Supporting Information

Oxidation and adsorption of antimony(III) from surface water using a novel Al_2O_3-supported Fe-Mn binary oxides nanoparticles: Effectiveness, dynamic quantitative mechanisms, and life cycle analysis

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Fig. S5 The ratios of Mn species (Mn(II), Mn(III), and Mn(IV)) to total Mn over reaction.

Section S1. Preparation of Fe-Mn@Al_2O_3

In brief, under vigorous magnetic stirring and N_2 purging, 40 mL $FeSO_4$ solution (0.05 mol/L) was added into 300 mL deionized water with 0.41 g of Al_2O_3. After mixing for 10 min, 40 mL of $KMnO_4$ solution (0.0167 mol/L) was added dropwise into the mixture under vigorous stirring. Then, a 5 mol/L NaOH solution was added till a pH value of 7–8. The suspension was continuously stirred for 1 h, and sealed and aged in dark for 12 h to ensure complete reaction and full growth of the particles. Finally, the solids settled by gravity were washed three times with deionized water and vacuum-dried in a freeze drier (SCIENTZ-10N, Ningbo, China) at -40 ^{o}C. The resultant composite contained 0.22 g Fe-Mn binary oxides and 0.41 g alumina oxide (i.e., a Fe:Al_2O_3 molar ratio of 1:2). The amounts of Al_2O_3 added in the system were changed to 0.20 g, 0.82 g, and 2.00 g under otherwise identical conditions to prepare Fe-Mn@Al_2O_3 with a Fe:Al_2O_3 molar ratio of 1:1, 1:4, and 1:10, respectively.

Section S2. Sorption kinetic models

Several kinetic models are applied to simulate the Sb sorption kinetic data. The commonly used pseudo-first-order (**equation 1**) and pseudo-second-order kinetic models (**equation 2**)[1] are given as follows:

$$In(q_e - q_t) = Inq_e - K_1 t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where q_t (mg/g) and q_e (mg/g) are the sorbed amounts of Sb at time t (h) and equilibrium, respectively, and K_1 (h^{-1}) and K_2 (g/(mg·h) are pseudo-first-order and pseudo-second-order sorption rate constants, respectively.

The Weber and Morris intraparticle diffusion model is based on Fick's second law of diffusion and described by **equation 3**:[2]

$$q_t = k_i t^{0.5} + C_{\mathrm{i}} \tag{3}$$

where k_i is the intraparticle diffusion rate constant ($mg/(g \cdot h^{-0.5})$) and C_i is the intercept related to the boundary layer effect (mg/g). The values of K_i and C_i can be obtained from the slope and intercept of the linear plots of q_t versus $t^{0.5}$.

The external mass transfer model is described by **equation 4**:[3]

$$-\frac{dC}{dt} = k_f a(C - C_s) \tag{4}$$

where k_f is the mass transfer coefficient (cm/s), C and C_s are the concentration of Sb in bulk solution and at interface (mg/L), respectively, and a (m^2/m^3) is the specific area available for mass transfer per unit volume of the contactor (2.26×10^5 m^2/m^3);

Assume the antimony sorption fits linear isotherm (**equation 5**):

$$q_e = \frac{q_m k C_S}{1 + C_S} \tag{5}$$

where k is the sorption equilibrium coefficient, q_m is the maximum sorption capacity of Fe-Mn@Al_2O_3 (mg/g), and q_e is the adsorption capacity which can be calculated by the following **equation 6**:

$$q_e = \frac{V}{m}(C_0 - C_s) \tag{6}$$

where V is the contactor volume (0.05 L), m is the mass of Fe-Mn@Al_2O_3, and C_0 is the initial Sb concentration in bulk solution (mg/L). Combine equations 4-6, yielding **equation 7**:

$$-\frac{dc}{dt} = k_f a[C - \frac{1}{2}(\sqrt{(\frac{q_m m}{V} - C_0 + \frac{1}{k})^2 + \frac{4C_0}{k}}) - \frac{q_m m}{V} + C_0 - \frac{1}{k})] \tag{7}$$

To describe the sorption data with the model, the concentration of Sb in the bulk solution (C) is derived as a function of time (t):

$$C = b\exp[-ht] + C_0 - b \tag{8}$$

In equation 8, h and b are the fitting parameters of the external mass transfer model: $h = k_f a$

and $b = C_0 - \frac{1}{2}(\sqrt{(\frac{q_m m}{V} - C_0 + \frac{1}{k})^2 + \frac{4C_0}{k}}) - \frac{q_m m}{V} + C_0 - \frac{1}{k})$

Thus equation 8 is applied to fit the experimental results with h and b as fitting parameters.

Section S3. Sorption isotherm models

Langmuir (**equation 9**) and Freundlich (**equation 10**) models were applied to fit the sorption isotherm data.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{9}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{10}$$

where q_e and C_e represents the equilibrium Sb uptake (mg/g) and the equilibrium concentration of Sb in the solution (mg/L), respectively, q_m is the maximum adsorption capacity of Fe-Mn@Al_2O_3 (mg/g), K_L is the Langmuir constant (mg/L), K_F is the Freundlich affinity coefficient ((mg/g)/(mg/L)^n), and n is the exponential coefficient.

