ) of the samples was calculated based on absorption coefficient ( $\alpha$ ) and frequency  
233 of light radiation ( $\nu$ ) as displayed in the following formula:

$$234 \quad \alpha h\nu = A(h\nu - E_g)^{\frac{n}{2}} \quad (1)$$

235 where  $h$  and  $n$  are the Planck's constant and optical absorption index, respectively. For the  
236 calculation of  $E_g$ ,  $(\alpha h\nu)^2$  was plotted versus  $h\nu$  as exhibited in Fig. 3a, b and c. Accordingly,  $E_g$   
237 values obtained for g-C<sub>3</sub>N<sub>4</sub>, ZnFe LDH and g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH nanocomposite were 3.14, 3.76  
238 and 2.98 eV, respectively. The results indicated reduction in the band gap energy of the g-  
239 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH heterojunction nanocomposite in comparison with the individual compounds of  
240 g-C<sub>3</sub>N<sub>4</sub> and ZnFe LDH. The decreased band gap energy of the heterojunction nanocomposite  
241 resulted in the intensified catalytic decomposition of TC due to the reduced recombination rate of  
242  $e^-/h^+$  pairs generated in the catalytic system (Kim and Kan, 2016).

## 243 3.2. Comparative study results

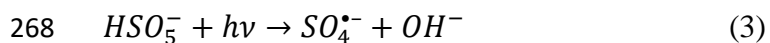
244 Preliminary experiments were performed to specify the role of individual processes in the  
245 removal of TC antibiotic. In this regard, the adsorption process usually play unavoidable role  
246 during elimination of the target pollutant using heterogeneous catalysts. Thus, the treatment  
247 process was conducted in the presence of g-C<sub>3</sub>N<sub>4</sub>, ZnFe LDH and g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH under dark  
248 condition without the addition of Oxone to determine the adsorption potential of the synthesized  
249 binary heterojunction nanocomposite and its components. The results of this set of experiments  
250 are shown in Fig. S1. Using g-C<sub>3</sub>N<sub>4</sub>, ZnFe LDH and g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH compounds, the  
251 adsorption efficiencies of 8.0, 8.8 and 9.2% were obtained. Accordingly, the Langmuir model  
252 was applied to predict maximum adsorption capacity of the samples (Soltani et al., 2009;  
253 Darvishi Cheshmeh Soltani et al., 2011):

$$254 \frac{C_e}{q_e} = \frac{1}{kq_m} + \frac{1}{q_m} C_e \quad (2)$$

255 where  $q_m$  ( $\mu\text{M/g}$ ) expresses the maximum capacity of the adsorbent to adsorb TC molecules,  
256 while  $q_e$  ( $\mu\text{M/g}$ ) represents the capacity of adsorption at specific equilibrium time. The constant  
257  $K$  defines the affinity of solid adsorbent for the TC molecules ( $\text{L}/\mu\text{M}$ ). Based on the Langmuir-  
258 based isotherm modeling, the  $q_m$  values of 0.36, 0.50 and 0.65  $\mu\text{M/g}$  were obtained when g-  
259 C<sub>3</sub>N<sub>4</sub>, ZnFe LDH and g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH compounds were used as adsorbents, respectively. The  
260 results indicated insignificant contribution of the adsorption process to the removal of TC. In the  
261 following, Oxone alone, photolysis using UV lamp alone and the combined process of  
262 Oxone/photolysis were utilized for the removal of TC without the heterogeneous catalyst. The  
263 application of Oxone, photolysis and Oxone/photolysis resulted in the degradation efficiency of  
264 5.6, 9.2 and 42.0%, respectively (Fig. 4a). Obviously, the sole use of Oxone and photolysis led to



265 the negligible degradation of TC, while their combination resulted in the notable efficiency of  
266 42.0%. This can be explained by the fact that UV irradiation activates Oxone to generate free  
267 oxidizing radicals in the reactor:

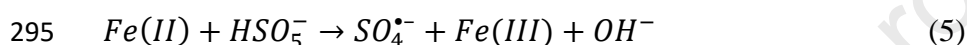
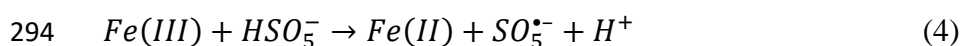


269 As shown in Fig. 4a, the utilization of g-C<sub>3</sub>N<sub>4</sub>/Oxone (23.6%) and g-C<sub>3</sub>N<sub>4</sub>/photolysis (32.8%) led  
270 to the enhanced degradation of TC in comparison with the sole use of Oxone (5.6%) or  
271 photolysis (9.2%). For the g-C<sub>3</sub>N<sub>4</sub>/Oxone process, no remarkable degradation efficiency of TC  
272 was attained when g-C<sub>3</sub>N<sub>4</sub> alone was applied for the activation of Oxone, suggesting low  
273 reactivity of g-C<sub>3</sub>N<sub>4</sub> toward the Oxone to generate radical species (Feng et al., 2018). In  
274 agreement with our results, Chen et al. (2021) reported an insignificant degradation efficiency of  
275 9.4% in the g-C<sub>3</sub>N<sub>4</sub>/Oxone treatment system for the removal of 4-chlorophenol (Chen et al.,  
276 2021a). For the g-C<sub>3</sub>N<sub>4</sub>/photolysis, the catalytic properties of the synthesized g-C<sub>3</sub>N<sub>4</sub> arise from  
277 its narrow band gap energy and consequently high photo-sensitivity (Gholami et al., 2020). The  
278 binary heterojunction nanocomposite of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH was employed to perform the rest of  
279 experiments. Using g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone and g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/photolysis processes, the  
280 degradation efficiencies of 57.2 and 68.4% were attained, respectively, which indicated the  
281 major contribution of ZnFe LDH to the degradation of TC. In a similar study, Zhao et al. (2018)  
282 utilized both Fe-Co LDH/Oxone and CoMn<sub>2</sub>O<sub>4</sub>/Oxone treatment systems for the degradation of  
283 an organic dye. They reported a degradation efficiency of 60% within short reaction time which  
284 was associated with high Oxone activation potential of the layered compounds and rapid  
285 generation rate of the sulfate radical (Zhao et al., 2018). In the case of ZnFe LDH, high activation  
286 potential and superior chemical stability is ascribed to the valence changes between Zn and Fe  
287 ions (Zhao et al., 2018).

