# Effect of peroxymonosulfate pre-oxidation followed by Fe-based coagulation on the mitigation of organic matter and the formation of disinfection byproducts

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**Text S1.** The assessment methods of potential health risk

To ensure the safety of drinking water, evaluating the potential health risks associated with the investigated DBPs under various scenarios is significant. Thus, cytotoxicity index (CTI) and genotoxicity index (GTI) were used to assess potential health risk of determined DBPs, which have been previously used to investigate the disinfection by-product toxicity [1, 2]. The CTI was calculated by dividing the concentration of each DBPs by the $LC_{50}$ (the dose of reducing 50% viability of the cells, Table S1, Eq 1) [3]. The GTI was calculated by dividing the concentration of each DBPs by the genotoxicity potency (the dose of inducing a Tail DNA value, Table S1, Eq 2) [3, 4]. $C_x$ represented each DBP. $LC_{50x}$ and genotoxicity $potency_x$ were the $LC_{50}$ and genotoxicity potency of each DBP, respectively.

$$CTI = \sum \frac{C_x}{LC_{50x}} \quad (1)$$

$$GTI = \sum \frac{C_x}{\text{genotoxiciy potency}_x} \quad (2)$$

**Table S1.** Water quality characteristics of water samples included in this study

| Water sample | DOC (mg/L) | DON (mg/L) | $NH_4^+$–N (mg/L) | $NO_2^-$–N (mg/L) | $NO_3^-$–N (mg/L) | SUVA (L/mg·m) | $Cl^-$ (μM) |
|---|---|---|---|---|---|---|---|
| Natural water | 2.5 | 4.1 | 0.51 | 0.004 | 1.4 | 0.96 | 104.5 |
| Tyr solution | 5.4 | 0.7 | 0 | 0 | 0 | 2.6 | 200.0 |
| HA solution | 5.0 | 0.5 | 0.1 | 0.003 | 0.7 | 3.3 | 200.0 |

**Table S2.** Parameters of GC/ECD to measure DBPs.

| GC/ECD: | Agilent 7890A |
|---|---|
| Columns: | HP-5, 30 m × 0.32 mm ID, 0.25-μm film thickness |
| Carrier gas: | Nitrogen, constant flow at 2 mL per minute |
| Injection volume: | 1 μL |
| Vaporizing chamber temperature: | 200 °C |
| GC column | Initial temperature of 34 °C for 6 min, then an increase of 7 °C per min to 70 °C, which was held for 0 min, and finally an increase of 50 °C per min to 200 °C, which was held for 2 min |
| Detector temperature: | 300 °C |

**Table S3.** Minimum quantitation limits of DBPs by GC/ECD

| DBPs | TCM | TCAL | DCAN | TCAN | DCAM | TCAM |
|---|---|---|---|---|---|---|
| LOD (μg/L) | 0.03 | 0.01 | 0.01 | 0.01 | 0.45 | 0.05 |

**Table S4.** The residual PMS in natural water, HA solution and Tyr solution after 30 min pre-oxidation

| Water sample | Natural water | HA solution | Tyr solution |
|---|---|---|---|
| Active oxygen (mg/L) | 2.74 | 2.8 | 2.78 |

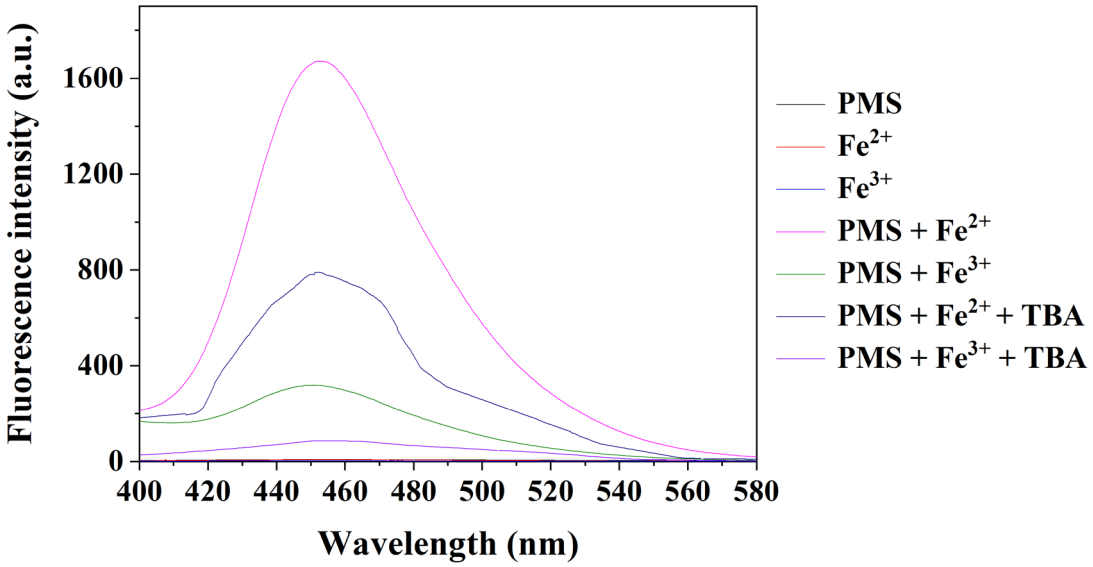


**Fig. S1.** Fluorescence intensities of coumarin reacting with different solutions. Conditions: [coumarin] = 1 mM, [PMS] = 200.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 200.0 μM, [TBA (HO• scavenger)] = 10.0 mM, reaction time = 30 s.