Section S4. The total oxidation efficiencies of Fe-Mn@Al_2O_3 and Fe-Mn+Al_2O_3 towards Sb(III)

The total oxidation efficiencies of Fe-Mn@ Al_2O_3 and Fe-Mn+Al_2O_3 towards Sb(III) are calculated based on mass balance.

(1) Reaction conditions: Initial Sb(III) concentration = Total Sb concentration = 5000 μg/L, solution volume = 50 mL, Fe-Mn@Al_2O_3 =100 mg/L, Fe-Mn+Al_2O_3 = 100 mg/L (Fe-Mn = 33 mg/L and Al_2O_3 = 67 mg/L), and initial solution pH = 6.4.

(2) Equilibrium aqueous Sb(III) concentration = 242.4 μg/L for Fe-Mn@ Al_2O_3 and 587.7 μg/L for Fe-Mn+Al_2O_3.

(3) The Sb-laden Fe-Mn@Al_2O_3 and Sb-laden Fe-Mn+Al_2O_3 were collected at the end of the experiment, the sample was gently rinsed twice with deionized water to remove soluble Sb, dissolved in 50 mL of 9.6 mol/L HCl solution, and analyzed for aqueous Sb(III) concentrations. Dissolved Sb(III) concentration = 235.1 μg/L for Fe-Mn@Al_2O_3 and 523.4 μg/L for Fe-Mn+Al_2O_3.

(4) The initial total Sb = 5000 μg/L× 0.05 L = 250 μg

For Fe-Mn@Al_2O_3, the Sb(III) content after reaction = (242.4+235.1) μg/L× 0.05 L = 23.88 μg

For Fe-Mn+Al_2O_3, the Sb(III) content after reaction = (587.7+523.4) μg/L× 0.05 L = 55.55 μg

(5) For Fe-Mn@Al_2O_3, the total oxidation efficiency towards Sb(III) = (250 μg - 23.88 μg) /250 μg × 100% = 90.4%

For Fe-Mn+Al_2O_3, the total oxidation efficiency towards Sb(III) = (250 μg -55.55 μg) /250 μg × 100% = 77.8%

Therefore, till equilibrium, the total oxidation efficiency towards Sb(III) was 90.4% for Fe-Mn@Al_2O_3 and 77.8% for Fe-Mn+Al_2O_3.

Table S1 Molar ratios of Fe:Mn and Fe:Al_2O_3 for different types of Fe-Mn@Al_2O_3.

Composites	Fe:Mn molar ratios		Fe:Al_2O_3 molar ratios	
	Theoretical values	Measured values	Theoretical values	Measured values
Fe-Mn	3:1	(2.83±0.02):1		
Fe-Mn@Al_2O_3 (1:1)		(2.96±0.06):1	1:1	1:(1.05±0.01)
Fe-Mn@Al_2O_3 (1:2)		(2.91±0.12):1	1:2	1:(1.92±0.13)
Fe-Mn@Al_2O_3 (1:4)		(2.85±0.02):1	1:4	1:(4.18±0.18)
Fe-Mn@Al_2O_3 (1:10)		(2.89±0.09):1	1:10	1:(9.78±0.09)

Table S2 Specific surface areas, pore sizes, and pore volumes of Fe-Mn, Al_2O_3, and Fe-Mn@Al_2O_3 at different Fe:Al_2O_3 molar ratios.

Composites	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Al_2O_3	265.53	0.493	9.34
Fe-Mn	208.54	0.419	7.44
Fe-Mn@Al_2O_3 (1:1)	230.84	0.486	8.09
Fe-Mn@Al_2O_3 (1:2)	225.88	0.471	8.16
Fe-Mn@Al_2O_3 (1:4)	221.16	0.464	8.39

Table S3 Preparation costs of Fe-Mn@Al_2O_3 with different Fe:Al_2O_3 molar ratios.

Fe:Al_2O_3 molar ratios	Preparation costs[a] (CNY/t)
1:0	8715
1:1	5957
1:2	5038
1:4	4303
1:10	3701

[a] The preparation cost was calculated based on the precursor (industrial grade) costs without considering the operational expenses. The market price was 3200 CNY/t for Al_2O_3 (98.6%), 410 CNY/t for $FeSO_4 \cdot 7H_2O$ (98.0%), and 15000 CNY/T for $KMnO_4$ (99.3%).

Table S4 Pseudo-first-order, pseudo-second-order, intraparticle diffusion, and external mass transfer models applied for simulating total Sb sorption kinetics and the corresponding fitting parameters (Errors given as standard deviation).

