Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Appendix A. Supplementary data

Degradation of Sulfapyridine antibiotics by chlorination in a pilot-scale water distribution system: kinetics, THMs, and DFT studies

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Text S1 The introduction of pilot-scale WDS.

The WDS has three loops. Each loop is approximately 80 m in length and 150 mm in diameter. The pipe materials of three loops are ductile iron pipe, stainless steel and polyethylene plastic pipes (PE pipes). This system had the velocity controller and temperature controller. The flow rates could be adjusted from 0.2-1.8 m/s, and the temperature could be adjusted from 0 ℃ to 40 ℃. In addition, this system was also equipped with an automatic detector, including free residual chlorine (FAC), turbidity, pH and so on. The ductile iron pipe was mostly used in this research, although stainless steel and PE pipes were tested. Experimental water circulated in the loop came from the municipal drinking water network in Hangzhou City.

Text S2 Dissociation reaction

(a) FAC

In aqueous solutions, due to dissociation reaction, residual chlorine generally has two forms of ClO^- and HClO as Equation (S1) .

$$[FAC] = [HClO] + [ClO^-] \quad \text{(S1)}$$

Dissociation：$HClO \Leftrightarrow ClO^- + H^+$ pKa=7.54 Decomposition：$HClO \rightarrow HCl + O_2$ (S2)

Where, pKa is the dissociation constant of HClO, and there is pKa=lgKa. Then the Ka can be described as Equation (S3)

$$Ka = \frac{[ClO^-][H^+]}{[HClO]} \quad \text{(S3)}$$

The proportions of HClO and ClO^- in aqueous solutions α_1 and α_2 can be determined as Equations (S4-S5).

$$\alpha_1 = \frac{[H^+]}{[H^+] + k_a^{HClO}} \quad \text{(S4)}$$

$$\alpha_2 = \frac{k_a^{HClO}}{[H^+] + k_a^{HClO}} \quad \text{(S5)}$$

Where $[H^+]$can be determined by the pH of the reaction system.

(b) SPD

SPD also dissociates in aqueous solutions, and the dissociation is described as

Equations (S7-S8).

$$[SPD]_{tot} = [SPD^+] + [SPD] + [SPD^-]$$

$$SPD^+ = SPD + H^+ \qquad pk_{a1}^{SPD} = 2.74 \qquad \text{(S7)}$$

$$SPD = SPD^- + H^+ \qquad pk_{a2}^{SPD} = 8.29 \qquad \text{(S8)}$$

pk_{a1} and pk_{a2} are the first-order and second-order dissociation constants of SPD respectively and $pk_{a1} = pk_{a2}$, pk_{a1} and pk_{a2} are calculated as Equations (S9-S10).

$$k_{a1}^{SPD} = \frac{[SPD][H^+]}{[SPD^+]} \qquad \text{(S9)}$$

$$k_{a2}^{SPD} = \frac{[SPD^-][H^+]}{[SPD]} \qquad \text{(S10)}$$

Then the proportions of the three components of SPD can be described as Equations (S11-S13).

$$\beta_1 = \frac{[H^+]^2}{[H^+]^2 + [H^+]k_{a1}^{SPD} + k_{a1}^{SPD}k_{a2}^{SPD}} \qquad \text{(S11)}$$

$$\beta_2 = \frac{[H^+]k_{a1}^{SPD}}{[H^+]^2 + [H^+]k_{a1}^{SPD} + k_{a1}^{SPD}k_{a2}^{SPD}} \qquad \text{(S12)}$$

$$\beta_3 = \frac{k_{a1}^{SPD}k_{a2}^{SPD}}{[H^+]^2 + [H^+]k_{a1}^{SPD} + k_{a1}^{SPD}k_{a2}^{SPD}} \qquad \text{(S13)}$$

The relationship between the total reaction and the orthogonal reaction of each component in the Equations (S14-S15).

