1	Efficient	antibiotics	removal	via th	e synergistic	effect o	f manganese	ferrite and	MoS <sub>2</sub>
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- 2 Huan Yi <sup>a,b,c,1</sup>, Cui Lai <sup>b,c,1</sup>, Eydhah Almatrafi <sup>c,1</sup>, Xiuqin Huo <sup>b</sup>, Lei Qin <sup>b</sup>, Yukui Fu <sup>b</sup>,
- 3 Chenyun Zhou<sup>a,b,c</sup>, ZhuotongZeng<sup>a,b,c,\*</sup>, Guangming Zeng<sup>a,b,c,\*</sup>
- 4 <sup>a</sup> Department of Dermatology, Second Xiangya Hospital, Central South University,
- 5 Changsha 410011, P.R. China;
- 6 <sup>b</sup> College of Environmental Science and Engineering and Key Laboratory of
- 7 Environmental Biology and Pollution Control (Ministry of Education), Hunan
- 8 University, Changsha, Hunan 410082, P.R. China;
- 9 <sup>c</sup> Center of Research Excellence in Renewable Energy and Power Systems, Center of
- 10 Excellence in Desalination Technology, Department of Mechanical Engineering,
- 11 Faculty of Engineering-Rabigh, King Abdulaziz University, Jeddah 21589, Saudi
- 12 Arabia.
- 13
- 14

E-mail address: zgming@hnu.edu.cn (G.M. Zeng), zengzhuotong@csu.edu.cn(Z.T. Zeng ).

<sup>\*</sup> Corresponding author

Tel.: +86-731-88822754; fax: +86-731-88823701.

<sup>1</sup> These authors contribute equally to this article.

# 15 Abstract

16 The use of antibiotics for beings is a most significant milestone in present era. 17 However, owing to the excessive use, a large amount of antibiotics accumulated in 18 water, leading to serious pollution. An efficient method is urgently needed to treat the 19 antibiotics pollution. Photo-Fenton process is a green method with utilizing solar 20 energy. Catalyst is important. This work combines manganese ferrite MnFe<sub>2</sub>O<sub>4</sub> and 21 MoS<sub>2</sub> to synthesize MnFe<sub>2</sub>O<sub>4</sub>-MoS<sub>2</sub> (FMG) composite as the catalyst of photo-Fenton 22 process, which shows good performance on tetracycline antibiotics degradation. Light 23 intensity exhibits positive correlation with the catalytic activity.  $h^+$ , •OH and  ${}^{1}O_{2}$ 24 participate in tetracycline degradation.  $h^+$  plays a key role in tetracycline removal. 25 •OH has a little impact on tetracycline removal, but it has a great impact on the 26 mineralization ability of this photo-Fenton process. Additionally, cycling experiments 27 confirm the stability of FMG. And owing to its magnetism, FMG can be easily 28 recycled by external magnetic field. This photo-Fenton process over FMG with 29 utilizing the synergism of MnFe<sub>2</sub>O<sub>4</sub> and MoS<sub>2</sub> is a promising method for antibiotics 30 pollution treatment.

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32 Key words: Antibiotics removal; Photo-Fenton; MnFe<sub>2</sub>O<sub>4</sub>; MoS<sub>2</sub>; Easy recycle.

