Mechanistic Insight into Suppression of Bromate Formation by Dissolved Organic Matters in Sulfate Radical-Based Advanced Oxidation Processes

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研究背景及问题的提出

硫酸根高级氧化工艺

$SO_4^{\bullet-}$-Advanced Oxidation Process (SR-AOP)

- PPCPs degradation
- Undesired byproducts 溴酸盐（BrO_3^-）

饮用水国标10 μg/L

纯水中：$Br^- \xrightarrow{SO_4^{\bullet-}} Br^\bullet/Br_2^{\bullet-} \Rightarrow HOBr \Rightarrow BrO_3^-$

NOM：0.5~2.0 mg/L NOM显著抑制BrO_3^-的产生

$Br^- \xrightarrow{SO_4^{\bullet-}} Br^\bullet/Br_2^{\bullet-} \Rightarrow HOBr \Rightarrow BrO_3^-$

NOM → Br-DBP ?

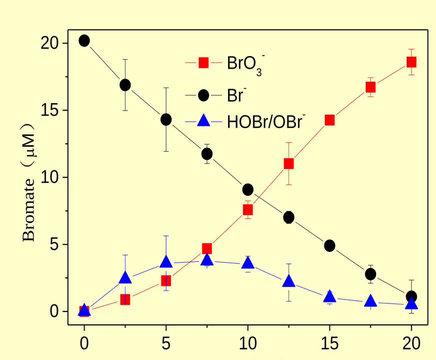
正反：Fang and Shang:

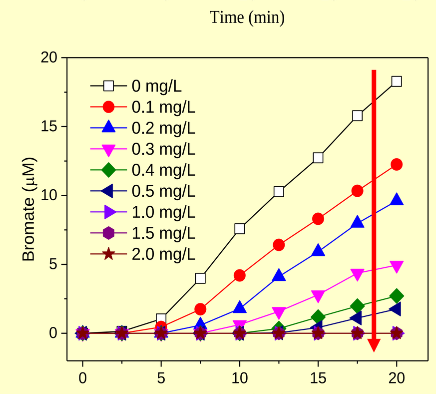
反方：Lutze et al.: Inorganic Br⁻ balance ?

矛盾的抑制机制

$SO_4^{\bullet-}$ + NOM + O_2 → $O_2^{\bullet-}$

$HOBr/Br_2^{\bullet-}$ → $Br^\bullet/Br^-$





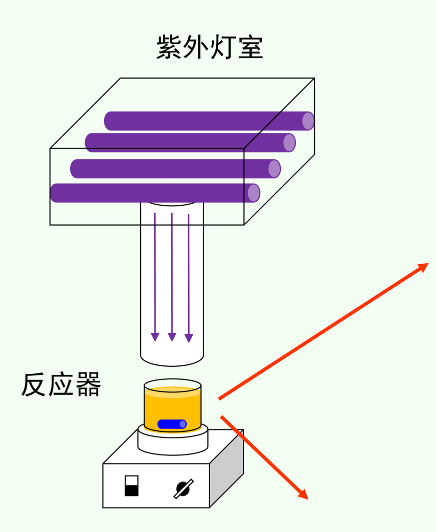
Fang and Shang, Environ. Sci. Technol. 2012, 46(16), 8976-8983.
Lutze et al., Water Res. 2014, 53, 370-377.

研究方法

（一）实验研究

□ 准直光束UV辐照装置

- 四支低压汞灯（254 nm, GPH212T5L/4, 10 W, Heraeus）
- 玻璃反应器的体积为100 mL，水的光程为4.00 cm。
- 其在254 nm处的入射光强为(8.69±0.37) × 10^{-8} Einstein L^{-1} s^{-1}。



□ Experimental solutions:
- 1mM PDS, 20 μMBr⁻
- pH=7.0, 10 mM phosphate buffer
- NOM model compounds:
  - Oxalate
  - phenol, l-tyrosine, critic acid, tBuOH and MeOH

□ Analytical methods:
HOBr: HPLC; BrO_3^-, Oxalate: IC; TOBr: TOX.