$$\frac{\mathrm{d}[\mathrm{SPD}]_{\mathrm{tot}}}{\mathrm{dt}} = -k_2[\mathrm{FAC}][\mathrm{SPD}] = -\sum_{\mathrm{i}=1}^{2}\sum_{\mathrm{j}=1}^{3} k_{\mathrm{ij}}\alpha_{\mathrm{i}}[\mathrm{FAC}]\beta_{\mathrm{j}}[\mathrm{SPD}]$$

$$= -[\mathrm{SPD}][\mathrm{FAC}]\cdot\left\{\begin{array}{l} k_{11}\cdot\dfrac{[\mathrm{H}^+]}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{[\mathrm{H}^+]^2}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{12}\cdot\dfrac{[\mathrm{H}^+]}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{k_{\mathrm{a1}}^{\mathrm{SPD}}[\mathrm{H}^+]}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{13}\cdot\dfrac{[\mathrm{H}^+]}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{k_{\mathrm{a1}}^{\mathrm{SPD}}\cdot k_{\mathrm{a2}}^{\mathrm{SPD}}}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{21}\cdot\dfrac{k_{\mathrm{a}}^{\mathrm{HOCl}}}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{[\mathrm{H}^+]^2}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{22}\cdot\dfrac{k_{\mathrm{a}}^{\mathrm{HOCl}}}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{k_{\mathrm{a1}}^{\mathrm{SPD}}[\mathrm{H}^+]}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{23}\cdot\dfrac{k_{\mathrm{a}}^{\mathrm{HOCl}}}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{k_{\mathrm{a1}}^{\mathrm{SPD}}\cdot k_{\mathrm{a2}}^{\mathrm{SPD}}}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}} \end{array}\right\}+\mathrm{b} \qquad \text{(S14)}$$

$$k_2 = \left\{\begin{array}{l} k_{11}\cdot\dfrac{[\mathrm{H}^+]}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{[\mathrm{H}^+]^2}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{12}\cdot\dfrac{[\mathrm{H}^+]}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{k_{\mathrm{a1}}^{\mathrm{SPD}}[\mathrm{H}^+]}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{13}\cdot\dfrac{[\mathrm{H}^+]}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{k_{\mathrm{a1}}^{\mathrm{SPD}}\cdot k_{\mathrm{a2}}^{\mathrm{SPD}}}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{21}\cdot\dfrac{k_{\mathrm{a}}^{\mathrm{HOCl}}}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{[\mathrm{H}^+]^2}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{22}\cdot\dfrac{k_{\mathrm{a}}^{\mathrm{HOCl}}}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{k_{\mathrm{a1}}^{\mathrm{SPD}}[\mathrm{H}^+]}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}}+ \\ k_{23}\cdot\dfrac{k_{\mathrm{a}}^{\mathrm{HOCl}}}{[\mathrm{H}^+]+k_{\mathrm{a}}^{\mathrm{HOCl}}}\cdot\dfrac{k_{\mathrm{a1}}^{\mathrm{SPD}}\cdot k_{\mathrm{a2}}^{\mathrm{SPD}}}{[\mathrm{H}^+]^2+[\mathrm{H}^+]k_{\mathrm{a1}}^{\mathrm{SPD}}+k_{\mathrm{a1}}^{\mathrm{SPD}}k_{\mathrm{a2}}^{\mathrm{SPD}}} \end{array}\right\}+\mathrm{b} \qquad \text{(S15)}$$

