Supporting Information

Detection, identification and control of polar iodinated disinfection byproducts in chlor(am)inated secondary wastewater effluents

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Fig. S12. DOC concentration in secondary wastewater effluent sample A_1 with different dosages of coagulant and resin.

Table S1. Characteristics of the secondary wastewater effluent samples A_1 and A_2

1. Structure Proposing of the Compound with *m/z* 199 at RT 2.33 min

As shown in Fig. 1, the compound with *m/z* 199 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). Fig. S2 shows the product ion scan spectrum of this compound: a loss of 44 was observed, indicating a carboxyl group. After subtraction of one iodine atom and a carboxyl group from *m/z* 199, the remaining part is 29 (i.e.,199 – 126.9 – 44 = 29), for which a reasonable combination should be C_2H_4. Accordingly, this compound was proposed to be 3-iodo-propanoic acid.

2. Structure Proposing of the Compound with *m/z* 257 at RT 1.74 min

As shown in Fig. 1, the compound with *m/z* 257 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). Fig. S3 shows the product ion scan spectrum of this compound: the consecutive loss of two 44 were observed, indicating two carboxyl group. After subtraction of one iodine atom and two a carboxyl group from *m/z* 257, the remaining part is 42 (i.e.,257 – 126.9 – 88 = 42), for which a reasonable combination should be C_3H_6. Accordingly, this compound was proposed to be $HOOC(CH_2)_2CHICOOH$.

3. Structure Proposing of the Compound with *m/z* 285 at RT 2.82 min

As shown in Fig. 1, the compound with *m/z* 285 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). Fig. S4 shows the product ion scan spectrum of this compound: the consecutive loss of two 44 were observed, indicating two carboxyl group. After subtraction of one iodine atom and one a carboxyl group from *m/z* 285, the remaining part is 70 (i.e.,285 – 126.9 – 88 = 70). Notably, this compound has an *m/z* value which is 28 larger than the compound with *m/z* 257 (which was proposed to be $HOOC(CH_2)_2CHICOOH$), and thus it was proposed to contain one more aldehyde group or C_2H_4 than $HOOC(CH_2)_2CHICOOH$. However, no loss of 28 was occurred in the product ion scan spectrum of this compound so a reasonable combination of the remaining part should be C_5H_{10}. Accordingly, this compound was proposed to be $HOOC(CH_2)_4CHICOOH$.

4. Structure Proposing of the Compound with *m/z* 317 at RT 7.14 min

As shown in Fig. 1, the compound with *m/z* 317 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). The relatively long RT (7.14 min) suggests that this compound was aromatic (Zhai and Zhang, 2011). Notably, this compound has an *m/z* value which is 28 larger than the compound with *m/z* 303 (which was proposed to be 5-iodo-3-(1-propen-1yl)-4-hydroxybenzoic acid), and thus it was proposed to contain one more CH_2 than 5-iodo-3-(1-propen-1yl)-4-hydroxybenzoic acid. Accordingly, this compound was proposed to be 5-iodo-3-(1-buten-1-yl)-4-hydroxybenzoic acid.

5. Structure Proposing of the Compound with *m/z* 331 at RT 8.01 min

As shown in Fig. 1, the compound with *m/z* 331 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). The relatively long RT (8.01 min) suggests that this compound was aromatic (Zhai and Zhang, 2011). Notably, this compound has

an *m/z* value which is 14 larger than the compound with *m/z* 317 (which was proposed to be 5-iodo-3-(1-buten-1-yl)-4-hydroxybenzoic acid), and thus it was proposed to contain one more CH_2 than 5-iodo-3-(1-buten-1-yl)-4-hydroxybenzoic acid. Accordingly, this compound was proposed to be 5-iodo-3-(1-penten-1-yl)-4-hydroxybenzoic acid.

