Supporting Information for:

Improving understanding of operational conditions for oxidant application during NOM and manganese treatment.

Chu X.,[1], Agostino A.,[1] Rao N.R.H., [1] Moradi S.,[1,a] Bustamante H.,[2] Power K.,[2] Henderson R.K.,[1] Leslie G.L[1]

[1] *School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia*

[2] *Sydney Water, 1 Smith Street, Parramatta NSW 2125, Australia*

[a] *Artificial Intelligence Centre of Excellence (AI CoE), NCS Group, Sydney, NSW, 2113, Australia*

* Corresponding author – g.leslie@unsw.edu.au

1. Materials and methods

1.1 Nepean Water Filtration Plant (WFP) process flow diagram

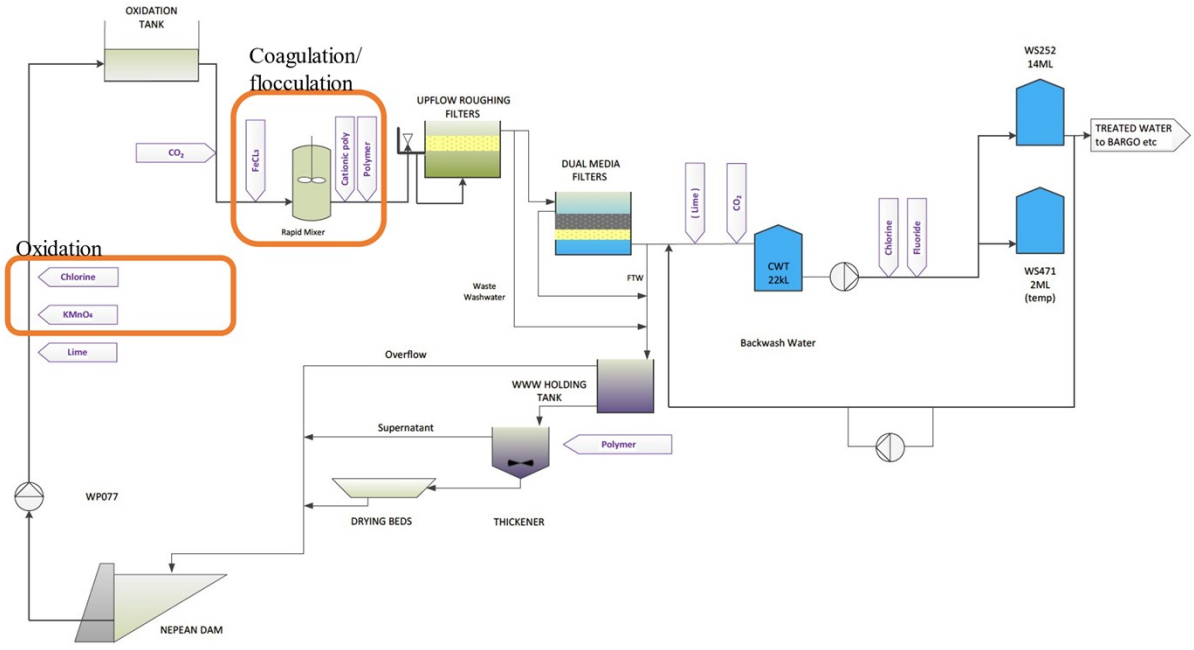

Fig. S1. Nepean WTP process flow diagram with oxidation and coagulation/flocculation processes circled.

1.2 Historical data of Nepean WTP

Historical data of manganese concentration in the raw and finished water; and the $KMnO_4$ doses in the treatment plant was plotted in **Fig. S2**. (Data from Sydney Water Corporation.)

