

# Supporting information for Kinetics of Chromium(III) Oxidation by Manganese(IV) Oxides

## Using Quick Scanning X-Ray Absorption Fine Structure Spectroscopy (Q-XAFS)

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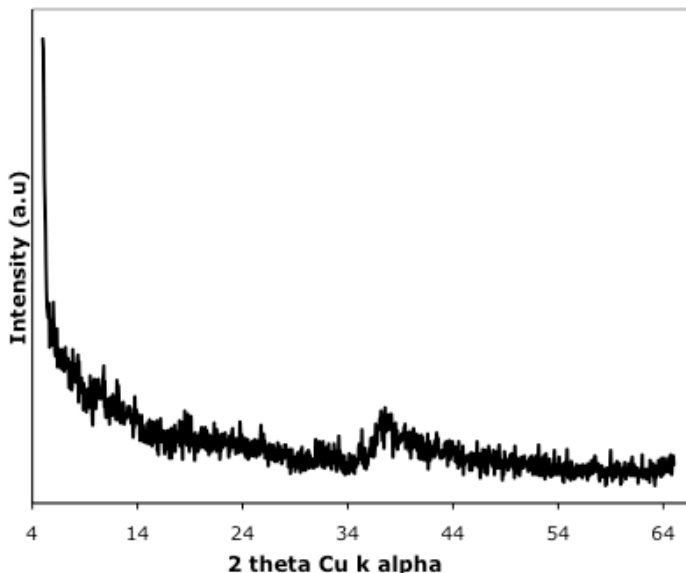


Figure S1: XRD pattern of hydrous manganese oxide.

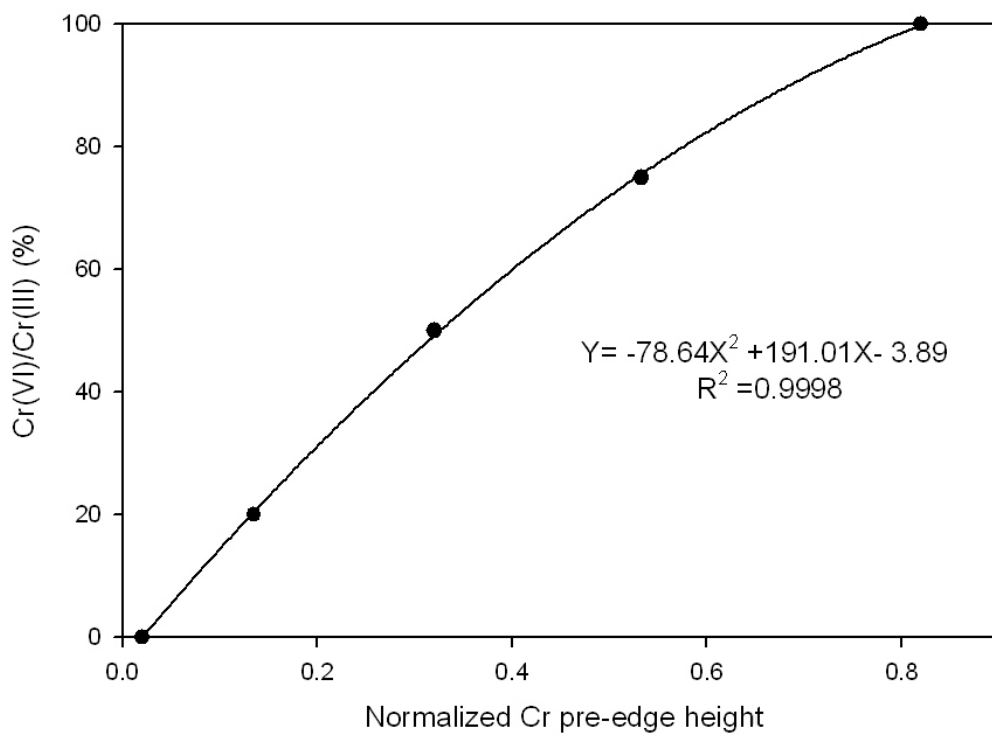


Figure S2- Chromium pre-edge height calibration curve. Height of Cr(VI) pre-edge was measured from XANES spectra of standard solution mixtures of 100mM [chromium]<sub>total</sub> Cr(III) + Cr(VI). The mixtures are respectively 0 % Cr(III)- 100 % Cr(VI), 25 % Cr(III)- 75 % Cr(VI), 50 % Cr(III)- 50 % Cr(VI), 80 % Cr(III)- 20 % Cr(VI), and 100 % Cr(III)- 0 % Cr(VI).

