SUPPORTING INFORMATION

Effect of Cu(II) on Mn(II) Oxidation by Free Chlorine to Form Mn Oxides at Drinking Water Conditions

Guiwei Li,[†,‡,§] Weiyi Pan,[‡] Lili Zhang,[†] Ziqiao Wang,[†] Baoyou Shi[†,§]

and Daniel E. Giammar*[,‡]

[†]Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[‡]Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States

[§]University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding author.

E-mail address: giammar@wustl.edu

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TEM (transmission electron microscopy) sample preparation. Transmission electron microscopy (TEM) was used to visualize particle size. During the oxidation of Mn(II), 10 μL of the MnO_x-containing suspension was placed on a carbon-coated copper grid and then dried at room temperature.

SEM (scanning electron microscope) sample preparation. As the oxidation of Mn(II) could be greatly affected by its initial concentration, a dose of Mn(II) of 100 μg/L was adopted in all the experiments of this study. This is a typical regulatory level of Mn in finished water as well as a typical concentration of Mn found in drinking water distribution systems. As a result, it could be very challenging to collect particles from water samples for the characterization of Mn(II) oxidation products. However, it was found that after Mn(II) oxidation, there were some fine Mn particles deposited on the surface of stir bars used for water mixing. Particles were collected carefully from the stirrer bar for SEM characterization: the stir bar was first immersed in ethyl alcohol and sonicated to disperse Mn oxides; one drop of the MnO_x-containing alcohol was then placed on a silica wafer, and the alcohol evaporated before the sample was taken to the SEM for characterization.

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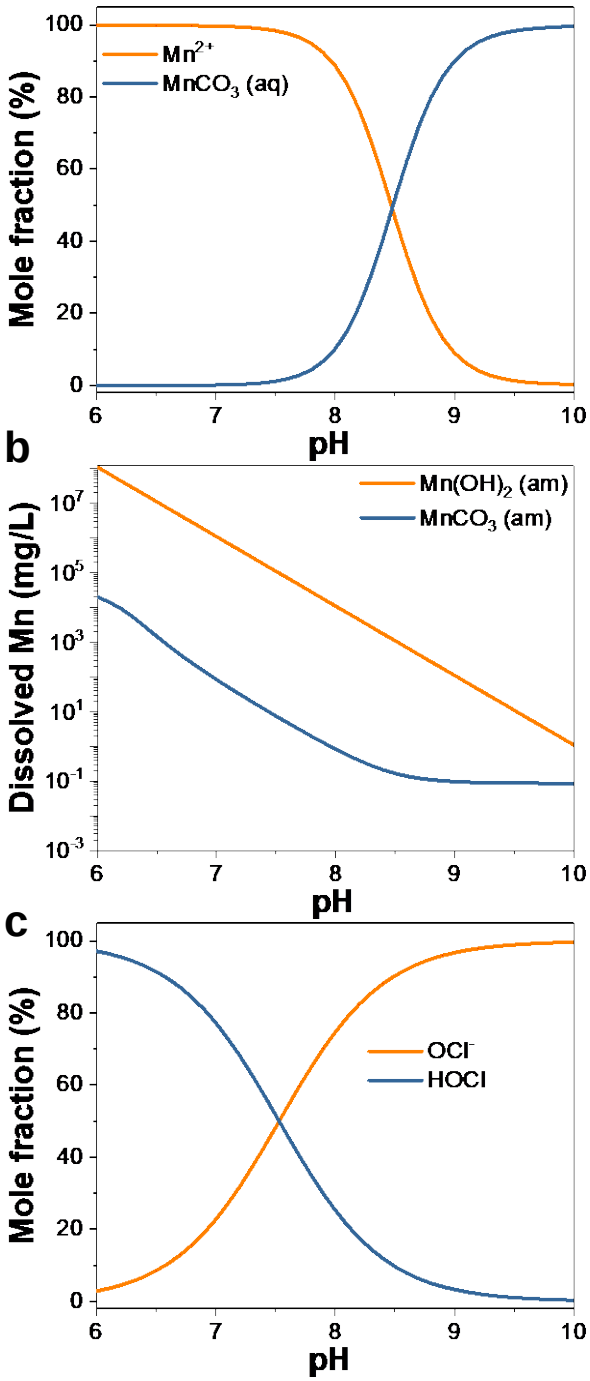

Figure S1. (a) Speciation of dissolved Mn(II) (100 μg/L) in an open system with DIC in equilibrium with atmospheric CO_2 at 25 ℃. (b) Solubility of $MnCO_3$ with DIC in equilibrium with atmospheric CO_2 at 25 ℃, and the solubility of $Mn(OH)_2$ without DIC at 25 ℃. (c) Speciation of free chlorine (HOCl + OCl^-) with different pH. Visual MINTEQ 3.1 was used for the calculation.