6. Structure Proposing of the Compound with *m/z* 357 at RT 5.13 min

As shown in Fig. 1, the compound with *m/z* 357 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). The relatively long RT (5.13 min) suggests that this compound was aromatic (Zhai and Zhang, 2011). Notably, this compound has an *m/z* value which is 26 larger than the compound with *m/z* 331 (which was proposed to be 5-iodo-3-(1-penten1-yl)-4-hydroxybenzoic acid), and thus it was proposed to contain one more CH_2 than 5-iodo-3-(1-penten-1-yl)-4-hydroxybenzoic acid. Accordingly, this compound was proposed to be 5-iodo-3-(1-hepten-1,5-diyl)-4-hydroxybenzoic acid.

7. Structure Proposing of the Compound with *m/z* 361 at RT 7.65 min

As shown in Fig. 1, the compound with *m/z* 361 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). The relatively long RT (7.65 min) suggests that this compound was aromatic (Zhai and Zhang, 2011). Notably, this compound has an *m/z* value which is 44 larger than the compound with *m/z* 317 (which was proposed to be 5-iodo-3-(1-buten-1-yl)-4-hydroxybenzoic acid), and thus it was proposed to contain one more carboxyl group than 5-iodo-3-(1-buten-1-yl)-4-hydroxybenzoic acid. Accordingly, this compound was proposed to be 5-iodo-3-(1-buten-1-yl)-4-hydroxy-1,2-benzenedicarboxylic acid.

8. Structure Proposing of the Compound with *m/z* 377 at RT 6.30 min

As shown in Fig. 1, the compound with *m/z* 377 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). The relatively long RT (6.30 min) suggests that this compound was aromatic (Zhai and Zhang, 2011). Notably, this compound has an *m/z* value which is 16 larger than the compound with *m/z* 361 (which was proposed to be 5-iodo-3-(1-buten-1-yl)-4-hydroxy-1,2-benzenedicarboxylic acid), and thus it was proposed to contain one more hydroxyl group than 5-iodo-3-(1-buten-1-yl)-4-hydroxy-1,2-benzenedicarboxylic acid. Accordingly, this compound was proposed to be 5-iodo-3-(1-buten-1-yl)-1,4-dihydroxy-1,2-benzenedicarboxylic acid.

9. Structure Proposing of the Compound with *m/z* 399/401/403 at RT 3.67 min

Fig. S10 shows the MRM chromatogram (399→126.9, 401→126.9, 403→126.9) and the product ion scan spectra of ion cluster *m/z* 399/401/403 of the sample. The relatively long RT (3.67 min) suggested that this compound was likely aromatic (Zhai and Zhang, 2011). An isotopic peak abundance ratio of *m/z* 399/401/403 at 9:3:1 was observed in the MRM spectrum of the ion cluster, indicating that this compound should contain two chlorine atoms. In the product ion scan spectra of *m/z* 399, 401 and 403, the consecutive loss of two 44 were observed, indicating two carboxyl group. Since this ion cluster was detected by PIS *m/z* 126.9, it should at least contain one iodine

atom. After subtraction of one benzene ring, two chlorine atom, two benzoic acid and one iodine atom from *m/z* 399/401/403, the remaining part was 41, for which a reasonable combination should be C_3H_5. Accordingly, this compound was proposed to be 3,5-dichlo-6-iodo-4-(1-propen-1-yl) -1,2-benzenedicarboxylic acid.

10. Structure Proposing of the Compound with *m/z* 417 at RT 3.86 min

As shown in Fig. 1, the compound with *m/z* 417 has only one isotopic peak, indicating that this compound should contain only I (without containing Cl or Br). The relatively long RT (3.86 min) suggested that this compound was likely aromatic (Zhai and Zhang, 2011). Fig. S11 shows the product ion scan spectrum of this compound: a loss of 44 were observed, indicating one carboxyl group, a loss of 28 were observed, indicating one aldehyde group and a loss of 16 were observed, indicating one hydroxyl group. Notably, this compound has an *m/z* value which is 44 larger than the compound with *m/z* 373 (which was proposed to be 3,5-diiodo-4-hydroxybenzoic acid), and thus it was proposed to contain one more carboxyl group than 3,5-diiodo-4-hydroxybenzoic acid. Accordingly, this compound was proposed to be 3,5-diiodo-4-hydroxy-1-hydroxylbenzaldehyde.