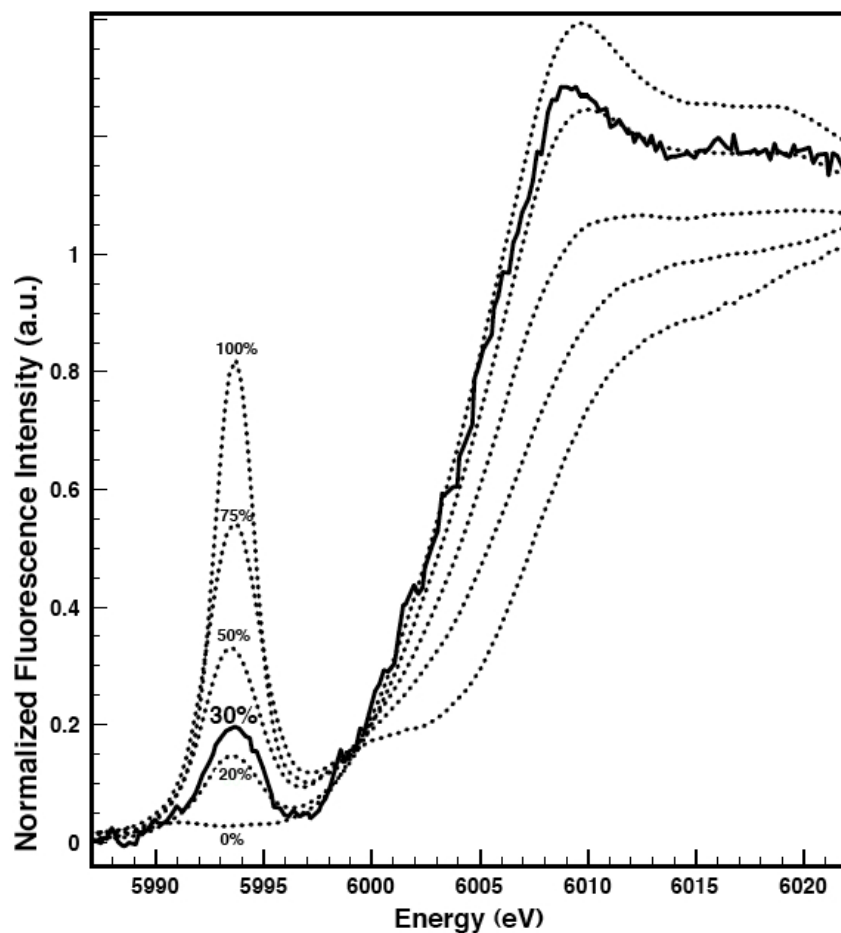


Figure S3 – Percentage of Cr(VI) produced in 4 minutes. Bold line: spectrum of Cr(III) oxidation kinetics at 240 second reaction time (average of two 0.75s Q-XAFS spectra), at pH 2.5,  $[\text{Cr(III)}]_0=100\text{mM}$ ,  $[\text{HMO}]=20\text{g/L}$ . Dashed lines: XANES spectra for standard solution mixtures of  $100\text{mM}$   $[\text{chromium}]_{\text{total Cr(III) + Cr(VI)}}$ : 100 % Cr(VI), 75 % Cr(VI), 50 % Cr(VI), 20 % Cr(VI), and 0 % Cr(VI).