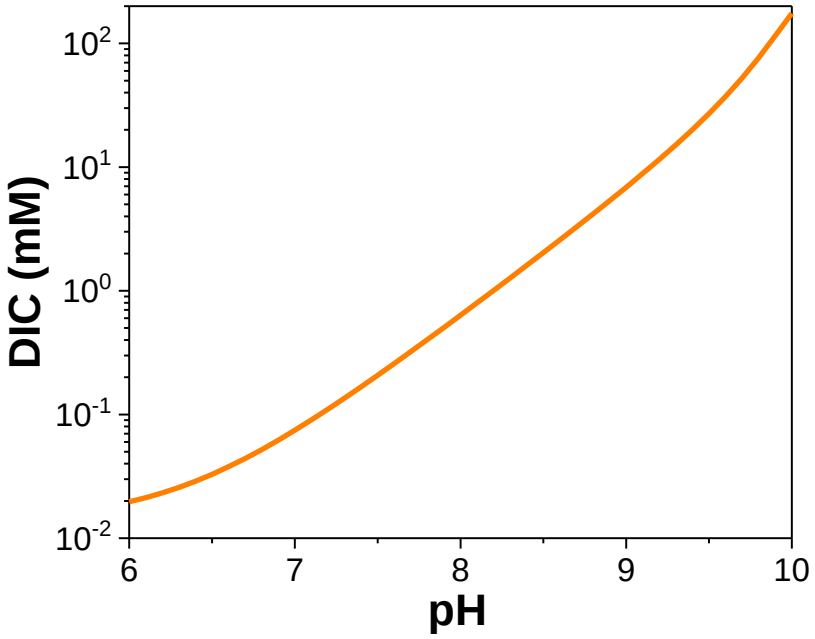

Figure S2. Concentrations of DIC in equilibrium with atmospheric CO_2 calculated by Visual MINTEQ3.1, based on a CO_2 partial pressure of 400 ppm.

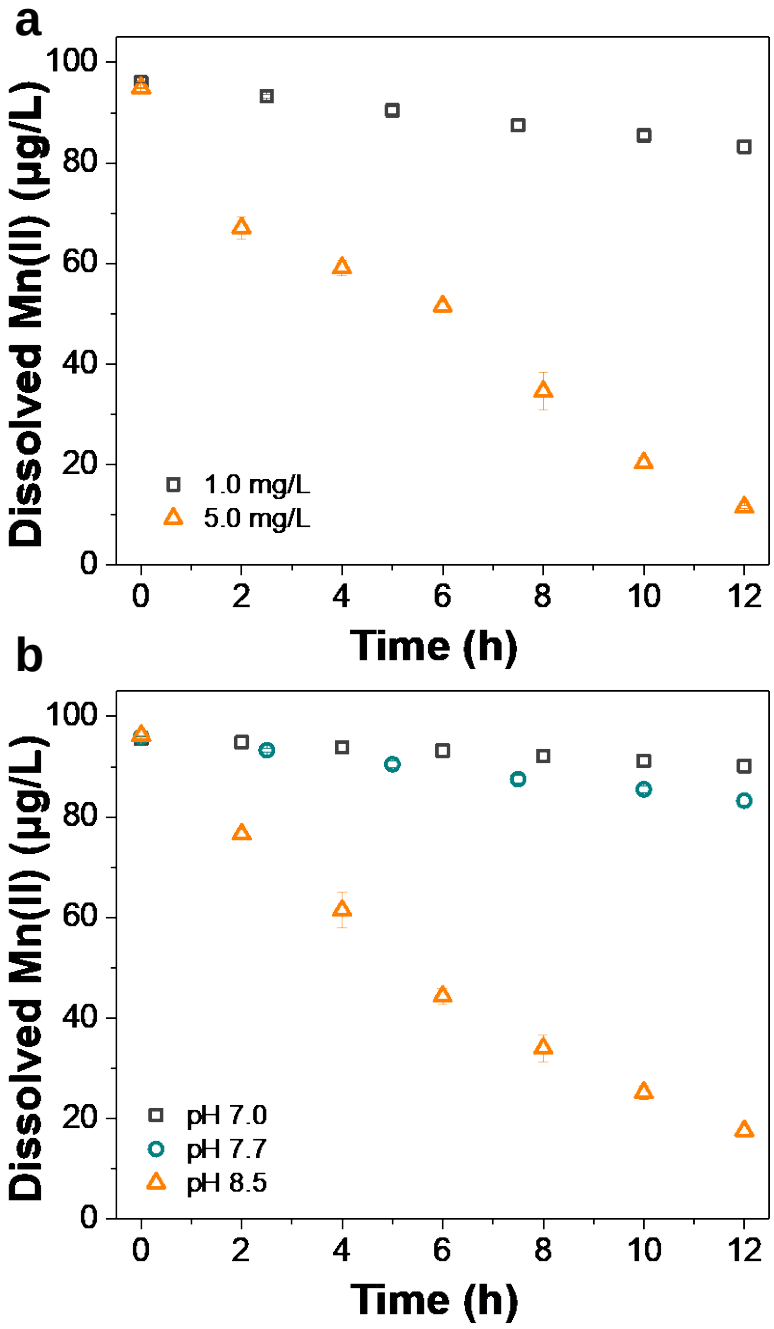

Figure S3. Oxidation of 100 µg/L (1.82 µM) Mn(II) (a) by different concentrations of chlorine at pH 7.7 ± 0.1 and (b) by 1.0 mg/L Cl_2 (14.1 µM)) at different pH. Other experimental conditions: NaCl = 1.0 mM, open to air. The error bars are the standard deviations of duplicate experiments.

