Supporting Information

Transformation of carbon dots by ultraviolet irradiation, ozonation, and chlorination processes: Kinetics and mechanisms

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Scheme S1: Radicals' generation in ultraviolet irradiation, ozonation, and chlorination processes.

Ultraviolet irradiation:[1, 2]

$CDs \xrightarrow{hv} h^{+} + e^{-}$——(1)

$h^{+} + OH^{-} \rightarrow \cdot OH$——(2)

$O_2 + e^{-} \rightarrow O_2^{\cdot -}$——(3)

Ozonation:[3]

$O_3 + OH^{-} \rightarrow HO_2^{-} + O_2$——(4)

$O_3 + HO_2^{-} \rightarrow \cdot OH + O_2^{\cdot -} + 2OH^{-}$——(5)

Chlorination:[4]

$HOCl \rightarrow \cdot OH + Cl \cdot$——(6)

$OCl^{-} \rightarrow O^{\cdot -} + Cl \cdot$——(7)

Scheme S2: Radical interconversion reactions [5-8]

$NO_3^{-} + \cdot OH \rightarrow NO_3 \cdot + OH^{-}$——(8)

$CO_3^{2-} + \cdot OH \rightarrow CO_3^{\cdot -} + OH^{-}$——(9)

$HCO_3^{-} + \cdot OH \rightarrow CO_3^{\cdot -} + H_2O$——(10)

$SO_4^{2-} + \cdot OH \rightarrow SO_4^{\cdot -} + OH^{-}$——(11)

$Cl^{-} + \cdot OH \rightarrow Cl \cdot + OH^{-}$——(12)

$ClOH^{\cdot -} + H^{+} \rightarrow Cl \cdot + OH^{-}$——(13)

$ClOH^{\cdot -} + Cl^{-} \rightarrow Cl_2^{\cdot -} + OH^{-}$——(14)

$CO_3^{2-} + Cl \cdot \rightarrow CO_3^{\cdot -} + Cl^{-}$——(15)

$HCO_3^{-} + Cl \cdot \rightarrow CO_3^{\cdot -} + H^{+} + Cl^{-}$——(16)

$CO_3^{2-} + ClO \cdot \rightarrow ClO^{-} + CO_3^{\cdot -}$——(17)

Table S1. Primary properties of various water samples.

Parameter	Unit	Zhujiang River water	Tap water	WWTP effluent water	South China Sea water
pH	-	7.12	7.48	6.89	8.23
TOC	mg L^{-1}	3.025	1.217	4.165	0.3597
Na^{+a}	mg L^{-1}	16.83	11.35	37.20	10241
$K^{+\,a}$	mg L^{-1}	4.62	3.68	10.87	396
$Cu^{2+\,a}$	μg L^{-1}	0.98	/	/	50.18
$Mg^{2+\,a}$	mg L^{-1}	3.97	3.21	7.01	1459
$Al^{3+\,a}$	μg L^{-1}	6.51	22.7	9.27	3.36
$Cl^{-\,b}$	mg L^{-1}	14.58	11.20	49.86	18984.02
HCO_3^-	mg L^{-1}	4.98	3.62	3.03	6.01
SO_4^{2-b}	mg L^{-1}	28.23	16.89	39.68	2706.02

[a] Detected by ICP-MS.

[b] Detected by anions-ion chromatography.

Table S2. Scavengers used, RSs quenched and rate constants with quenched reactive species.

	Quencher	RSs Quenched	Removal Rate (%)	Inhibition (%)
UV	Blank	\	66.5	0
	$Na_2C_2O_4$	h^+	39.1	41.2
	$K_2Cr_2O_7$	e^-	63.8	4.1
	IPA	•OH	56.0	15.8
	TEMPO	$O_2^{\bullet-}$	27.4	58.8
	NaN_3	$^1O_2$	43.7	34.3
O_3	Blank	\	81.7	0
	IPA	•OH	77.7	4.9
	TEMPO	$O_2^{\bullet-}$	33.0	59.6
	NaN_3	$^1O_2$	54.2	33.7
NaClO	Blank	\	30.3	0
	0.1 μM $Na_2S_2O_3$	Cl• /ClO•	14.5	52.1
	0.1 μM $Na_2S_2O_3$	Cl• /ClO•	0	100

