

**Degradation of diclofenac in urine by electro-permanganate process driven by microbial fuel cells**

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**Table S1** Compositions of mineral element

Composition	Chemical Formula	Concentration (g L <sup>-1</sup> )
Manganese sulfate	MnSO <sub>4</sub> ·H <sub>2</sub> O	0.5
Friglycollamic acid	C <sub>6</sub> H <sub>9</sub> NO <sub>6</sub>	1.5
Magnesium sulfate	MgSO <sub>4</sub> ·7H <sub>2</sub> O	3
Cobalt chloride	CoCl <sub>2</sub> ·6H <sub>2</sub> O	0.1
Calcium chloride	CaCl <sub>2</sub>	0.1
Sodium chloride	NaCl	1
Ferric sulfate	FeSO <sub>4</sub> ·7H <sub>2</sub> O	0.1
Zinc sulfate	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	0.1
Copper sulfate	CuSO <sub>4</sub> ·5H <sub>2</sub> O	0.01
Boric acid	H <sub>3</sub> BO <sub>3</sub>	0.01
Sodium molybdate	Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	0.01
Potassium aluminum sulfate	AlK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	0.01

**Table S2** Compositions of vitamin solution

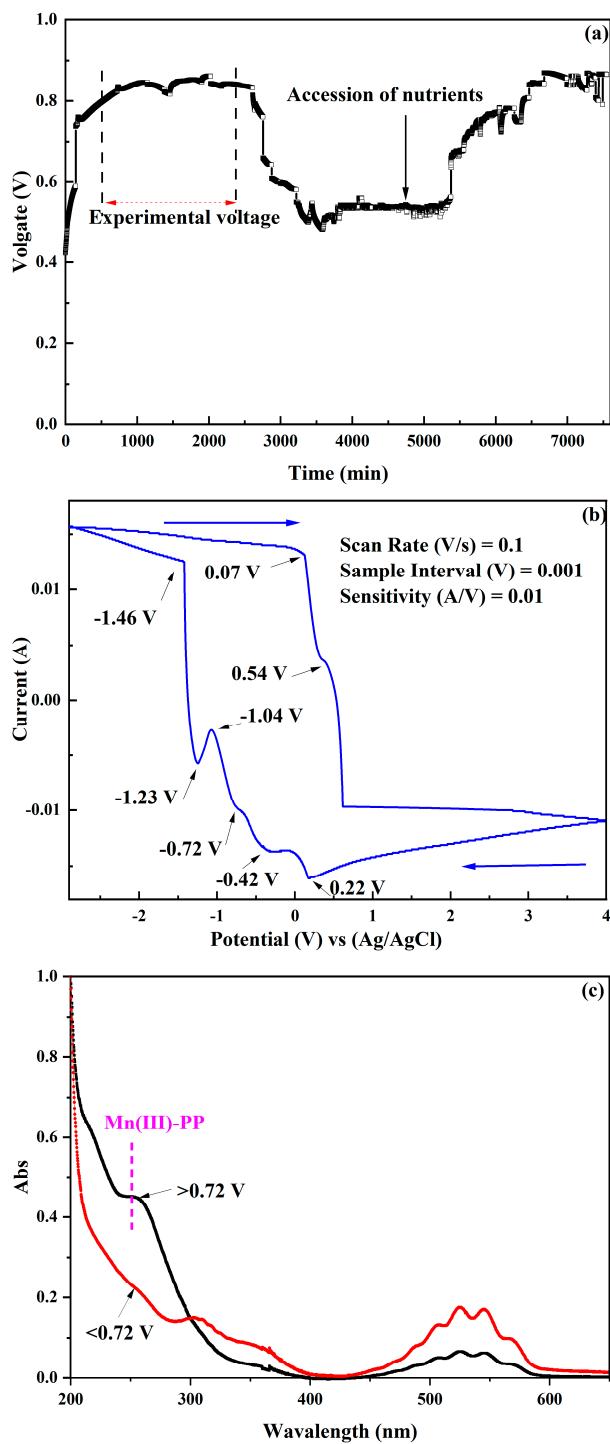
Composition	Chemical formula	Concentration (mg L <sup>-1</sup> )
Vitamin B-2	C <sub>17</sub> H <sub>20</sub> N <sub>4</sub> O <sub>6</sub>	5
Lipoic acid	C <sub>8</sub> H <sub>14</sub> O <sub>2</sub> S <sub>2</sub>	5
Vitamin B-3	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	5
Vitamin B-1	C <sub>12</sub> H <sub>16</sub> N <sub>4</sub> OS-HCl	5
Vitamin B-5	C <sub>9</sub> H <sub>17</sub> NO <sub>5</sub>	5
4-aminobenzoic acid	C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	5
Vitamin H	C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> S	2
Folic acid	C <sub>19</sub> H <sub>19</sub> N <sub>7</sub> O <sub>6</sub>	2
Vitamin B-6	C <sub>8</sub> H <sub>12</sub> ClNO <sub>3</sub>	10
Vitamin B-12	C <sub>63</sub> H <sub>88</sub> CoN <sub>14</sub> O <sub>14</sub> P	0.1

