Supplementary Materials for

Degradation of Diclofenac by Bisulfite Coupled with Iron and Manganous Ions: Dual mechanism, DFT-assisted Pathway Studies, and Toxicity Assessment

Hongbin Wang[1,2,3], Shijie Kuang[1], Youlun Su[1], Xu Ren[1,3,4], Bowen Yang[1], Yongliang Sun[2*]

1, School of Architecture and Civil Engineering, Chengdu University, Chengdu 610106, China

2, Sichuan Academy of Eco-Environmental Sciences, Chengdu 610041, China

3, Sichuan City Solid Waste Energy and Building Materials Conversion Technology Engineering, Chengdu University, Chengdu 610106, China

4, Postdoctoral Research Station in Environmental Science and Engineering, Sichuan University, Chengdu 610065, China

[*]Corresponding author's E-mail: syliang825@163.com

Text S1. Sequential batch experiments

Fig. S1 investigated sequential batch experiments with DCF and BS spiked orderly in Fe(III)/Mn(II)/BS system. The result showed that after 2 mins, DCF alone didn't be degraded because of probable depletion of BS. By contrast, when DCF and BS were added simultaneously (every 2 mins), DCF was still degraded better, whereas the increase of each subsequent addition occurred simultaneously with the lower slightly decreasing degradation effect. The reasons were as follows: 1) Conversion of Fe(II)/Fe(III) or Mn(II)/Mn(III) could constantly consume BS to produce active radicals, obtaining favorable DCF removal rate. 2) The associated reactions (Equation (1), (2), (3) and (4)) in system would generate mass H^+, inhibiting the form of BS to cause slightly decreasing degradation [1-4]. 3) Mn(III) would be rapidly consumed through oxidation, reduction and disproportionation reaction (Equation (5), (6), and (7)) [3][5].This experiment again affirmed that BS played an essential role in Fe(II)/Fe(III) and Mn(II)/Mn(III) circulation, providing an effective solution to remove high concentration DCF in Fe(III)/Mn(II)/BS system.

$$SO_4^{\bullet-} + HSO_3^- \rightarrow SO_3^{\bullet-} + SO_4^{2-} + H^+ \qquad K = 1.3\times 10^8 \sim 2.5 \times 10^9\ M^{-1}\ s^{-1} \qquad (1)$$

$$Fe^{3+} + HSO_3^- \rightarrow FeSO_3^+ + H^+ \qquad K \approx 1 \times 10^3\ M^{-1}\ s^{-1} \qquad (2)$$

$$SO_5^{\bullet-} + HSO_3^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} + H^+ \qquad K = 1.2 \times 10^4\ M^{-1}\ s^{-1} \qquad (3)$$

$$2Mn^{3+} + HSO_3^- + H_2O \rightarrow 2Mn^{2+} + SO_4^{2-} + 3H^+ \qquad (4)$$

$$Mn^{3+} + HSO_3^- \rightarrow Mn^{2+} + SO_3^{\bullet-} + 3H^+ \qquad (5)$$

$$Mn^{3+} + DCF \rightarrow Mn^{2+} + Products \qquad (6)$$

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+ \qquad (7)$$

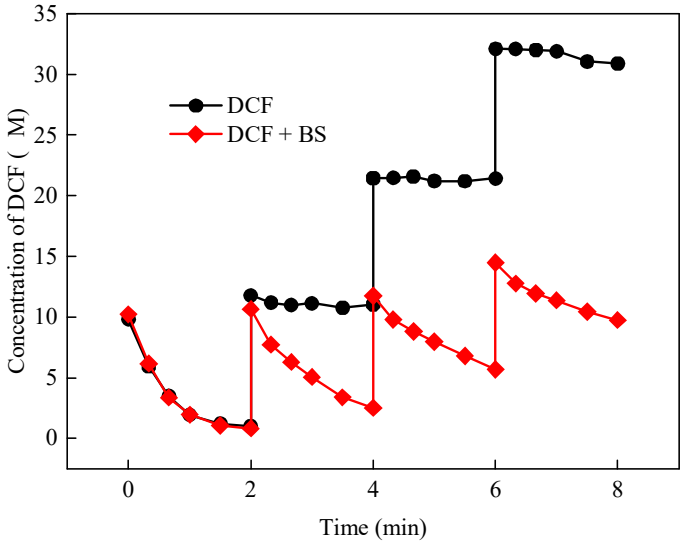
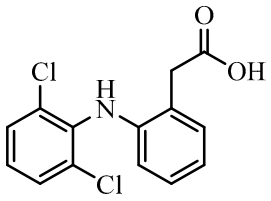
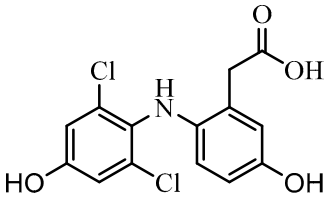
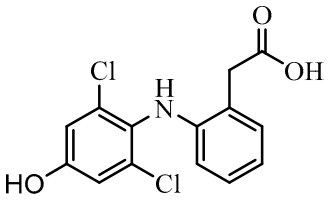
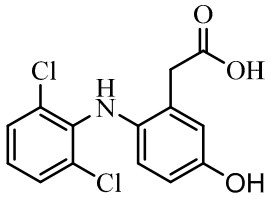
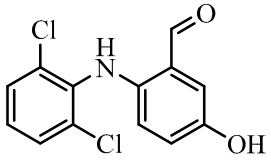
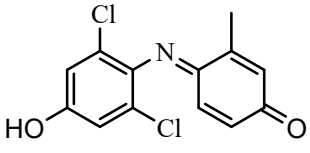
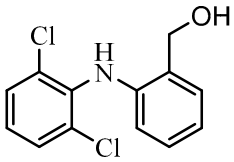