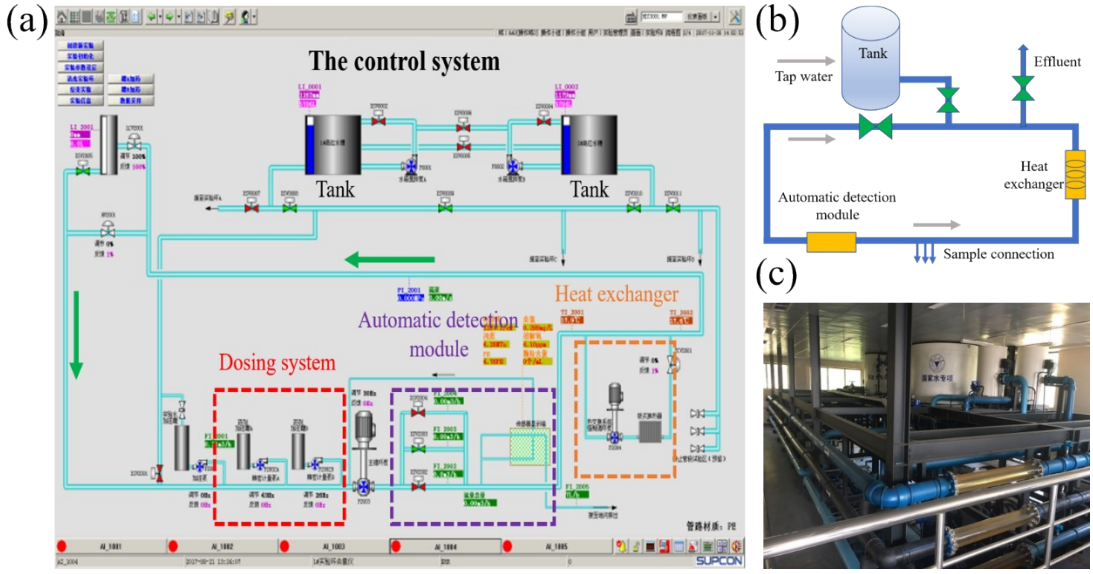


Fig. S1 Schematic representation of WDS. (a): The control system for the WDS. (b): The illustration of WDS model. (c): The pilot-scale WDS in experiments.

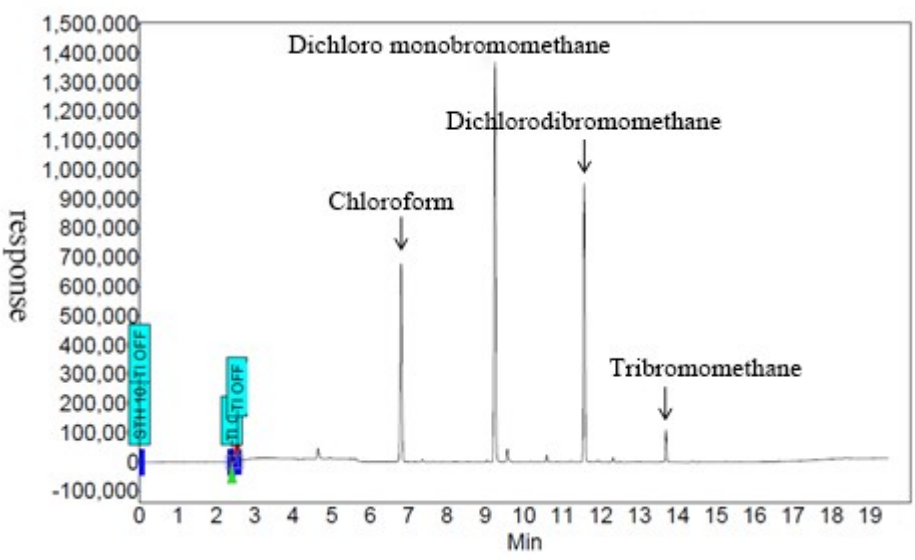


Fig. S2 GC-ECD chromatogram of trihalomethane.

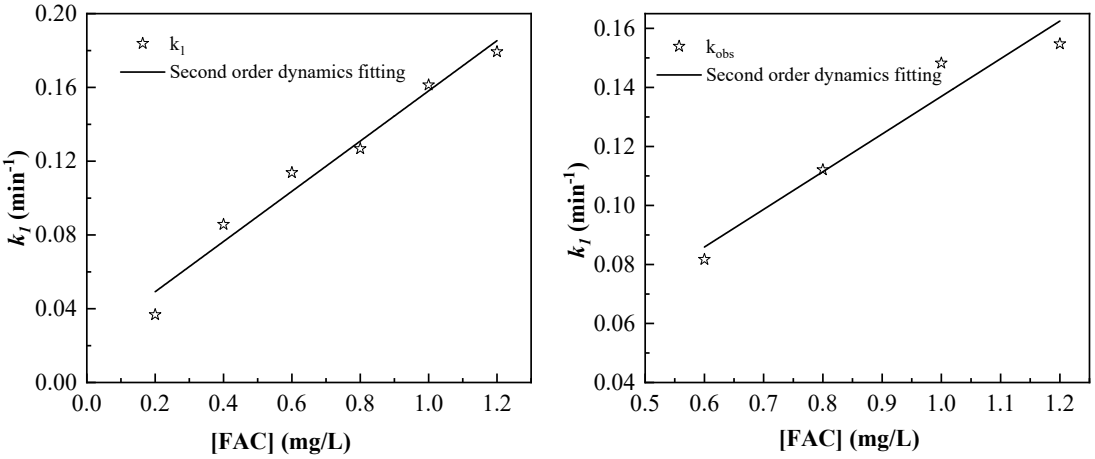


Fig. S3 (a) Second order dynamic fitting in WDS; (b) Second order dynamics fitting in beaker tests;