Table S3. The comparison of the MFC-PM process with the other methods for the degradation of DCF

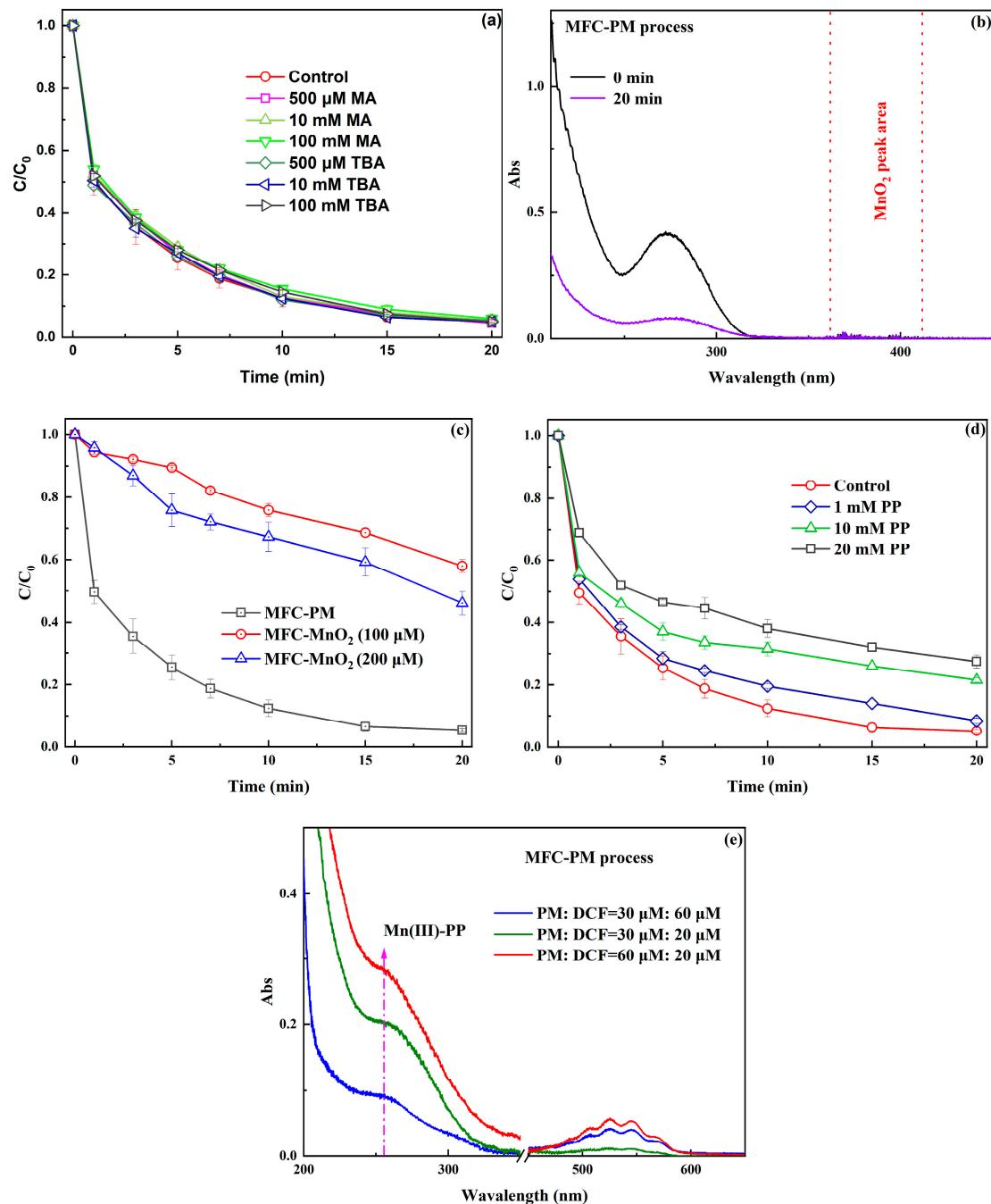
System	Reaction conditions	Rection efficiency	k value	Ref
CoFe <sub>2</sub> O <sub>4</sub> /oxone system	[DCF] <sub>0</sub> = 10 mg L <sup>-1</sup> , Initial pH = 5.0	99 % (30 min)	13.8 s <sup>-1</sup>	[1]
Photoelectrocatalytic system	[DCF] <sub>0</sub> = 5 mg L <sup>-1</sup> , Initial pH = 6.23	71.9% (6 h)	0.0036 s <sup>-1</sup>	[2]
Pyrite nanoparticles	[DCF] <sub>0</sub> = 25 mg L <sup>-1</sup> , Initial pH = 3.0	100% (3 min)	0.461 s <sup>-1</sup>	[3]
hydrodynamic cavitation in conjunction with UV/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub>	[DCF] <sub>0</sub> = 20 mg L <sup>-1</sup> , Initial pH = 3.0	94.78% (120 min)	1.56 s <sup>-1</sup>	[4]