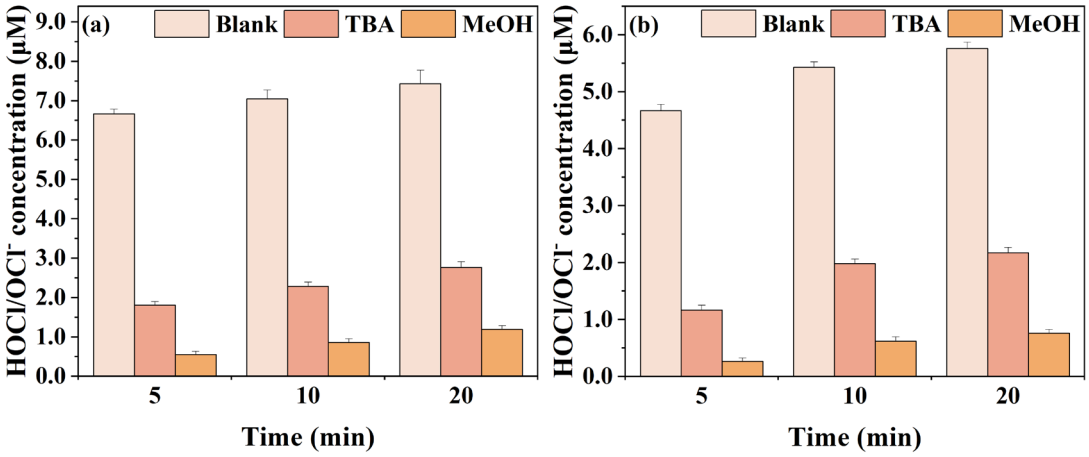


**Fig. S2.** The HOCl/OCl$^-$ formation in ultrapure water during the PPFeC process (a: $Fe^{2+}$, b: $Fe^{3+}$). Condition: [PMS] = 200.0 μM, [$Cl^-$] = 200.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 200.0 μM, [MeOH (both HO• and $SO_4^{\bullet-}$ scavenger)] = 10.0 mM, [TBA (HO• scavenger)] = 10.0 mM, pre-oxidation time = 0, sedimentation time = 5, 10 and 20 min.