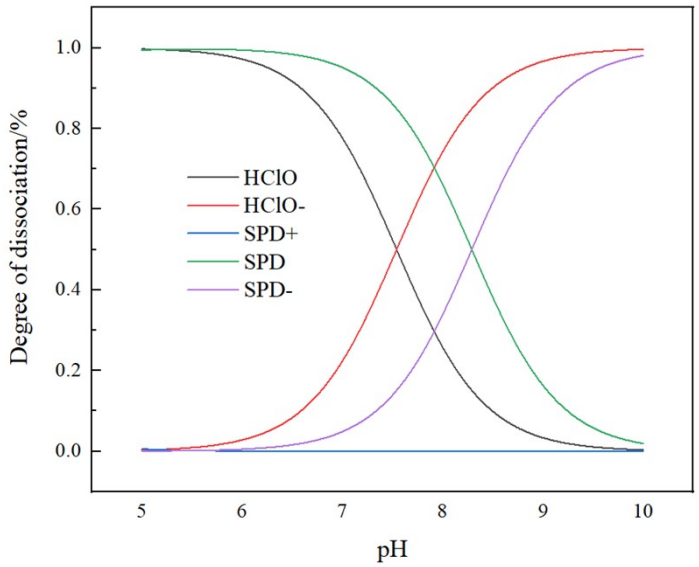


Fig.S4 Distribution coefficient of each component at different pH

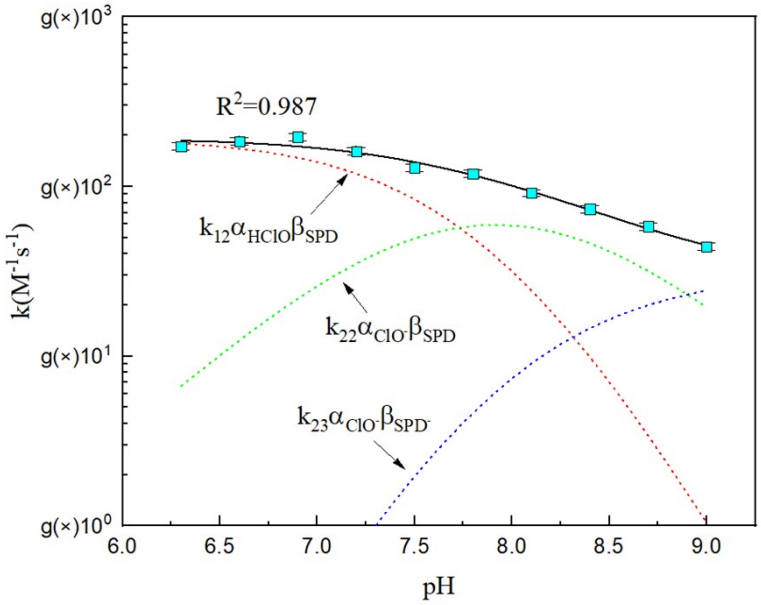
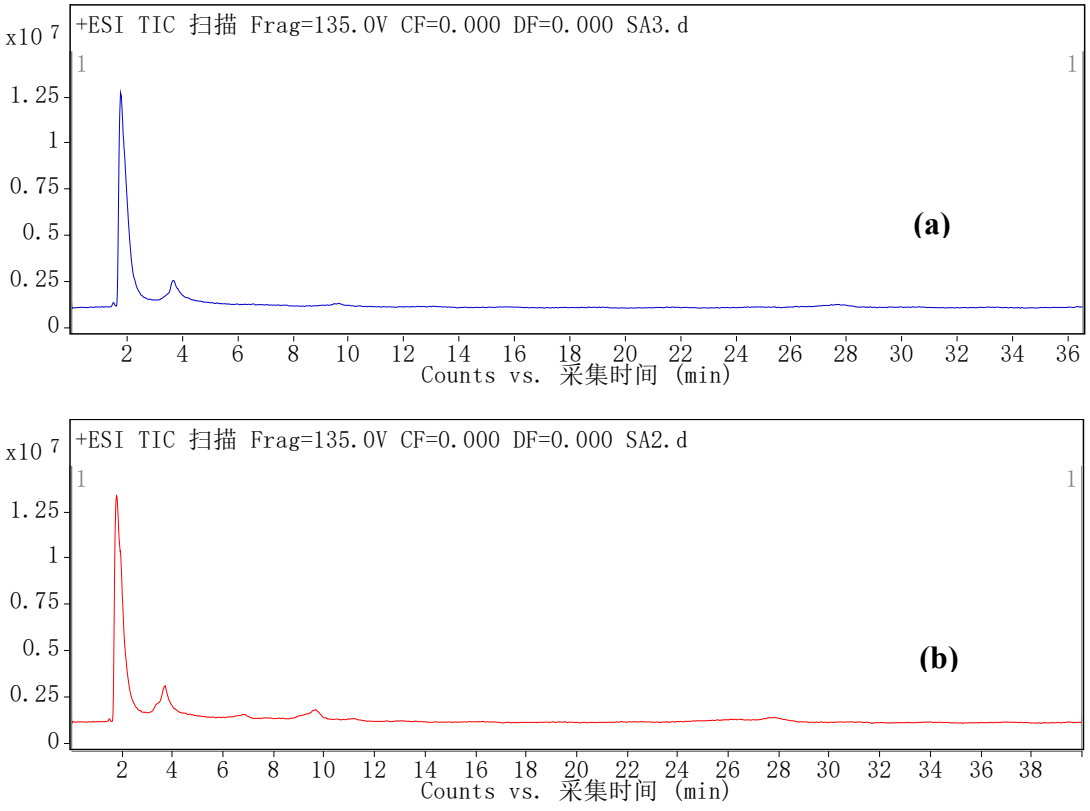