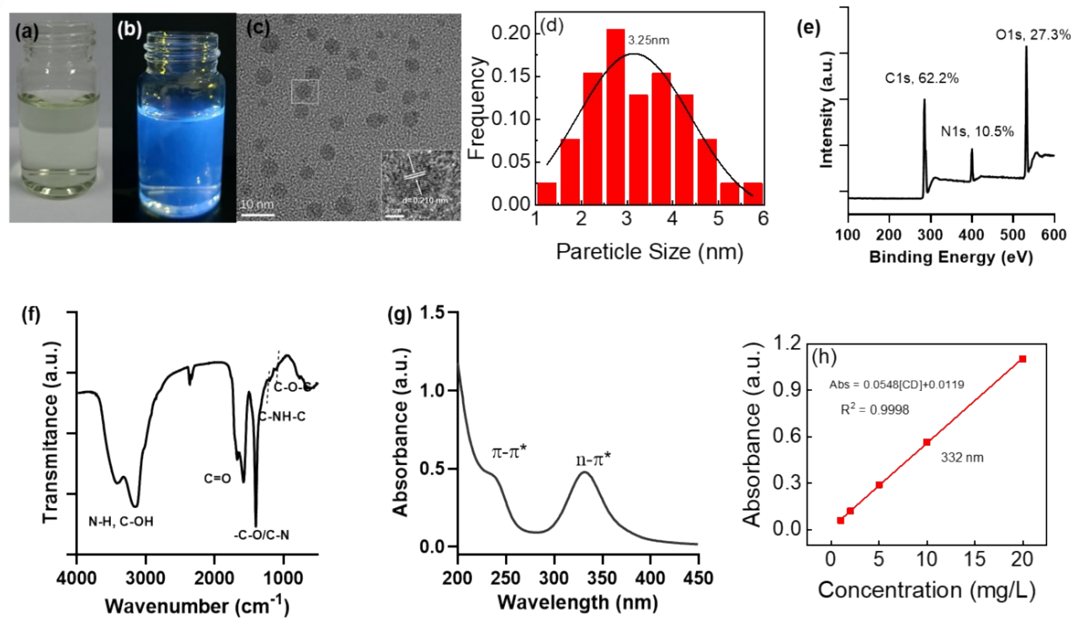


Fig. S1. Characterizations of the prepared CDs, the photographs of the (a) visible color of CDs and (b) fluorescence color under UV lamp irradiation; (c) TEM images and (d) diameter distribution of CDs, (e) XPS, (f) FT-IR spectra of CDs, (g) UV-vis absorption spectra of CDs and (h) liner correlation between CD concentration and its UV-vis absorbance with wavelength of 332 nm.

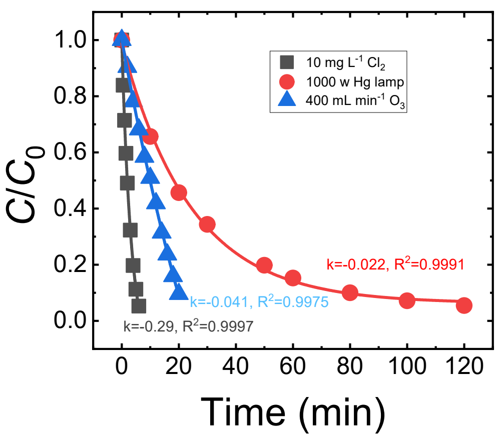


Fig. S2. Reaction kinetics of sodium indigo disulfonate treated by 1000W mercury lamp irradiation, 400 mL /min ozone oxidation, and chlorination with 10 mg/L Cl_2, respectively.

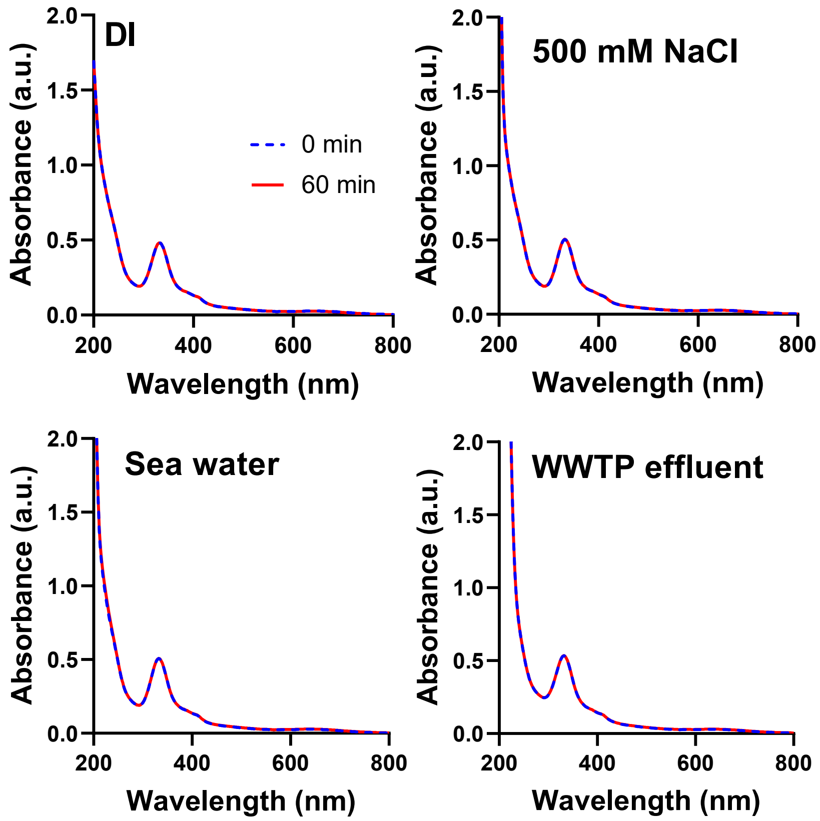


Fig. S3. UV−vis absorption spectra of CDs in various solutions including DI water, DI water with 500 mM NaCl, sea water, and WWTP effluent at pH=7.0.