（二）模拟计算（Kintecus）

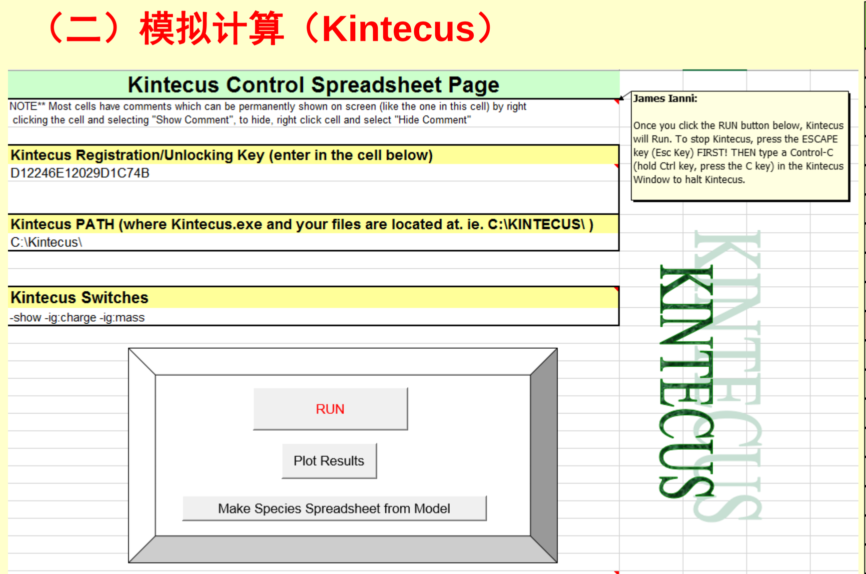


Table 1. Calculated rate constants for photochemical reactions.

Oxidants	quantum yield (Φ, mol per Einstein)	molar absorptivity (ε, M^{-1} cm^{-1})	k_{obs} (s^{-1})
$S_2O_8^{2-}$	0.9	21.1	6.32×10^{-4}
HSO_5^-	0.52	13.8	2.39×10^{-4}
SO_5^{2-}	0.52	149.5	2.59×10^{-3}
H_2O_2	0.5	21.1	3.51×10^{-4}
HO_2^-	0.5	228	3.80×10^{-3}
HOBr	0.75	110	2.75×10^{-3}
OBr^-	0.5	10	1.66×10^{-4}
Br_2	0.5	100	1.66×10^{-3}

Table 2. The second-order rate constants between dissolved organic model compounds and the reactive species involved in UV/PDS/Br⁻/Organic matters systems.

Compounds	k($SO_4^{\bullet-}$)	k(OH•)	k(Br•)	k($Br_2^{\bullet-}$)	k(HOBr/OBr⁻)
Phenol	8.8×10^9 M^{-1} s^{-1}	6.6×10^9 M^{-1} s^{-1}	u.k.	6.1×10^6 M^{-1} s^{-1}	1.8×10^5 M^{-1} s^{-1} (pH=7)
L-tyrosine	3.2×10^9 M^{-1} s^{-1}	5.0×10^9 M^{-1} s^{-1}	u.k.	u.k.	2.6×10^5 M^{-1} s^{-1} (pH=7.2~7.5)
Citric acid	1.2×10^6 M^{-1} s^{-1}	3.0×10^8 M^{-1} s^{-1}	u.k.	u.k.	u.k.
Oxalic acid	1.1×10^6 M^{-1} s^{-1}	7.6×10^6 M^{-1} s^{-1}	5.5×10^7 M^{-1} s^{-1}	u.k.	4.0×10^1 M^{-1} s^{-1} (pH=6)
tBuOH	4.0×10^5 M^{-1} s^{-1}	6.0×10^8 M^{-1} s^{-1}	4.2×10^4 M^{-1} s^{-1}	u.k.	$<10^{-4}$ M^{-1} s^{-1}
MeOH	1.1×10^7 M^{-1} s^{-1}	9.7×10^8 M^{-1} s^{-1}	3.0×10^5 M^{-1} s^{-1}	4.4×10^3 M^{-1} s^{-1}	$<10^{-4}$ M^{-1} s^{-1}
3-Buten-2-ol	u.k.	5.9×10^9 M^{-1} s^{-1}	u.k.	u.k.	10^5~10^6 M^{-1} s^{-1}
Cinnamic acid	u.k.	8.0×10^9 M^{-1} s^{-1}	u.k.	u.k.	10^5~10^6 M^{-1} s^{-1}