UV-activated persulfate process	[DCF] <sub>0</sub> = 8.88 mg L <sup>-1</sup> , Initial pH = 6.0	83% (60 min)	5.0×10 <sup>-4</sup> s <sup>-1</sup>	[5]
pulsed corona discharge system	[DCF] <sub>0</sub> = 5 mg L <sup>-1</sup> , Initial pH = 6.0	100% (10 min)	-	[6]
Fenton reaction system	[DCF] <sub>0</sub> = 5 mg L <sup>-1</sup> , Initial pH = 4.0	95 % (180 s)	0.164 s <sup>-1</sup>	[7]
ultrasonic irradiation	[DCF] <sub>0</sub> = 14.81 mg L <sup>-1</sup> , Initial pH = 7.0	67% (80 min)	1.79 s <sup>-1</sup>	[8]
US/ZnO	[DCF] <sub>0</sub> = 10 mg L <sup>-1</sup> , Initial pH = 2.0	85% (15 min)	-	[9]
Photoelectro-oxidation	[DCF] <sub>0</sub> = 10 mg L <sup>-1</sup> , Initial pH = 5.6	85% (2h)	0.0191 s <sup>-1</sup>	[10]
MFC-PM	[DCF] <sub>0</sub> = 17.77 mg L <sup>-1</sup> , Initial pH = 3.0	94.75% (20 min)	9.30 s <sup>-1</sup>	This work

