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 HNO_3	40 °C	30 min + 30 min sonication	Burger, et al. [5]
7.7 M HNO_3 + 15.4 M HNO_3 + H_2O_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 M H_2SO_4 + 0.5 M oxalic acid	NS	NS	Kijima, et al. [10]
0.074 M HNO_3 + 6 g/L hydroxylamine sulfate	NS	2 h	Cerrato, et al. [11]; Knocke, et al. [12]
0.148 M HNO_3 + 4 g/L hydroxylamine sulfate	NS	6 h	Tobiason, et al. [13] Islam, et al. [14]
0.01M HNO_3 + 0.1M $NH_2OH.HCl$	Room Temperature	0.5h	Chao [15]

NS: not specified

2. Manganese oxide thermodynamic solubility constant calculation:

Table S2: Thermodynamic data of common manganese oxides and hydroxides

Minerals	Formula	AOS	ΔG°$_f$ (kj/mol)	K_{sp}	Source
Pyrochroite	$Mn(OH)_2$	+II	-615.71	1.5×10^{-13}	Hem et Lind [16]
Hausmannitte	Mn_3O_4	(+II,+III)	-1283.34	1.0×10^{-119}	
Bixbyte	Mn_2O_3	+III	-881.16	1.6×10^{-34}	Hem [17]
Groutite	α-MnOOH	+III	-556.08	1.6×10^{-13}	Fritsch, et al. [18]; Sun, et al. [19]
Feitknechtite	β-MnOOH	+III	-547.11	4.0×10^{-17}	Sun, et al. [19]
Manganite	γ-MnOOH	+III	-557.72	1.6×10^{-15}	Hem et Lind [16]
Nsutite	γ-MnO_2	+IV	-461.91	Insoluble*	Kitchaev, et al. [20]
Ramsdellite	R-MnO_2	+IV	-460.00	Insoluble*	
K-Birnessite	δ-(K,Mn)O_2	+IV	-580.64	Insoluble*	Birkner et Navrotsky [21]
Na-Birnessite	δ-(Na,Mn)O_2	+IV	-556.00	Insoluble*	
Ca-Birnessite	δ-(Ca,Mn)O_2	+IV	-546.65	Insoluble*	
Pyrolusite	β-MnO_2	+IV	-465.19	Insoluble*	Hem et Lind [16]

*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(III) or Mn(II) [22, 23].*

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.

$$\alpha A + \beta B \leftrightarrow \gamma C + \delta D \qquad (S1.1)$$

With (α,β,γ,δ): stoichiometric coefficients

$$\Delta G°_f = \gamma \Delta_f G°_C + \delta \Delta_f G°_D - \left(\alpha \Delta_f G°_A + \beta \Delta_f G°_B\right) \qquad (S1.2)$$

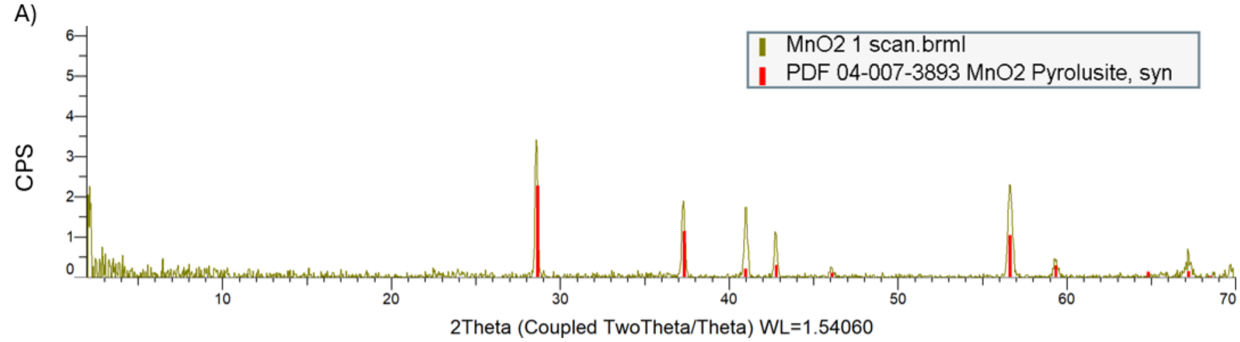
$$K_{sp} = e^{\frac{-\Delta G°_f}{RT}} \qquad (S1.3)$$