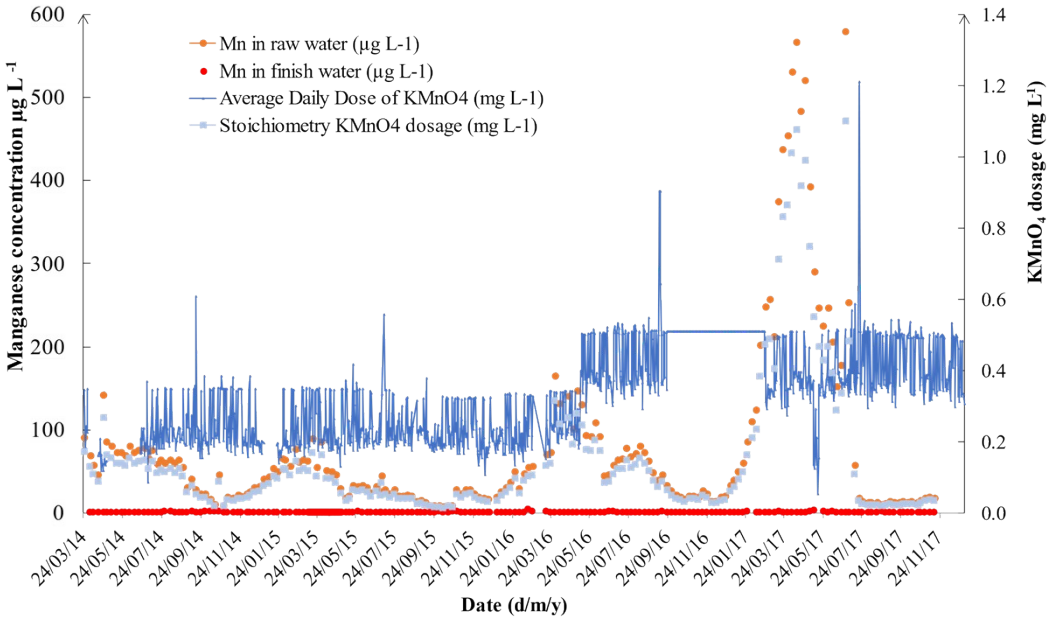

Fig. S2. Historical data for the manganese concentrations in the raw and finished water; the potassium permanganate dose in the WFP and the calculated stoichiometric $KMnO_4$ dosages relative to raw manganese concentration.

From March 2014 to December 2017, the manganese concentration fluctuated at a level below 100 µg L^{-1} with peaks every March to May. In April 2017, the manganese concentration in raw water peaked at around 500 µg L^{-1}, followed by a dramatic drop back to a normal value below 100 µg L^{-1}. However, despite the fluctuation of the manganese level in the feed water, the dose of $KMnO_4$ used in the treatment process remained stable, with only one increase from approximately 0.3 to 0.5 mg L^{-1} and for most of the time the dose was higher than what was stoichiometrically required to remove manganese (**Fig. S2**). Nevertheless, the manganese concentrations in the finished water were always maintained at desirable values below 30 µg L^{-1} (guideline= 0.05 mg L^{-1} (1–3) even with the most extreme scenario in April 2017. This indicated the $KMnO_4$ treatment had successfully reacted with and removed almost all the manganese in water despite the doses being overdose or underdose. From the perspective of DWTP, lower manganese concentrations mean less taste and odour problems or less potential damage on the pipelines.

1.3 Liquid chromatography-organic carbon detection

Within the LC-OCD system, a weak cation exchange size-exclusion column on basis of polymethacrylate was coupled (250 mm x 20 mm, Toyopearl TSK HW 50S, Tosoh Bioscience, Japan). The mobile phase of phosphate buffer solution (2.5 g L^{-1} KH_2PO_4 and 1.5 g L^{-1} $Na_2HPO_4 \cdot 2H_2O$) of pH 6.85 operates at flow rate of 1.1 mL min^{-1}. Injection volume was set at 1 mL. Potassium hydrogen phthalate and potassium nitrate were used for OCD and OND detector calibration, respectively. Humic substance molecular weights were calibrated using Suwannee River standard II humc (HA) and fulvic acids (FA) from International Humic Substances Society (IHSS). The average molecular weights for IHSS-FA and IHSS-HA molecular weights were determined to be 711 and 1066 Da, respectively. Result integration was processed on the ChromCalc software (DOC-Labor, Germany). LC-OCD fractionates NOM to biopolymers, humic substances, building blocks, low molecular weight neutrals (LMWN) and low molecular weight acids (LMWA) accordingly. More detailed analysis had been previously described by Huber et al., (2011) (5).