# 33 1. Introduction

34 Antibiotics have been widely used as antibacterial agents in treating disease for beings (Yu et al., 2021b). High influent concentration, like 1616 ng $\cdot$ L<sup>-1</sup> of tetracycline (TC), 35 36 was detected in municipal sewage treatment plant (Shao and Wu, 2020). This lead to a 37 serious pollution, and antibiotics would increase chemical oxygen demand and 38 negatively affect the microbial community structure in water (Yi et al., 2019; Stokes 39 et al., 2020; Yu et al., 2021c). Notably, antibiotic pollution is happening directly to 40 humans. According to global ICU infection data, drug resistance caused by overuse of 41 antibiotics will lead to an estimated 10 million deaths a year in 2050 (O'Neill, 2016). 42 Treatment for antibiotics is urgently needed. However, owing to the stubborn ring 43 structure and the developed bacterial resistance, using common wastewater treatment 44 technologies (e.g. adsorption, membrane separation, and biological treatment) cannot 45 remove TC efficiently (Fu et al., 2020; Li et al., 2020a; Yu et al., 2021a). Photocatalytic process has been proved to be a good solution for TC removal (Yi 46 47 et al., 2018; Li et al., 2020b; Yang et al., 2020). Owing to the hard sedimentation and 48 centrifugation process at industrial scale, fabricating a magnetic composite catalyst 49 that can be easily recycled via magnetic separation. Spine ferrite is an ideal material 50 with showing soft magnetic property and high catalytic activity, like ZnFe<sub>2</sub>O<sub>4</sub> for 51 photo induced PMS activation (Zhong et al., 2021). MnFe<sub>2</sub>O<sub>4</sub> is a popular cubic spine 52 ferrite with functional surface, showing high adsorption ability (Hou et al.; Gautam et al., 2017; Wang et al., 2020). And it exhibits good biocompatibility. However, 53

54 photocatalytic system based on MnFe<sub>2</sub>O<sub>4</sub> is not efficient. Molybdenum disulfide 55 (MoS<sub>2</sub>), a common used photocatalyst, has large surface area and suitable band gap 56 for visible-light absorption (Pang et al., 2019). But, the photocatalytic process over 57 MoS<sub>2</sub> cannot generate enough radicals to degrade TC owing to the low valence band 58 (VB) edge potential, and it is difficult to recycle the catalyst from this process 59 (Samakchi et al., 2018; Liu et al., 2019). Combining MnFe<sub>2</sub>O<sub>4</sub> and MoS<sub>2</sub> shows the 60 potential to solve these drawbacks simultaneously. Apart from being the main component of catalyst,  $MoS_2$  can act as co-catalyst to accelerate the  $Mn^{2+}/Mn^{3+}$  and 61  $Fe^{2+}/Fe^{3+}$  cycle to improve the catalytic efficiency. 62

63 This work reports the photo-Fenton process catalyzed by MnFe<sub>2</sub>O<sub>4</sub>/MoS<sub>2</sub> (FM) 64 composites. Mo, Mn and Fe with variable valence benefit the transfer of electrons in 65 the process to improve the oxidation efficiency. The stable and recyclable catalytic 66 performance of FM is tested. The effects of different mass ratio of FM, TC 67 concentration and light intensity on the performance of TC degradation are studied. 68 The intermediate products ad detected and the degradation pathway are discussed to 69 better know the process action. The role of radicals generated in the process and 70 mechanism are also investigated. Overall, this photo-Fenton process over FM exhibits 71 potential practical utility for aqueous organic pollutants treatment.

- 72 **2. Experimental**
- 73 2.1 Synthesis of catalysts

All the reagents are analytical grade. Deionized water was used in the experiment,

75	and the resistivity was 18.2 M $\Omega$ • cm (Milli-Q Millipore). The composite FM
76	synthesized via a solvothermal process with ethylene glycol as the solution is marked
77	as FMG, including four steps: (i) $MnCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ (with 1 : 2 in mol)
78	are dissolved in 20 mL ethylene glycol, then adding 7.2 g sodium acetate (NaAc) and
79	2.0 g polyethylene glycol to obtain solution A after 60 min stirring; (ii)
80	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and thiourea (1 : 40 in mol) are dissolved in 20 mL ethylene
81	glycol to obtain solution B after 30 min ultrasonication; (iii) adding A to B under
82	stirring to get mixture solution; (iv) transfer to Teflon-lined autoclave, heat to 180°C
83	and maintain for 22 h (Shen et al., 2015). The mixture with mol ratio of Mn (in A):
84	Mo (in B) located at 1 : 1, 10 : 1 and 1 : 10 are obtained to synthesize various
85	composites and marked as 1FMG, 10FMG, 0.1FMG, respectively. Parallel synthesis
86	process without step (ii) and (iii) was used to obtain pure MnFe <sub>2</sub> O <sub>4</sub> (FG). MoS <sub>2</sub> (MG)
87	was prepared through the parallel synthesis process without step (i) and (iii).
88	2.2 Characterization of catalysts