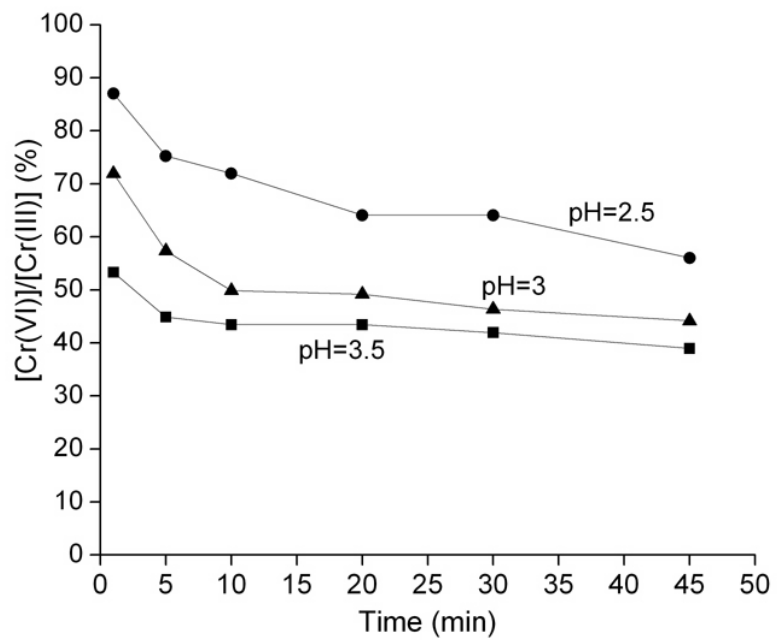


Figure S4 -Percentage of Cr(VI)/Cr(III) in the HMO pastes based on the pre-edge feature at 5993.5eV, at pH 2.5, 3, and 3.5