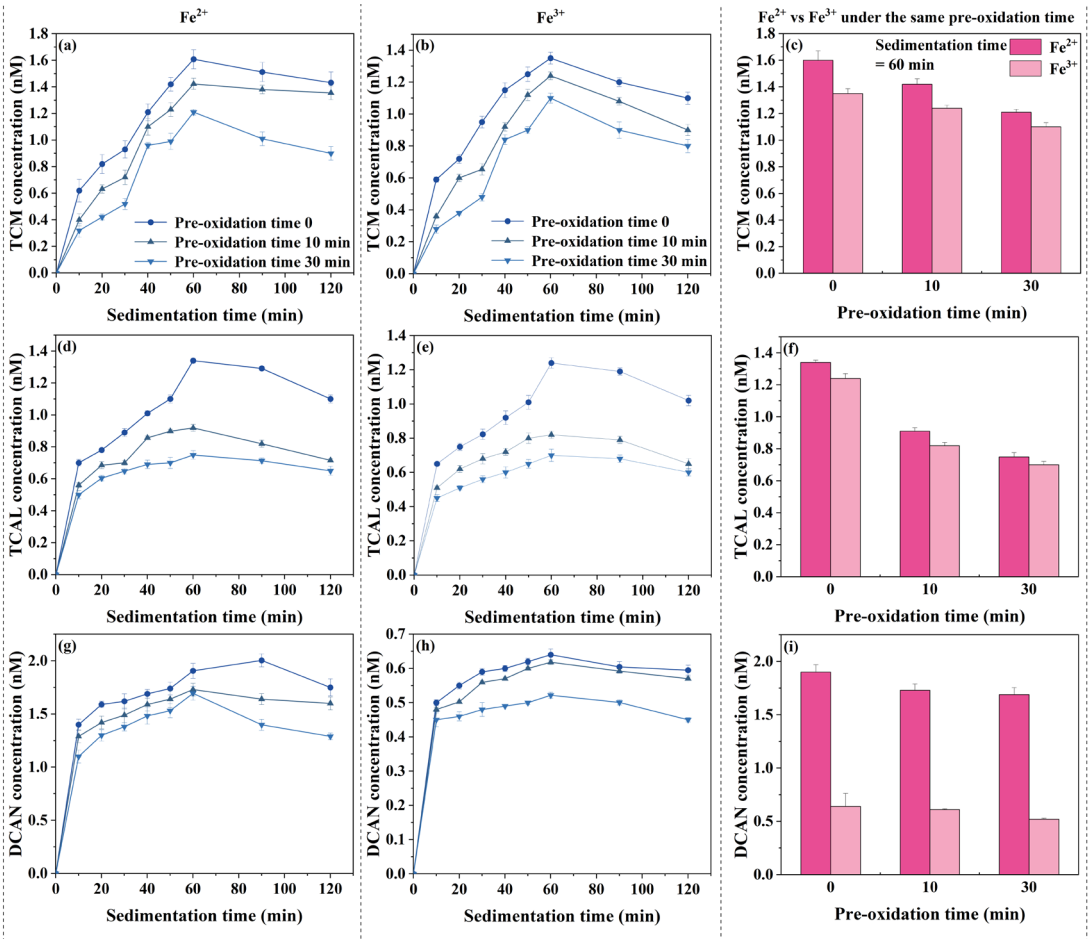


**Fig. S3.** Effects of pre-oxidation time and sedimentation time on the formation of TCM (a and b), TCAL (d and e) and DCAN (g and h) during the PPFeC process. Condition: DOC (HA solution) = 2.5 mg/L, [PMS] = 200.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 200.0 μM, pre-oxidation time = 0, 10 and 30 min, sedimentation time = 10, 20, 30, 40, 50, 60, 90 and 120 min. Fig. c, Fig. f and Fig. i compare the TCM, TCAL and DCAN concentrations, respectively, between $Fe^{2+}$ and $Fe^{3+}$ under the same pre-oxidation time (sedimentation time = 60 min).

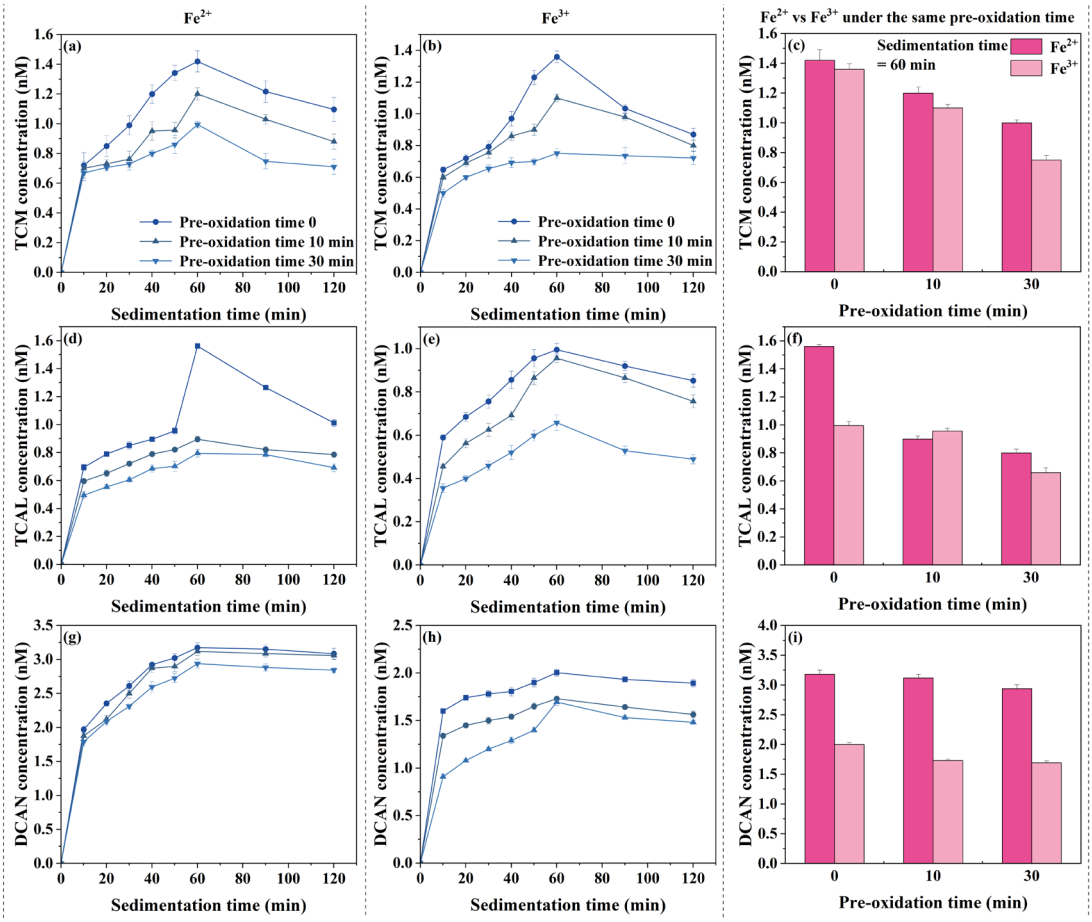


**Fig. S4.** Effects of pre-oxidation time and sedimentation time on the formation of TCM (a and b), TCAL (d and e) and DCAN (g and h) during the PPFeC process. Condition: DOC (Tyr solution) = 5.4 mg/L, [PMS] = 200.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 200.0 μM, pre-oxidation time = 0, 10 and 30 min, sedimentation time = 10, 20, 30, 40, 50, 60, 90 and 120 min. Fig. c, Fig. f and Fig. i compare the TCM, TCAL and DCAN concentrations, respectively, between $Fe^{2+}$ and $Fe^{3+}$ under the same pre-oxidation time (sedimentation time = 60 min).