X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha+) is used to investigate the surface elemental compositions. Scanning electron microscopy (SEM, SIGMA HD), transmission electron microscopy (TEM) and high resolution TEM (TEM, JEOL JEM 2100) are employed to show the information of morphology and crystal lattice. The specific surface area and pore size are recorded by Brunauer-Emmett-Teller (BET, ASAP 2020 Plus HD88). UV-vis diffuse reflectance spectrophotometer (DRS, Hitachi U4100 UV), Mott-Schottky (M-S) analysis, and 96 linear sweep voltammetry (LSV) are employed to study the optical properties.

97 2.3 Photo-Fenton experiments

98 All the water samples are filtrated by 0.45 um filter membrane. TC is added to 99 water to obtain 10 mg/L solution. 20 mg catalyst is added to 100 mL TC solution. 100 Dark reaction is performed firstly to reach the adsorption/desorption equilibrium. Then, 101 the solution is irradiated with Xe lamp (>420nm, CELHXF300) for 1 h. Reaction 102 solution is collected at given time interval and then filtered through 0.45 µm membrane 103 filters. The concentration of TC is analyzed via Shimadzu UV-vis spectrophotometer 104 (characteristic band at 357 nm). TC intermediate products are determined by 105 high-performance liquid chromatography-mass spectrometry (HPLC-MS, 1290/6460 106 Triple Quad). The test method of HPLC-MS is same as that in our previous work (Yang et al., 2018). Mineralization of TC solution was analyzed by testing the total 107 108 organic carbon (TOC) on Analytik Jena AG (Multi N/C 2100). 109 2.4 Detection of generated radicals Trapping tests are used to explore the role of these active species (i.e.,  $h^+$ ,  $\bullet O_2^-$ , 110 111 <sup>1</sup>O<sub>2</sub> and •OH) in TC degradation. Tetramethylpiperidine (TEMPOL), Isopropanol (IPA), 112 Ethylenediamine tetraacetic acid disodium salt (EDTA-2Na), and L-tryptophan (LTP) are used as the scavengers for  $\bullet O_2^-$ ,  $\bullet OH$ , h<sup>+</sup>, and  $^1O_2$ , respectively. LC-MS is also used 113 114 to detect the intermediates generated in the TC photodegradation process with adding 115 the scavengers.

116 **3. Results and discussion** 

# 117 3.1 Characterizations

# 118 3.1.1 Surface element analysis

119	Surface elemental compositions of the samples are analyzed by XPS. Fig. 2a
120	shows the full-scale spectrum. Binding energy (BE) of Fe 2p, Mn 2p, O 1s, Mo 3d
121	and S 2p are detected in 1FMG, 10FMG and 0.1FMG composites. Fe, Mn and O exist
122	in FG. However, beside Mo and S, O also exist in MG, possibly ascribed to the
123	oxygen of adsorbed -OH form ethylene glycol or $H_2O$ molecules from air.
124	Fig. 2b is the high resolution spectrum of Fe 2p. It can observe two obvious
125	peaks at ~724 eV and ~711 eV that are respectively belonged to the BE of Fe $2p_{1/2}$
126	and Fe $2p_{3/2}$ , and a satellite peak at 718.2 eV is ascribed to the presence of Fe <sup>3+</sup> .
127	Moreover, both $Fe^{3+}$ and $Fe^{2+}$ existed in Fe $2p_{1/2}$ and Fe $2p_{3/2}$ . The BE at 709.9 eV and
128	711.4 eV belonged to $Fe^{3+}$ and $Fe^{2+}$ of Fe 2p <sub>3/2</sub> , while 722.9 eV and 725.2 eV BE
129	belong to $Fe^{3+}$ and $Fe^{2+}$ of Fe $2p_{1/2}$ (Zhao et al., 2020). Based on the peak area, the
130	content of $Fe^{3+}$ and $Fe^{2+}$ can be obtained, which is different in composites and FG.
131	The ratio of $Fe^{2+}$ in 0.1FMG is nearest to that in FG. This reveals that reactions
132	happened between $MnFe_2O_4$ and $MoS_2$ . Since $Fe^{3+}$ and $Fe^{2+}$ co-existed in FMG and
133	FG, it is reasonable to believe the presence of $Mn^{3+}$ and $Mn^{2+}$ .
134	In the Mn 2p spectrum (Fig. 2c), the binding energy of $Mn^{3+}$ (645.8 eV) and
135	$Mn^{2+}$ (641.3 eV) can be divided from $Mn 2p_{3/2}$ peak. The content of $Mn^{3+}$ and $Mn^{2+}$ in
136	the prepared samples is also not the same, and the ratio of $Mn^{3+}$ and $Mn^{2+}$ in 0.1FMG