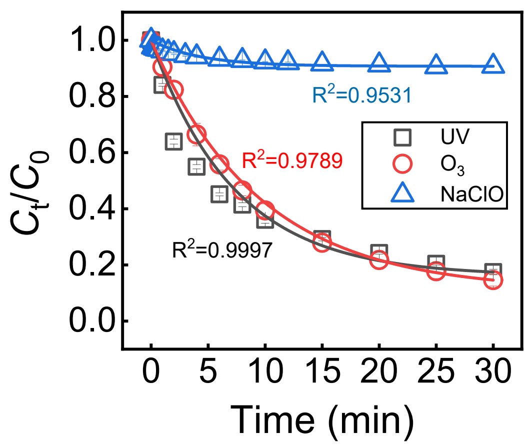


Fig. S4. Degradation kinetics of CDs in three typical disinfection processes including UV irradiation, ozonation, and chlorination.

Fig. S5. Visual change of color and fluorescence intensity of pristine CDs and after treated by three disinfection processes.

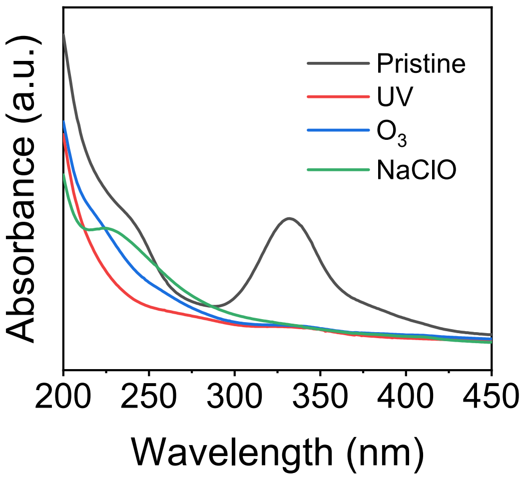


Fig. S6. UV-vis spectra change of pristine CDs and after treated by three disinfection processes.

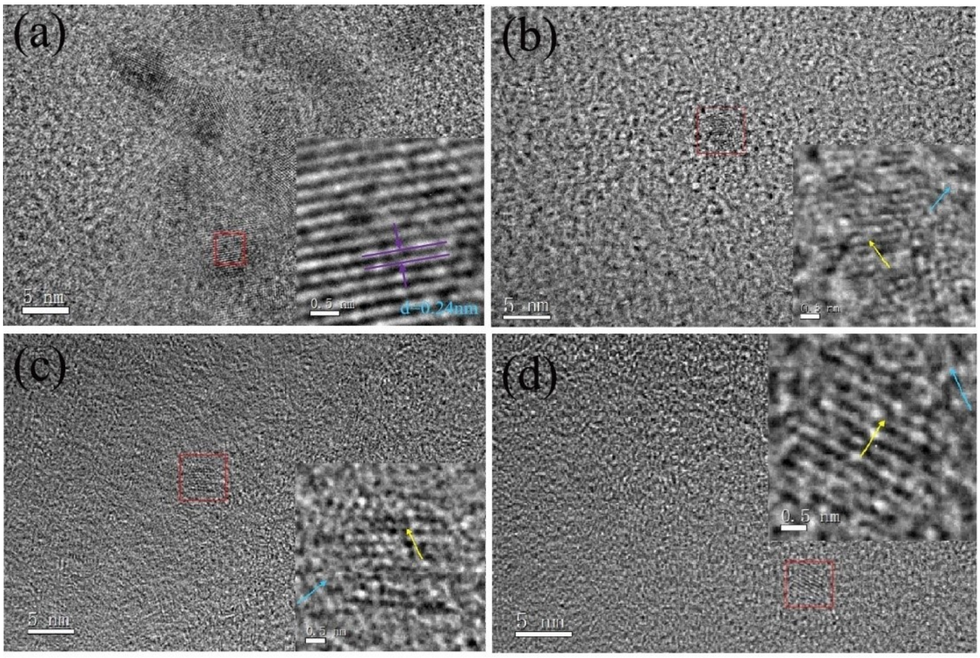


Fig. S7. HR-TEM images of the pristine and three different disinfectants-treated CDs. (a) Pristine CDs, (b) UV irradiated-CDs, (c) O_3 treated CDs, (d) chlorinated-CDs. yellow arrows indicate intact region, blue arrows show damaged regions of CDs.