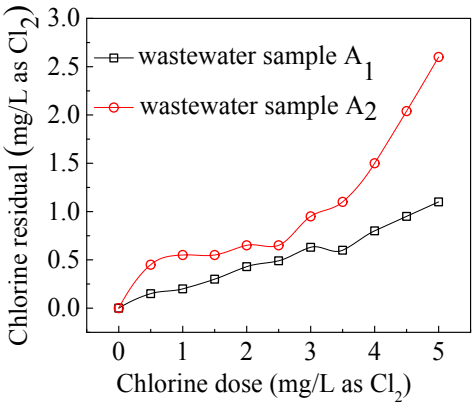

Fig. S1. Residual chlorine with different chlorine doses.

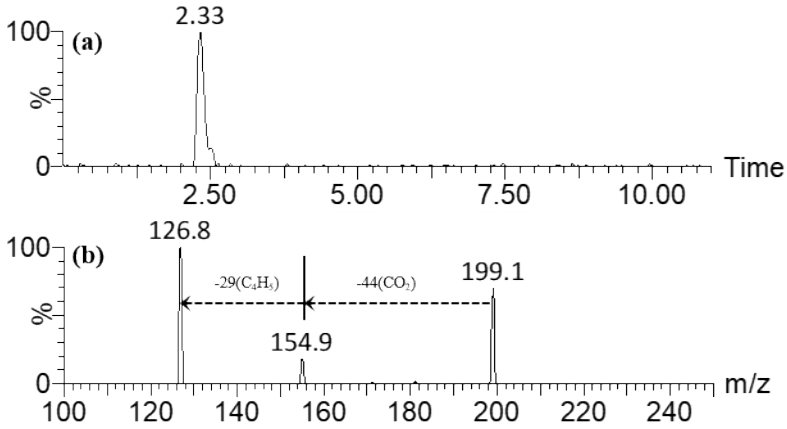

Fig. S2. (a) UPLC/ESI-tqMS MRM (199→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 199 of chlorinated secondary wastewater effluent sample A_1 at RT 2.33 min.

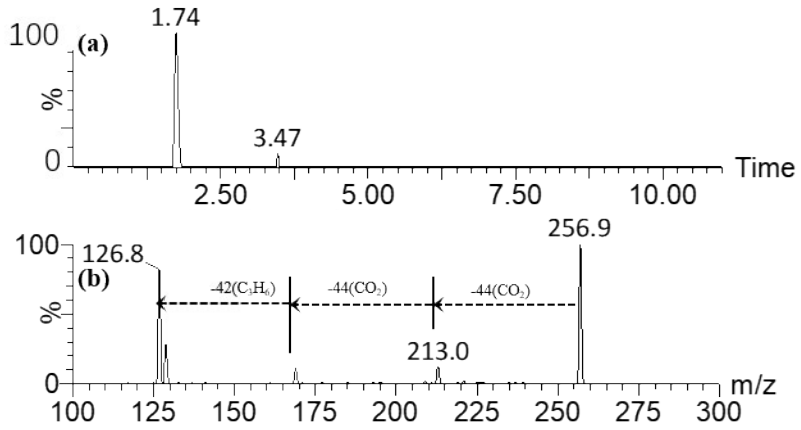

Fig. S3. (a) UPLC/ESI-tqMS MRM (257→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 257 of chlorinated secondary wastewater effluent sample A_1 at RT 1.74 min.