137 is closest to FG, which is consistent with the findings in Fe 2p spectrum.  $Mn^{3+}$  can

better capture holes to improve catalytic performance (Chen et al., 2014). Moreover,
Mn 2p1/2 (652.5 eV) is observed.

140	High resolution spectrum of O 1s is shown in Fig. 2d. BE at 529.7 eV is ascribed
141	to lattice oxygen, while BE at $\sim$ 531 eV (530.9 eV in 1FMG, 531.4 eV in 10FMG,
142	531.1 eV in 0.1FMG and 531.7 eV in FG) might be owing to the adsorbed oxygen
143	from -OH, $H_2O$ or air. Additionally, the satellite peak of FG at 531.5 eV confirms the
144	presence of lattice oxygen Mn-O.
145	Mo 3d spectrum is shown in Fig. 2e. The peak appeared at 226.0 eV belongs to
146	the BE of S 2s. Mo $3d_{5/2}$ and $3d_{3/2}$ peak with Mo <sup>6+</sup> are observed in all the samples. In
147	0.1FMG and FG, $Mo^{4+}$ can be divided from Mo $3d_{5/2}$ . However, the content of $Mo^{4+}$
148	divided from $3d_{5/2}$ is lower than $Mo^{6+}$ . It suggests that Mo is oxidized in the reaction,
149	leading to the generation of $MoO_x$ (x=2 or 3), which can also provide active sites (Vesel
150	et al., 2018). This can explain the low signal of $MoS_2$ in XRD.
151	S-O is found in S 2p spectrum (the rightmost peak in Fig. 2f) (Chen et al., 2020).
152	Corresponding to Mo, the least oxidation of S occurs in MG, and the next is 0.1FMG.
153	S $2p_{3/2}$ (162.4 eV) and $2p_{1/2}$ (163.6 eV) peaks are found. The spin-orbit energy
154	separation of 1.2 eV is consistent with $MoS_2$ . Besides, XPS valence spectra of FG and

MG are measured to obtain the VB. As shown in Fig. S1, the VB value of FG and MG

156 is 2.94 V and 0.12 V, respectively.



Fig. 2 XPS analysis of the samples: (a) survey spectra, (b) Fe 2p, (c) Mn 2p, (d) O 1s, (e) Mo 3d, (f) S 2p.
3.1.2 Morphology

160 Morphology and microstructure of samples are performed by SEM and TEM. 161 SEM images are presented in Fig. S2. FG show spherical shape with pores. MG also 162 exhibits spherical shape, but the surface is smooth. Both the size of FG and MG is not 163 uniform. Morphologies of 1FMG, 10FMG and 0.1FMG are also observed in TEM 164 images (Fig. 3), which are consistent with SEM. As can be seen from Fig. 3a, 1FMG 165 exhibits stick-like shape with the size at  $\sim 2 \times 0.3$  µm. These sticks are well dispersed