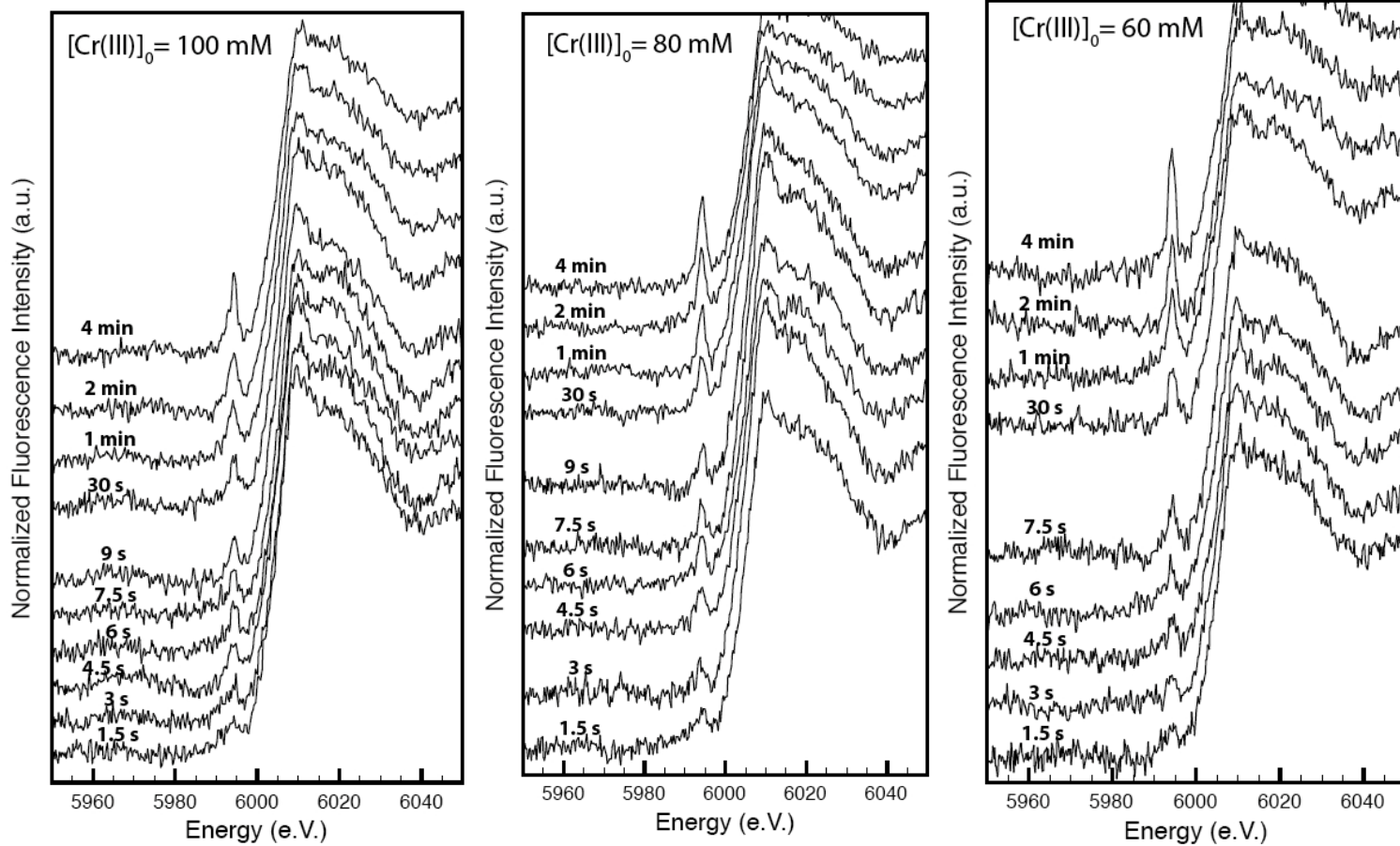


Figure S5-S1

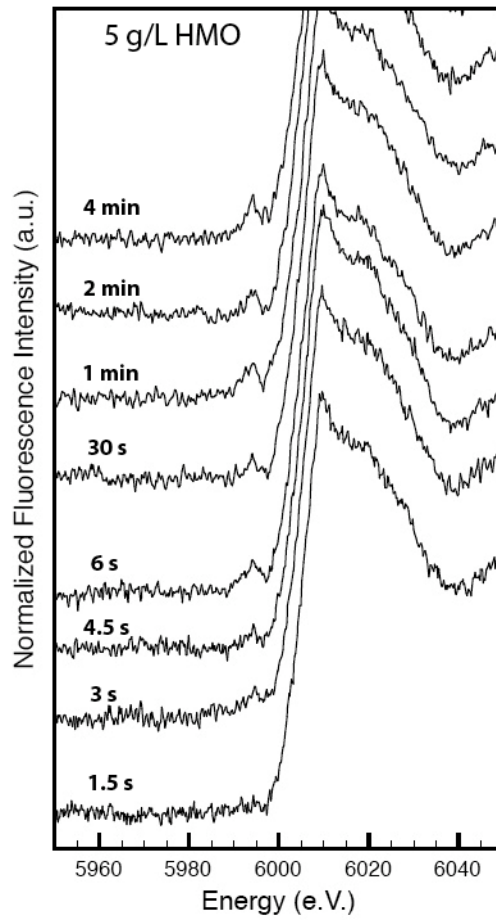