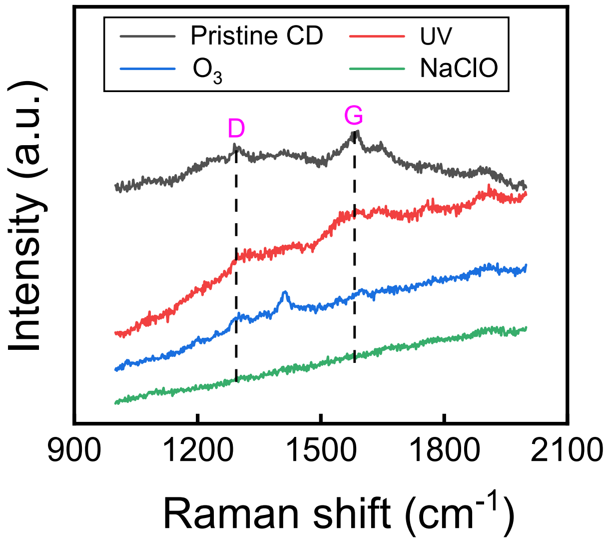


Fig. S8. Raman spectra of CDs before and after treatment by different disinfection processes.

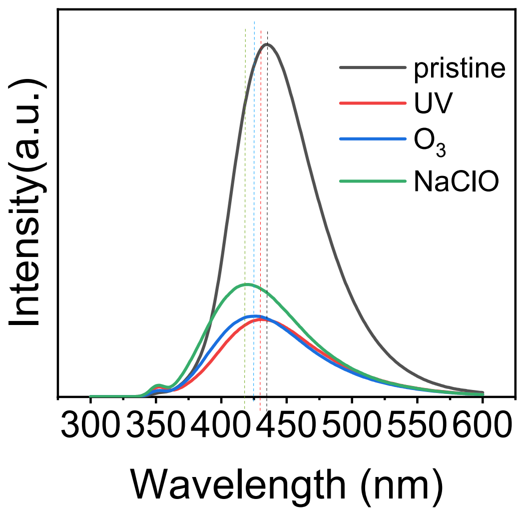


Fig. S9. The emission spectra of pristine and treated CDs excited at wavelength of 350 nm.

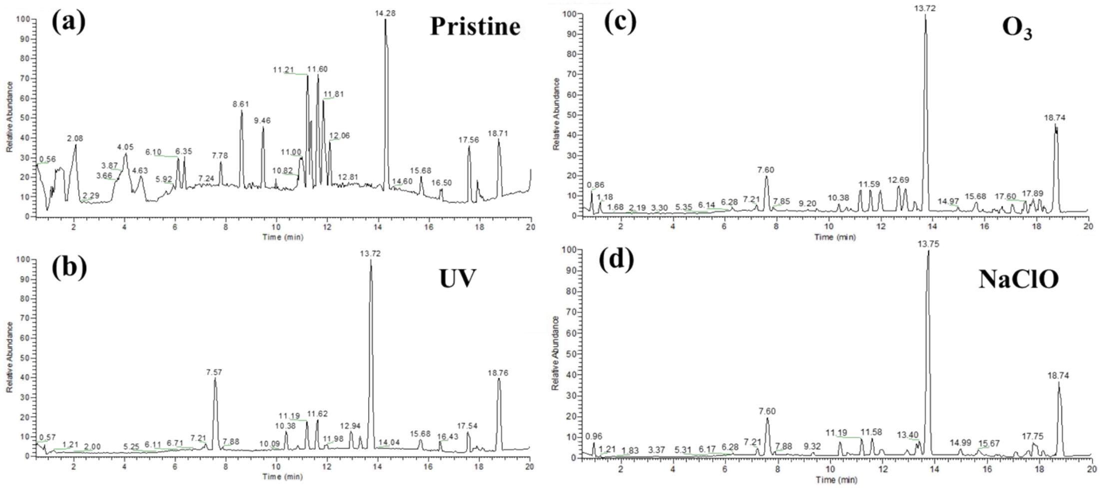


Fig. S10. HPLC chromatograms of CDs before and after transformation, (a) the pristine CDs, (b-d) CDs treated with UV, ozone and chlorine, respectively