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

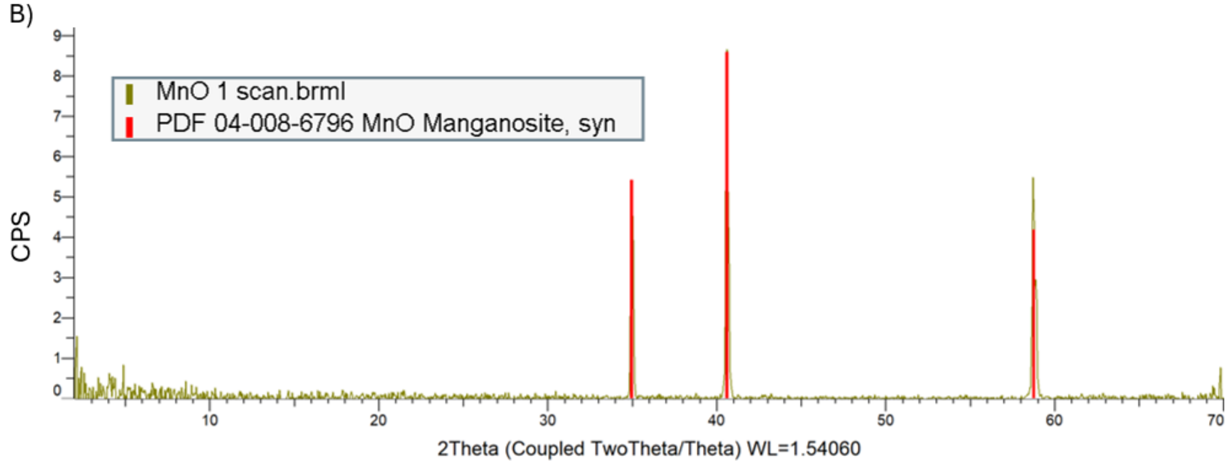
Manganese oxides	**Solubility equilibria considered**
Pyrochroite [$Mn(OH)_2$]	$Mn(OH)_2 \leftrightarrow Mn^{2+} + 2HO^-$
Hausmannite [Mn_3O_4]	$Mn_3O_4 + 4H_2O \leftrightarrow Mn^{2+} + 2Mn^{3+} + 4HO^-$
Bixbyite [Mn_2O_3]	$Mn_2O_3 + 3H_2O \leftrightarrow 2Mn^{3+} + 6HO^-$
Groutite [α-MnOOH]	$\alpha - MnOOH + H_2O \leftrightarrow Mn^{3+} + 3HO^-$
Feitknechtite [β-MnOOH]	$\beta - MnOOH + H_2O \leftrightarrow Mn^{3+} + 3HO^-$
Manganite [γ-MnOOH]	$\gamma - MnOOH + H_2O \leftrightarrow Mn^{3+} + 3HO^-$