166	and not accumulated. The corresponding HRTEM images show two lattice fringes
167	with lattice spacing at 0.21 nm and 0.26 nm, belonging to (400) and (311) plane of
168	MnFe <sub>2</sub> O <sub>4</sub> , respectively. It can be observed that 10FMG shows regular spherical shape
169	with a diameter at ~0.4 $\mu m$ . Three kinds of lattice spacing and crystal planes are
170	observed in HRTEM images, including 0.21 nm (400), 0.26 nm (311) and 0.30 nm
171	(220) (Zhang et al., 2014; Wang et al., 2017). All of them are the crystal planes of
172	MnFe <sub>2</sub> O <sub>4</sub> . No MoS <sub>2</sub> crystal plane is observed in the HRTEM images of 1FMG and
173	10FMG. There are two possible reasons: i) the content of $MoS_2$ is low, ii) $MoS_2$ is
174	surrounded by MnFe <sub>2</sub> O <sub>4</sub> . Therefore, only MnFe <sub>2</sub> O <sub>4</sub> lattice can be observed from the
175	surface. The shape of 0.1FMG performed in Fig. 3c is spherical but not regular with
176	multiple sizes. No crystal lattice was magnified by HRTEM, indicating the formation
177	of amorphous substance. It is speculated that amorphous MoS <sub>2</sub> is formed outside the
178	$MnFe_2O_4$ in 0.1FMG.



180 Fig. 3 TEM and HR-TEM images of (a, b) 1FMG, (c, d) 10FMG, and (e, f) 0.1FMG.

# 181 3.1.3 Surface area and pore size

182 The surface area and pore distribution of these prepared samples are explored via 183 nitrogen adsorption-desorption isotherms experiments. As can be seen in Fig. 4a, the 184 basic shape of N<sub>2</sub> adsorption-desorption isotherm of all the samples are typical IV 185 type, indicating the presence of mesoporous. Moreover, the samples possess H3-type 186 hysteric ring that suggest the slit structures. The BET surface area in descending order is: 10FMG > MG > 1FMG > FG > 0.1FMG (Table 1). The pore diameter distributions 187 188 are shown in Fig. 4b-f. Pores of FG and 10FMG range from 1 nm to 100 nm. 0.1 189 FMG pores are in the range of 0-90 nm. 1FMG Pores range from 0 nm to 60 nm. MG 190 shows the least range of pore diameter (0-40 nm), corresponding to the least average 191 pore diameter (4.6 nm). The BET specific surface area and pore size of different 192 catalysts are different. The specific surface area of the catalyst can explain the 193 exposure of the surface active site. The contact between the active site and the target 194 contaminant is also affected by the structure of the catalyst.



196 Fig. 4 N<sub>2</sub> adsorption-desorption isotherm of all the samples (a), and pore diameter distribution of FG

Samples	1FMG	10FMG	0.1FMG	FG	MG
BET surface (m <sup>2</sup> /g)	9.03	13.62	4.34	8.78	9.93
Total pore volume (cm <sup>3</sup> /g)	0.027	0.032	0.135	0.070	0.014
Average pore diameter (nm)	9.05	8.75	14.99	17.76	4.60

198 Table 1 BET surface, average pore volume and average pore diameter of the prepared samples

### 199 3.1.4 Optical property

200 Related optical properties of the prepared samples are explored by UV-vis DRS 201 and LSV analysis. According to the DRS in Fig. 5a, all the samples can absorb visible 202 light. LSV curve (Fig. 5b) suggests that all the samples are conductive. Compared 203 with 1FMG, 10FMG and 0.1FMG composites show higher conductivity. Additionally, 204 a peak at 0.85 V appears in FG and a peak at 1.23 V appears in MG. Differently, a 205 peak at 1.00 V appears in 10FMG and a peak at 1.04 V appears in 0.1FMG. No peaks 206 are found in 1FMG. This indicates there has been a reaction between MnFe<sub>2</sub>O<sub>4</sub> and 207 MoS<sub>2</sub> to form FMG composites. M-S analyses of FG and MG are shown in Fig. S3. It 208 can be found that FG is a p-type semiconductor (negative slope in M-S plot) with the 209 value of Fermi level at 2.12 V vs. vs. Ag/AgC1. The bottom of FG VB is more positive 210 (~0.2 eV) than Fermi lever. Therefore, VB value of FG can be calculated to be 2.52 V vs. NHE, which is close to the VB value (2.94 V) determined by XPS-VB. The M-S 211 plot of MG exhibits positive slop with the value of Fermi level at -0.08 V vs. vs. 212 213 Ag/AgCl. For MG, Fermi level is more positive (~0.2 eV) than the bottom of