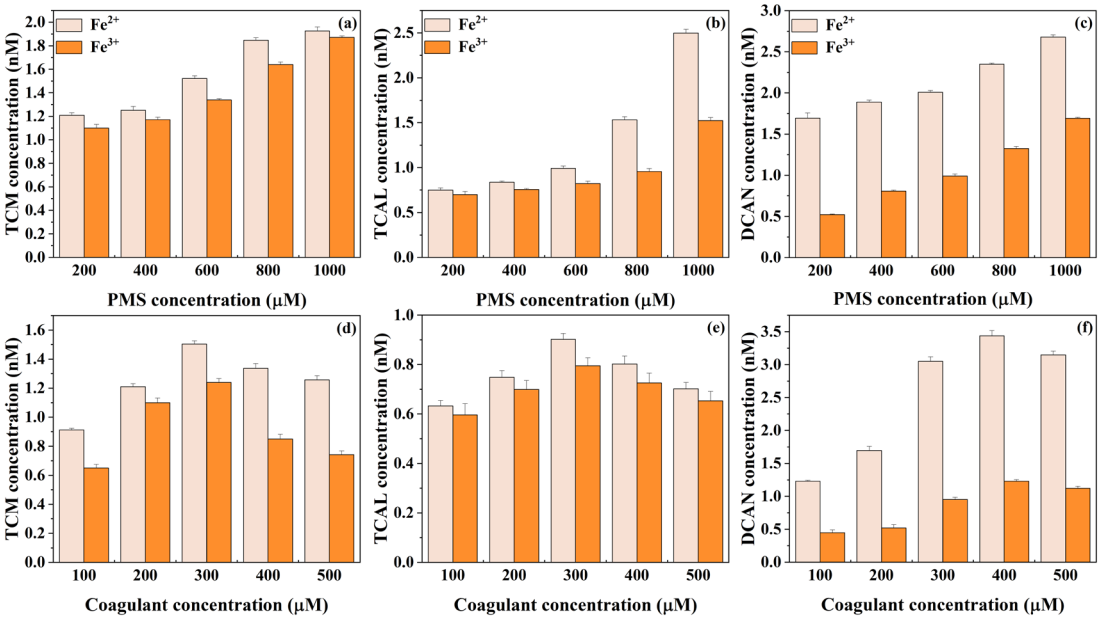


**Fig. S5.** Effects of PMS concentration (a, b and c) and coagulant concentration (d, e and f) on the formation of TCM (a and d), TCAL (b and e) and DCAN (c and f) during the PPFeC process. Condition: DOC (HA solution) = 5.0 mg/L, [PMS] = 200.0, 400.0, 600.0, 800.0 and 1000.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 100.0, 200.0, 300.0, 400.0 and 500.0 μM, pre-oxidation time = 30 min, sedimentation time = 60 min.

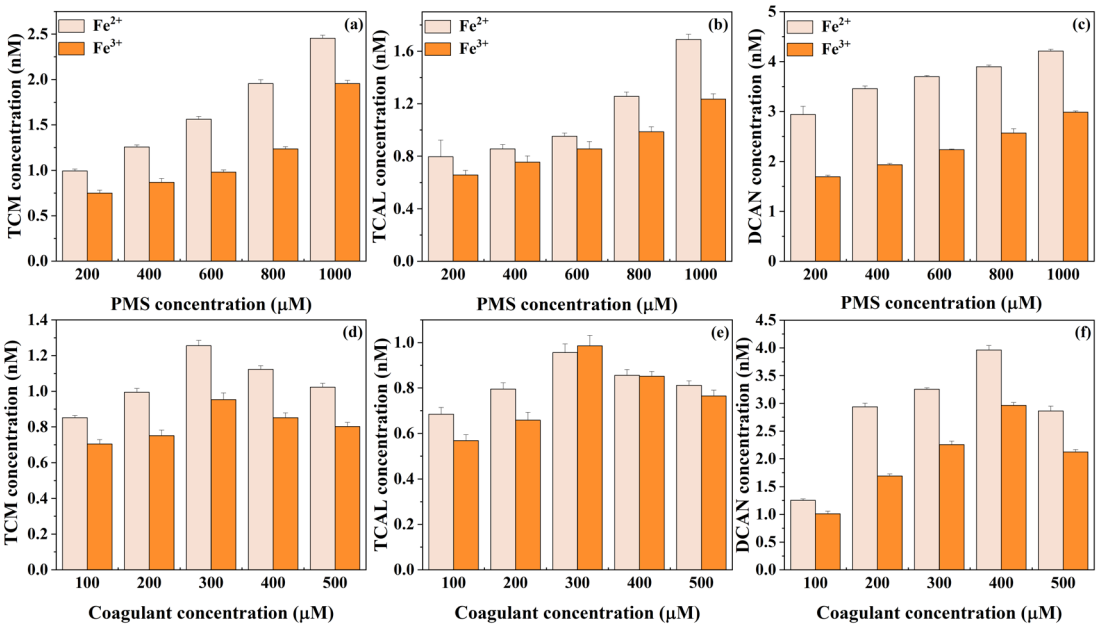


**Fig. S6.** Effects of PMS concentration (a, b and c) and coagulant concentration (d, e and f) on the formation of TCM (a and d), TCAL (b and e) and DCAN (c and f) during the PPFeC process. Condition: DOC (Tyr solution) = 5.4 mg/L, [PMS] = 200.0, 400.0, 600.0, 800.0 and 1000.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 100.0, 200.0, 300.0, 400.0 and 500.0 μM, pre-oxidation time = 30 min, sedimentation time = 60 min.