1.4 Fluorescence EEMs

Five common excitation/emission peaks were defined for marine and terrestrial DOM: humic-like **Peak A** ($\lambda_{ex/em} = 260/380 - 460nm$); humic-like **Peak C** ($\lambda_{ex/em} = 350/420 - 480nm$); marine humic-like **Peak M** ($\lambda_{ex/em} = 312/380 - 420nm$); tyrosine-like, protein-like **Peak B** ($\lambda_{ex/em} = 275/310nm$); tryptophan-like, protein-like **Peak T** ($\lambda_{ex/em} = 275/340nm$).

1.5 Floc strength and breakage model

The floc strength co-efficient log (C) value depends on the floc size measurement so that the results could only be compared within the same experiment setup. The stable floc size exponent γ value could be determined from the slope of the model and it represented the floc breakge pattern with increasing shear forces. Parker et al., (1972) suggested that floc breakage was dominated by floc fragmentation when γ remained 0.5, whilst erosion mechanisms dominated with $\gamma = 1$, and $\gamma = 2$ suggested surface erosion breakage (6).

Table S1. Average velocity gradient (shear rate) (s^{-1}) under different impeller stirring speed. Data under 22 °C was used for this study.

Velocity gradients (s^{-1})		
Speed [RPM]	Temperature (°C)	
	20	22
10	3.5	3.6
20	10.0	10.3

30	18.4	18.8
40	28.3	29.0
50	39.6	40.5
60	52.0	53.5
70	65.5	67.1
80	80.1	82.0
90	95.5	97.9
100	111.9	114.6
110	129.1	132.2
120	147.1	150.7
130	165.8	169.9
140	185.3	189.9
150	205.5	210.6
160	226.4	232.0
170	248.0	254.1
180	270.2	276.3
190	193.0	300.2
200	316.4	324.2

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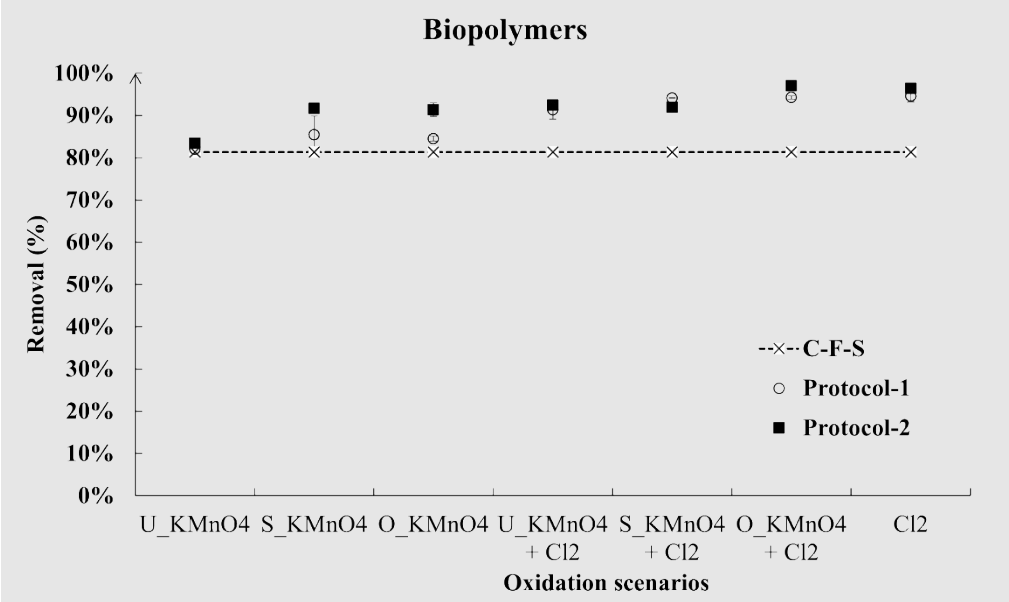
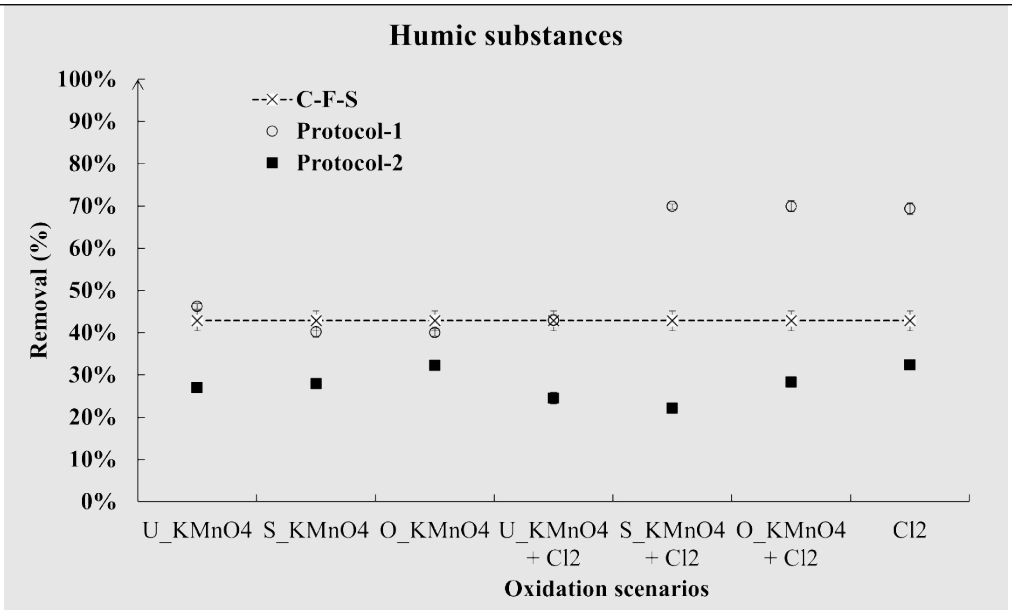
66 2. Results