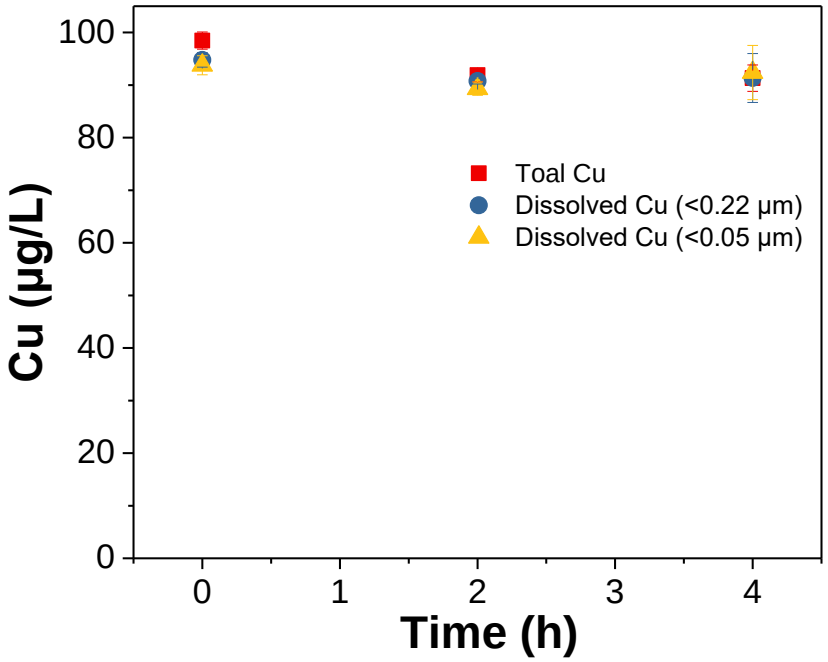

Figure S4. Concentration of dissolved Cu(II) in solutions without Mn(II) or chlorine present. Experimental conditions: NaCl = 1.0 mM, pH = 7.7 ± 0.1, open to air. The error bars are the standard deviations of duplicate experiments.

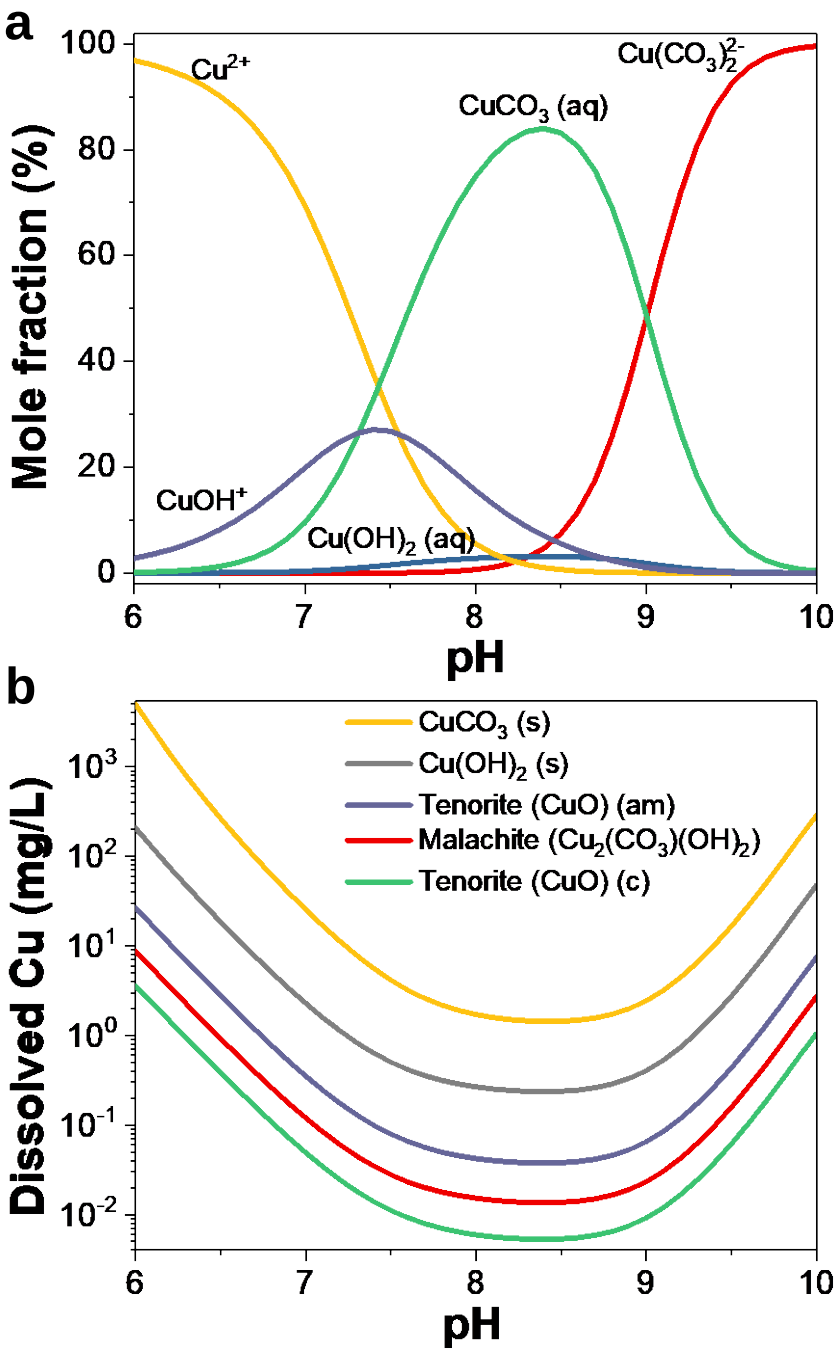

Figure S5. (a) Solubility of Cu(II) minerals and (b) dissolved species of Cu(II) (100 µg/L) at pH ranging from 6.0 to 10.0. T = 25 °C, NaCl = 1.0 mM, DIC in equilibrium with atmosphere at pH ranging from 6.0 to 9.0. The calculations were performed using Visual MINTEQ 3.1.