u.k., unknown

No.	Reactions	Rate constants	No.	Reactions	Rate constants
#Photolysis			49	$Br_2^{\bullet-}$ + OBr^- ==> BrO• + $2Br^-$	6.20E+07
1	$S_2O_8^{2-}$ ==> $SO_4^{\bullet-}$ + $SO_4^{\bullet-}$		50	$Br_2^{\bullet-}$ + OH• ==> HOBr + Br^-	1.00E+09
2	HSO_5- ==> $SO_4^{\bullet-}$ + OH•		51	$Br_2^{\bullet-}$ + OH^- ==> $BrOH^{\bullet-}$ + Br^-	2.70E+06
3	SO_5^{2-} ==> $SO_4^{\bullet-}$ + $O^{\bullet-}$		52	Br_2 + Br^- ==> Br_3^-	9.60E+08
4	H_2O_2 ==> OH• + OH•		53	Br_2 + HO_2• ==> $Br_2^{\bullet-}$ + O_2 + H^+	1.10E+08
5	HO_2^- ==> OH• + $O^{\bullet-}$		54	Br_2 + $O_2^{\bullet-}$ ==> $Br_2^{\bullet-}$ + O_2	5.60E+09
6	HOBr ==> OH• + Br•		55	Br_2 + H_2O ==> HOBr + Br^-	9.70E+01
7	OBr^- ==> $O^{\bullet-}$ + Br•		56	Br_2 + H_2O_2 ==> 2HBr + O_2	1.30E+03
8	Br_2 ==> Br• + Br•		57	Br_3^- ==> Br_2 + Br^-	5.50E+07
#reactions between SO4•- and OH•			58	Br_3^- + HO_2• ==> $Br_2^{\bullet-}$ + HBr + O_2	1.00E+07
9	$SO_4^{\bullet-}$ + OH^- ==> SO_4^{2-} + OH•	7.00E+07	59	Br_3^- + $O_2^{\bullet-}$ ==> $Br_2^{\bullet-}$ + Br^- + O_2	3.80E+09
10	$SO_4^{\bullet-}$ ==> H^+ + SO_4^{2-} + OH•	6.60E+02	60	HOBr + Br^- + H^+ ==> Br_2 + H_2O	5.00E+09
11	$SO_4^{\bullet-}$ + OH• ==> HSO_5-	1.00E+10	61	HOBr + HO_2^- ==> Br^- + H_2O + O_2	7.60E+08
12	$SO_4^{\bullet-}$ + HSO_5^- ==> SO_4^{2-} + $SO_5^{\bullet-}$	1.00E+06	62	HOBr + H_2O_2 ==> HBr + H_2O + O_2	3.50E+04
13	$SO_4^{\bullet-}$ + SO_5^{2-} ==> SO_4^{2-} + $SO_5^{\bullet-}$	1.00E+08	63	HOBr + OH• ==> BrO• + H_2O	2.00E+09
14	$SO_5^{\bullet-}$ + $SO_5^{\bullet-}$ ==> $S_2O_8^{2-}$ + O_2	2.20E+08	64	HOBr + $O_2^{\bullet-}$ ==> $BrOH^{\bullet-}$	3.50E+09
15	$SO_5^{\bullet-}$ + $SO_5^{\bullet-}$ ==> $SO_4^{\bullet-}$ + $SO_4^{\bullet-}$ + O_2	2.10E+08	65	HOBr + HO_2• ==> $BrOH^{\bullet-}$ + H^+	3.50E+09