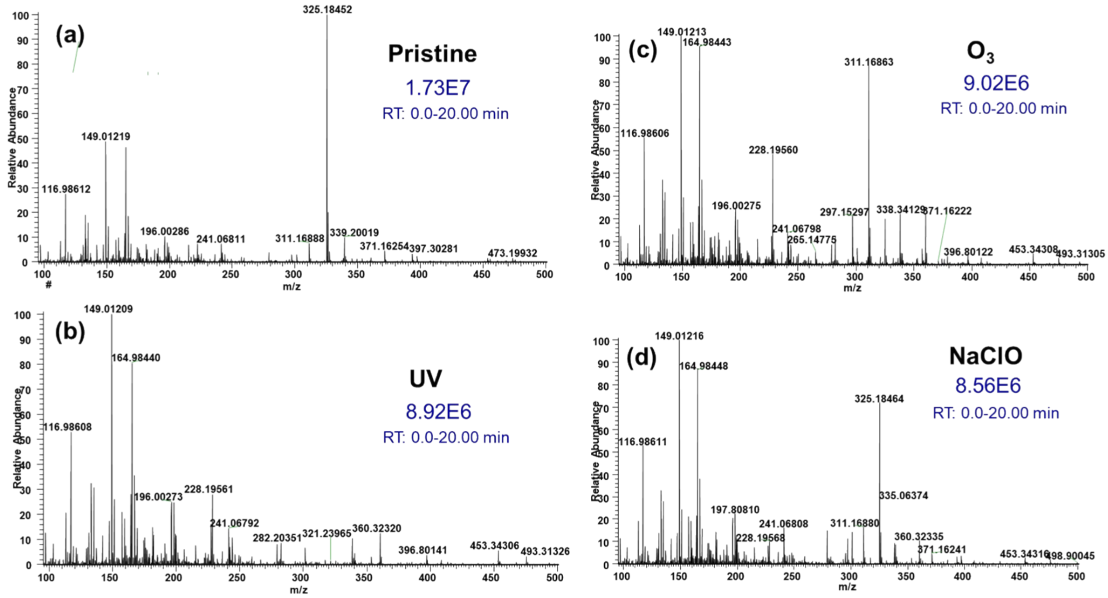
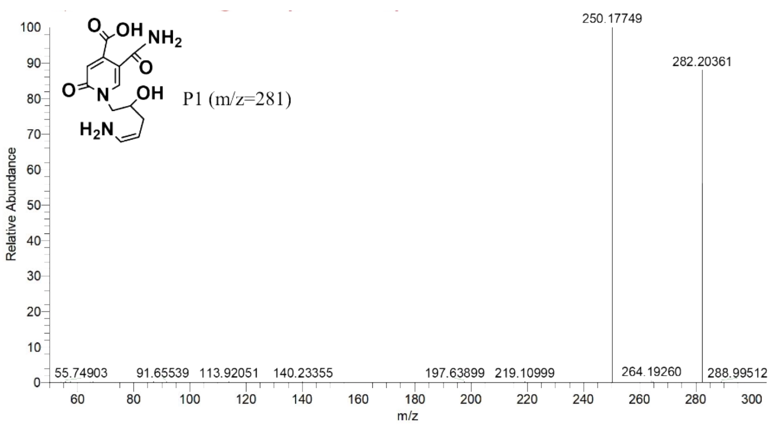
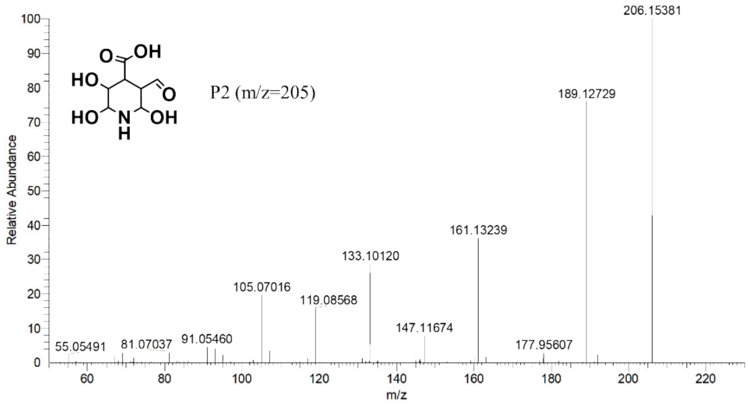
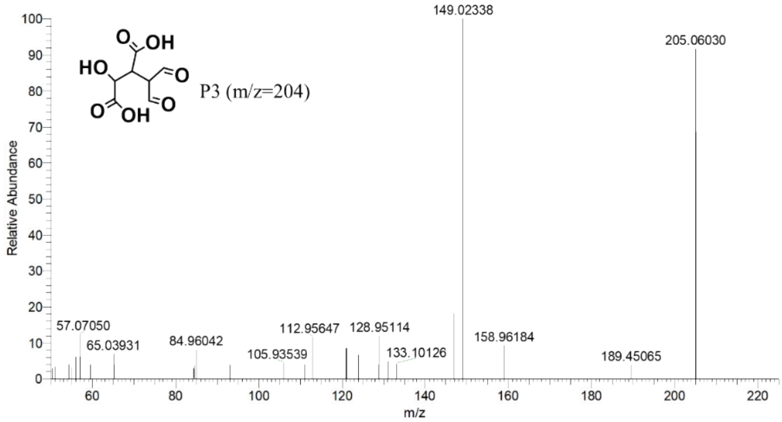