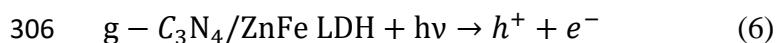




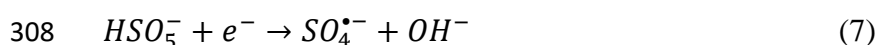
288 Similarly, a bimetallic LDH catalyst containing Co and Mn was successfully used by He et al.  
 289 (2021) for the degradation of nitroimidazoles through the activation of Oxone. Based on their  
 290 analysis and interpretation, the alteration of bimetallic valence in Co-Mn LDH structure donated  
 291 electron for the activation of Oxone (He et al., 2021a). The presence of Fe ions in the structure of  
 292 ZnFe LDH improves the generation of free oxidizing radicals (Soltani et al., 2018; Guo et al.,  
 293 2021):

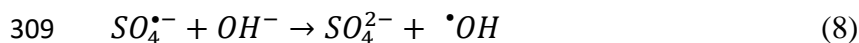


296 In addition, it is demonstrated that the combination of g-C<sub>3</sub>N<sub>4</sub> and layered double hydroxide  
 297 compounds such as ZnFe LDH enhances water treatment efficiency in comparison with that of  
 298 LDH alone or pure g-C<sub>3</sub>N<sub>4</sub> due to the reduced e<sup>-</sup>/h<sup>+</sup> recombination rate (Jo and Tonda, 2019;  
 299 Song et al., 2019). Furthermore, as can be observed in Fig. 4a, the efficiency of 92.4% was  
 300 obtained when the g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis process was used for the decomposition  
 301 of TC. In this regard, the binary heterojunction nanocomposite is not only played the  
 302 heterogeneous activator role for Oxone to form radical species but also acted as the  
 303 heterogeneous photocatalyst for UV light irradiation. Under UV light irradiation, the e<sup>-</sup>/h<sup>+</sup> pairs  
 304 of the binary g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH heterojunction were produced due to the stimulation of both g-  
 305 C<sub>3</sub>N<sub>4</sub> and ZnFe LDH (Song et al., 2019; Zeng et al., 2020):



307 Meanwhile, the generated electrons react with Oxone to form both <sup>•</sup>OH and SO<sub>4</sub><sup>•-</sup> radicals:





310 Because of the asymmetrical structure of Oxone and the conversion of sulfate to hydroxyl  
 311 radicals, simultaneous formation of such radicals is feasible (Feng et al., 2018). Jin and  
 312 coworkers used g-C<sub>3</sub>N<sub>4</sub> in combination with Co<sub>3</sub>O<sub>4</sub> for the activation of Oxone to degrade TC.  
 313 Based on their results, a degradation efficiency of 99% was obtained under visible light  
 314 irradiation of Xenon lamp (Jin et al., 2020). Ultimately, the synergy percent was calculated  
 315 considering the application of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone, g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/photolysis and g-  
 316 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis processes by the following equation:

$$317 \quad Synergy (\%) = \frac{k_{g-C_3N_4/ZnFe\ LDH/Oxone/Photolysis} - (k_{g-C_3N_4/ZnFe\ LDH/Oxone} + k_{g-C_3N_4/ZnFe\ LDH/Photolysis})}{k_{g-C_3N_4/ZnFe\ LDH/Oxone/Photolysis}}$$

318 (9)

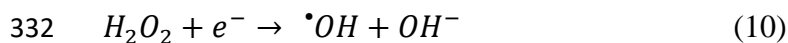
319 According to the obtained reaction rate constants (Fig. 4b), the synergy percent of 18.9% was  
 320 calculated using the above formula, indicating the significant increase in the degradation rate of  
 321 TC when both Oxone and photolysis were simultaneously utilized in the presence of g-  
 322 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH. Progress in the mineralization of the target compound was also checked within  
 323 the reaction time of 30 min based on the results of TOC analysis. As a result, the mineralization  
 324 efficiency of 33.5% was obtained within the short reaction time of 30 min.

### 325 3.3. Enhancing techniques

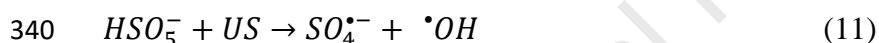
326 To further enhance efficiency of the g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis process in the removal  
 327 of TC, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ultrasound (US) were implemented as chemical and  
 328 physical enhancing agents, respectively. The results are provided in Fig. 5a. Using H<sub>2</sub>O<sub>2</sub>, the  
 329 degradation efficiency of TC increased from 92.4 to 100% within the reaction time of 30 min.