16	$SO_4^{\bullet-}$ + $SO_4^{\bullet-}$ ==> $S_2O_8^{2-}$	7.00E+08	66	OBr^- + H_2O_2 ==> Br^- + H_2O + O_2	1.20E+06
17	$SO_4^{\bullet-}$ + $S_2O_8^{2-}$ ==> $S_2O_8^{\bullet-}$ + SO_4^{2-}	6.50E+05	67	OBr^- + OH• ==> BrO• + OH^-	4.50E+09
18	OH• + H_2O_2 ==> HO_2• + H_2O	2.70E+07	68	OBr^- + $O_2^{\bullet-}$ + H_2O ==> Br• + $2OH^-$ + O_2	2.00E+08
19	OH• + OH• ==> H_2O_2	5.50E+09	69	HOBr + $SO_4^{\bullet-}$ ==> BrO• + SO_4^{2-} + H^+	2.00E+09
20	HO_2• + H_2O_2 ==> O_2 + OH• + H_2O	3.00E+00	70	OBr^- + $SO_4^{\bullet-}$ ==> BrO• + SO_4^{2-}	4.50E+09
21	$O_2^{\bullet-}$ + H_2O_2 ==> O_2 + OH• + OH^-	1.30E-01	#Bromate formation		
22	HO_2• + HO_2• ==> O_2 + H_2O_2	8.30E+05	72	BrO• + BrO• ==> OBr^- + BrO_2^-	5.00E+09
23	HO_2• + $O_2^{\bullet-}$ ==> O_2 + HO^{2-}	9.70E+07	73	BrO• + BrO_2^- ==> OBr^- + BrO_2•	3.40E+08
24	OH• + HO_2• ==> O_2 + H_2O	6.60E+09	74	$Br_2^{\bullet-}$ + BrO_2^- ==> OBr^- + BrO• + Br^-	8.00E+07
25	OH• + $O_2^{\bullet-}$ ==> O_2 + OH^-	7.00E+09	75	OH• + BrO_2^- ==> BrO_2• + OH^-	1.90E+09
26	OH• + HO_2^- ==> HO_2• + OH^-	7.50E+09	76	OH• + BrO_2• ==> BrO_3^- + H^+	2.00E+09
27	OH• + OH^- ==> $O^{\bullet-}$ + H_2O	1.20E+10	77	BrO_2• + BrO_2• ==> Br_2O_4	1.40E+09
28	OH• + $S_2O_8^{2-}$ ==> $S_2O_8^{\bullet-}$ + OH^-	1.40E+07	78	Br_2O_4 ==> BrO_2• + BrO_2•	7.00E+07
#Reactions between SO4•- and Br-			79	Br_2O_4 ==> BrO_3^- + BrO_2- + H^+	7.00E+08
29	$SO_4^{\bullet-}$ + Br^- ==> SO_4^{2-} + Br•	3.50E+09	#Reactions between the radicals with phosphate ions		
#Reactions including Br-			80	OH• + HPO_4^{2-} ==> $HPO_4^{\bullet-}$ + OH^-	1.50E+05
30	OH• + Br^- ==> $BrOH^{\bullet-}$	1.10E+10	81	OH• + $H_2PO_4^-$ ==> $HPO_4^{\bullet-}$ + H_2O	2.00E+04