#### 215 -0.08 V vs. NHE.

217 Fig.5 (a) UV-Vis absorption spectra and (b) LSV curve of the prepared samples.

#### 218 3.2 Catalytic test

219 TC, a broad-spectrum antibiotic, is widely used in treating bacterial infections for 220 human health. With the increase of daily dosage, TC emissions into water have been rising. The accumulated TC is a potential hazard for beings. TC is chosen as the main 221 target pollutant to test the performance and stability of FMG under visible-light 222 irradiation. The prepared FMG in this work is anticipated to show high catalytic 223 224 activity. The effects of different mass ratio of MnFe<sub>2</sub>O<sub>4</sub>/MoS<sub>2</sub>, TC concentration, and light intensity on catalytic performance are investigated. The stability of catalyst is 225 226 studied by cycling experiments. The intermediate products in TC degradation process 227 is explored by LC-MS. Before irradiation, 1 h of dark adsorption needs to be carried 228 out to reach absorption equilibrium (Fig. S4). 229 Fig. 6a shows the degradation efficiency of the prepared samples on 10 mg/L TC.

230 1FMG shows the best performance with the efficiency located at 76.4%. 10FMG and

231 0.1FMG can remove 57.2% and 60.0% TC in 1 h, respectively, higher than the

degradation efficiency of FG (19.5%) and MG (4.4%). This indicating there is a synergism between  $MnFe_2O_4$  and  $MoS_2$  in FMG composites for TC degradation. Fig. 2b exhibits the performance of these samples on 20 mg/L TC degradation. The results are consistent with the degradation efficiency on 10 mg/L TC. Compared the results in Fig. 6a and Fig. 6b, it can be found that the concentration of TC has an impact on the degradation efficiency. The lower concentration leads to higher efficiency, which is beneficial for practical TC (like 1.62 mg/L) treatment.

Afterwards, the effect of light intensity is investigated by adjusting the distance between the light source and TC solution surface. The distance is set at 5 cm, 10 cm and 15 cm, corresponding to  $398.75 \text{ mW/cm}^2$ ,  $333.97 \text{ mW/cm}^2$  and  $203.82 \text{ mW/cm}^2$ , and the TC degradation efficiency reaches 76.4%, 71.2% and 68.2%, respectively. With the decrease of light intensity, the efficiency is also reduced. The degradation efficiency is reduced by ~4% with the decrease of 100 mW/cm<sup>2</sup>.

245 The stability is an important factor as a catalyst. In this work, the stability and 246 reusability of 1FMG are tested by cyclic experiments. As shown in Fig. 6d, the 247 photo-Fenton process over 1FMG can degrade 76.4% of TC. 1FMG are recycled via 248 magnetic separation. In the second and third run, TC degradation reaches 72.2% and 249 70.1%, respectively. The reduced efficiency might be owing to the reduced adsorption 250 capacity (from 48.1% to 28.5% and 27.6%). After the first use, some TC or intermediates remain in 1FMW and are not been eluted out, shielding part of the 251 active sites and leading to a decrease in degradation efficiency. 252



Fig. 6 Degradation efficiency of prepared samples in (a) 10 mg/L TC and (b) 20 mg/L TC; (c) TC
degradation over 1FMG under different intensity of light, (d) Cycling runs of 1FMG on TC
photodegradation. Conditions: [Catalyst] = 0.2 g/L, [TC] = 10 mg/L.