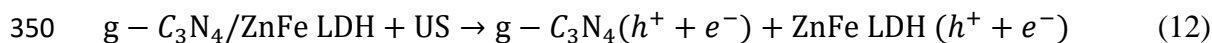
330 The addition of hydrogen peroxide improves the formation of  $\cdot\text{OH}$  radicals in the reactor as  
 331 represented in the following equation:



333 The addition of  $\text{H}_2\text{O}_2$  in the presence of ZnFe LDH is considerably reactive for the degradation  
 334 of pollutants through the interaction with Fe ions (Feng et al., 2018). The complete degradation  
 335 of TC was achieved within the reaction time of 25 min when US was applied as enhancing agent.  
 336 The US alone is used for the degradation of various pollutants as well as its integration with  
 337 other treatment processes (Gagol et al., 2019; Fedorov et al., 2022). Actually, the formation of  
 338  $\cdot\text{OH}$  is expected under ultrasonic irradiation as a result of the water dissociation (Soltani et al.,  
 339 2019). In the meantime, Oxone can be further activated under ultrasonic irradiation:



341 The US creates microcirculation zones in the fluid causing formation, growth and collapse of  
 342 cavitation bubbles (“hot spot” phenomenon) around the solid heterojunction nanocomposite  
 343 because of lower tensile strength toward the solid-liquid intersection, leading to the intensified  
 344 water dissociation and “sonoluminescence” phenomenon. During the “sonoluminescence”  
 345 phenomenon, light is emitted as a result of cavitation bubbles collapse with extremely high  
 346 temperature and pressure, thereby exciting the heterojunction catalyst of g- $\text{C}_3\text{N}_4/\text{ZnFe}$  LDH to  
 347 generate more  $e^-/h^+$  pairs (Gholami et al., 2020). The US-induced  $e^-/h^+$  pairs were significantly  
 348 segregated by the binary heterojunction nanocomposite as depicted in the following equation (He  
 349 et al., 2020):



351 Consequently, the implementation of US led to more enhancing effect on effectiveness of the g-  
 352 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis process than that of H<sub>2</sub>O<sub>2</sub>.

### 353 3.4. Antioxidant effect

354 Alcoholic compounds of TBA and EtOH were added to the g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis  
 355 process in order to indirectly specify the contribution of free oxidizing radicals to the degradation  
 356 of TC. The experiments were performed under the same operational parameters. For this  
 357 purpose, the degradation efficiencies of TC and corresponding reaction rate constants ( $k_{obs}$ ) were  
 358 determined in the presence of TBA and EtOH in comparison with the scavenger-free treatment  
 359 reactor. TBA is recognized as potential  $\cdot OH$  scavenger ( $6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), which is higher than its  
 360  $SO_4^{\cdot -}$  scavenging potential ( $4.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) (Fedorov et al., 2020). Nevertheless, EtOH can  
 361 scavenge both  $\cdot OH$  ( $1.2\text{-}2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) and  $SO_4^{\cdot -}$  ( $1.6\text{-}7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ), thus it can be used to  
 362 quench both  $\cdot OH$  and  $SO_4^{\cdot -}$  radicals (Xie et al., 2019). In the presence of TBA and EtOH, the  
 363 degradation efficiency of TC decreased from 92.4% ( $k_{obs}$ :  $0.0847 \text{ min}^{-1}$ ) to 80.4% ( $k_{obs}$ :  $0.0543$   
 364  $\text{min}^{-1}$ ) and 52.4% ( $k_{obs}$ :  $0.0261 \text{ min}^{-1}$ ), respectively (Fig. 5a and b). Based on these data, the  
 365 following equations were used to prove the role of  $\cdot OH$  and  $SO_4^{\cdot -}$  radicals in the degradation of  
 366 TC antibiotic:

$$367 \text{ Role of } \cdot OH = \frac{k_{obs} - k_{obs,TBA}}{k_{obs}} \times 100 \quad (13)$$

$$368 \text{ Role of } SO_4^{\cdot -} = \frac{k_{obs,TBA} - k_{obs,EtOH}}{k_{obs}} \times 100 \quad (14)$$

369 Based on the above equations, the role of  $\cdot OH$  in the degradation of TC was 36.0%, while the  
 370 role of  $SO_4^{\cdot -}$  was 33.3%. This indicated that  $\cdot OH$  played a little more notable role than  $SO_4^{\cdot -}$  in  
 371 the decomposition of TC by the g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis process. In agreement with



372 our results, Ramachandran et al. (2021) confirmed the major role of both  $\text{SO}_4^{\cdot-}$  and  $\cdot\text{OH}$  radicals  
373 in the degradation of organic dye utilizing NiCo-LDH/Oxone process (Ramachandran et al.,  
374 2021).

### 375 *3.5. Effect of operating parameters*

376 The main operating parameters of solution pH, TC concentration, catalyst dosage and Oxone  
377 concentration were selected to assess effectiveness of the g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis  
378 process under variable operating conditions and to determine the optimum conditions for the  
379 operation of the treatment process (Fig. 6). Three distinct initial pHs of 4.5 (natural pH), 7.0  
380 (neutral pH) and 9.0 (basic pH) were selected to determine the influence of solution pH on the  
381 reactor performance. At pH values of 4.5, 7.0 and 9.0, the degradation efficiencies of TC were  
382 92.4, 95.2 and 98.8%, respectively (Fig. 6a). Thus, the degradation of TC slightly increased with  
383 increasing the initial pH. Acidic pH causes disintegration of the generated free oxidizing radicals  
384 resulting in the reduced process performance. The enhanced efficiency of the process at basic pH  
385 could be related to the presence of more hydroxyl ions ( $\text{OH}^-$ ) on the heterojunction  
386 nanocomposite surface which can get further oxidized to hydroxyl radicals (Karim and  
387 Shriwastav, 2021). Moreover, in the presence of  $\text{OH}^-$  ions, sulfate radicals are converted to  
388 hydroxyl radicals with higher oxidizing potential (Cai et al., 2015; Xie et al., 2019). Under basic  
389 conditions, the intense affinity between the heterojunction nanocomposite and negatively  
390 charged TC molecules may improve the degradation efficiency of TC. Furthermore, the TC  
391 molecule with rich electrical density on its ring system is prone to attract  $\cdot\text{OH}$  radicals, resulting  
392 in the enhanced elimination of TC in basic conditions (Jo and Tonda, 2019). However, it should  
393 be noted that excessive  $\text{OH}^-$  ions accumulated on the nanocomposite surface react with as-  
394 generated holes, reducing degradation of the target pollutant.