**Table S4.** The reaction kinetics of DCF removal in different PM concentrations, external resistances and water matrices by the MFC-PM process

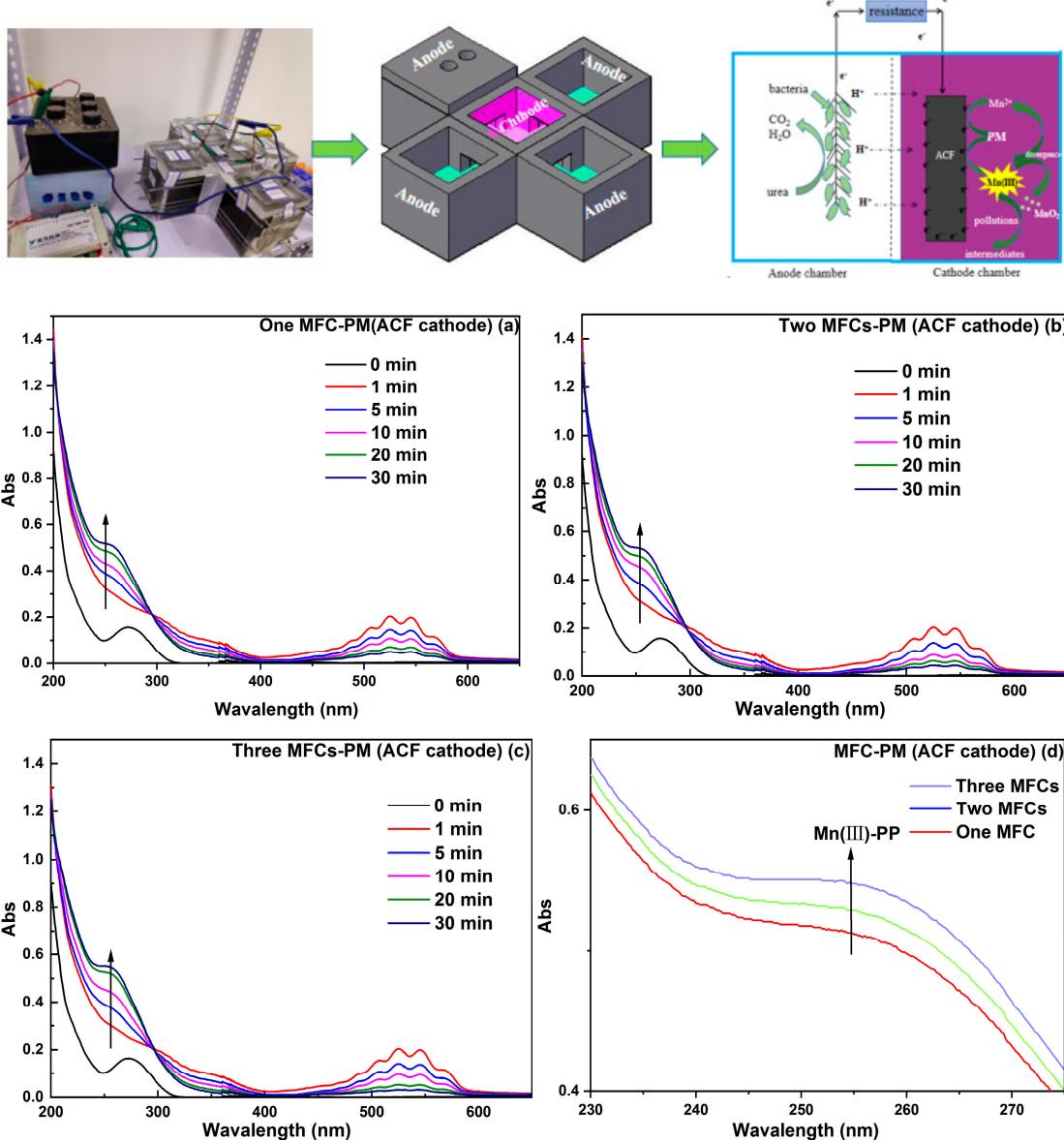
PM dosages	k value (min <sup>-1</sup> )	R <sup>2</sup>
15 μM	0.051	0.85
30 μM	0.138	0.92
45 μM	0.192	0.94
60 μM	0.129	0.93
75 μM	0.390	0.91
External resistances	k value (min <sup>-1</sup> ) (within 3 min)	R <sup>2</sup>
0 Ω	0.321	0.89
500 Ω	0.319	0.92
2000 Ω	0.279	0.94
5000 Ω	0.243	0.90
Water matrices	k value (min <sup>-1</sup> )	R <sup>2</sup>
Tap water	0.106	0.91
Surfaces water	0.083	0.97
Ultrapure water	0.155	0.96



**Figure S1.** The change of voltage with time (a), cyclic voltammetry curve of PM (b), and UV-vis spectrum of PM under different potentials (c).

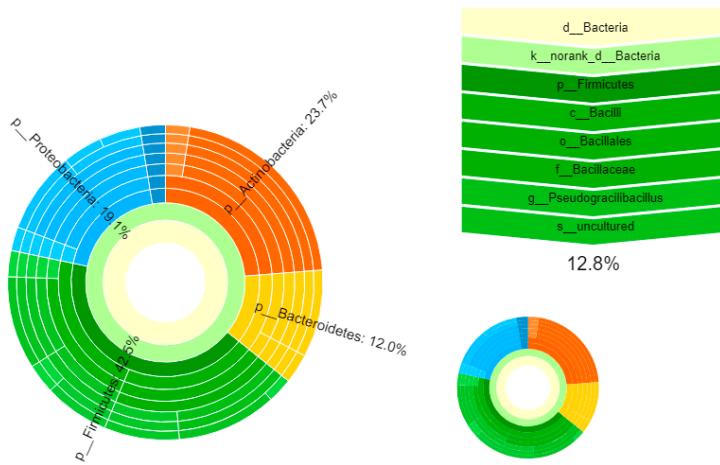


**Figure S2.** Effect of MA, TBA (a), UV-vis spectra of the the MFC-PM processes (b), effect of MnO<sub>2</sub> (c) and PP (d) on the removal of DCF, and the peaks of Mn(III)aq (e) in different PM/DCF ratios with 10 mM PP.