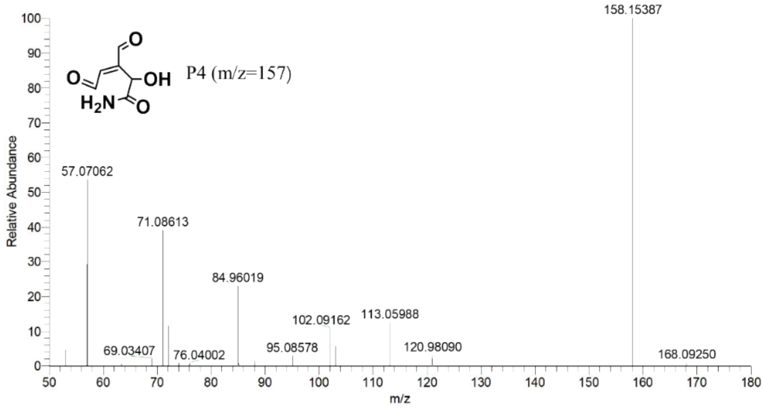
Fig. S11. Positive ion mode mass spectrometry of CDs before and after transformation, (a) the pristine CDs, (b-d) CDs treated with UV, ozone and chlorine, respectively.

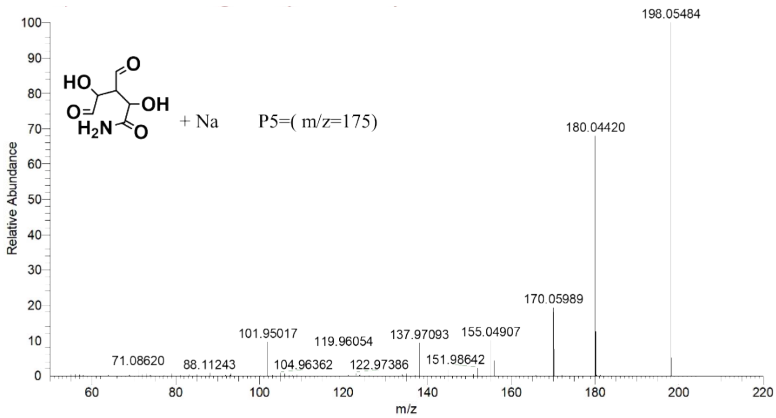
Possible intermediates in UV and O_3 treatments:

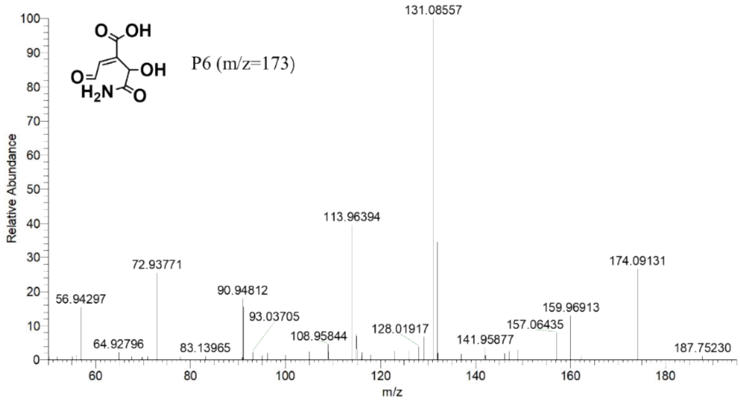



P2 (m/z=205)
Relative Abundance
m/z
206.15381
189.12729
161.13239
133.10120
105.07016
119.08568
147.11674
177.95607
55.05491
81.07037
91.05460


P3 (m/z=204)
Relative Abundance
m/z
149.02338
205.06030
57.07050
65.03931
84.96042
105.93539
112.95647
128.95114
133.10126
158.96184
189.45065


P4 (m/z=157)
Relative Abundance
m/z
158.15387
57.07062
71.08613
84.96019
102.09162
113.05988
69.03407
76.04002
95.08578
120.98090
168.09250


+ Na
P5=(m/z=175)
Relative Abundance
m/z
198.05484
180.04420
170.05989
101.95017
119.96054
137.97093
155.04907
71.08620
88.11243
104.96362
122.97386
151.98642