Fig. S5 k_2 and pH model of SPD chloride in WDS and beaker tests.



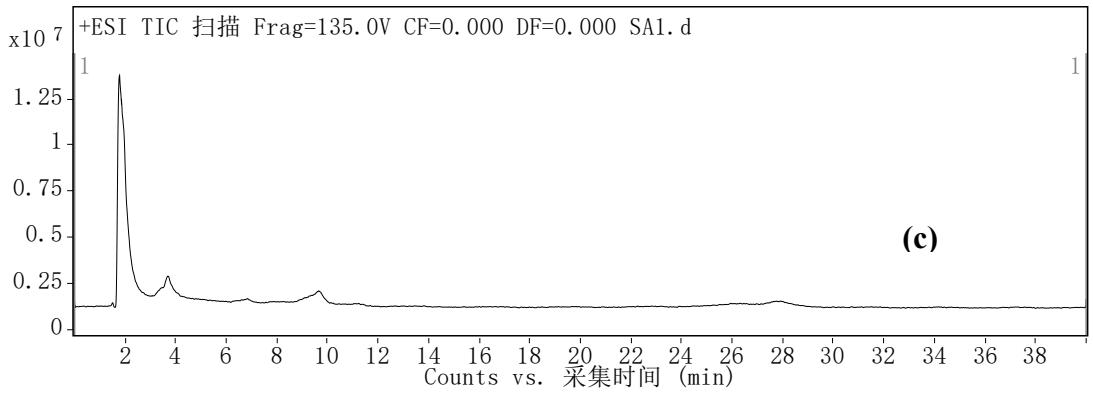
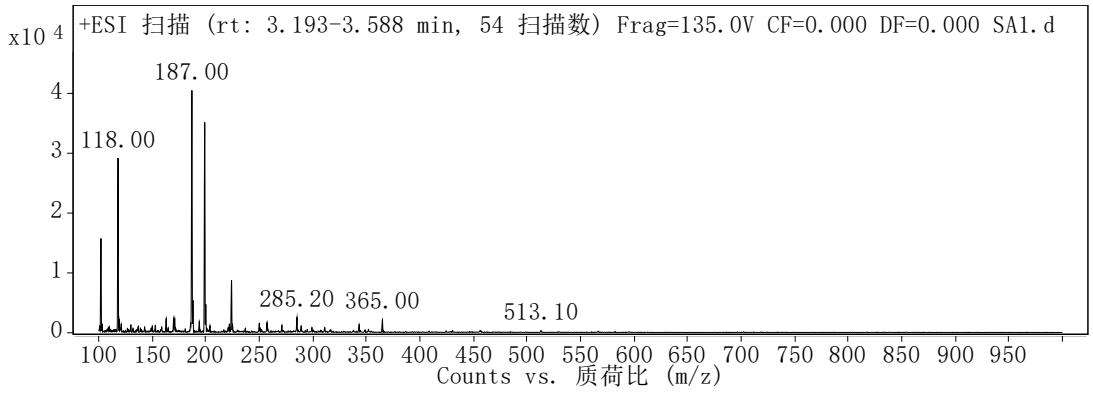
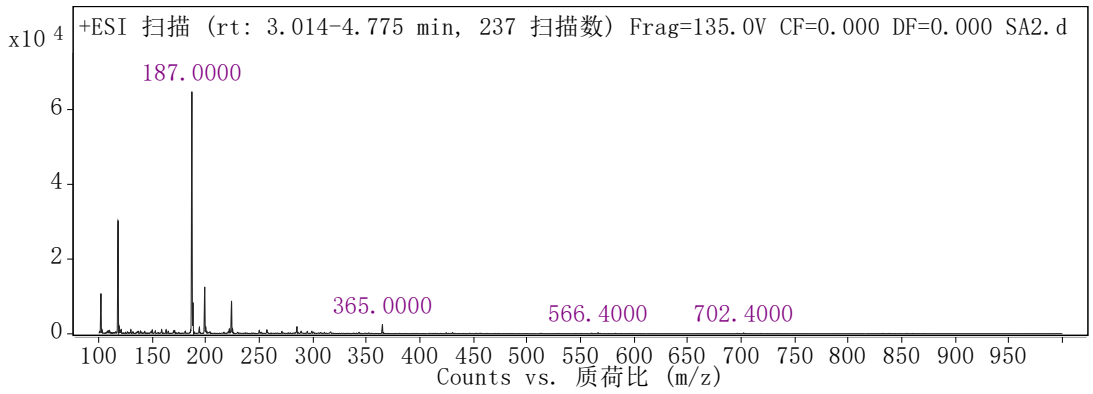