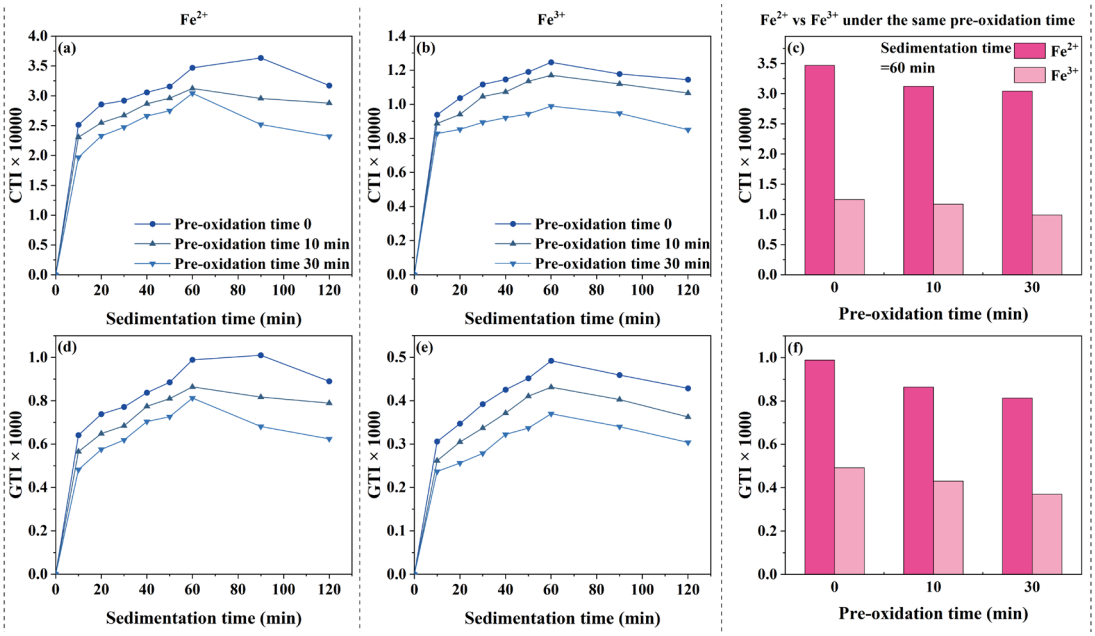


**Fig. S7.** Effects of pre-oxidation time and sedimentation time on the CTI (a and b) and GTI (d and e) during the PPFeC process. Condition: DOC (HA solution) = 5.0 mg/L, [PMS] = 200.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 200.0 μM, pre-oxidation time = 0, 10 and 30 min, sedimentation time = 10, 20, 30, 40, 50, 60, 90 and 120 min. Fig. c and Fig. f compare the CTI and GTI, respectively between $Fe^{2+}$ and $Fe^{3+}$ under the same pre-oxidation time (sedimentation time = 60 min).

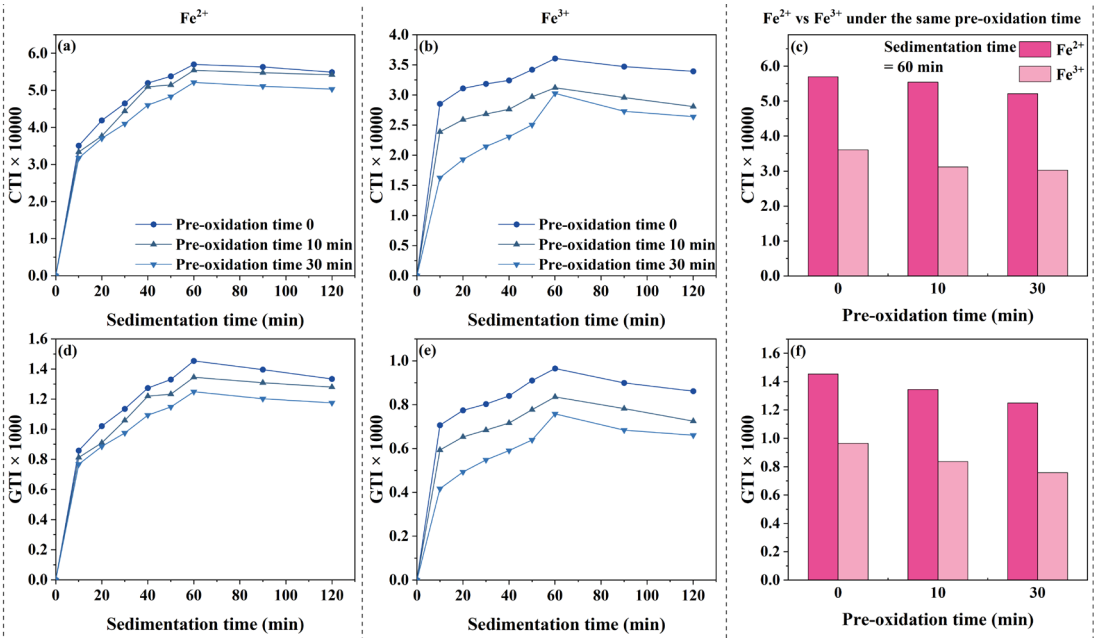


**Fig. S8.** Effects of pre-oxidation time and sedimentation time on the CTI (a and b) and GTI (d and e) during the PPFeC process. Condition: DOC (Tyr solution) = 5.4 mg/L, [PMS] = 200.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 200.0 μM, pre-oxidation time = 0, 10 and 30 min, sedimentation time = 10, 20, 30, 40, 50, 60, 90 and 120 min. Fig. c and Fig. f compare the CTI and GTI, respectively between $FeSO_4$ and $Fe_2(SO_4)_3$ under the same pre-oxidation time (sedimentation time = 60 min).