67 2.1 NOM characterisation using liquid chromatography – organic carbon detection

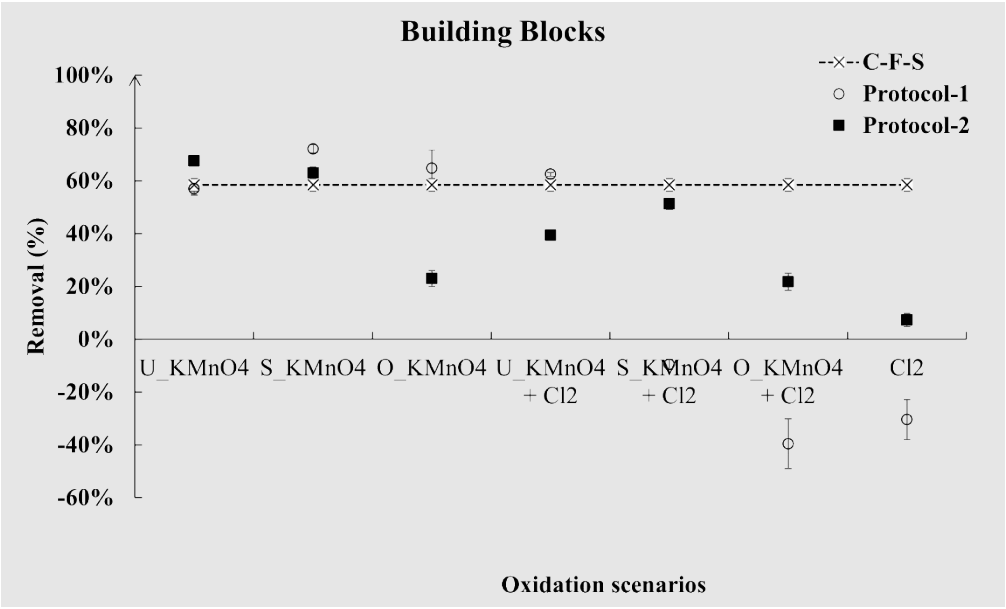
(a)