257 The degradation products of TC over 1FMG are detected via HPLC-MS (Fig. 7). 258 The peak at m/z=444.4 representing TC is decreasing during the reaction process. 259 Peaks located at other m/z positions appear successively after irradiation. The peaks at 260 m/z=274.3 and 318.3 are decreasing as the reaction time increased. And after 60 min of irradiation, peaks at m/z=116.2, 158.2, 188.3 and 204.3 appear, indicating the 261 262 production of smaller molecules. These small molecular products are more 263 biodegradable. Based on the m/z value, the intermediates can be obtained. Possible degradation pathways of TC are presented (Inset in Fig. 7). There are two main 264 reactions in TC degradation over 1FMG: one is N-demethylation reaction that 265

266 dominated by h<sup>+</sup>, the other one is dehydration/hydroxylation reaction that dominated



267 by •OH (Deng et al., 2018).



Fig. 7 Degradation intermediates of TC detected by LC-MS. Inset is the possible degradation pathways

271 3.3 Role of radical species

Trapping tests are used to analyze the role of radical species generated in the photo-Fenton process over 1FMG. TEMPOL, IPA, EDTA-2Na, and LTP are used as the scavengers for  $\cdot O_2^-$ ,  $\cdot OH$ , h<sup>+</sup>, and  $^1O_2$ , respectively. As shown in Fig. 8a, after adding the scavengers, all the degradation efficiencies decrease. EDTA-2Na shows the highest inhibit effect with the degradation efficiency reduced to 55.0%. This suggests that h<sup>+</sup> plays the most important role in TC degradation. Moreover, compared with the degradation efficiency of the process without adding scavengers, 5.1%, 2.8%

<sup>270</sup> of TC in the photo-Fenton process over 1FMG.

and 4.9% of the efficiency is reduced after adding TEMPOL, IPA and LTP, respectively. Trapping  $\cdot O_2^-$ ,  $\cdot OH$ , and  $^1O_2$  has a little negative impact on TC degradation, indicating that  $\cdot O_2^-$ ,  $\cdot OH$ , and  $^1O_2$  also play a role in the oxidation process.

283 LC-MS is used to detect the products of trapping test. Degradation results are 284 consistent with that of trapping tests that are determined by UV-Vis spectrophotometer. Possible TC degradation pathways after adding scavengers are also proposed. Fig. 8b 285 286 shows the LC-MS spectra of the TC degradation intermediates of the photo-Fenton 287 process with adding TEMPOL, which are similar to that of normal photo-Fenton 288 process. The degradation pathway is the same to that in Fig. 7. This suggests that no  $\cdot O_2^-$  is generated in the reaction, but the addition of TEMPOL as an organic leads to a 289 290 competition with TC, so having a little effect on LC-MS spectra. Besides, we also 291 found that compared the LC-MS spectrum in 0 min with that after 60 min of reaction, 292 most TC is not be removed after adding EDTA-2Na (Fig. 8c). And notably, it can be 293 found that nearly no small molecules (m/z<360) are produced after adding IPA (Fig. 294 8d), while smaller products (m/z<200) can be detected after adding LTP (Fig. 8e). 295 Aromatic ring and naphthol ring were hardly to be broken when IPA was added to trap 296 •OH, affecting the mineralization process. And TOC removal of the TC solution with 297 adding TEMPOL, IPA, EDTA-2Na, and LTP was about 57%, 28%, 33% and 60%, respectively. It could be concluded that: i)  $h^+$  plays a key role in TC removal, ii) •OH 298 299 has a great impact on the mineralization ability of the photo-Fenton process.



301 Fig. 8 (a) Trapping tests: 5 mmol scavengers in 100 mL 10 mg/L TC solution; LC-MS spectra and

302 proposed possible TC degradation pathways of the photo-Fenton process after adding (b) TEMPOL, (c)

<sup>303</sup> EDTA-2Na, (d) IPA, and (e) LTP.

