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1 Microwave catalytic activities of supported catalysts MFe₂O₄@CMT

- 2 (M=Ni, Co) for dimethyl phthalate degradation
- 3 Wenli Qin^a, Xinyi Zhang^a, Zefei Chen^a, Xueya Liu^a, Manqing Ai^b, Pingping Zhang^b,
- 4 Ying Ye^b, Zengling Ma^{a1}
- 5 a National and Local Joint Engineering Research Center of Ecological Treatment
- 6 Technology for Urban Water Pollution, College of Life and Environmental Science,
- 7 Wenzhou University, Wenzhou, 325035, P.R. China
- 8 b Ocean College, Zhejiang University, Zhoushan, 316021, P.R. China

9 1. Materials information

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Table S1 The content of the main elements in simulated seawater

Elements	Cl-	Na ⁺	Mg^{2+}	SO ₄ ²⁻	Ca ²⁺	\mathbf{K}^+	Br⁻	others
Content (g L ⁻¹)	18.30	9.78	1.08	2.46	0.35	0.31	0.042	0.23

11 2. Pore structure analysis

Table S2 BET surface area and pore characteristics of PCCF and PCNF

Sample	Surface are (m ² g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Average pore size (nm)
PCCF	8.995	0.231	0.058	8.36
PCNF	11.22	0.256	0.067	7.12

13 3. Permittivity and Permeability

14 The frequency dependence of EM parameters of ferrite/corncob composite were

15 detected using vector network analyzer in the range of 1-18 GHz. As shown in Fig.

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¹ Corrersponding author: Zengling Ma, Email: mazengling@wzu.edu.cn; Tel.: +86-0577-86689079; fax: +86-0577-86689079.

S1a and S1b, the real (ε') and imaginary permittivities (ε'') of CC were 22.74 - 206.14 16 and 63.25 - 194.33, respectively. The ε' and ε'' kept decreasing with the increasing of 17 frequency. Consequently, their dielectric loss tangents (tan $\delta_e = \varepsilon''/\varepsilon'$, Fig. S1c) were 18 generally invariant at 0.94 to 2.74. When coated with ferrite, the ε' were between 3.33 19 and 3.73 of PCCF, 3.62 and 3.83 of PCNF, which were smaller than that of CC; the ε'' 20 of PCCF and PCNF fluctuated slightly with frequencies between 0.06 and 1.24. It is 21 well known that $\varepsilon'' \approx \sigma/2\pi\varepsilon_0 f$ according to the free electron theory (Chen *et al.* 2012a), 22 where σ is the conductivity of the sample; that is, higher ε'' values require higher 23 conductivities. The ε'' values of ferrite/corncob composite are almost increased 24 slightly with frequency, indicating that the poorer conductivity of ferrite/corncob 25 composite than that of CC. Consequently, the tan δ_e value of ferrite/corncob 26 composite increased to the maximum value at 2.74 of CC, 0.26 of PCCF, 0.10 of 27 PCNF, where larger tan δ_e values show higher dielectric loss. It is indicated that the 28 coating of ferrite/corncob will not increase the conductivity of the sample, resulted in 29 PCCF and PCNF showed lower permittivity than CC. 30

Fig. S1d and S1e showed the frequency dependence of the relative complex permeability of ferrite/corncob composite. Because of the absence of magnetic components, the real (μ') and imaginary permeability (μ'') of CC were lower than that of PCCF and PCNF. Nevertheless, the μ' and μ'' values of PCCF showed slightly higher than PCNF exhibited highest value, the maximum μ' and μ'' value were 1.57 and 0.91, respectively. As a result, the magnetic loss tangent (tan $\delta_m = \mu''/\mu'$, Fig. S1f) of CC and PCNF were below 0.030, while the maximum magnetic loss tangent of

- 38 PCCF was 1.07. The complex permittivity and permeability values of ferrite/corncob
- 39 composite suggest that the presence of ferrite will enhance the EM wave absorption,



40 mainly induced by magnetic loss.