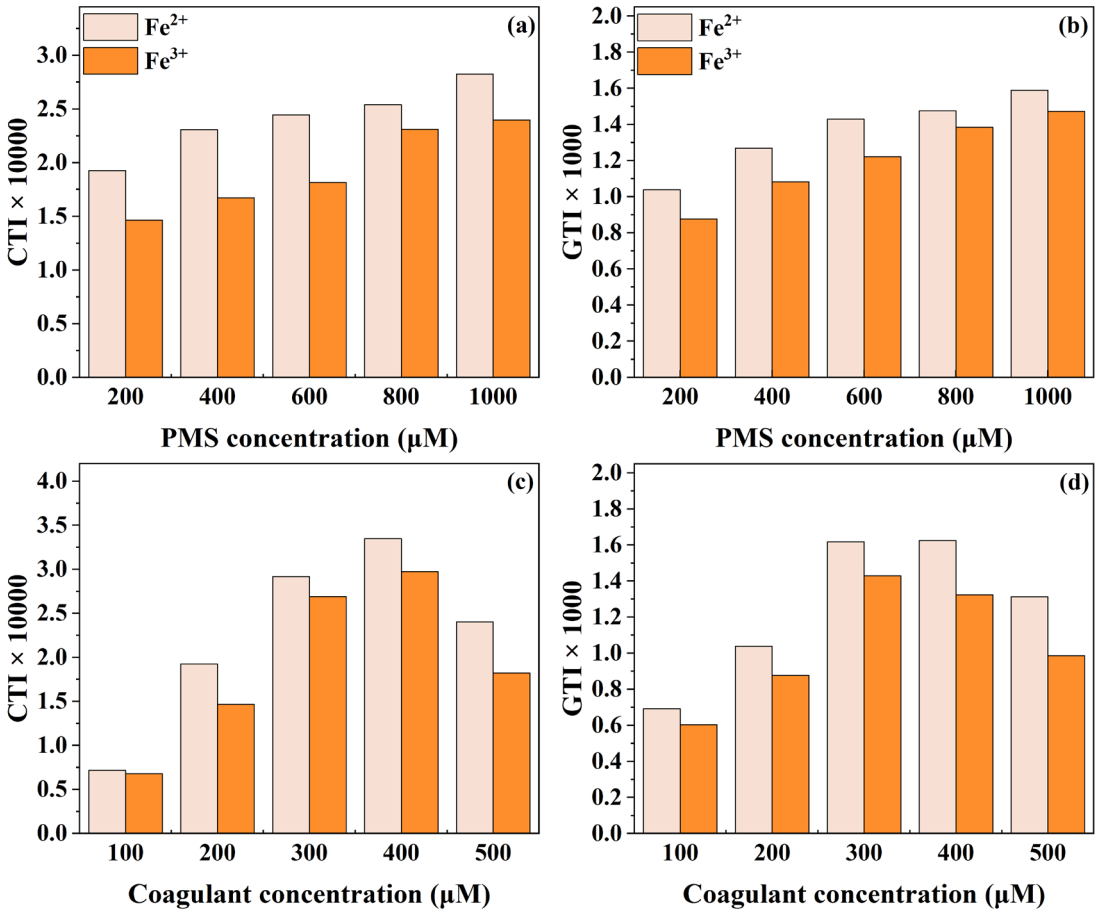


**Fig. S9.** Effects of PMS concentration and coagulant concentration on the CTI (a and c) and GTI (b and d) during the PPFeC process. Condition: DOC (natural water) = 2.5 mg/L, [PMS] = 200.0, 400.0, 600.0, 800.0 and 1000.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 100.0, 200.0, 300.0, 400.0 and 500.0 μM, pre-oxidation time = 30 min, sedimentation time = 60 min.