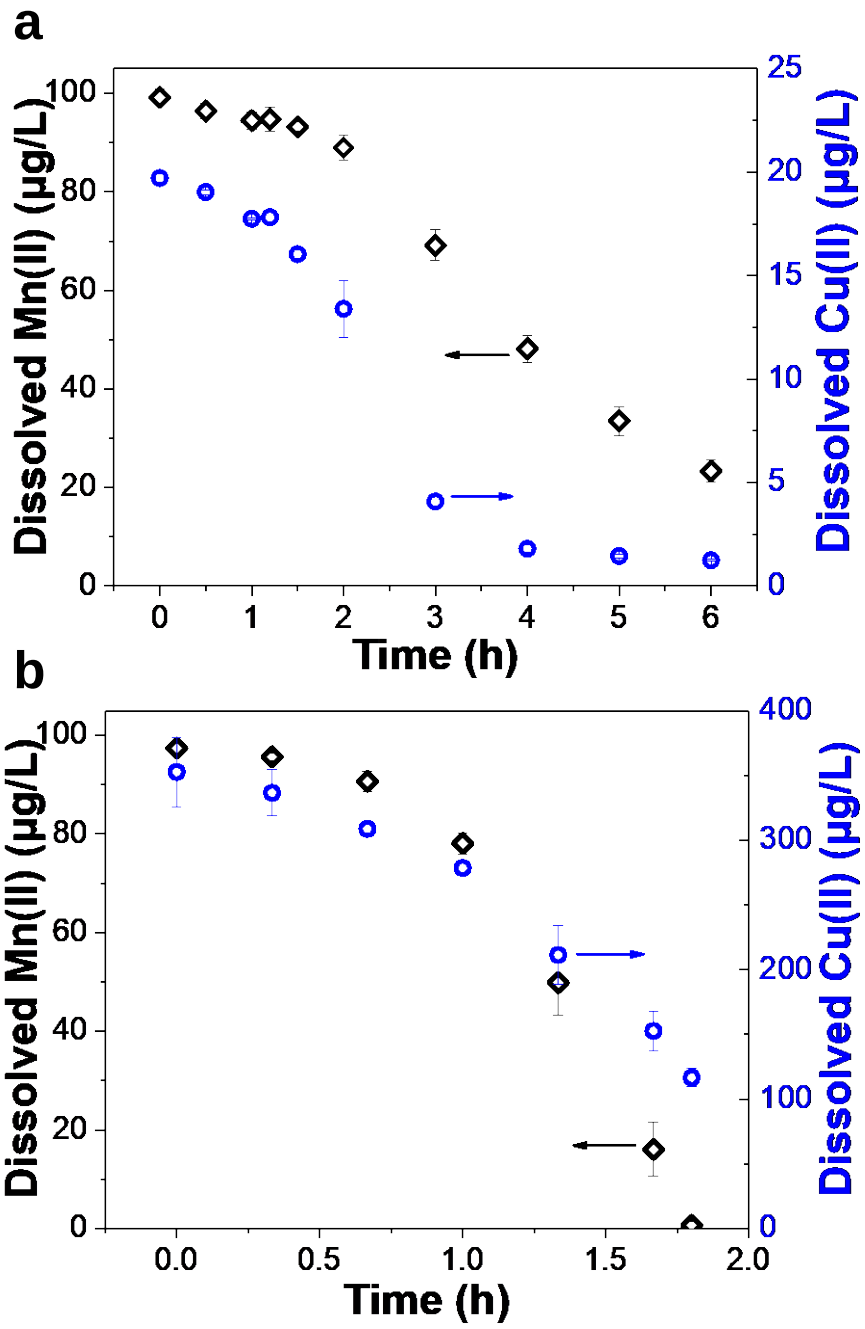

Figure S6. Decrease of dissolved Cu(II) and Mn(II) concentrations during the oxidation of Mn(II) by free chlorine: (a) initial Cu(II) dose = 20 µg/L, (b) initial Cu(II) dose = 400 µg/L. Experimental conditions: NaCl = 1.0 mM, Cl_2 = 1.0 mg/L, pH = 7.7 ± 0.1, open to air. The error bars are the standard deviations of duplicate experiments.

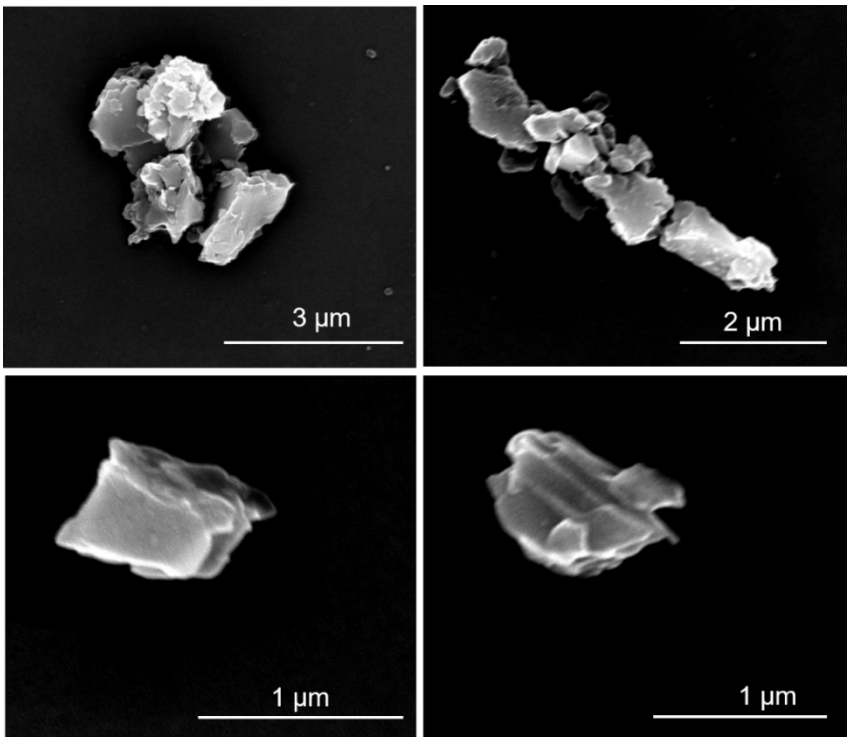

Figure S7. SEM images of MnO_x particles formed from the Mn(II) oxidation in the presence of dissolved Cu(II). Experimental conditions: NaCl = 1.0 mM, Mn(II) = 100 µg/L, Cu(II) (added in the form of $CuSO_4$) = 100 µg/L, pH = 7.7 ± 0.1, open to air; reaction proceeded for 4 hours. Four images were collected to make them more representative and they were all for the same batch of solid sample.