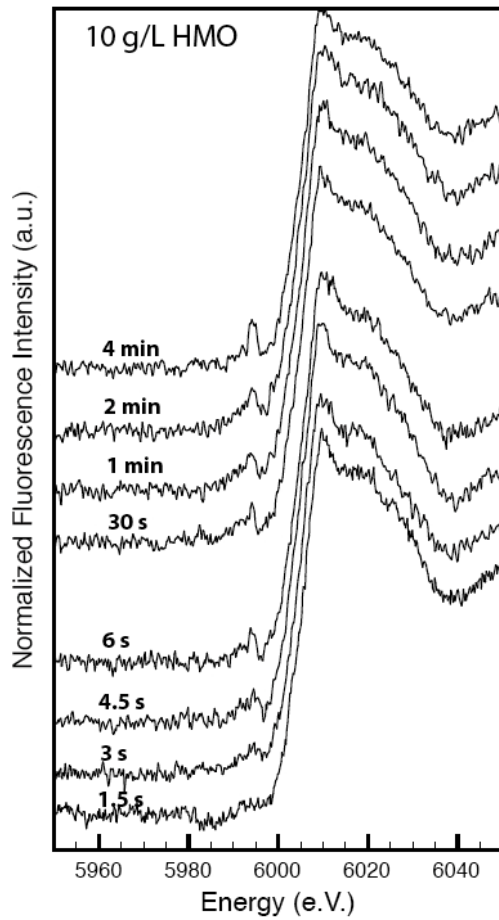
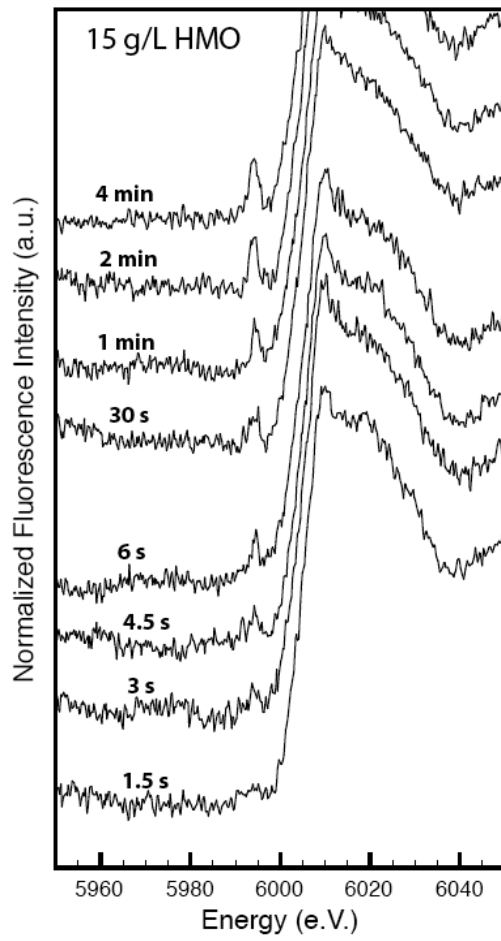
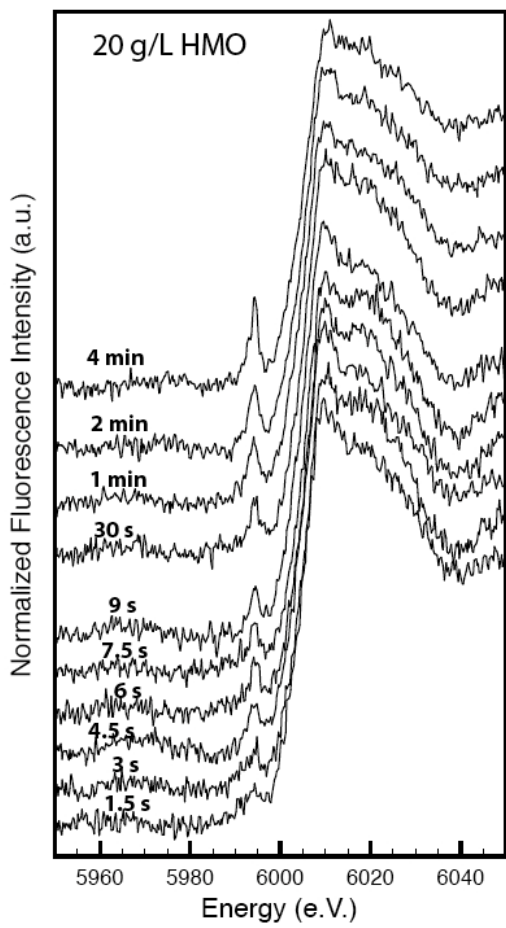