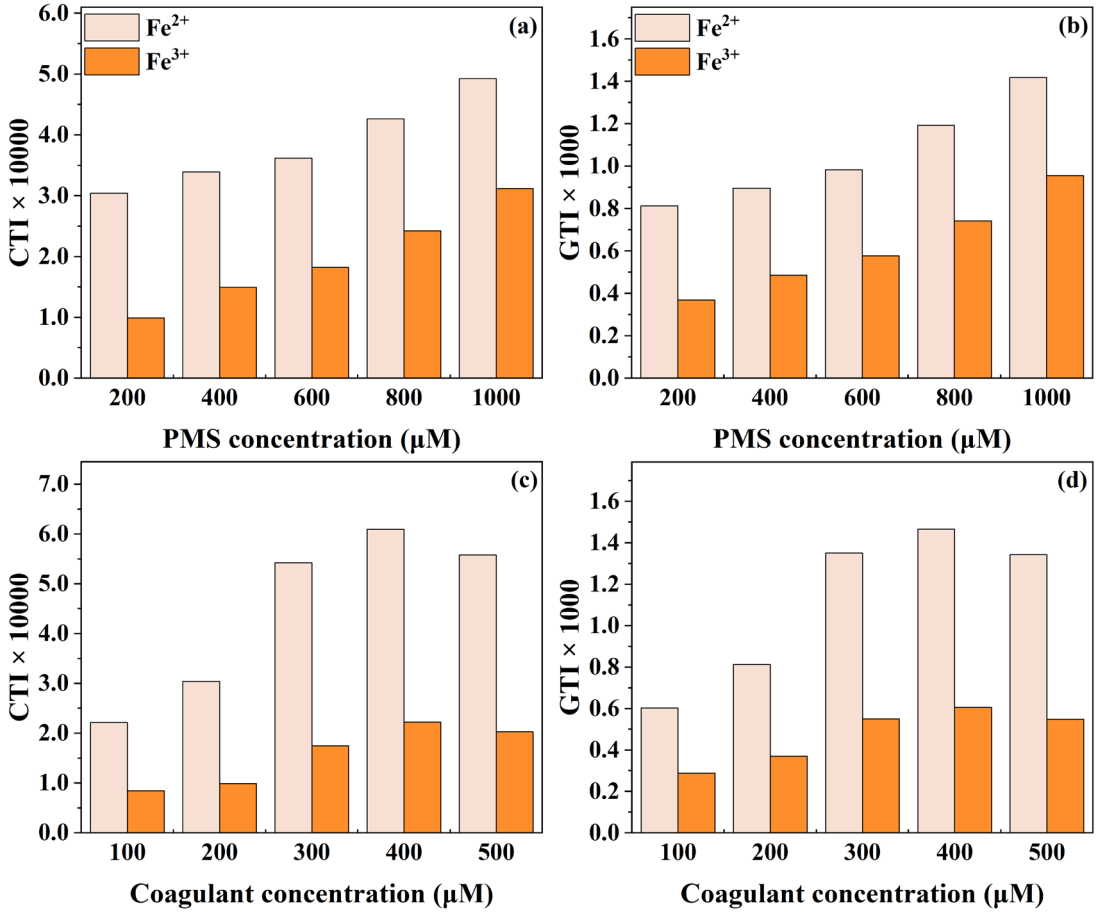


**Fig. S10.** Effects of PMS concentration and coagulant concentration on the CTI (a and c) and GTI (b and d) during the PPFeC process. Condition: DOC (HA solution) = 5.0 mg/L, [PMS] = 200.0, 400.0, 600.0, 800.0 and 1000.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 100.0, 200.0, 300.0, 400.0 and 500.0 μM, pre-oxidation time = 30 min, sedimentation time = 60 min.

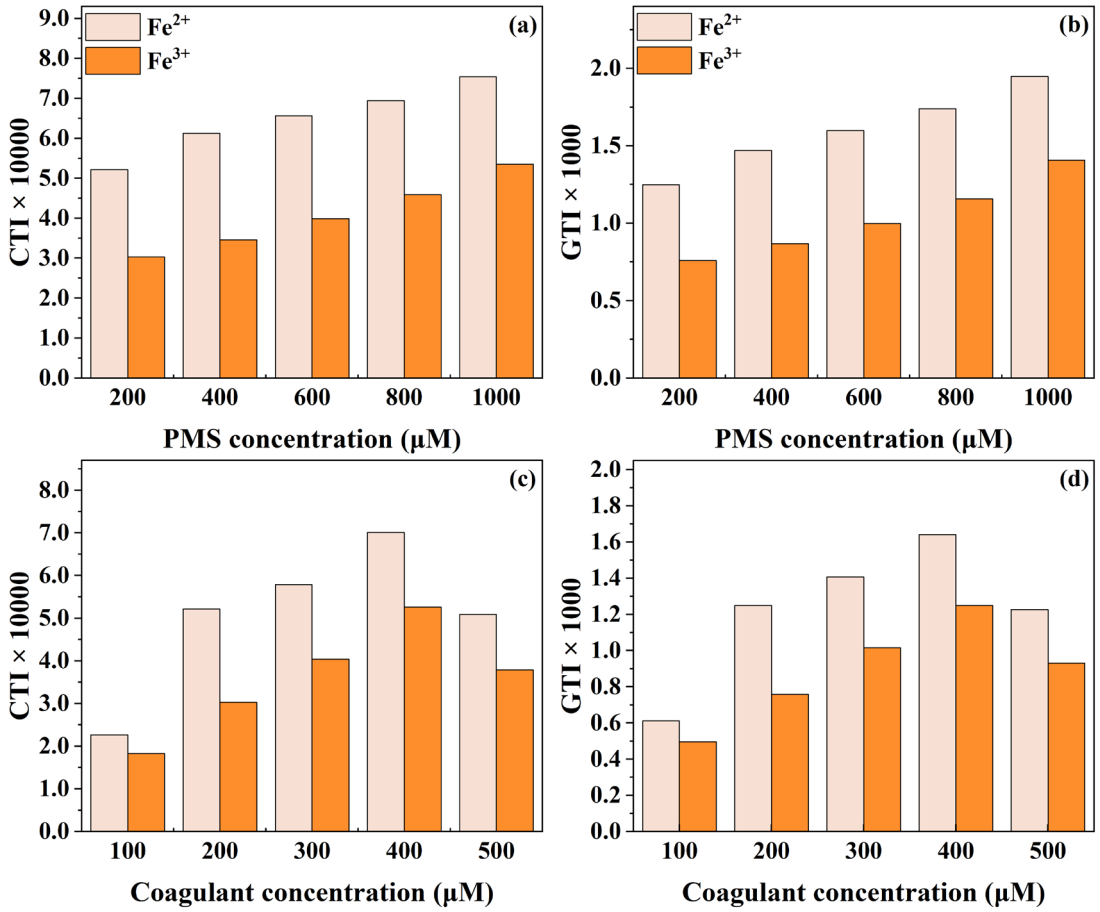


**Fig. S11.** Effects of PMS concentration and coagulant concentration on the CTI (a and c) and GTI (b and d) during the PPFeC process. Condition: DOC (Tyr solution) = 5.4 mg/L, [PMS] = 200.0, 400.0, 600.0, 800.0 and 1000.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 100.0, 200.0, 300.0, 400.0 and 500.0 μM, pre-oxidation time = 30 min, sedimentation time = 60 min.