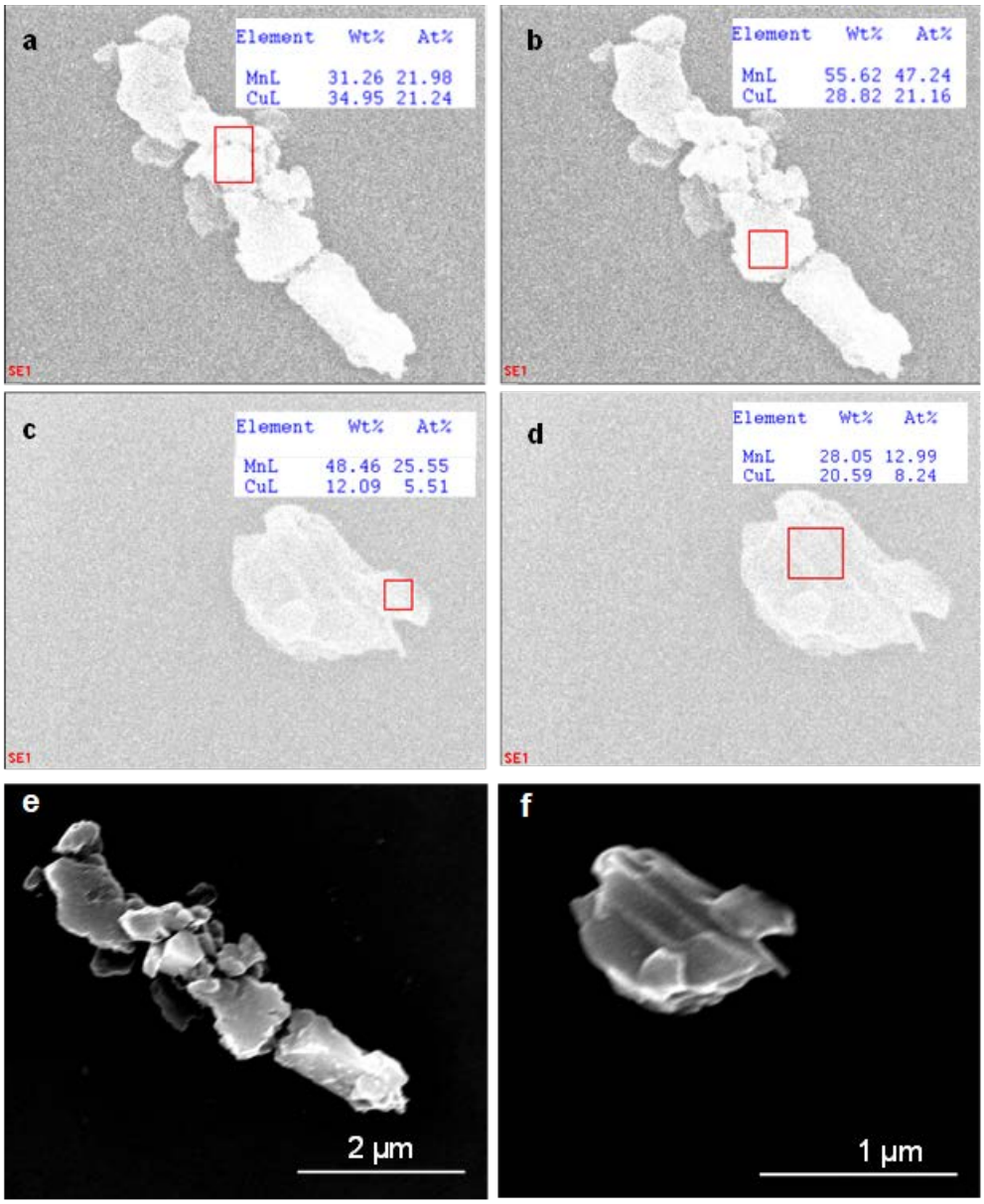

Figure S8. (a) and (b), Mn and Cu contents detected by EDS at two locations on the surface of MnO_x-Cu(II) particle_1; (c) and (d), Mn and Cu contents detected by EDS at two locations on the surface of MnO_x-Cu(II) particle_2. (e) and (f) are for clearer viewing of MnO_x particulates.