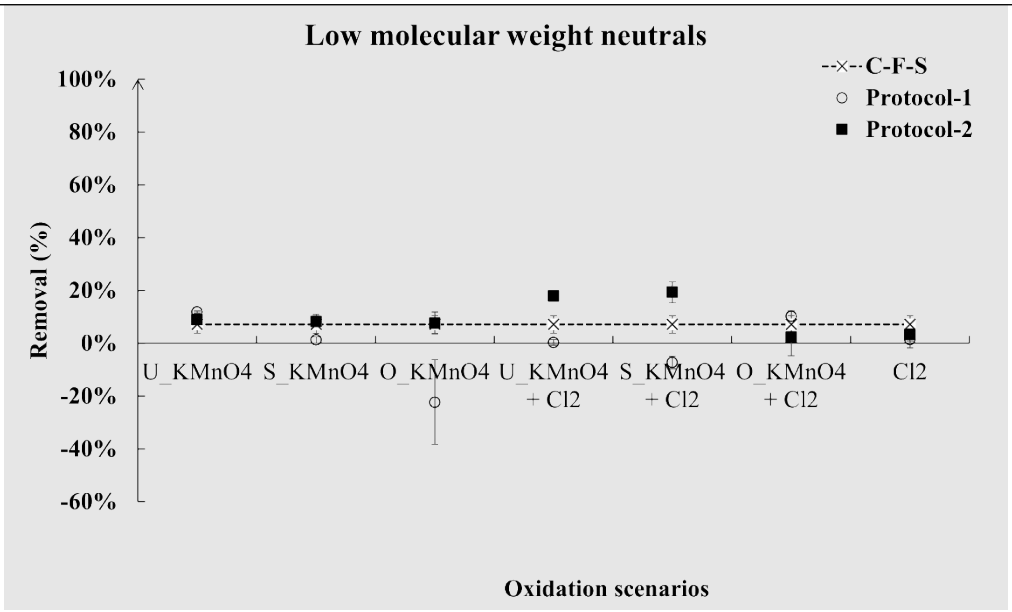
(b)


Humic substances
C-F-S
Protocol-1
Protocol-2
Removal (%)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
U_KMnO4
S_KMnO4
O_KMnO4
U_KMnO4 + Cl2
S_KMnO4 + Cl2
O_KMnO4 + Cl2
Cl2
Oxidation scenarios

(c)


Building Blocks
C-F-S
Protocol-1
Protocol-2
Removal (%)
100%
80%
60%
40%
20%
0%
-20%
-40%
-60%
U_KMnO4
S_KMnO4
O_KMnO4
U_KMnO4 + Cl2
S_KMnO4 + Cl2
O_KMnO4 + Cl2
Cl2
Oxidation scenarios

(d)



(e)

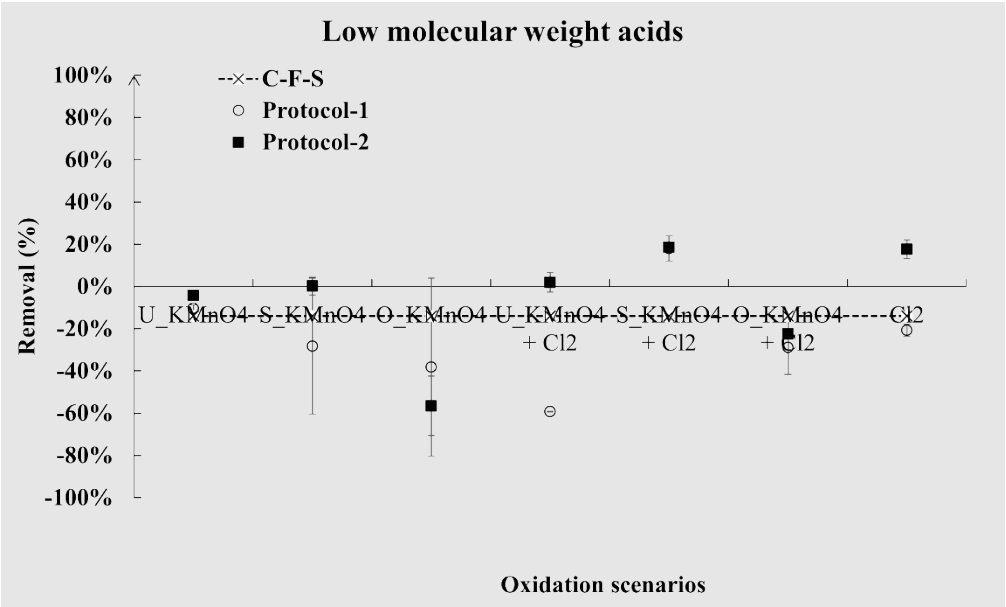


Fig. S3. Fraction concentrations from LC-OCD for coagulation, pre-oxidation enhanced coagulation and post-oxidation after coagulation: (a) Biopolymer; (b) Humic substances; (c) Building blocks, (d) LMWN, (e) LMWA.