3. **XRD spectrums of the four reference manganese oxides**

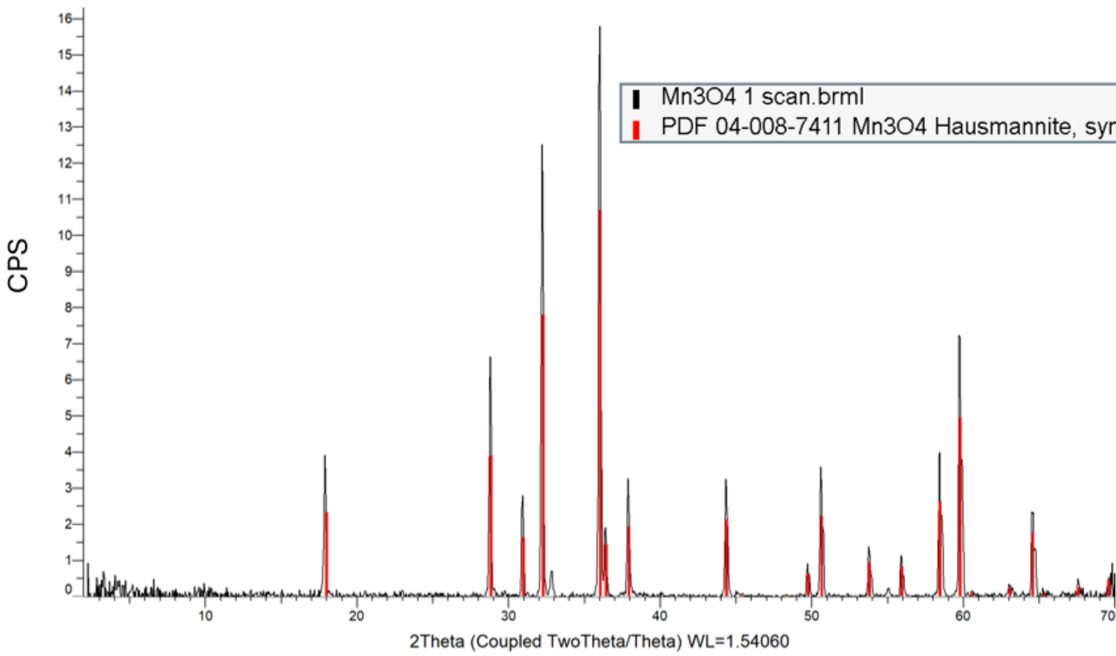
A)



B)



C)



D)

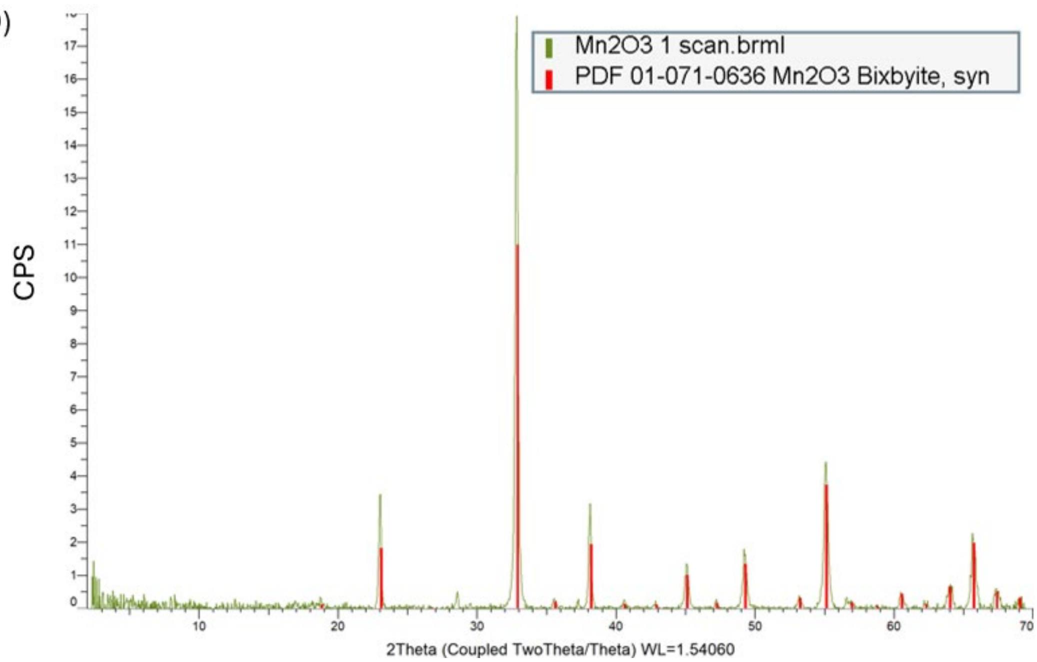


Figure S1: XRD spectra used to determine the structure of (A) MnO_2; (B) MnO; (C) Mn_3O_4 and (D) Mn_2O_3.

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