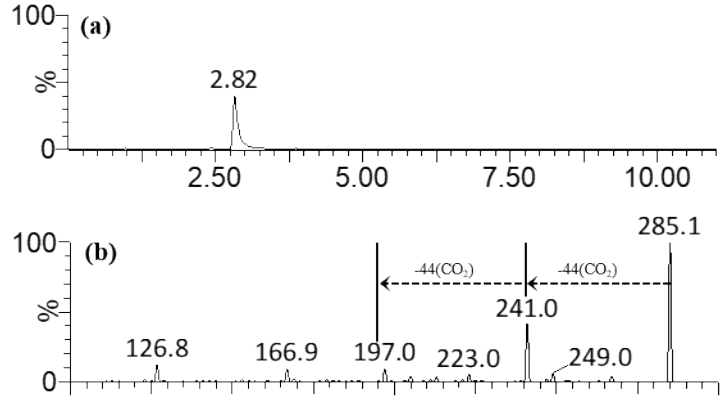

Fig. S4. (a) UPLC/ESI-tqMS MRM (285→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 285 of chlorinated secondary wastewater effluent sample A_1 at RT 2.82 min.

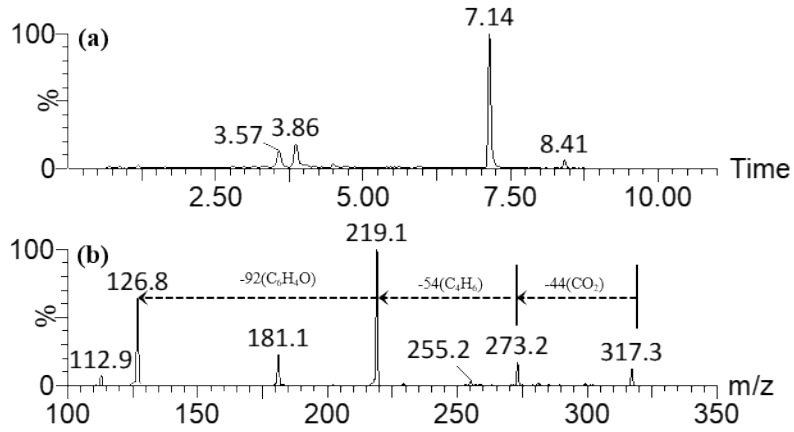

Fig. S5. (a) UPLC/ESI-tqMS MRM (317→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 317 of chlorinated secondary wastewater effluent sample A_1 at RT 7.14 min.

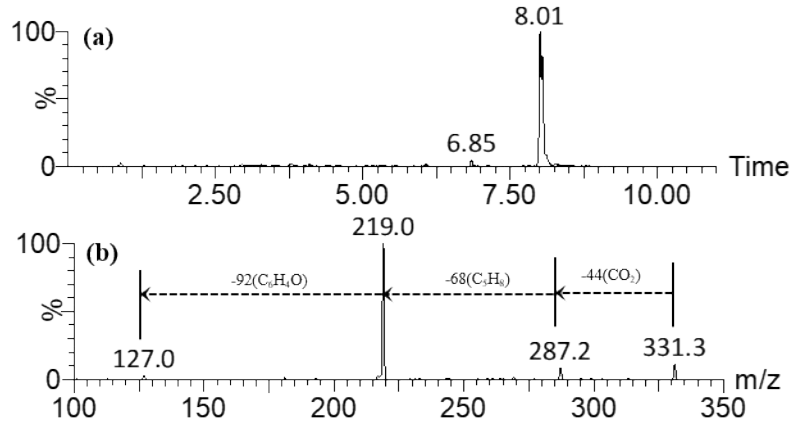

Fig. S6. (a) UPLC/ESI-tqMS MRM (331→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 331 of chlorinated secondary wastewater effluent sample A_1 at RT 8.01min.

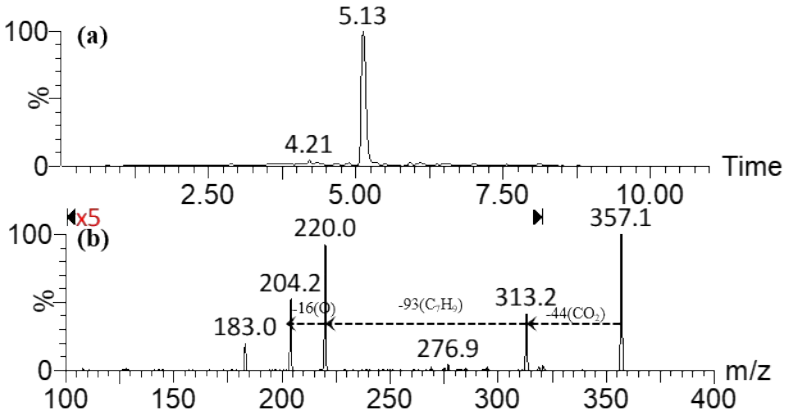

Fig. S7. (a) UPLC/ESI-tqMS MRM (357→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 357 of chlorinated secondary wastewater effluent sample A_1 at RT 5.13 min.