Figure S5-S2  
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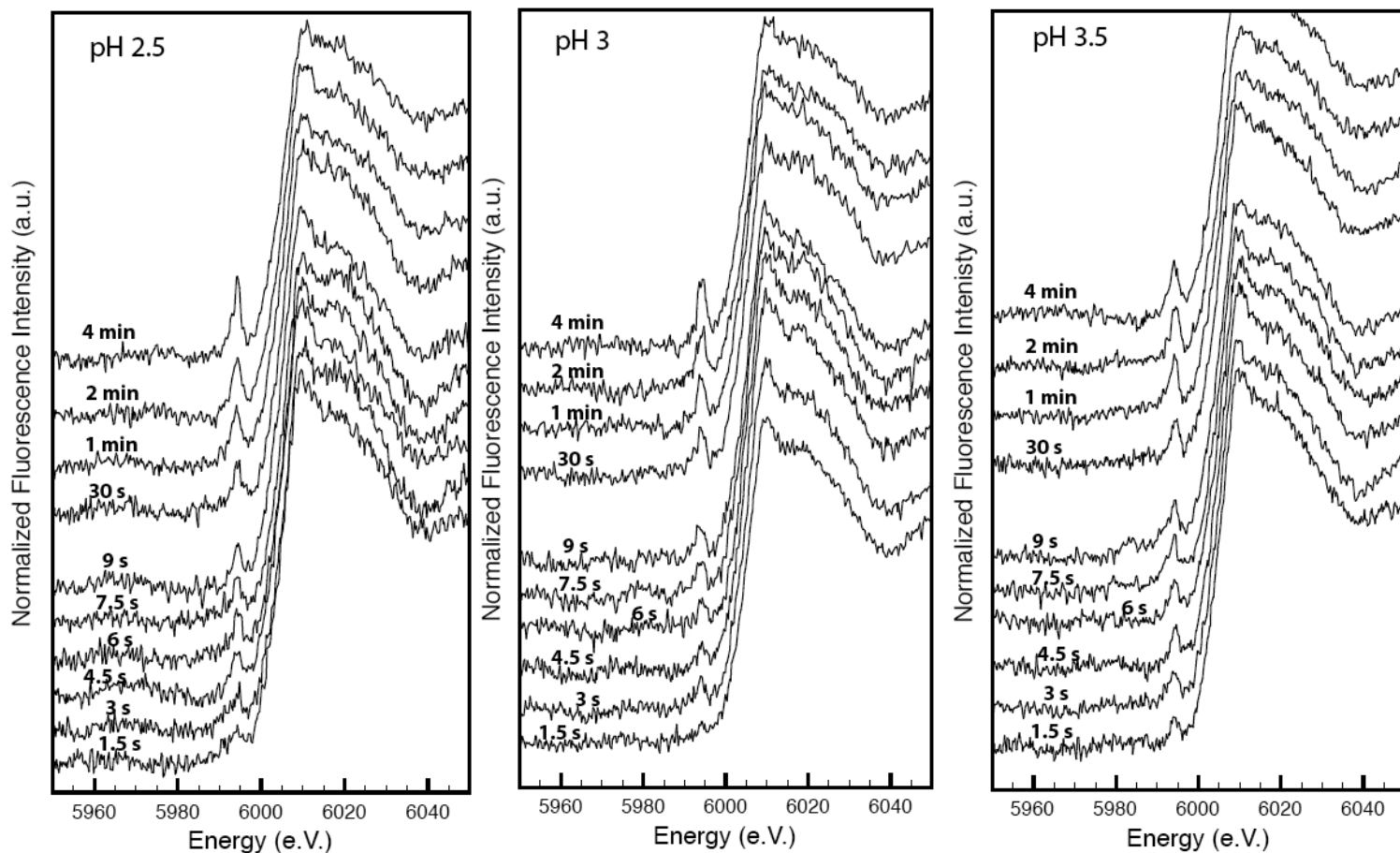


Figure S5-S3

Figure S5 – S5-S1) Effect of Cr concentration – pH 2.5; 20 g/L HMO; [Cr(III)]= 100 mM, 80 mM, and 60 mM S5-S2) Effect of Mn concentration –pH 2.5; [Cr(III)]= 100 mM; 20, 15, 10, and 5 g/L S5-S3) Effect of pH – [Cr(III)]= 100 mM; 20 g/L HMO; pH 2.5, 3, and 3.5. Each spectrum is an average of two 0.75 s spectra.