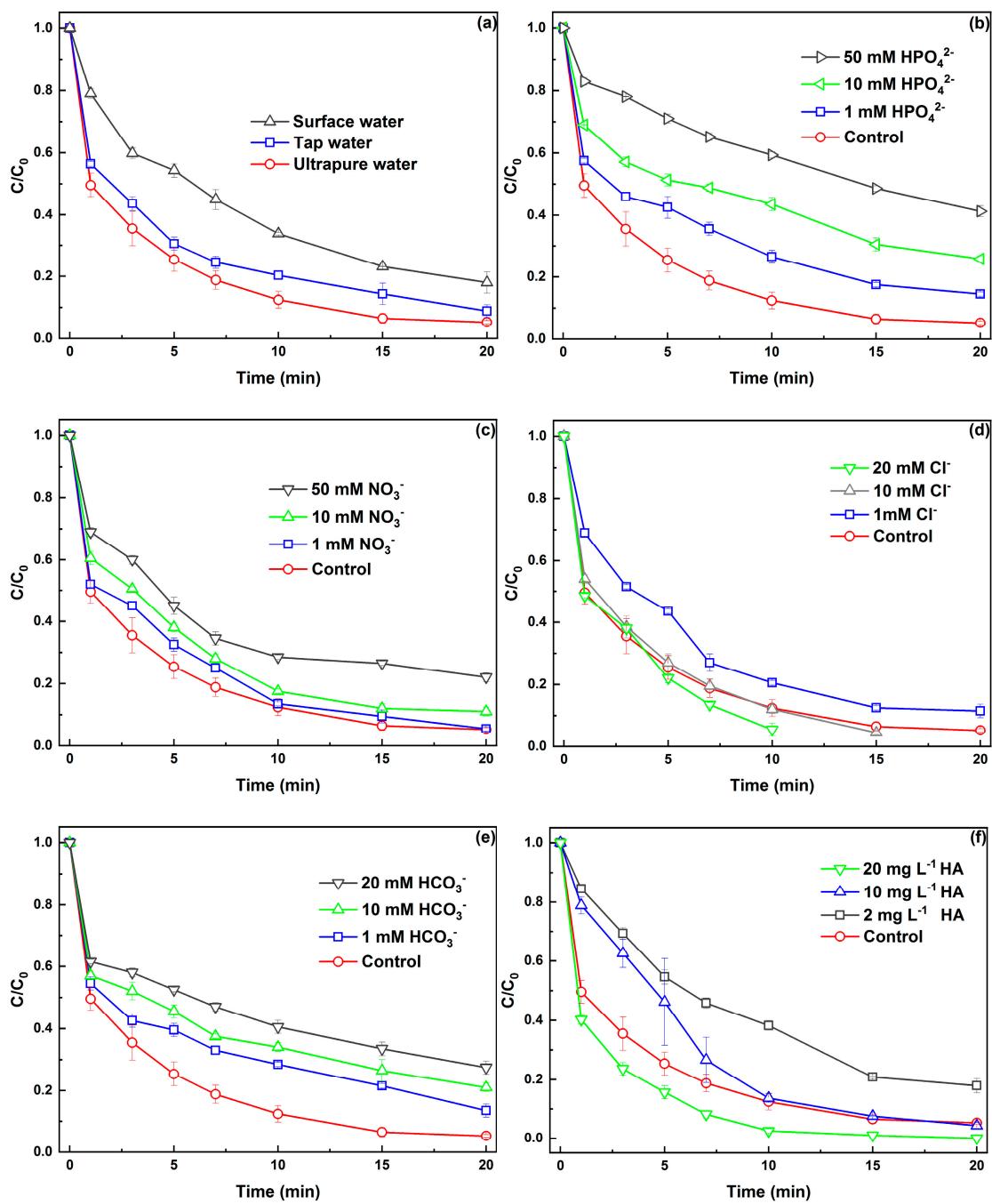


**Figure S3.** Diagram of MFC with muti-anodes and single cathode and UV-vis spectra with one anode (a), two anodes (b), three anodes (c) in the MFC-PM (ACF cathode) system (ACF was used as cathode electrode), and the comparison of peaks of  $\text{Mn}(\text{III})_{\text{aq}}$  with different number of anodes (d).