31	Br• + H_2O ==> $BrOH^{\bullet-}$ + H^+	1.40E+00	82	H_2O_2 + $HPO_4^{\bullet-}$ ==> $H_2PO_4^-$ + HO_2•	2.70E+07
32	Br• + OH^- ==> $BrOH^{\bullet-}$	1.06E+10	83	$SO_4^{\bullet-}$ + HPO_4^{2-} ==> $HPO_4^{\bullet-}$ + SO_4^{2-}	1.20E+06
33	$BrOH^{\bullet-}$ ==> OH• + Br^-	3.30E+07	84	$SO_4^{\bullet-}$ + H2PO_4^- ==> $HPO_4^{\bullet-}$ + HSO_4^-	5.00E+04
34	$BrOH^{\bullet-}$ ==> Br• + OH^-	4.20E+06	#Acid dissociation rxns		
35	$BrOH^{\bullet-}$ + H^+ ==> Br• + H_2O	4.40E+10	85	HOBr <==> OBr^- + H^+	8.8
36	$BrOH^{\bullet-}$ + Br^- ==> $Br_2^{\bullet-}$ + OH^-	1.90E+08	86	HSO_5^- <==> H^+ + SO_5^{2-}	9.2
37	Br• + Br^- ==> $Br_2^{\bullet-}$	1.20E+10	87	H_2O_2 <==> H^+ + HO_2^-	11.6
38	Br• + Br• ==> Br_2	1.00E+09	88	HO_2• <==> $O_2^{\bullet-}$ + H^+	4.8
39	Br• + H_2O_2 ==> HO_2• + Br^-	4.00E+09	89	H_3PO_4 <==> $H_2PO_4^-$ + H^+	2.1
40	Br• + HO_2• ==> Br^- + H^+ + O_2	1.60E+08	90	$H_2PO_4^-$ <==> HPO_4^{2-} + H^+	7.2
41	Br• + OBr^- ==> BrO• + Br^-	4.00E+09	91	HPO_4^{2-} <==> PO_4^{3-} + H^+	12.3
42	$Br_2^{\bullet-}$ ==> Br• + Br^-	1.90E+04	#Reactions between the radicals and OMs		
43	$Br_2^{\bullet-}$ + $Br_2^{\bullet-}$ ==> Br_2 + Br^- + Br^-	1.90E+09	92	H2C2O4 + $Br_2^{\bullet-}$ ==> CO_2 + Br^- + Br^-	1.00E+05
44	$Br_2^{\bullet-}$ + Br• ==> Br_2 + Br^-	2.00E+09	93	H2C2O4 + Br• ==> CO_2 + Br^-	5.50E+07
45	$Br_2^{\bullet-}$ + H_2O_2 ==> HO_2• + $2Br^-$ + H^+	5.00E+02	94	H2C2O4 + $SO_4^{\bullet-}$ ==> CO_2 + SO_4^{2-}	1.10E+06
46	$Br_2^{\bullet-}$ + HO_2• ==> HBr + Br^- + O2	1.00E+08	95	H2C2O4 + OH• ==> CO_2 + OH^-	7.70E+06
47	$Br_2^{\bullet-}$ + HO_2• ==> Br_2 + HO_2^-	4.40E+09	96	$CO_2^{\bullet-}$ + O_2 ==> CO_2 + $O_2^{\bullet-}$	2.00E+09
48	$Br_2^{\bullet-}$ + O_2•- ==> Br^- + Br^- + O_2	1.70E+08	97	$H_2C_2O_4$ + HOBr ==> products	4.00E+01