43 Fig. S1 Frequency dependence of (a) real permittivity, (b) imaginary permittivity, (c) dielectric loss tangent,

44 (d) real permeability, (e) imaginary permeability, and (f) magnetic loss tangent of CC, PCCF, and PCNF

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with volume fraction of 50 % and thickness of 2 mm.

Table S3 The comparation between the different EM wave absorbing materials

	Thickness (mm)	Maximum RL (dB)
CC	2.72	-1.82
PCCF	1.82	-39.79
PCNF	6.47	-23.47
Porous Carbon fiber (Guan et al., 2007)	2.9	-15.5
Porous Fe (Chen et al., 2012b)	2.0	-21.9
Rice Husk Ash (Liu et al. 2014)	2.0	-12.5
Halloysite-Fe (Zhang et al., 2014)	2.0	-0.8
Polypropylene/montmorillonite/polypyrrole (Moučka et al., 2011)	100	-60.0

47 4. Degradation



53 values of DMP solution after PCCF and PCNF microwave enhanced Fenton-like performance; (d)

54 MW enhanced Fenton-like performance of PCCF and PCNF when hydroxyl radical quenching

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- 56

Table S4 DMP degradation first-order kinetic reaction fitting kinetic constant

agent added after 1 min MW

Catalyst	<i>k</i> (min ⁻¹)
PCCF	0.3975
PCNF	0.8902
PCCF in salinity	0.1561

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Table S5 Experimental details and the DMP removal rate of AOPs systems

Catalyst	Type of reaction	Catalyst dosage	DMP concentration (mg L ⁻¹)	Time (min)	Degradation rate (%)	Reference
Hydroxylamine	Electro-Fenton (Fe ²⁺ : 10	0.5 μM	10	20	96.7	Li, et al., 2022
sulfate	mM)	·				
Graphene-WO ₂	Dielectric barrier discharge	40 mg L ⁻¹	10	60	90.60	Han et al 2022
Shiphene (19)	plasma system	10 116 2	10		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	,,
Z-scheme iron				360		
oxide/mpg-	Photocatalytic	10 g I -1	20		92	Lietal 2021
C ₃ N ₄ /BiOBr/polythi	Thotocatarytic	1.0 g L	20)2	Li, et al., 2021
ophene						
CaEa O @CMT	Microwave-assisted Fenton	$2.0 \sim 1^{-1}$	500 u ~ I -1	6	00	This non on
CoFe ₂ O ₄ @CM1	(H ₂ O ₂ : 200 mg L ⁻¹)	2.0 g L ¹	500 µg L .		90	This paper
	Microwave-assisted Fenton	2 0 1 -1	500 Il	6	00	TTI :
$N1Fe_2O_4(@CMT)$	(H ₂ O ₂ : 200 mg L ⁻¹)	2.0 g L ⁻¹	500 μg L ⁻¹		99	I nis paper

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Table S6 Information on intermediates

Compound	Structure	Formula	m/z
DMP		$C_{10}H_{12}O_4$	196
M1	ОН	$C_8H_{10}O_3$	154
M2		$C_8H_9O_2$	137
M3	COOH	$C_8H_8O_4$	168



62 4. XPS after reaction

- 63 Table S7 Surface elemental and group composition (%) of PCCF and PCNF before and after
- 64

reaction.