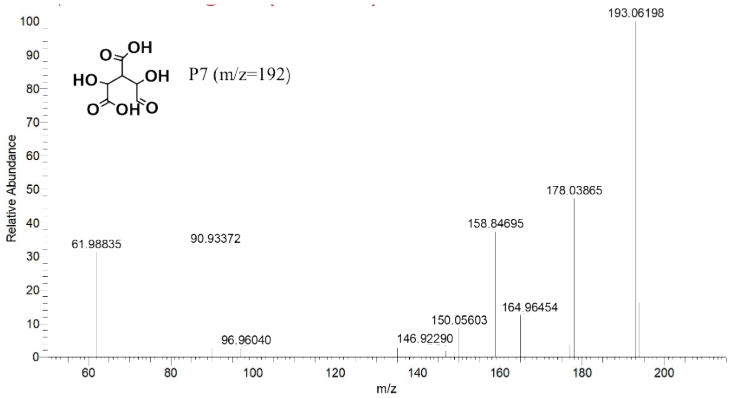
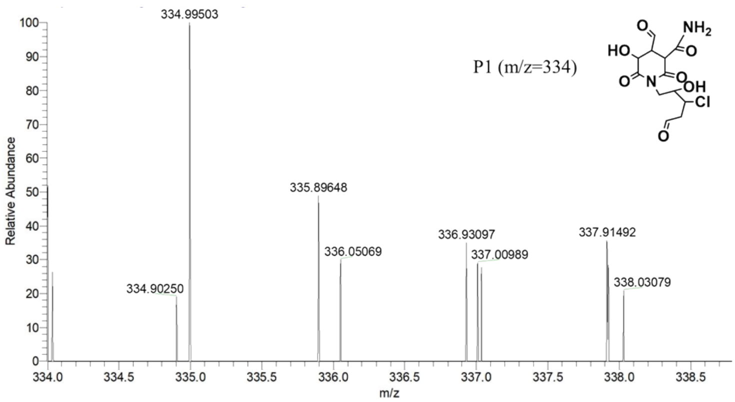
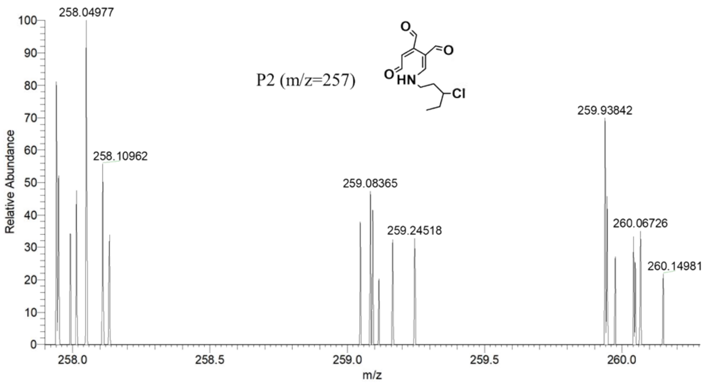


Fig. S12. Proposed structures of some possible products in UV and ozone treatment.

Possible intermediates in NaClO treatment:





