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Supplementary materials:

1. Examples of digestion methods used in the literature to characterize Mn content in solids

Table S1: Examples of digestion methods formerly used to characterize Mn content in solids.

Chemicals used	Temperature (°C)	Incubation time (h)	References	
0.2 M oxalic acid + 0.2 M ammonium oxalate	NS	overnight	Albers, et al. [1]	
4 M HCl + 2 g/L oxalic acid	NS	NS	Breda, et al. [2]; de Vet, et al. [3]	
3 M HNO ₃	Boiling	NS	Bruins, et al. [4]	
9.3 M HNO₃	40 °C	30 min + 30 min sonication	Burger, et al. [5]	
7.7 M HNO ₃ + 15.4 M HNO ₃ + H ₂ O ₂ (30%) (optional: +HCl)	95 °C	4 h	McCormick, et al. [6]; United States Environmental Protection Agency (USEPA) [7]	
12.4 M HCl	80 °C	NS	Almquist, et al. [8]; Tali [9]	
$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M oxalic}$ acid	NS	NS	Kijima, et al. [10]	
0.074 M HNO₃ + 6 g/L hydroxylamine sulfate	NS	2 h	Cerrato, et al. [11]; Knocke, et al. [12]	
0.148 M HNO ₃ + 4 g/L NS NS		6 h	Tobiason, et al. [13] Islam, et al. [14]	
0.01M HNO ₃ + 0.1M NH ₂ OH.HCl	Room Temperature	0.5h	Chao [15]	

NS: not specified

2. Manganese oxide thermodynamic solubility constant calculation:

Minerals	Formula	AOS	ΔG° _f (kj/mol)	K _{sp}	Source
Pyrochroite	Mn(OH) ₂	+11	-615.71	1.5×10 ⁻¹³	Hem et Lind
Hausmannitte	Mn ₃ O ₄	(+ <i>,</i> +)	-1283.34	1.0×10 ⁻¹¹⁹	[16]
Bixbyte	Mn ₂ O ₃	+111	-881.16	1.6×10 ⁻³⁴	Hem [17]
Groutite	α-MnOOH	+111	-556.08	1.6×10 ⁻¹³	Fritsch, et al. [18]; Sun, et al. [19]
Feitknechtite	β-MnOOH	+111	-547.11	4.0×10 ⁻¹⁷	Sun, et al. [19]
Manganite	γ-MnOOH	+11	-557.72	1.6×10 ⁻¹⁵	Hem et Lind [16]
Nsutite	γ-MnO₂	+IV	-461.91	Insoluble*	Kitchaev, et
Ramsdellite	R-MnO ₂	+IV	-460.00	Insoluble*	al. [20]
K-Birnessite	δ-(K,Mn)O ₂	+IV	-580.64	Insoluble*	Birkner et
Na-Birnessite	δ-(Na,Mn)O ₂	+IV	-556.00	Insoluble*	Navrotsky [21]
Ca-Birnessite	δ-(Ca,Mn)O ₂	+IV	-546.65	Insoluble*	
Pyrolusite	β-MnO ₂	+IV	-465.19	Insoluble*	Hem et Lind [16]

Table S2: Thermodynamic data of common manganese oxides and hydroxides

For each Mn oxide considered, the chemical equation used for the calculations is presented in Table S3. The equations are balanced for a basic environment to trace the main pH found in biological water

treatment for manganese removal.

Gibbs energy from the solubility equation has been calculated using Equations S1.1 and S1.2 using for each component their Gibbs energy of formation taken from NBS table [23], except for manganese oxides or hydroxides, for which this value depends on their mineralogy arrangement [19, 21]. Then, the solubility constant is determined using Equation S1.3.

The calculation method is presented below. The thermodynamic equilibrium constant (K_{sp}) was calculated at 25°C and atmospheric pressure. *Mn(IV) oxides are completely insoluble, so no K_{sp} can be calculated for these species without considering a reduction of Mn(IV) to Mn(II) or Mn(II) [22, 23].

$$\alpha A + \beta B \leftrightarrow \gamma C + \delta D \tag{S1.1}$$

With $(\alpha,\beta,\gamma,\delta):$ stoichiometric coefficients

$$\Delta G^{\circ}_{f} = \gamma \Delta_{f} G^{\circ}_{C} + \delta \Delta_{f} G^{\circ}_{D} - \left(\alpha \Delta_{f} G^{\circ}_{A} + \beta \Delta_{f} G^{\circ}_{B} \right)$$
(S1.2)

$$K_{sp} = e^{\frac{-\Delta G^{\circ}_{f}}{RT}}$$
(S1.3)

Table S3: Chemical reaction for the solubility of Mn oxides presented in this study.

Manganese oxides	Solubility equilibria considered		
Pyrochroite [Mn(OH) ₂]	$Mn(OH)_2 \leftrightarrow Mn^{2+} + 2HO^-$		
Hausmannite [Mn₃O₄]	$Mn_{3}O_{4} + 4H_{2}O \leftrightarrow Mn^{2+} + 2Mn^{3+} + 4HO^{-}$		
Bixbyite [Mn ₂ O ₃]	$Mn_2O_3 + 3H_2O \leftrightarrow 2Mn^{3+} + 6HO^-$		
Groutite [α-MnOOH]	$\alpha - Mn00H + H_20 \leftrightarrow Mn^{3+} + 3H0^-$		
Feitknechtite [β-MnOOH]	$\beta - Mn00H + H_20 \leftrightarrow Mn^{3+} + 3H0^{-}$		
Manganite [γ-MnOOH]	$\gamma - Mn00H + H_20 \leftrightarrow Mn^{3+} + 3H0^-$		

3. XRD spectrums of the four reference manganese oxides





Figure S1: XRD spectra used to determine the structure of (A) MnO₂; (B) MnO; (C) Mn₃O₄ and (D) Mn₂O₃.

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