	Catalant	С	1s	O 1s		
	Catalyst	C-C/C=C	С-ОН	H ₂ O	-OH	Fe-O
PCCF	Before	84.12	15.88	15.82	43.87	40.31
	After	81.74	18.26	3.29	51.02	45.69
PCNF	Before	82.36	17.64	14.32	47.36	38.32

	After	78.22	21.78	1.85	54.84	43.31
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4. Health risk evaluation 66

The non-carcinogenic risk (HI) is which is calculated according to Eqs. S1-S4. 67

 $BW \times AT$

$$HI = \frac{CDI}{RfD}$$
(S1)

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$$CDI_{drinking} = \frac{C \times U \times EF \times ED}{BW \times AT}$$

70 (S2)

$$CDI_{skin} = \frac{I \times A_{sd} \times FE \times ED}{BW \times AT \times f}$$

72 (S3)

$$_{73} \qquad I = 2 \times 10^{-3} \times k \times C \times (6 \times \tau \times TE/\pi)^{0.5}$$
(S4)

76 When the HI value is less than 1, it indicates that the exposure dose does not cause non-carcinogenic risk to human body. An HI value greater than 1 indicates a 77 non-carcinogenic health risk to humans. 78

Table S8 PAEs concentrations in surface water of rivers and lakes in some places in China and 79

80				oversea				
Site	DMP	DEP	DiBP	DBP	BBP	DEHP	DOP	Reference
Somme River Water,	0.02~0.25	0.26~6.98	/	0.22~3.86	ND	5.16~20.8	ND	Net, et al., 2014
France								
Kaveri River, India	0.02	0.24	/	0.25	0.04	0.51	0.03	Selvaraj, et al., 201
False Creek Harbor,	<0.5	<0.5	/	<0.5	<0.5	<0.5	<0.5	Mackintosh, et a
Spain								2009
Manzanares and	ND	ND	/	0.25~1.76	ND	ND	/	Dominguez-Morueo
Halama rivers, Spain								et al., 2014
Xuanwu Lake, China	0.003~0.085	0.015~0.32	0.16~0.92	0.94~3.60	ND	0.087~0.63	ND	Zeng, et al., 2008

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81 Notes: 1) ND: not detected; 2) /: not determined.

Meaning **Reference value** Unit CDI Long-term daily intake mg·(kg·d)⁻¹ _ *RfD* Reference value mg·(kg·d)⁻¹ _ SF (kg·d)·mg⁻¹ Slope factor of carcinogenic pollutants С Contaminant concentration mg·L⁻¹ 1.825 (Male) U Daily drinking water quantity 1.350 (Female) L·d⁻¹ 1.000 (Children) EF 365 d·a⁻¹ Exposured frequency 74 (Male) ED Exposured duration 78 (Female) а 12 (Children) BW Average weight 64.8 (Male) 55.1 (Female) kg 26.8 (Children) 27010 (Male) AT 28470 (Female) d Average exposured time 4380 (Children) Ι Amount of contaminants absorbed by mg·cm⁻²·times⁻¹ skin 17000 (Male) Surface area of the human body 15000 (Female) cm² Asd 8490 (Children) times·d⁻¹ FE Bathing frequency 0.3 TE Bath time 0.4 h Intestinal adsorption ratio 1 f

Table S9 Meaning, reference value, and unit of each symbol in the formula

k	Skin adsorption parameter	0.001	cm·h ⁻¹
τ	Contaminant lag time	1	h
RfD	Reference dose	0.1	mg·(kg·d) ⁻¹

83 Reference:

- 84 Chen, X, Lv, S, Zhang, P, Cheng, J, Liu, S, Ye, Y, 2012a. Fabrication and electromagnetic
- 85 performance of micro-tubular nanocomposites composed of monodisperse iron nanoparticles and
- 86 carbon. Journal of Magnetism and Magnetic Materials, 324(9):1745-1751.
- 87 Chen, X, Cheng, J, Lv, S, Zhang, P, Liu, S, Ye, Y, 2012b. Preparation of porous magnetic

88 nanocomposites using corncob powders as template and their applications for electromagnetic

89 wave absorption. *Composites Science and Technology*, 72(8):908-914.