2.2 NOM characterisation using fluorescence excitation-emission matrices

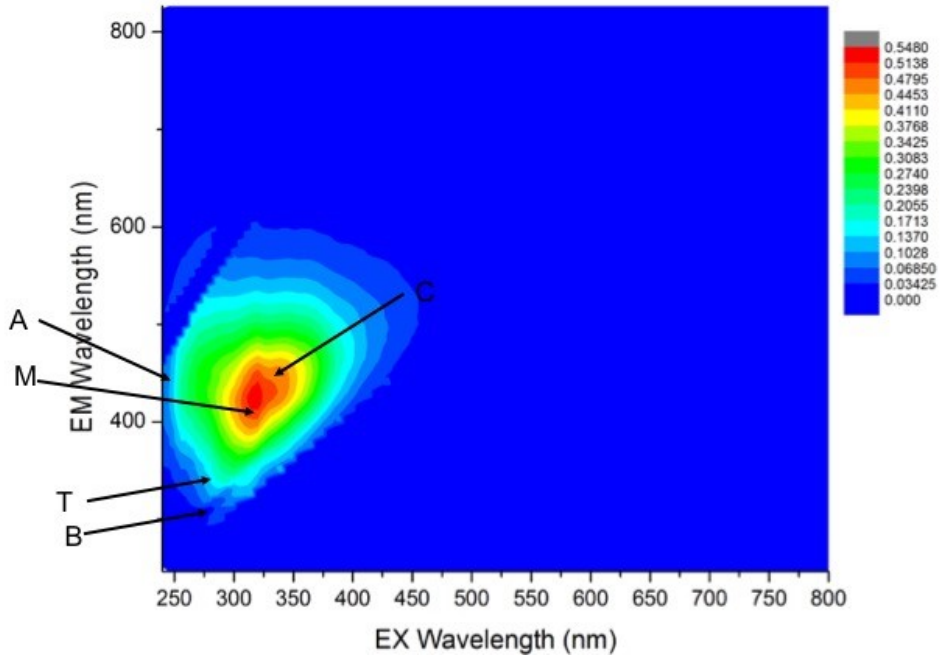


Fig. S4. Fluorescence EEM contour plot for the feed water with fluorescence peak A, B, C, M, T locations.

2.3 Floc breakage model

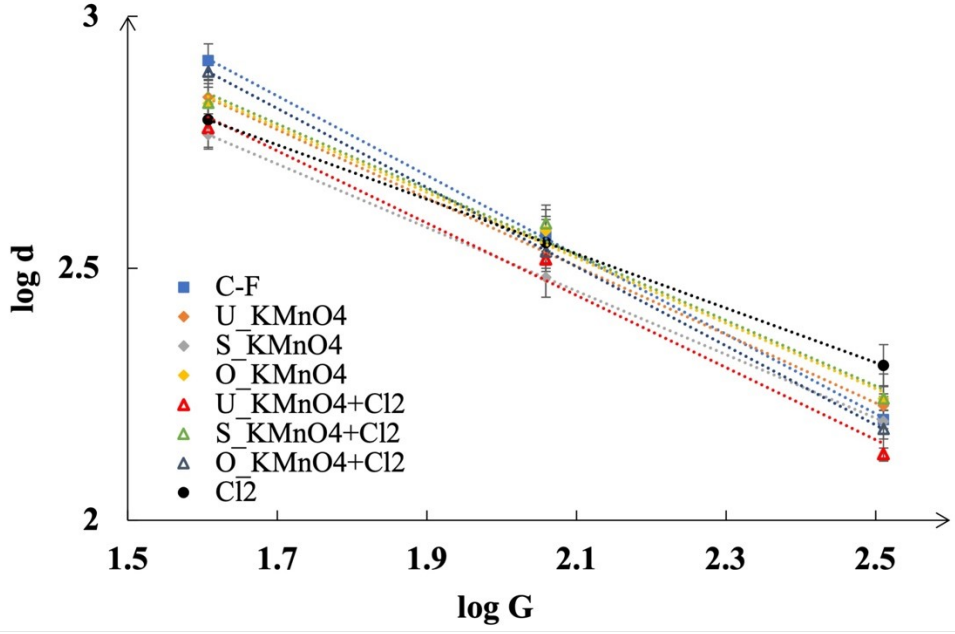


Fig. S5. Linear correlation of log (d) (steady floc size) and log (G) (shear rate) for the flocs generated from the seven oxidation scenarios in Protocol-1, and only C-F in Protocol-2.