结果与讨论

□ Bromate formation in the UV/PDS system in the absence and presence of oxalate.

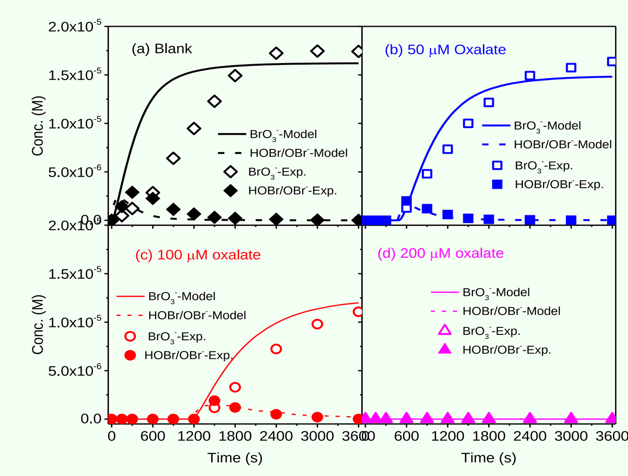


Figure 1. Effect of oxalate concentrations on bromate formation. (a) blank, (b) 50 μM oxalate, (c) 100 μM oxalate, (d) 200 μM oxalate.

□ In the absence of oxalate:
- complete conversion of Br⁻ to BrO_3^- achieved at 40 min.
- HOBr/OBr⁻ increased rapidly to its maximum (~2.9 μM) at 5 min and then decreased gradually

□ In the presence of oxalate, BrO_3^- evolution exhibited biphasic kinetics:
- Lag phase: undetectable in the initial 20 min.
- Secondary rapid phase: rapidly increased to approximate 12 μM from 20 min to 60 min.

□ Role of reactive radicals scavenging reactions by oxalate.

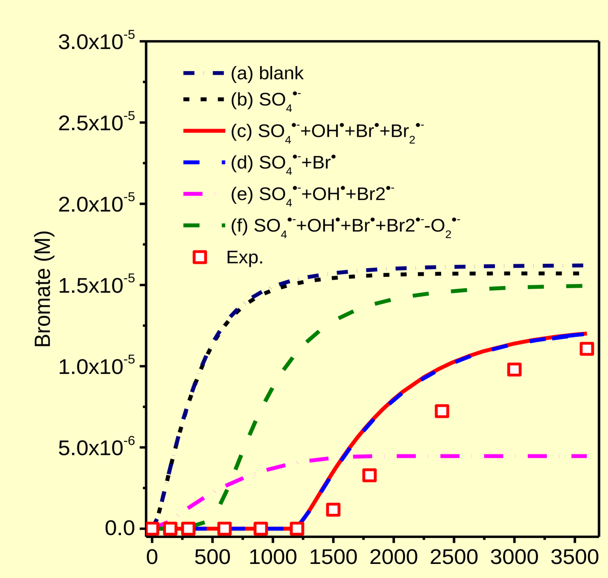


Figure 2. Contribution of radicals scavenging reactions to the suppression of bromate formation by oxalate.

$HC_2O_4^-$ + $SO_4^{\bullet-}$ = $CO_2^{\bullet-}$ + CO_2 + SO_4^{2-} + H^+, $k=1.1\times10^6$ M^{-1} s^{-1} (1)

$HC_2O_4^-$ + OH• = $CO_2^{\bullet-}$ + CO_2 + H_2O, $k=7.7\times10^6$ M^{-1} s^{-1} (2)

$HC_2O_4^-$ + Br• = $CO_2^{\bullet-}$ + CO_2 + Br^- + H^+, $k=5.5\times10^7$ M^{-1} s^{-1} (3)

$HC_2O_4^-$ + $Br_2^{\bullet-}$ = $CO_2^{\bullet-}$ + CO_2 + $2Br^-$ + H^+, $k=1\times10^5$ M^{-1} s^{-1} (4)

$CO_2^{\bullet-}$ + O_2 = CO_2 + $O_2^{\bullet-}$, $k=2.0\times10^9$ M^{-1} s^{-1} (5)

- □ **Scavenging of Br• by oxalate predominantly** contribute to the suppression of BrO_3^- formation, which might be ascribed to the higher scavenging capacity of Br• than OH• and $Br_2^{\bullet-}$ by oxalate.
- □ **$O_2^{\bullet-}$ formed from the reactions of oxalate with Br•** also contributed appreciably to the suppression of BrO_3^- formation.

□ Steady-state concentrations of reactive radicals.