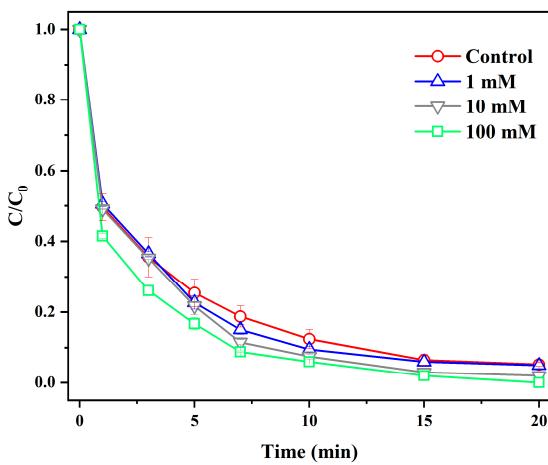
Community analysis sunburst plot on OTU level:



**Figure S4.** Taxonomy of microbial communities classified at the phylum level on the anode of MFC.



**Figure S5.** Effect of water matrices (a),  $\text{HPO}_4^{2-}$  (b),  $\text{NO}_3^-$  (c),  $\text{Cl}^-$  (d),  $\text{HCO}_3^-$  (e), and HA (f) on the removal of DCF in the MFC-PM system.



**Figure S6.** Effect of urea on the removal of DCF in the MFC-PM system.

#### References:

- [1] Deng, J.; Shao, Y.; Gao, N.; Tan, C.; Zhou, S.Hu, X. CoFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles as a highly active heterogeneous catalyst of oxone for the degradation of diclofenac in water. *J. Hazard. Mater.* 2013, 262, 836-844.
- [2] Hua, Z.; Dai, Z.; Bai, X.; Ye, Z.; Wang, P.; Gu, H.Huang, X. Copper nanoparticles sensitized TiO<sub>2</sub> nanotube arrays electrode with enhanced photoelectrocatalytic activity for diclofenac degradation. *Chem. Eng. J.* 2016, 283, 514-523.
- [3] Khabbaz, M.Entezari, M.H. Degradation of Diclofenac by sonosynthesis of pyrite nanoparticles. *J. Environ. Manage.* 2017, 187, 416-423.
- [4] Bagal, M.V.Gogate, P.R. Degradation of diclofenac sodium using combined processes based on hydrodynamic cavitation and heterogeneous photocatalysis. *Ultrason. Sonochem.* 2014, 21, 1035-1043.
- [5] Lu, X.; Shao, Y.; Gao, N.; Chen, J.; Zhang, Y.; Xiang, H.Guo, Y. Degradation of diclofenac by UV-activated persulfate process: Kinetic studies, degradation pathways and toxicity assessments. *Ecotox. Environ. Safe.* 2017, 141, 139-147.
- [6] Dobrin, D.; Bradu, C.; Magureanu, M.; Mandache, N.B.Parvulescu, V.I. Degradation of diclofenac in water using a pulsed corona discharge. *Chem. Eng. J.* 2013, 234, 389-396.
- [7] Bae, S.; Kim, D.Lee, W. Degradation of diclofenac by pyrite catalyzed Fenton oxidation. *Applied Catalysis B: Environmental.* 2013, 134-135, 93-102.
- [8] Nie, E.; Yang, M.; Wang, D.; Yang, X.; Luo, X.Zheng, Z. Degradation of diclofenac by ultrasonic irradiation: Kinetic studies and degradation pathways. *Chemosphere.* 2014, 113, 165-170.
- [9] Huang, T.; Zhang, G.; Chong, S.; Liu, Y.; Zhang, N.; Fang, S.Zhu, J. Effects and mechanism of diclofenac degradation in aqueous solution by US/Zn<sup>0</sup>. *Ultrason. Sonochem.* 2017, 37, 676-685.
- [10] Liu, S.; Zhao, X.; Zeng, H.; Wang, Y.; Qiao, M.Guan, W. Enhancement of photoelectrocatalytic degradation of diclofenac with persulfate activated by Cu cathode. *Chem. Eng. J.* 2017, 320, 168-177.