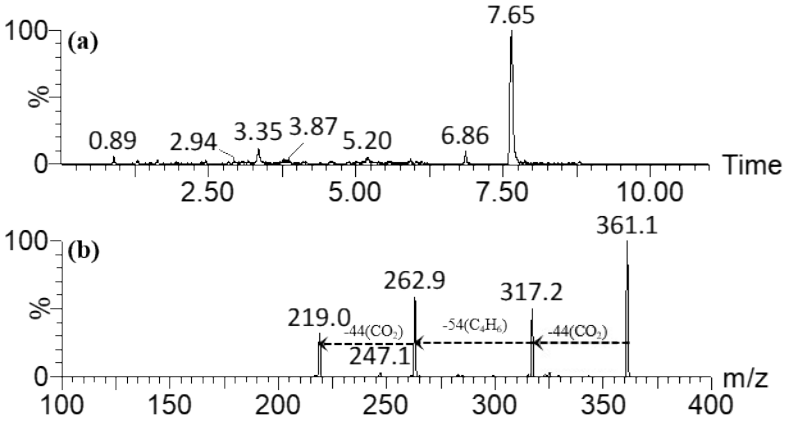

Fig. S8. (a) UPLC/ESI-tqMS MRM (361→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 361 of chlorinated secondary wastewater effluent sample A_1 at RT 7.65 min.

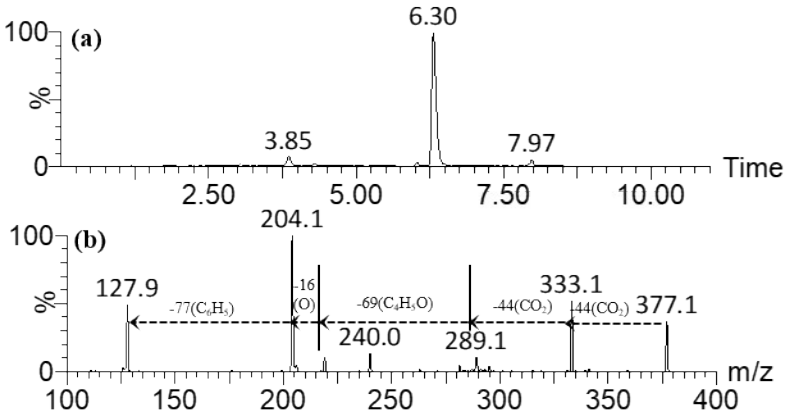

Fig. S9. (a) UPLC/ESI-tqMS MRM (377→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 377 of chlorinated secondary wastewater effluent sample A_1 at RT 6.30 min.