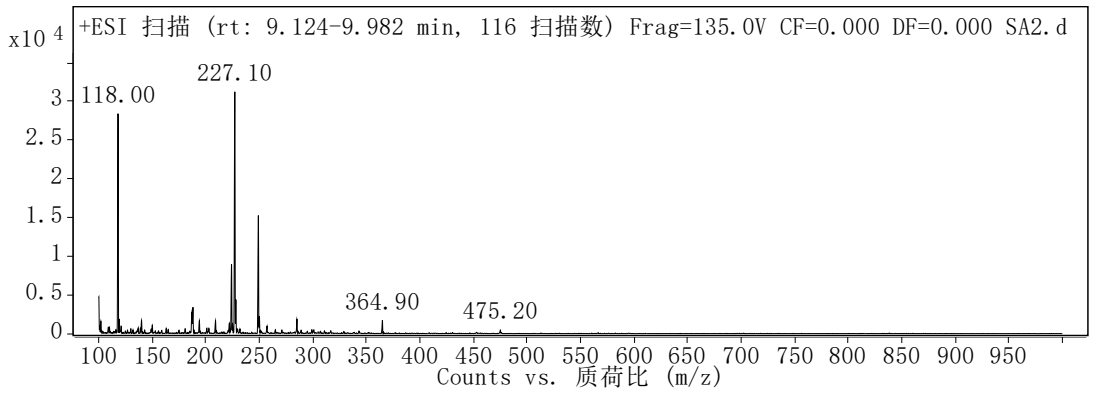


Fig S6 LC-MS scans in positive ion mode (ESI+): (a) (b) (c) 10 min, 20 min and 30 min reaction samples, respectively