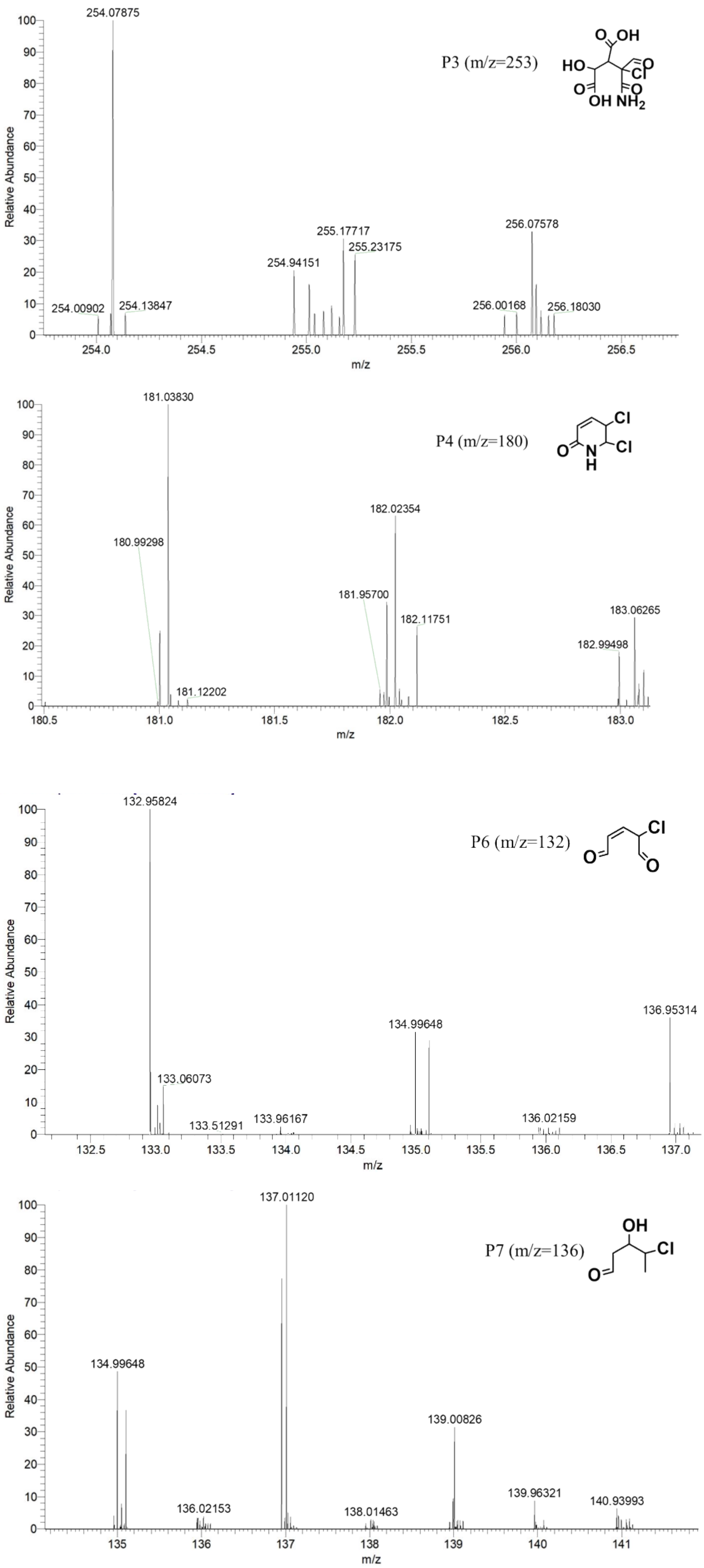


Fig. S13. Proposed structures of some possible products in chlorination treatment.

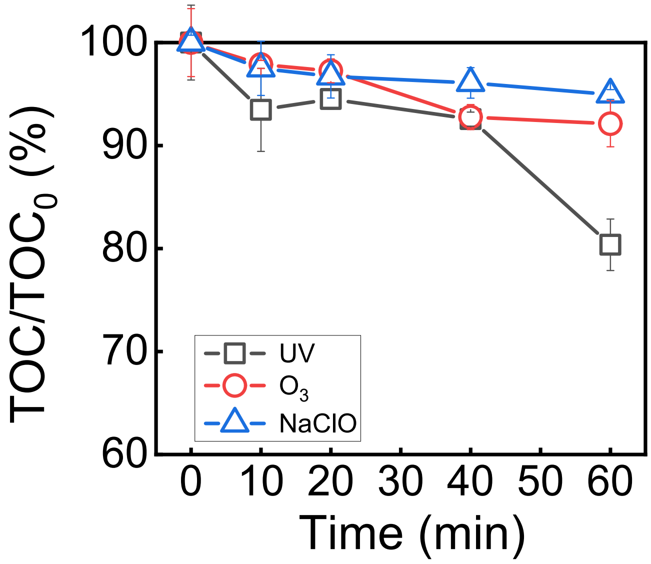


Fig. S14. Changes of total organic carbon (TOC) content before and after CDs transformation.

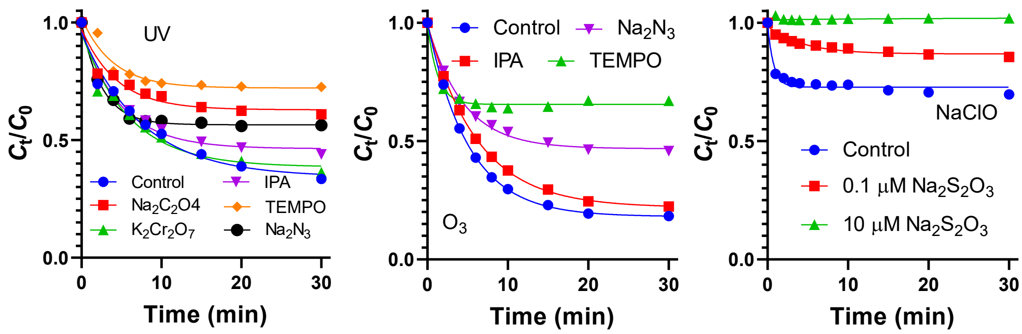


Fig. S15. Isopropanol (IPA, 10 mM), 2, 2 , 6, 6-tetramethylpiperidine-1-oxyl (TEMPO, 10 mM), potassium dichromate ($K_2Cr_2O_7$, 50 μM), sodium oxalate ($Na_2C_2O_4$, 10 mM), sodium azide (NaN_3, 10 mM), and sodium thiosulfate ($Na_2S_2O_3$, 0.1 or 10 μM) were applied as the trapping agent of •OH, $O_2^{\bullet -}$, e^-, h^+, $^1O_2$, and chlorine-active species (Cl• and ClO•).

Reference:

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