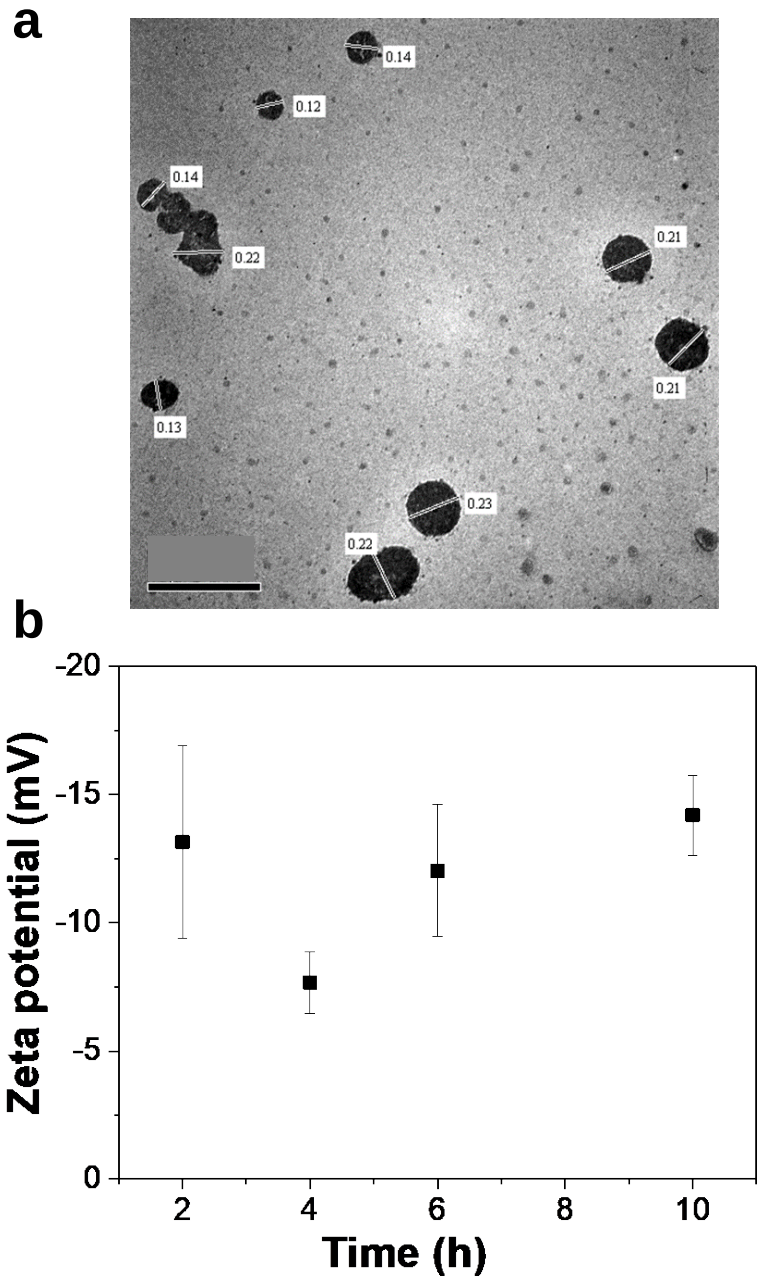

Figure S9. (a) TEM image and (b) zeta potential of the MnO_x particulates formed from the oxidation of Mn(II) by 5.0 mg/L Cl_2. Other experimental conditions: NaCl = 1.0 mM, Mn(II) = 100 μg/L, pH = 7.7 ± 0.1, open to air. The error bars are the standard deviations of triplicate measurements. The lines and numbers in (a) show the diameters of particles.

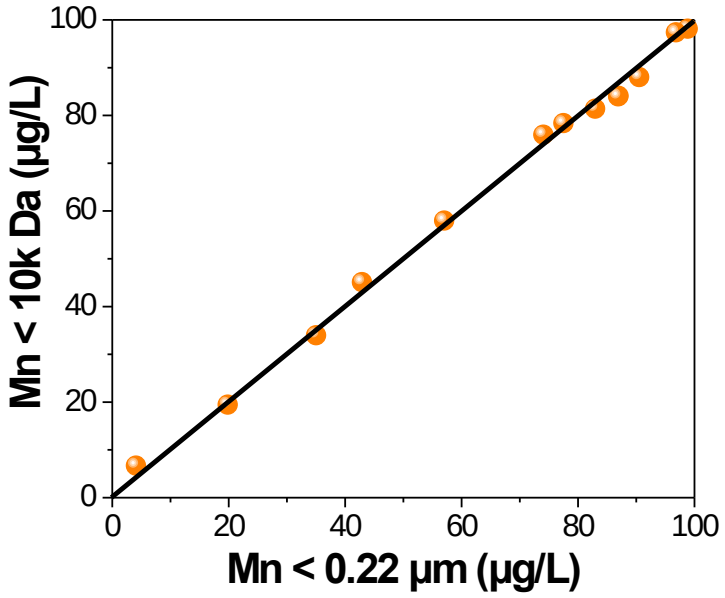

Figure S10. Comparison of Mn that passes through a 0.22 µm -filter and a 10k Da -filter in the Cu(II)-containing system. The solid line with a slope of 1 was drawn to indicate that the dissolved Mn(II) concentrations defined by the two kinds of filters were the same. Experimental conditions: NaCl = 1.0 mM, Mn(II) = 100 µg/L, Cu(II) = 100 µg/L, pH = 7.7 ± 0.1, open to air.