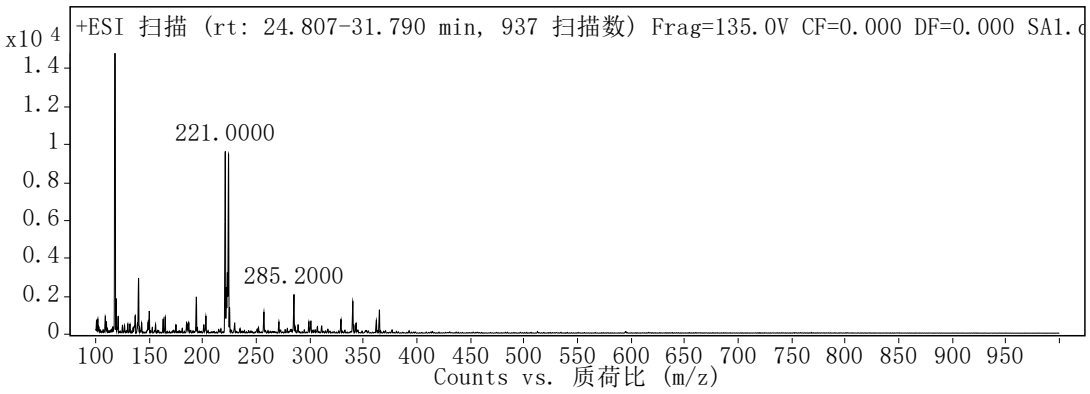


Fig. S7 Mass spectrum with different retention times. （a）3.19-3.59 min，m/z 199；（b）3.59-4.78 min，m/z 187（c）9.12-9.98 min，m/z 249（d）24.80-31.80 min，m/z 221

Table S1 Physiochemical characteristics of SPD

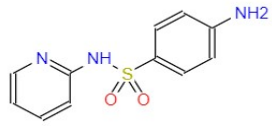
Chemical structure	Melocular formula	Boiling point	Melting point	Solubility in water
	$C_{10}H_{10}N_4O_2S$	473.5±51.0 °C	191-193°C	＜0.1 g/100 mL at 22 ºC

Table. S2 Parameter of injection system for purge and trap pretreatment.

Parameter name	Parameter value	Parameter name	Parameter value
Purge temperature	30	Analytical temperature	210
Purge time	15	Analysis time	3
Purge air flow	40	Baking temperature	250
Dry purge time	1.5	baking time	5
Dry purge flow	100	Injection volume of water sample	30

Table. S3 THMs standard curve.

Target analyte	Peak time	linear equation	R^2	Linear range	detection limit
Chloroform	6.90	Y=2067.2x+1542.3	0.9964	0~20	0.01
Dichloromethane	9.23	Y=20145x+1638	0.9985	0~20	0.01
Chlorodibromomethane	11.52	Y=21023x-1569.7	0.9923	0~20	0.01
Tribromomethane	13.72	Y=6457.3x+364.1	0.9945	0~20	0.01

Table. S4 The first order kinetic constant of the chlorination SPD reaction

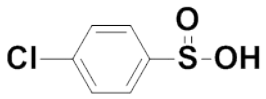
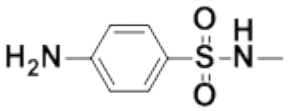
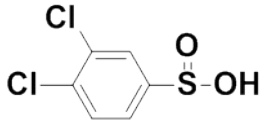
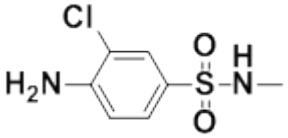
Residual chlorine concentration	k_1（min^{-1}）		R^2	
	WDS	Beaker tests	WDS	Beaker tests

（mg/L）				
0.2	/	$(3.68 \pm 0.24) \times 10^{-2}$		0.967
0.4	/	$(8.51 \pm 0.16) \times 10^{-2}$		0.967
0.6	$(8.07 \pm 0.22) \times 10^{-2}$	$(11.35 \pm 0.18) \times 10^{-2}$	0.994	0.998
0.8	$(11.14 \pm 0.61) \times 10^{-2}$	$(12.65 \pm 0.26) \times 10^{-2}$	0.985	0.998
1.0	$(14.74 \pm 0.98) \times 10^{-2}$	$(16.13 \pm 0.40) \times 10^{-2}$	0.978	0.997
1.2	$(15.46 \pm 1.25) \times 10^{-2}$	$(17.98 \pm 0.57) \times 10^{-2}$	0.962	0.995

Table. S5 The second order kinetic constants of chlorination SPD reaction (k_2)

condition	WDS	Beaker tests
k_2（$L \cdot mg^{-1} \cdot min^{-1}$）	$(12.89 \pm 2.22) \times 10^{-2}$	$(13.67 \pm 1.18) \times 10^{-2}$

Table S6 Molecular structures corresponding to different ionic fragment mass-to-charge ratios.

Retention time	（m/z）	Possible molecular formula	molecular weight
3.3 min	199		176
4.3 min	187		186
9.5 min	249		210
27.6 min	221		220