305	1FMG composite shows much higher degradation efficiency (76.4%) than that of FG
306	(19.5%) and MG (14.%), indicating there is a synergism between $MnFe_2O_4$ and $MoS_2$
307	in FMG composites for TC degradation. The presence of $Fe^{3+}/Fe^{2+}$ , $Mn^{3+}/Mn^{2+}$ and
308	$Mo^{6+}/Mo^{4+}$ plays an important role in the synergism. The reaction rate of Fe <sup>3+</sup> /Mn <sup>3+</sup> and
309	$Fe^{2+}/Mn^{2+}$ cycles is limited owing to the low electron transfer rate in the photo-Fenton
310	process over MnFe <sub>2</sub> O <sub>4</sub> . The introduction of MoS <sub>2</sub> promotes the electron cycle and
311	ensures the enough presence of metal ions with lower valence state (i.e., $Fe^{2+}$ , $Mn^{2+}$ and
312	$Mo^{4+}$ ) for $H_2O_2$ decomposition. Therefore, the photo-Fenton reaction efficiency can be
313	guaranteed. On the basis of above results, $h^+$ , •OH, and ${}^1O_2$ are generated in the
314	photo-Fenton process of 1FMG, and then participate in the TC degradation. The main
315	active species, $h^+$ , is generated in 1FMG VB after irradiation. The conversion of
316	$Fe^{2+}/Fe^{3+}$ , $Mn^{2+}/Mn^{3+}$ , and $Mo^{4+}/Mo^{6+}$ benefit the separation of photogenerated
317	electrons and $h^+$ . No $\bullet O_2^-$ is produced in the photo-Fenton process. The value of CB
318	(-0.08 V vs. NHE) is more positive than the redox potential needed for $\cdot O_2^-$
319	generation (E( $O_2/\bullet O_2^-$ )=-0.33 V vs. <i>NHE</i> ), confirming that $\bullet O_2^-$ cannot be produced.
320	•OH can be generated from the oxidation reaction of $\mathrm{H}_2\mathrm{O}$ owing to the higher VB
321	value than the redox potential of •OH/H <sub>2</sub> O (+2.38 V). $^{1}O_{2}$ can be generated from the
322	oxygen activation or the disproportionation reaction of •OH. The mechanism of the
323	active species generation in the photo-Fenton process over 1FMG and their roles in
324	TC degradation are presented in Fig. 9.



326 Fig. 9 Possible oxidation mechanisms over 1 FMG composite.

# 327 **4.** Conclusion

325

328 Overall, among these FMG composites, 1FMG are successfully synthesized 329 according to the detailed analysis on its component, structure, morphology and property. The conductive stick-like 1FMG ( $\sim 2 \times 0.3 \mu m$ ) composites are well dispersed 330 and not accumulated. Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, and Mn<sup>3+</sup> co-exist in IFMG, benefiting the 331 332 electrons transfer. Compared with other samples, 1FMG shows the best performance 333 for TC degradation with the removal efficiency reaches 76.4%. Lower TC concentration leads to higher efficiency, which is beneficial for practical TC (almost 334 <10 mg/L) treatment. Light intensity exhibits positive correlation with the catalytic 335 activity. Active species include  $h^+$ , •OH and  ${}^1O_2$  participate in TC photodegradation. 336 337 Although •OH has a little impact on TC removal, it act as a key role in the mineralization of TC. The excellent catalytic performance can be attributed to 338 following reasons: (i) the presence of metal ions with variable valence state can 339

345	Declaration of competing interest
344	1FMG shows great potentials in the applications of antibiotics treatment.
343	•OH promotes the mineralization of TC. Particularly, the photo-Fenton process over
342	high oxidation ability is also formed in the photo-Fenton process over 1FMG. (iv)
341	generation of $h^+$ . (ii) $h^+$ plays the main role in TC degradation. (iii) ${}^1O_2$ possessing
340	improve the separation of photogenerated electrons and $h^+$ , guaranteeing the enough

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