395 Increasing the dosage of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH from 0.05 to 0.2 g/L led to increasing the  
396 degradation of TC from 74.4 to 92.4%, respectively (Fig. 6b). However, its increase to 0.3 g/L  
397 resulted in a slight decrease in the degradation efficiency (86.8%). Increasing the amount of g-  
398 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH improves surface reactive sites forming more radical species such as  $\cdot\text{OH}$  and  
399  $\text{SO}_4^{\cdot-}$  to accelerate the degradation of TC antibiotic. Nevertheless, excessive amount of the  
400 nanocomposite catalyst may scavenge the generated radical species by metallic Zn or Fe sites,  
401 thereby reducing the radical species accessible for the decomposition of TC (Feng et al., 2018;  
402 Hong et al., 2020). Moreover, higher amounts of catalyst increase turbidity of the bulk solution  
403 leading to lower effectiveness of UV absorption by the heterojunction nanocomposite (Fernandes  
404 et al., 2020). The effect of solute (TC) concentration on its degradation was explored in the range  
405 of 10-55  $\mu\text{M}$  (Fig. 6c). Clearly, the efficiency increased from 60.0 to 92.4% with decreasing the  
406 initial concentration of TC from 55 to 25  $\mu\text{M}$ , respectively. At initial concentrations of 15 and 10  
407  $\mu\text{M}$ , the complete degradation of TC was achieved in 30 and 25 min, respectively. The increased  
408 process efficiency with decreasing TC concentration could be attributed to the reasons as follows  
409 (Dou et al., 2020): 1) The number of oxidizing species is constant in the reactor; thus, increasing  
410 TC concentration leads to the increased competition between limited oxidizing species to react  
411 with the target pollutant. 2) The transmittance of the bulk solution will be adversely influenced  
412 when the solute concentration increases. This results in the diminished adsorption of emitted  
413 photons by the heterojunction nanocomposite, thereby reducing the number of radical species in  
414 the reactor. 3) As-generated intermediate byproducts compete with the parent compound for  
415 interaction with radical species when the initial concentration of TC increases, declining the  
416 process efficiency.



417 The process efficiency increased with the addition of higher amounts of Oxone (Fig. 6d).  
418 Increasing Oxone from 0.1 to 0.5 mM improved the efficiency from 70.0 to 95.6%, respectively.  
419 As can be seen, the increase in the Oxone concentration from 0.4 to 0.5 mM caused negligible  
420 increase (about 3.0%) in the efficiency. Addition of optimized concentration of Oxone, as the  
421 source of oxidizing radicals, results in the formation of appropriate amounts of radical species  
422 such as  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  to efficiently decompose TC. At high concentration of Oxone, as-  
423 generated  $\text{SO}_4^{\cdot-}$  radicals interacts with itself generating weaker oxidizing agent of persulfate. In  
424 addition, it might be destroyed by excess Oxone molecules creating  $\text{SO}_5^{\cdot-}$  radical with lower  
425 oxidation potential; thus, unfavorably influencing the decomposition efficiency of TC (Hong et  
426 al., 2020). The results of bio-toxicity assessment on effluent of the g- $\text{C}_3\text{N}_4/\text{ZnFe}$   
427 LDH/Oxone/photolysis process showed the improved growth of gram-negative bacilli of *E. coli*  
428 (2000 CFU/100 mL) during the incubation in comparison with the untreated water sample (400  
429 CFU/100 mL). This pointed out the decrease in the bio-toxicity of the TC-contained water  
430 sample after the treatment process.

#### 431 4. Conclusions

432 In this investigation, the binary heterojunction nanocomposite of g- $\text{C}_3\text{N}_4/\text{ZnFe}$  LDH was  
433 fabricated and successfully applied for the catalytic decomposition of tetracycline antibiotic in  
434 the presence of Oxone and UV light irradiation. SEM-EDX, XRD and FTIR results revealed the  
435 synthesis of g- $\text{C}_3\text{N}_4/\text{ZnFe}$  LDH with suitable structure for the catalytic conversion of the target  
436 pollutant. The role of both hydroxyl and sulfate radicals in the degradation of the pollutant was  
437 indirectly verified using scavenging compounds. The treatment process effectiveness was  
438 enhanced using hydrogen peroxide and ultrasonic irradiation. Increasing the Oxone  
439 concentration and initial pH, along with decreasing the pollutant concentration, favored the



440 process efficiency. Operation of the process under natural pH conditions improves cost-  
441 efficiency of the process due to the lack of need to add chemical agents for pH adjustment. Based  
442 on the results, optimization of the dosage of the binary heterojunction nanocomposite is essential  
443 for the process operation. The growth of more colonies of *E. coli* indicated lower bio-toxicity of  
444 the treated water sample than that of untreated sample. Conclusively, the treatment process of g-  
445 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/photolysis can be effectively utilized for the remediation of aquatic  
446 environments contaminated by antibiotic compounds.