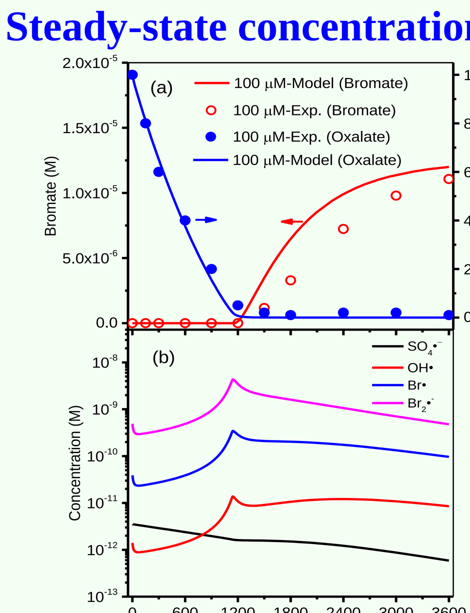


Figure 3. (a)Time-dependent bromate formation and (b)steady-state concentration of $SO_4^{\bullet-}$, OH•, Br• and $Br_2^{\bullet-}$ in UV/PDS/Br⁻ system in the presence of oxalate.

- □ In the lag phase (0~20 min): the steady-state concentration of Br• was relatively low (<1.0×10^{-10} M) due to the sustained scavenging of Br• by oxalate.
- □ When the 100 μM of oxalate was almost entirely degraded at 20 min, the steady-state concentration of Br• fast increase to 3.4×10^{-10} M which is comparable as that in the absence of oxalate (i.e., 5.0×10^{-10} M), resulting in the rapid BrO_3^- formation (secondary rapid phase).
- □ Similar trends between OH•, $Br_2^{\bullet-}$ and Br•.

✓Br• + OH^- <=> $BrOH^{\bullet-}$, $k_+=1.06\times10^{10}$ M^{-1} s^{-1}, $k_+=4.2\times10^6$ s^{-1}
✓$BrOH^{\bullet-}$ <=> OH• + Br^-, $k_+=3.3\times10^7$ s^{-1}, $k_-=1.1\times10^{10}$ M^{-1} s^{-1}
✓Br• + Br^- <=> $Br_2^{\bullet-}$, $k_+=1.2\times10^{10}$ M^{-1} s^{-1}, $k_-=1.9\times10^4$ s^{-1}

□ Bromate formation in the presence of dissolved organic model compounds.

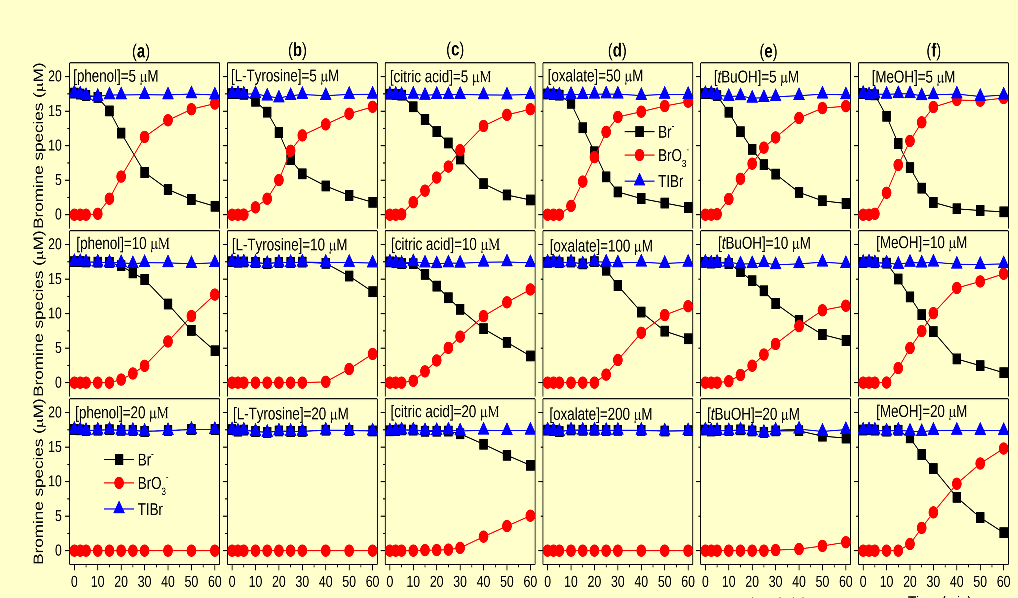
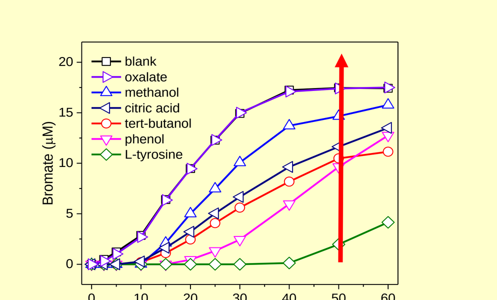