### Hydrous Manganese Oxide (HMO)

Hydrous manganese oxide (HMO), also referred in the literature to  $\delta$ -MnO<sub>2</sub>, was synthesized less than a week before carrying out experiments to minimize the effect of aging. HMO is characterized by a poorly ordered layered structure, high surface area, and a point of zero charge (PZC) equal to 2.7 (1-3). The HMO used in this study was synthesized using the method of Gadde and Laitinen (4). A Mn(II) nitrate solution was slowly (~30 mins) added to an alkaline permanganate solution while stirring. The molar ratio of MnNO<sub>3</sub>, KMnO<sub>4</sub>, and KOH was respectively 3:2:4. The oxide was repeatedly washed and centrifuged until a constant supernatant conductivity was obtained. After purging the mineral with helium, a specific surface area of 272.6 m<sup>2</sup>/g was measured via BET analysis using nitrogen as the adsorbate at 77.4K. SEM measurements of the mineral (data not shown) exhibited small, disordered aggregates with an average size smaller than 0.5 $\mu$ m. X-ray diffraction (XRD) pattern from 5 to 65 2 $\theta$  suggested a poorly ordered structure (Fig. S1). One small, broad peak was detected at about 37 2 $\theta$ , and a very small peak at 12.3 2 $\theta$ , which matches the XRD pattern of  $\delta$ -MnO<sub>2</sub> reported in (5).

Dissolution of HMO was studied using a stirred flow method at pH=2.5, 3, and 3.5 (39). With this method, one could test whether Mn dissolution into solution was occurring since Mn is removed from solution. A 8mL stirred flow chamber was filled with HMO at a suspension density of 1 g/L, and a solution of 0.05M KCl at pH 2.5, 3, or 3.5 (three different experiments) was used as the dissolution agent, at a flow rate of 0.5 mL/min. A few seconds before sealing the stirred flow chamber and beginning the flow, a small amount of 100mM HCl was quickly added to the reaction chamber to equilibrate the HMO at the correct pH (pH 2.5, 3, or 3.5). The effluent solution was collected continuously for 45 minutes, in 9 tubes (5 minute collection for each tube). Each tube contained 2.5 mL of effluent solution, which was analyzed for total manganese by ICP-Atomic Emission Spectroscopy.

## Elemental Measurements

All samples were diluted in a 15mM EDTA solution at pH 7, and dried in an oven for 8 hours at 45°C before analysis. Cr(VI) and Cr(III) were then separated by chromatography, using a G3268-80001 Agilent Column in a 15mM EDTA mobile phase at pH 7. Finally, the concentration of Cr(III), Cr(VI), and Mn<sub>aqueous</sub> were analyzed with an ICP-MS. The chemical equilibrium modeling system MINEQL+ (database version 4.6) revealed that at our experimental conditions, the major dissolved form of manganese was Mn<sup>2+</sup>. This assumption was confirmed by measuring manganese both by ICP-AES (total aqueous Mn) and by colorimetry (7) during one of our batch experiments. The concentration of Cr<sub>aqueous</sub> and Mn<sub>aqueous</sub> were also measured with an ICP-AES, and the results were compared with the ICP-MS data. The concentration of Mn<sub>aqueous</sub> measured with ICP-AES equaled the concentration of Mn<sub>aqueous</sub> measured with ICP-MS (almost a 0% difference), [Cr]<sub>aqueous</sub> measured with ICP-AES was very similar to [Cr(VI)]+[Cr(III)] measured with ICP-MS (difference less than 2%). The concentration of Cr(VI)<sub>aqueous</sub> was also measured by colorimetry using the s-diphenyl carbazide method (8), and compared to [Cr(VI)] measured with ICP-MS. An approximate 10% difference was found, which could be ascribed to the error range for the colorimetric method.

## Literature Cited

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