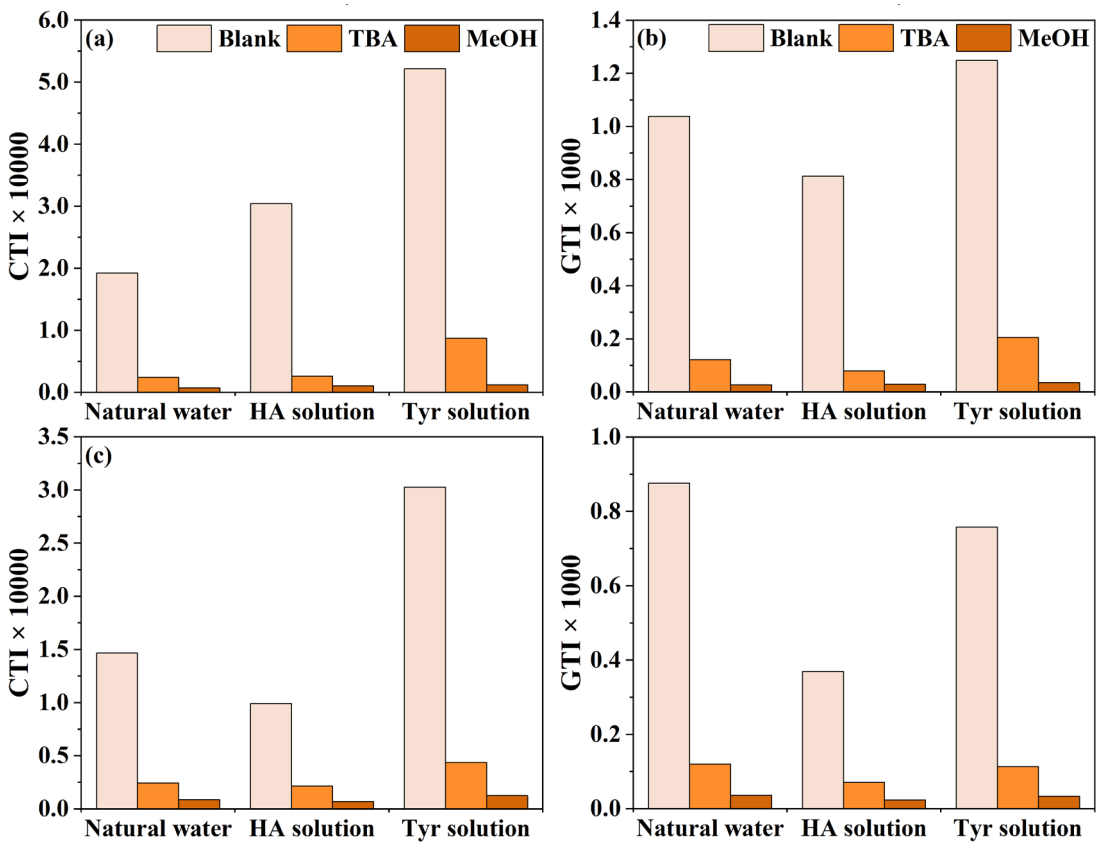


**Fig. S12.** The roles of PMS, $SO_4^{\bullet-}$ and HO• on the CTI (a, and c) and GTI (b, and d) during the PPFeC process (a and b: $Fe^{2+}$, c and d: $Fe^{3+}$). Condition: DOC (natural water) = 2.5 mg/L, DOC (HA solution) = 5.0 mg/L, DOC (Tyr solution) = 5.4 mg/L, [PMS] = 200.0 μM, [coagulant ($Fe^{2+}$ and $Fe^{3+}$)] = 200.0 μM, [MeOH (both $SO_4^{\bullet-}$ and HO• scavenger)] = 10.0 mM, [TBA (HO• scavenger)] = 10.0 mM, pre-oxidation time = 30 min, sedimentation time = 60 min.

## Reference

[1]Y. Yu, M.M Hossain, R. Sikder, Z. Qi, L. Huo, R. Chen, W. Dou, B. Shi, T. Ye, Exploring the potential of machine learning to understand the occurrence and health risks of haloacetic acids in a drinking water distribution system, Sci. Total Environ., 951 (2024) 175573. https://doi.org/10.1016/j.scitotenv.2024.175573.

[2]T. Li, C. Shang, Y. Xiang, R. Yin, Y. Pan, M. Fan, X. Yang, $ClO_2$ pre-oxidation changes dissolved organic matter at the molecular level and reduces chloro-organic byproducts and toxicity of water treated by the UV/chlorine process, Water Res., 216 (2022) 118341. https://doi.org/10.1016/j.watres.2022.118341.