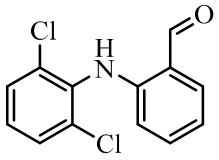
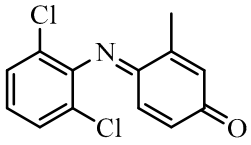
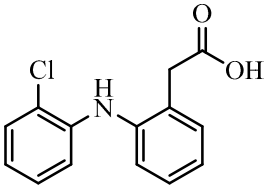
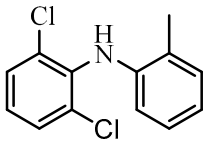
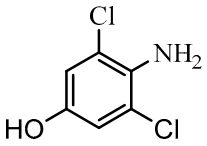
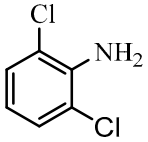
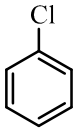
Figure S1. Variation of DCF concentration with time in Fe(III)/Mn(II)/BS system. Reaction conditions: $[DCF]_0 = [Fe(III)]_0 = 10$ μM, $[Mn(II)]_0 = 5$ μM, $[BS]_0 = 200$ μM, $[pH]_0 = 4.0$ T = 25 ℃. Annotation: add 1 mL 1 mM DCF and 1 mL 20 mM BS every 2 mins.

Table S1. The *CK* values of reactive radicals towards substrates

reactive species	concentration C (M)	$HO^{\bullet}$		$SO_4^{\bullet-}$	
		K (M^{-1} s^{-1})	CK (s^{-1})	K (M^{-1} s^{-1})	CK (s^{-1})
DCF	1.0×10^{-5}	7.5×10^{9} [6]	7.5×10^{4}	9.2×10^{9} [7]	9.2×10^{4}
TBA	1.0×10^{-2}	6.0×10^{8} [8]	6.0×10^{6}	8.4×10^{5} [9]	8.4×10^{3}
	1.0×10^{-1}		6.0×10^{7}		8.4×10^{4}
	5.0×10^{-1}		3.0×10^{8}		4.2×10^{5}
Me	1.0×10^{-1}	9.7×10^{8} [8]	9.7×10^{7}	1.0×10^{7} [9]	1.0×10^{6}
	5.0×10^{-1}		4.9×10^{8}		5.0×10^{6}

Table S2. Degradation products of DCF in Fe(III)/Mn(II)/BS system

Serial number	Molecular weight	Mass to charge ratio(*m/z*)	Formular	Proposed structure	$SO_4^{\bullet-}$ 200 μM BS	Mn(III) 1000 μM BS
DCF	295	296	$C_{14}H_{11}Cl_2NO_2$			
1	327	328	$C_{14}H_{11}Cl_2NO_4$		√	
2	311	312-1	$C_{14}H_{11}Cl_2NO_3$		√	
3	311	312-2	$C_{14}H_{11}Cl_2NO_3$		√	
4	281	282-1	$C_{13}H_9Cl_2NO_2$			√
5	281	282-2	$C_{13}H_9Cl_2NO_2$			√
6	267	268	$C_{13}H_{11}Cl_2NO$			√

Serial number	Molecular weight	Mass to charge ratio(*m/z*)	Formular	Proposed structure	$SO_4^{\bullet-}$ 200 μM BS	Mn(III) 1000 μM BS
7	265	266-1	$C_{13}H_9Cl_2NO$		√	√
8	265	266-2	$C_{13}H_9Cl_2NO$			√
9	261	262	$C_{14}H_{12}ClNO_2$		√	
10	251	252	$C_{13}H_{11}Cl_2N$		√	√
11	177	178	$C_6H_5Cl_2NO$			√
12	161	162	$C_6H_5Cl_2N$			√
13	113	114	C_6H_5Cl		√	

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