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638 **Figures captions**

639 **Fig. 1.** SEM images of g-C<sub>3</sub>N<sub>4</sub> (a) with EDX-Map (b), ZnFe LDH (c) with EDX-Map (d) and g-  
640 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH (e) with EDX-Map (f).

641 **Fig. 2.** XRD patterns (a) along with FT-IR spectra (b) of the g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH heterojunction  
642 and its components.

643 **Fig. 3.** DRS results and corresponding band gap energy of g-C<sub>3</sub>N<sub>4</sub> (a), ZnFe LDH (b) and g-  
644 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH (c).

645 **Fig. 4.** Degradation of TC under various treatment systems (a), together with the results of  
646 kinetic study (b). Experimental conditions: [TC]: 25 μM, [Oxone]: 0.4 mM, g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH  
647 dosage: 0.2 g/L, pH: natural (unadjusted).

648 **Fig. 5.** Effect of the presence of enhancers and scavengers (a) and kinetic results associated with  
649 the presence of scavengers (b). Experimental conditions: [TC]: 25 μM, [Oxone]: 0.4 mM, g-  
650 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH dosage: 0.2 g/L, pH: natural (unadjusted), [Co-existing compounds]: 0.01 M.

651 **Fig. 6.** Effect of initial pH (a), g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH dosage (b), TC concentration (c) and Oxone  
652 concentration (d). Experimental conditions: [TC]: 10-55 μM, [Oxone]: 0.1-0.5 mM, g-  
653 C<sub>3</sub>N<sub>4</sub>/ZnFe LDH dosage: 0.05-0.3 g/L, pH: 4.5, 7.0 and 9.0.

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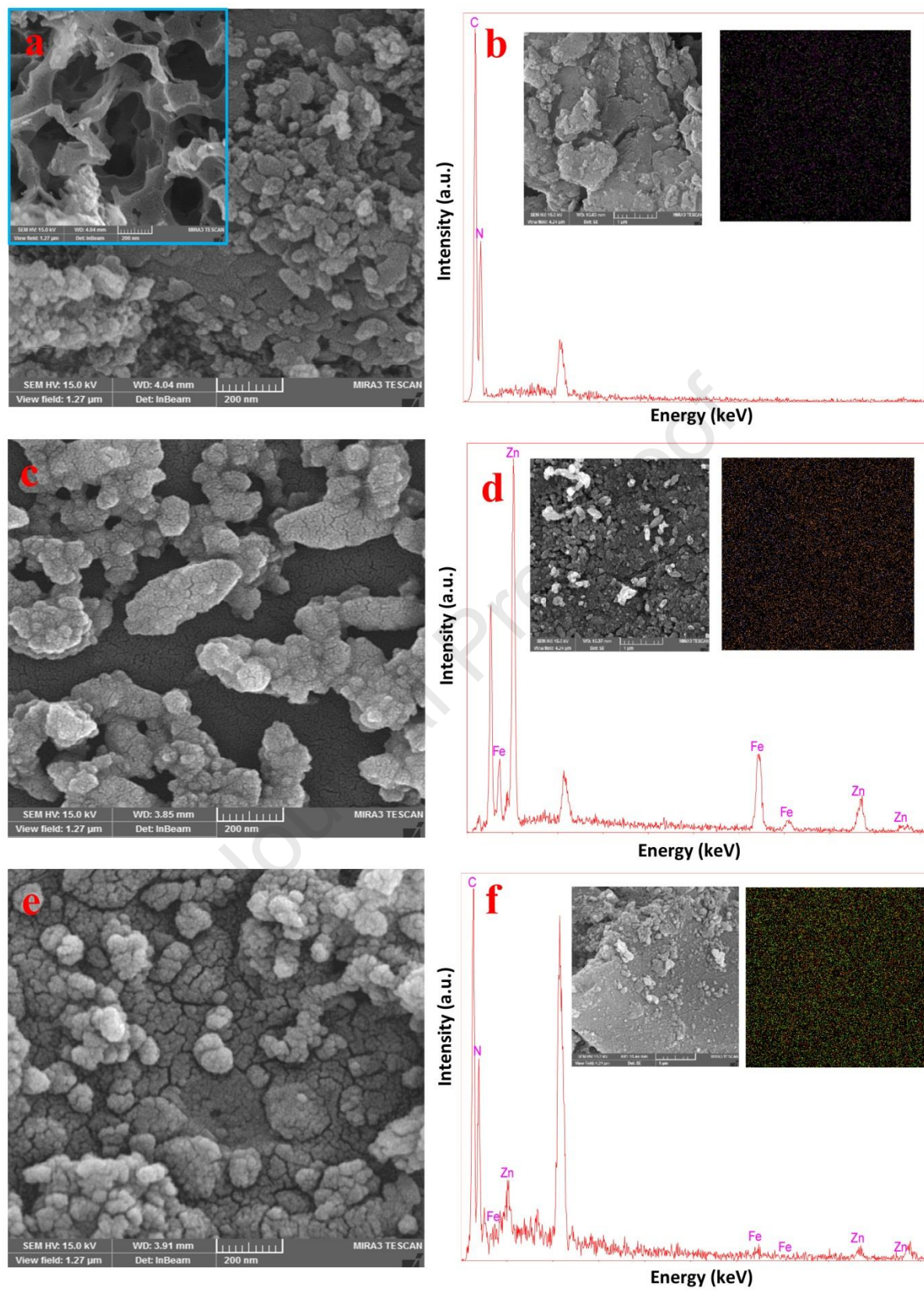