From the empirical expression suggested by Parker et al., (1972), the floc strength co-efficient C, and stable floc size exponent γ could be derived from linearization of log (steady floc size) and log (shear rate) (6). The shear rates of jar tester employed in this study were provided by the Platypus Jar Tester manufacturer. From **Fig. S5**, differences in the slopes and intercepts with y-axis were minor, indicating the different pre-oxidation scenarios did not vary floc breakage pattern or floc strength much.

2.4 Iron removal

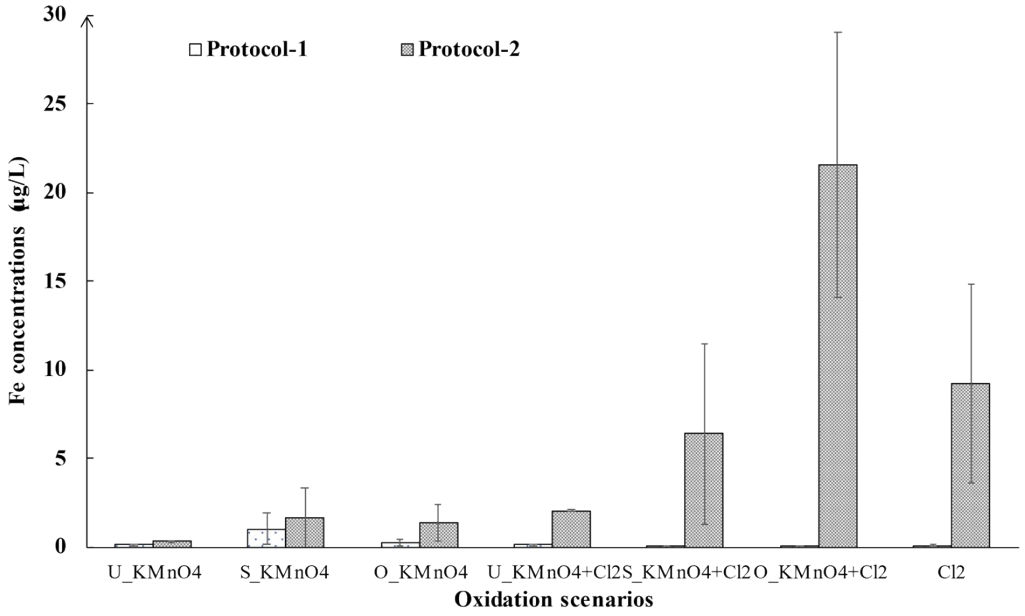


Fig. S6. Residual soluble iron concentration in Protocol-1 and 2. Soluble iron concentration in raw water = 758 ± 23.9 µg L^{-1}. Error reflects the standard deviation in measurements of independent triplicate tests.

3. References

1. EPA US. Drinking Water Health Advisory for Manganese. US Environ Prot Agency Off Water. 2004;1–49.

2. NHMRC (National Health and Medical Research Council). Australian Drinking Water Guidelines 6 2011 [Internet]. National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia,. 2011. 1244 p. Available from: https://www.nhmrc.gov.au/_files_nhmrc/file/publications/nhmrc_adwg_6_february_2016.pdf

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4. Huber SA, Balz A, Abert M, Pronk W. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND). Water Res. 2011;45(2):879–85.

5. Huber SA, Balz A, Abert M, Pronk W. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography–organic carbon detection–organic nitrogen detection (LC-OCD-OND). Water Res. 2011;45(2):879–85.

6. Parker DS, Kaufman WJ, Jenkins D. Floc breakup in turbulent flocculation processes. J Sanit Eng Div. 1972;98(1):79–99.