- 90 Dominguez-Morueco, N, Gonzalez-Alonso, S, Valcarcel, Y. 2014. Phthalate occurrence in rivers
- 91 and tap water from central Spain. Science of the Total Environment, 500-501: 139-146.
- 92 Han, S, Mao, D, Wang, H, Guo, H, 2022. An insightful analysis of dimethyl phthalate degradation
- 93 by the collaborative process of DBD plasma and Graphene-WO₃ nanocomposites. Chemosphere,
 94 291, 132774.
- Guan, H, Liu, S, Duan, Y, Zhao, Y, 2007. Investigation of the electromagnetic characteristics of
 cement based composites filled with EPS. Cement and Concrete Composites, 29(1):49-54.
- 97 Li, S X, Lai, C, Li, C G, Zhong, J T, He, Z F, Peng, Q Y, Liu, X, Ke, B H, 2021. Enhanced
- 98 photocatalytic degradation of dimethyl phthalate by magnetic dual Z-scheme iron oxide/mpg-
- 99 C₃N₄/BiOBr/polythiophene heterostructure photocatalyst under visible light. Journal of Molecular
- 100 Liquid, 342, 116947.
- 101 Li, D, Yu, J H, Jia, J L, He, H Y, Shi, W, Zheng, T, Ma, J, 2022. Coupling electrode aeration and
- 102 hydroxylamine for the enhanced Electro-Fenton degradation of organic contaminant: Improving
- 103 H_2O_2 generation, Fe^{3+}/Fe^{2+} cycle and N_2 selectivity. Water Research, 214: 118167.
- 104 Liu, S T, Chen, X G, Zhang, A B, Yan, K K, Ye, Y, 2014. Electromagnetic Performance of Rice
- 105 Husk Ash. Bioresources, 9(2):2328-2340.
- 106 Mackintosh, CE, Maldonado, JA, Ikonomou, MG, Gobas, FAPC. 2006. Sorption of phthalate
- 107 esters and PCBs in a marine ecosystem. Environmental Science & Technology, 40(11): 3481-3488.
- 108 Moučka, R, Mravčáková, M, Vilčáková, J, Omastová, M, Sáha, P, 2011. Electromagnetic

- 109 absorption efficiency of polypropylene/montmorillonite/polypyrrole nanocomposites. Materials &
- 110 Design, 32(4):2006-2011.
- 111 Net, S, Dumoulin, D, El-Osmani, R, Rabodonirina, S, Ouddane, B. 2014. Case Study of PAHs,
- 112 Me-PAHs, PCBs, Phthalates and Pesticides Contamination in the Somme River Water, France.
- 113 International Journal of Environmental Research, 8(4): 1159-1170.
- 114 Selvaraj, KK, Sundaramoorthy, G, Ravichandran, PK, Girijan, GK, Sampath, S, Ramaswamy, BR.
- 115 2015. Phthalate esters in water and sediments of the Kaveri River, India: environmental levels and
- 116 ecotoxicological evaluations. Environmental Geochemistry and Health, Health, 37: (1): 83-96.
- 117 Shen, Y, Xu, Q, Yin, X, Wang, M, Zhang, N, Wu, S, Zhang, Z, Gu, Z, Wang, H. 2010.
- 118 Determination and Distribution Features of Phthalate Esters in Xuanwu Lake. Journal of Southeast
- 119 University (Natural Science Edition), 40 (6): 1337-1 341. (in Chinese)
- 120 Zeng, F, Cui, KY, Xie, ZY, Liu, M, Li, YJ, Lin, YJ, Zeng, ZX, Li, FB. 2008. Occurrence of
- 121 phthalate esters in water and sediment of urban lakes in a subtropical city, Guangzhou, South
- 122 China. Environment International, 34(3): 372-380.
- 123 Zhang, A., Liu, S., Yan, K., Ye, Y., Chen, X. 2014. Facile preparation of MnFe₂O₄/halloysite
- 124 nanotubular encapsulates with enhanced magnetic and electromagnetic performances. RSC
- 125 Advances, 4, 13565.