Fig. 1

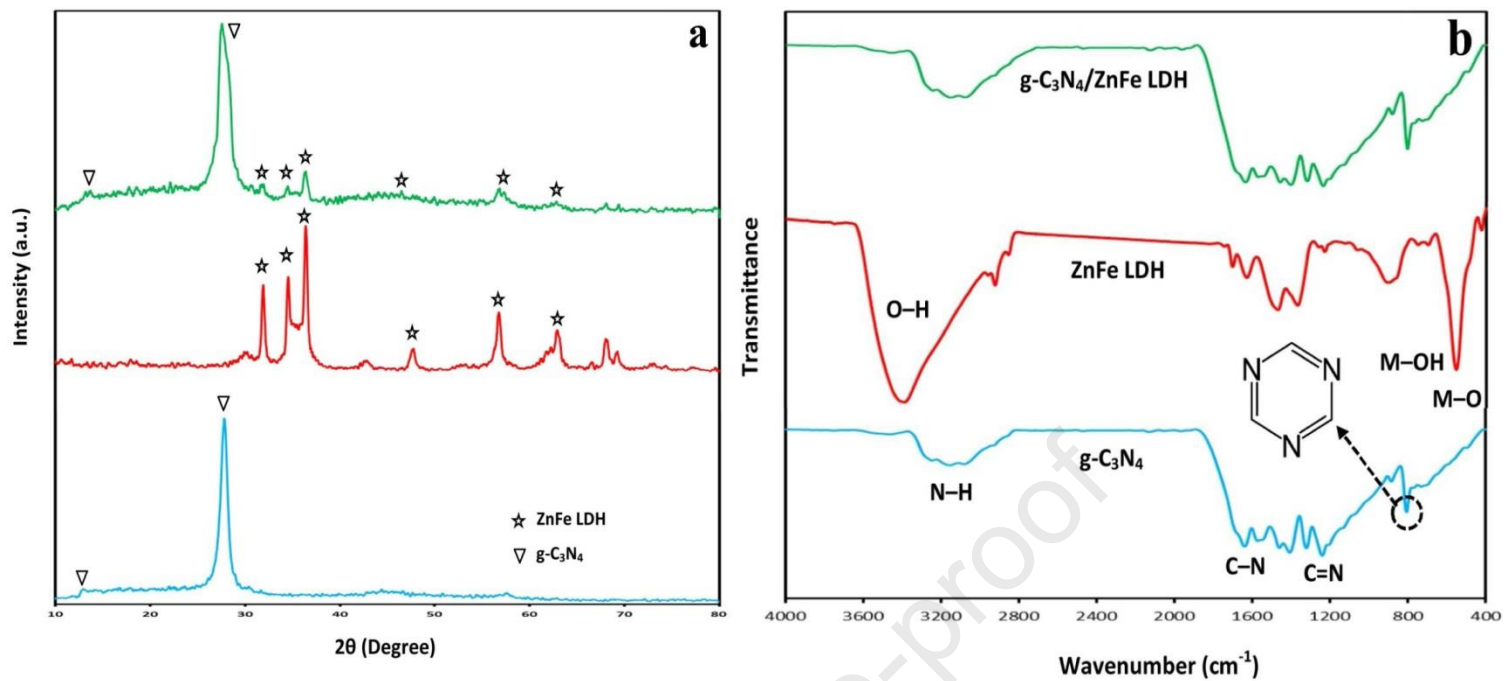


Fig. 2

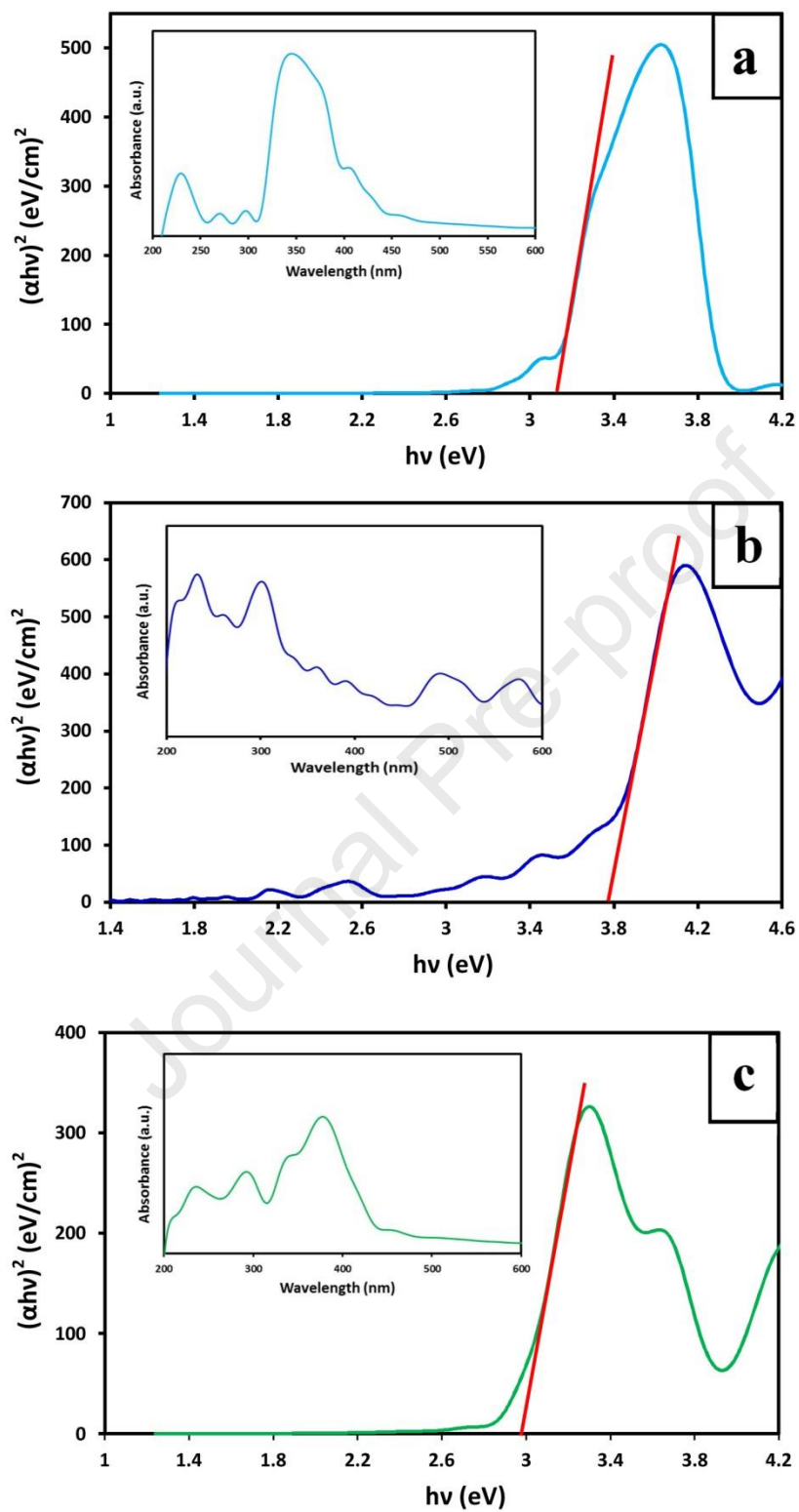


Fig. 3

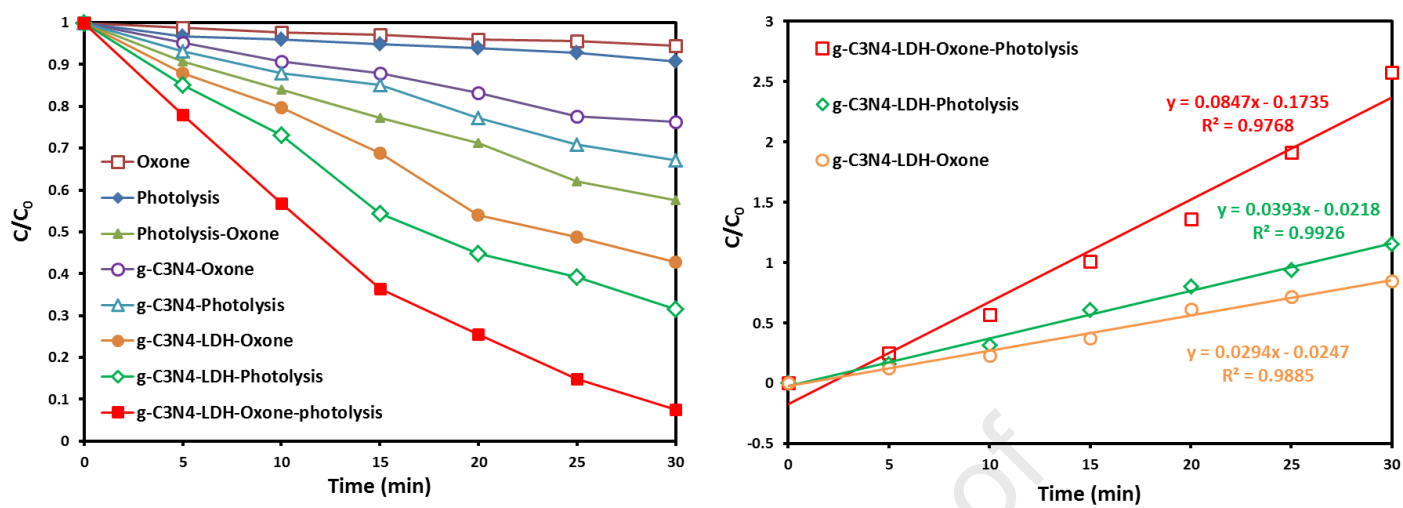


Fig. 4

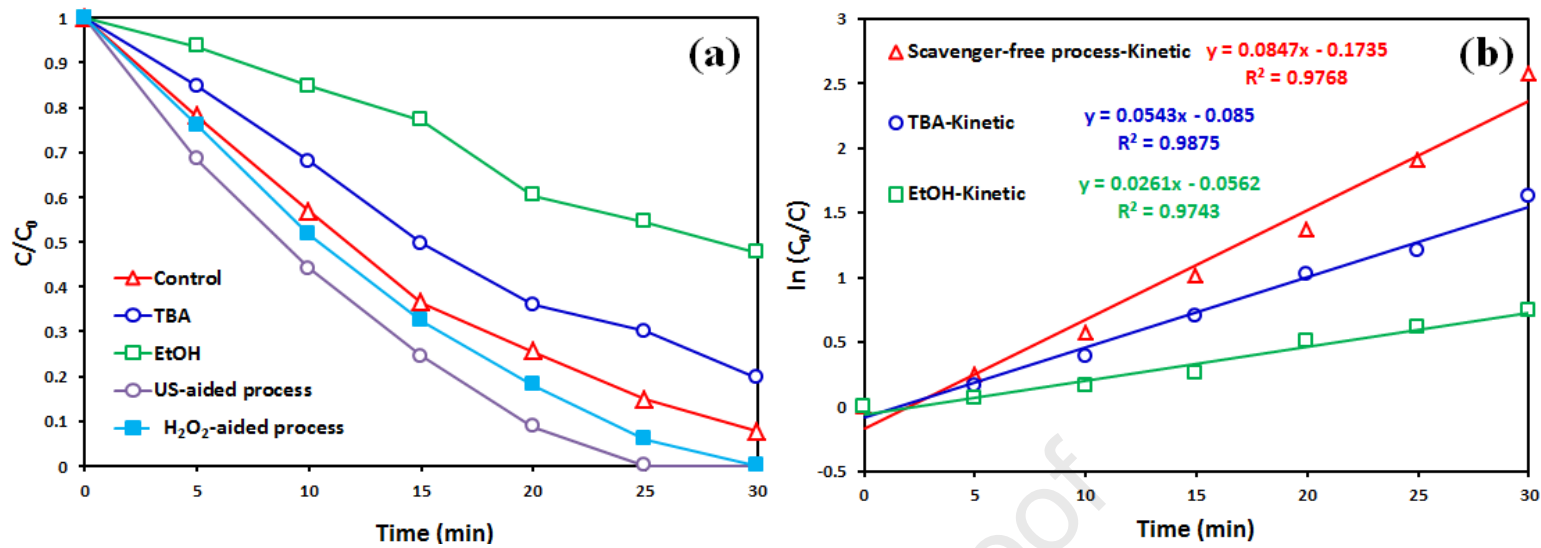


Fig. 5



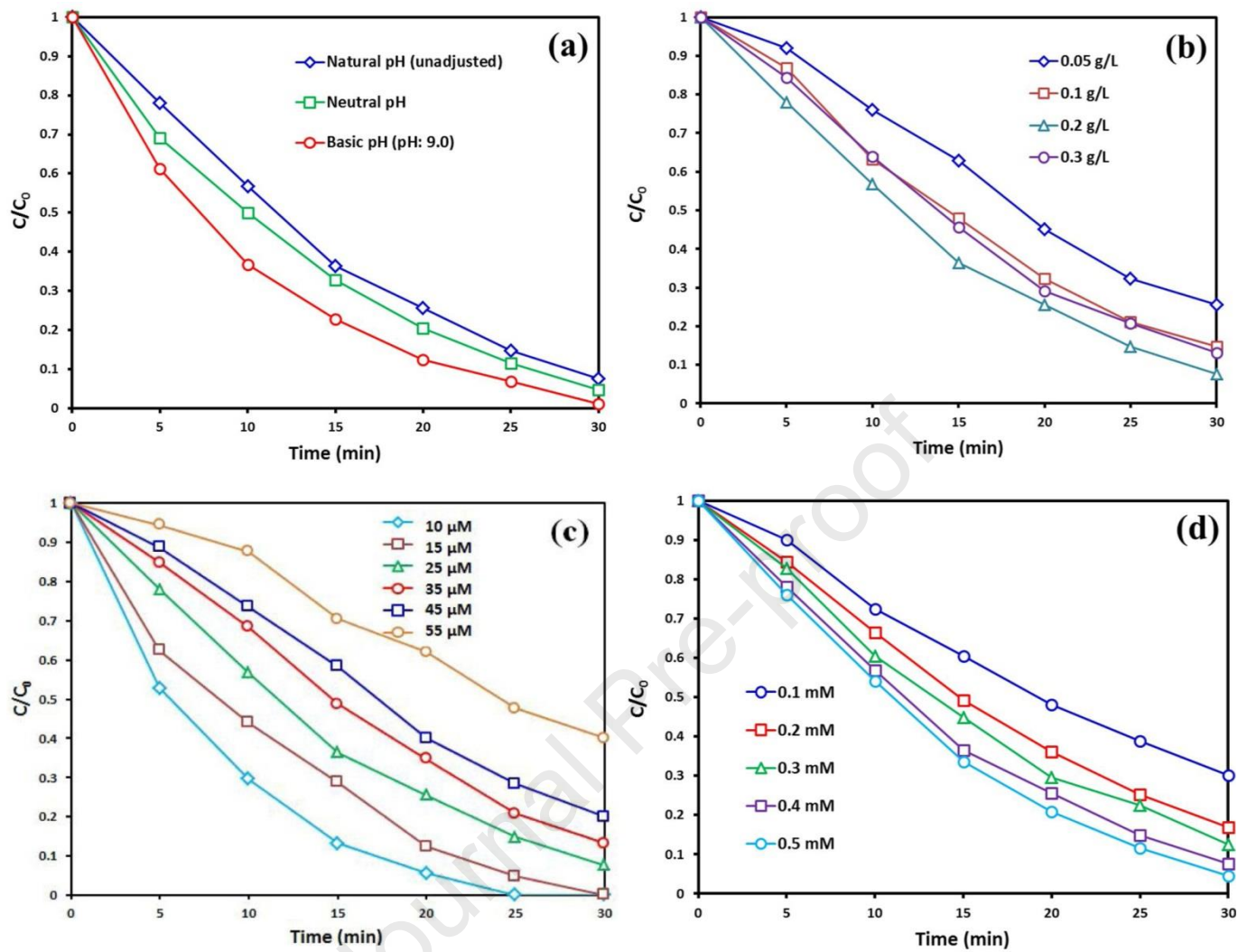


Fig. 6

**Research highlights**

- ✓ Binary heterojunction nanocomposite of g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH was synthesized as catalyst.
- ✓ Tetracycline was effectively decomposed by g-C<sub>3</sub>N<sub>4</sub>/ZnFe LDH/Oxone/UV process.
- ✓ Contribution of radical species to the degradation of tetracycline was determined.
- ✓ Bio-toxicity of the effluent toward microbial population was assessed.
- ✓ Enhancement of the process effectiveness was considered via ultrasound.

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### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the research project reported in this paper.

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