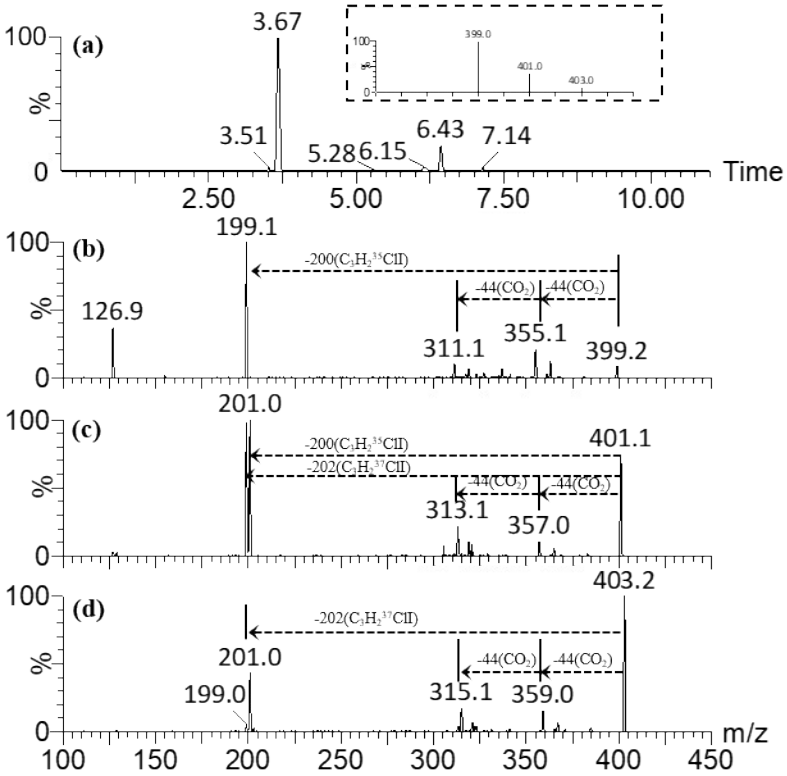

Fig. S10. (a) UPLC/ESI-tqMS MRM (399→126.9, 401→126.9, 403→126.9) chromatogram of chlorinated secondary wastewater effluent sample A_1; (b–d) UPLC/ESI-tqMS product ion scan spectra of *m/z* 399/401/403 of chlorinated secondary wastewater effluent sample A_1 at RT 3.67 min.

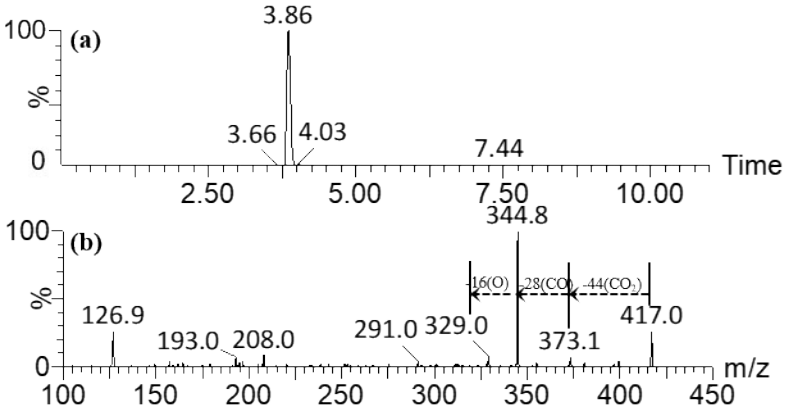

Fig. S11. (a) UPLC/ESI-tqMS MRM (417→126.9) chromatograms of chlorinated secondary wastewater effluent sample A_2; (b) UPLC/ESI-tqMS product ion scan spectrum of *m/z* 417 of chlorinated secondary wastewater effluent sample A_2 at RT 3.86 min.

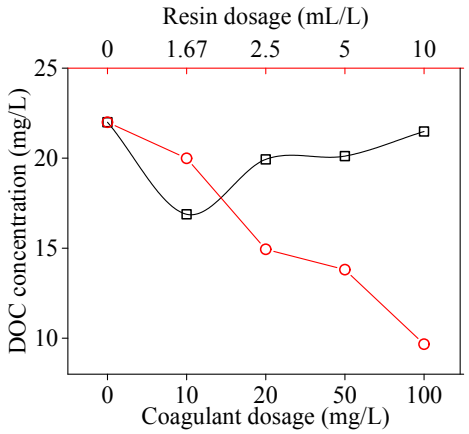

Fig. S12. DOC concentration in secondary wastewater effluent sample A_1 with different dosages of coagulant and resin.

Table S1
Characteristics of the secondary wastewater effluent samples A_1 and A_2

sample	pH	DOC as C (mg/L)	ammonia as N (mg/L)	I^- (μg/L)	UV_{254} (1/cm)
A_1	7.69	22.87	0.42	7.1	0.27
A_2	7.75	21.58	0.38	7.8	0.16