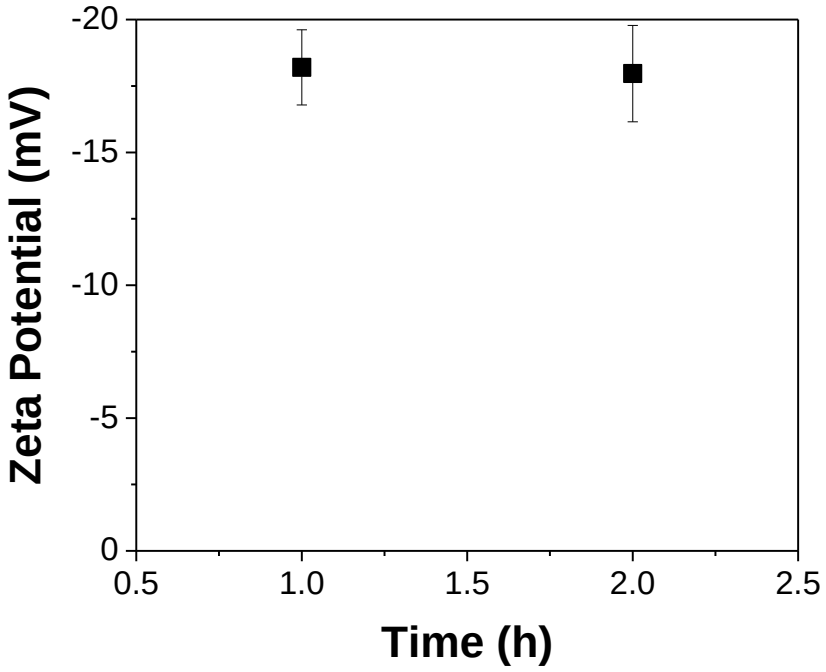

Figure S11. Zeta potential of Mn particles (MnO_x-Cu(II)) formed through Mn(II) oxidation in the system containing 100 μg/L Cu(II). Other experimental conditions: NaCl = 1.0 mM, Mn(II) = 100 μg/L, pH = 7.7 ± 0.1, Cl_2 = 1.0 mg/L, open to air. The error bars are the standard deviations of triplicate measurements.

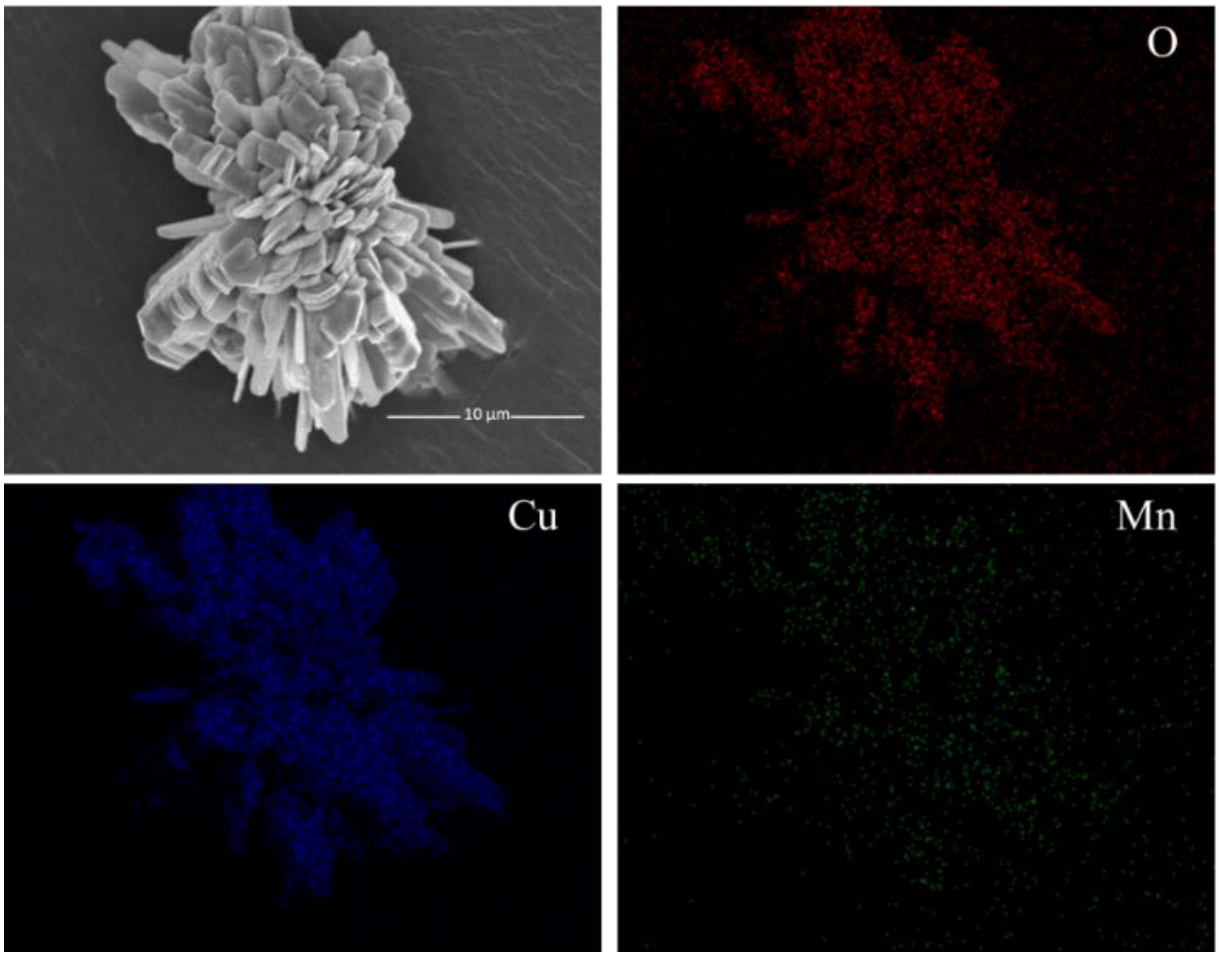

Figure S12. SEM image and EDS mapping of CuO particles collected after Mn(II) oxidation (reaction proceeded for 3 hours). Experimental conditions: NaCl = 1.0 mM, Cl_2 = 1.0 mg/L, CuO = 100 mg/L, Mn(II) = 100 µg/L, pH = 7.7 ± 0.1, open to air.