Figure 4. Bromate formation in the presence of model compounds in UV/PDS process.



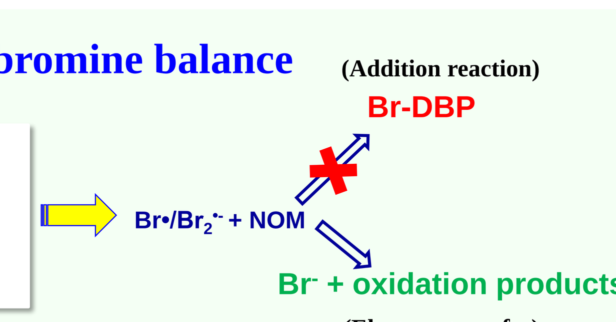
□ Suppression Effects:
l-tyrosine>phenol>tert-butanol>critic acid>MeOH>oxalate

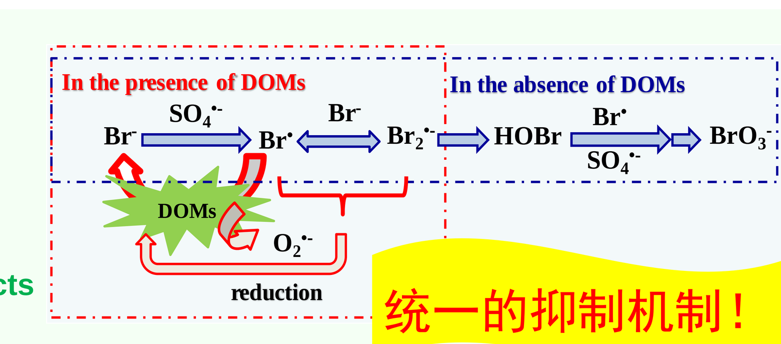
Amounts of PDS consumption for complete mineralization

- □ **L-tyrosine:** $C_9H_{11}NO_3$ + 23$S_2O_8^{2-}$ + $18H_2O$ = 46SO_4^{2-} + 9CO_2 + 46H^+ + HNO_3
- □ **Phenol:** C_6H_6O + 14$S_2O_8^{2-}$ + $11H_2O$= 28SO_4^{2-} + 6CO_2 + 28H^+
- □ **Tert-butanol:** $C_4H_{10}O$ + 12$S_2O_8^{2-}$ + $7H_2O$= 24SO_4^{2-} + 4CO_2 + 24H^+
- □ **Citric acid:** $C_6H_8O_7$ + 9$S_2O_8^{2-}$ + $5H_2O$= 18SO_4^{2-} + 6CO_2 + 18H^+
- □ **Methanol:** CH_4O + 3$S_2O_8^{2-}$ + H_2O= 6SO_4^{2-} + CO_2 + 6H^+
- □ **Oxalate:** $C_2O_4^{2-}$ + 1$S_2O_8^{2-}$ = 2SO_4^{2-} + 2CO_2

□ Inorganic bromine balance

✓ Inorganic bromine almost kept balance.
✓ TOBr < 1% of total bromine.





统一的抑制机制！

Acknowledgment

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主要研究成果：

1. Mechanistic Insight into Suppression of Bromate Formation by Dissolved Organic Matters in Sulfate Radical-Based Advanced Oxidation Processes. Chemical Engineering Journal 333 (2018) 200–205.