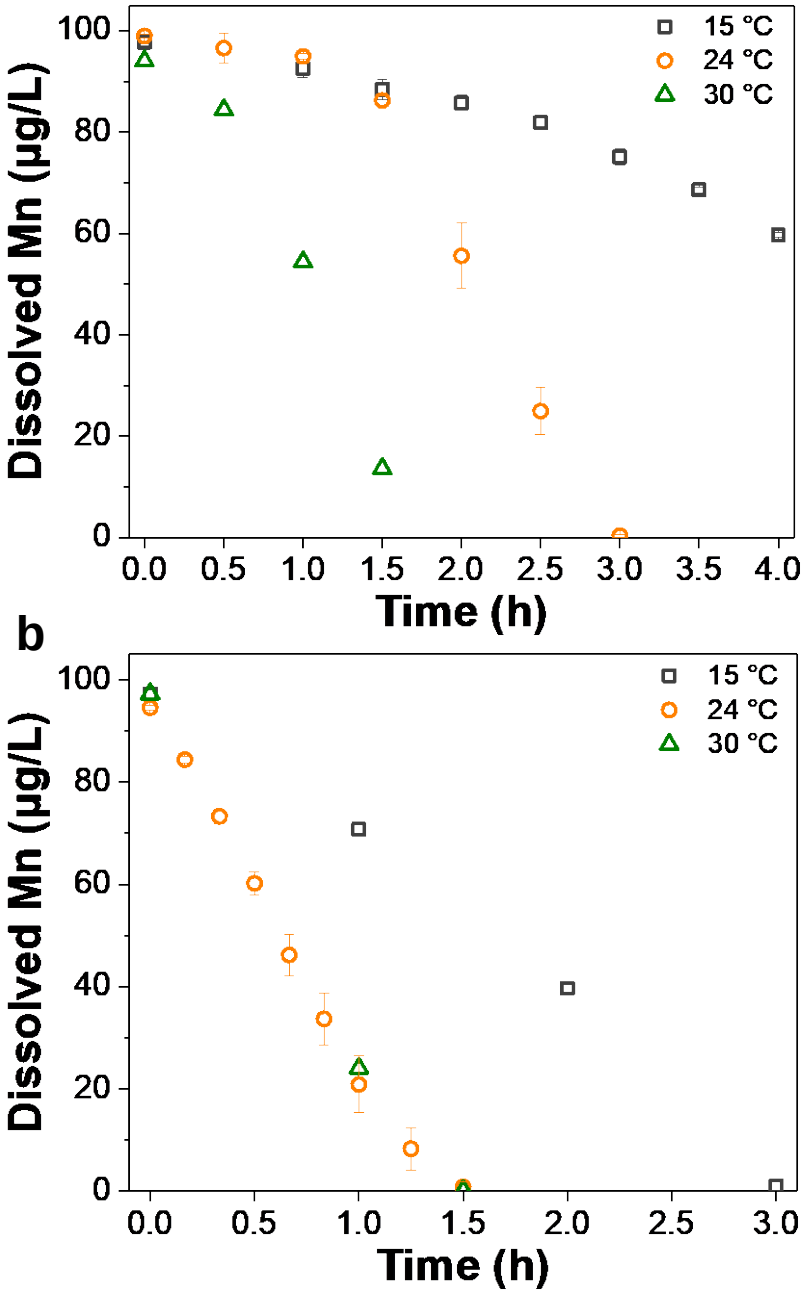

Figure S13. Effect of temperature on Mn(II) oxidation by chlorine in the presence of (a) 100 µg/L Cu(II) (added as $CuSO_4$) and (b) 100 mg/L CuO, respectively. Other experimental conditions: NaCl = 1.0 mM, Mn(II) = 100 µg/L, Cl_2 = 1.0 mg/L, pH = 7.7 ± 0.1, open to air. The error bars are the standard deviations of duplicate experiments.

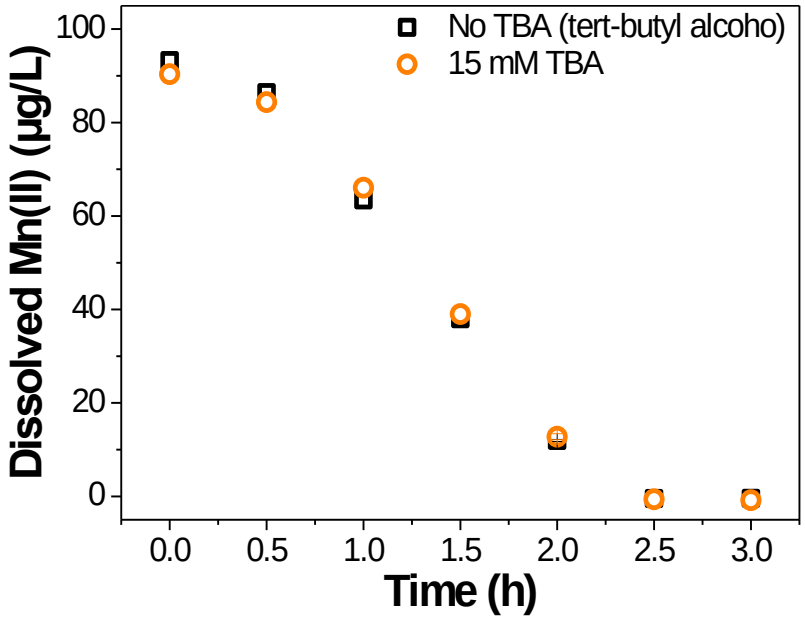

Figure S14. Effect of TBA on Mn(II) oxidation in the presence of 100 µg/L Cu(II), 1.0 mg/L Cl_2 at pH 7.7. Other conditions: NaCl = 1.0 mM, open to air.