Kinetic models	**Parameters**			**R^2**	**ARE**[i]	**NSD**[i]
Pseudo-first-order model	K_1^a (h^{-1}) 0.1386±0.0117	q_e^b(mg/g) 1.32±0.36	$h_1^c = K_1 q_e$ (mg/(g·h)) 0.1829	0.9524	25.09	52.91
Pseudo-second-order model	K_2^a (g/(mg·h)) 0.7140±0.1871	q_e^b(mg/g) 8.09±0.06	$h_2^c = K_2 q_e^2$ (mg/(g·h)) 46.73	0.9997	12.11	23.07
Intraparticle diffusion model	First stage (0-10 min)	k_1^d (mg/(g·$h^{0.5}$)) 21.1748±0.000	C_1^e (mg/g) 0	1.0000	0.02	0.02
	Second stage (10 min-4 h)	k_2^d (mg/(g·$h^{0.5}$)) 0.4785±0.0217	C_2^e (mg/g) 6.49±0.04	0.9918	2.85	2.95
	Third stage (4-24 h)	k_3^d (mg/(g·$h^{0.5}$)) 0.1110±0.0215	C_3^e (mg/g) 7.50±0.08	0.9639	4.95	4.82
External mass transfer model	$k_f^f = h/a^g$ (cm/s) $1.49\times10^{-6}\pm0.52\times10^{-6}$	h^h(1/h) 0.3380±0.1179	b^h (μg/L) 924.21±104.94	0.9285	11.88	15.76

[a] K_1 (h^{-1}) is the rate constant of the pseudo-first-order sorption, K_2 (g/(mg·h)) is the pseudo-second-order sorption rate constant. [b] q_e (mg/g) is Sb uptake at equilibrium time. [c] h_1 (mg/(g·h)) and h_2 (mg/(g·h)) are the initial rate of the pseudo-first-order sorption and the initial rate of the pseudo-second-order sorption, respectively. [d] k_i (mg/ (g·$h^{-0.5}$)) is the intraparticle diffusion rate constant. [e] C_i is the intercept related to the boundary layer effect (mg/g). [f] k_f (cm/s) is the mass transfer coefficient. [g] a (m^2/m^3) is the specific surface area available for mass transfer per unit volume of the contactor (2.26×10^5 m^2/m^3). [h] h (1/h) and b (mg/L) are the fitting parameters of the external mass transfer model. [i] The normalized standard deviation (NSD) and average relative error (ARE) were calculated to indicate the validity of kinetic models, which are defined as:

$$NSD = 100\sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left|\frac{(q_{ti}^{\exp} - q_{ti}^{cal})}{q_{ti}^{\exp}}\right|^2}$$

$$ARE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{(q_{ti}^{\exp} - q_{ti}^{cal})}{q_{ti}^{\exp}}\right|$$

where $q_{ti}^{\exp}$ and q_{ti}^{cal} (mg/g) are experimental values and calculated values by models of Sb uptake at time t, and N is the number of measurements.

Table S5 Regression parameters of sorption isotherm data of Sb onto Fe-Mn@Al_2O_3 by Langmuir and Freundlich models (Errors given as standard deviation).

Adsorption isotherm	**Sb species**	**Parameters**		**R^2**	**MPSD**[e]	**HYBRID**[e]
		q_m[a] (mg/g)	b[b] (L/mg)			
Langmuir	Sb(III)	272.22±33.33	0.09±0.03	0.9862	52.10	1239.88
	Sb(V)	66.68±13.34	0.04±0.01	0.9200	64.53	1676.06
		K_F[c] ((mg/g)/(mg/L)^n)	n[d]			
Freundlich	Sb(III)	29.23±3.05	0.56±0.03	0.9909	74.69	371.97
	Sb(V)	7.69±0.75	0.42±0.02	0.9856	24.79	135.49

[a] q_m is the Langmuir maximum sorption capacity (mg/g). [b] b is the Langmuir affinity constant (L/mg). [c] K_F is the Freundlich affinity coefficient ((mg/g)/(mg/L)^n). [d] n is the exponential coefficient. [e] The Marquardt's percent standard deviation (MPSD) and hybrid error function (HYBRID) indicated the validity of adsorption isotherm:

$$\mathrm{MPSD} = 100\sqrt{\frac{1}{N-P}\sum_{i=1}^{N}\left(\frac{q_{ti}^{exp}-q_{ti}^{cal}}{q_{ti}^{exp}}\right)^2}$$

$$\mathrm{HYBRID} = \frac{100}{\mathrm{N}-\mathrm{P}}\sum_{\mathrm{i}=1}^{\mathrm{N}}\left|\frac{(\mathrm{q}_{\mathrm{ti}}^{\mathrm{exp}} - \mathrm{q}_{\mathrm{ti}}^{\mathrm{cal}})^2}{\mathrm{q}_{\mathrm{ti}}^{\mathrm{exp}}}\right|$$

where $q_{ti}^{\exp}$ is the experimental data obtained from batch sorption tests (mg/g), and q_{ti}^{cal} is the estimated value from the isotherm for corresponding $q_{ti}^{\exp}$ (mg/g), N is the number of observations in the experimental sorption isotherm, and P is the number of parameters in the regression model.

Table S6 XPS results of Fe-Mn@Al_2O_3 before and after sorption of Sb(III).

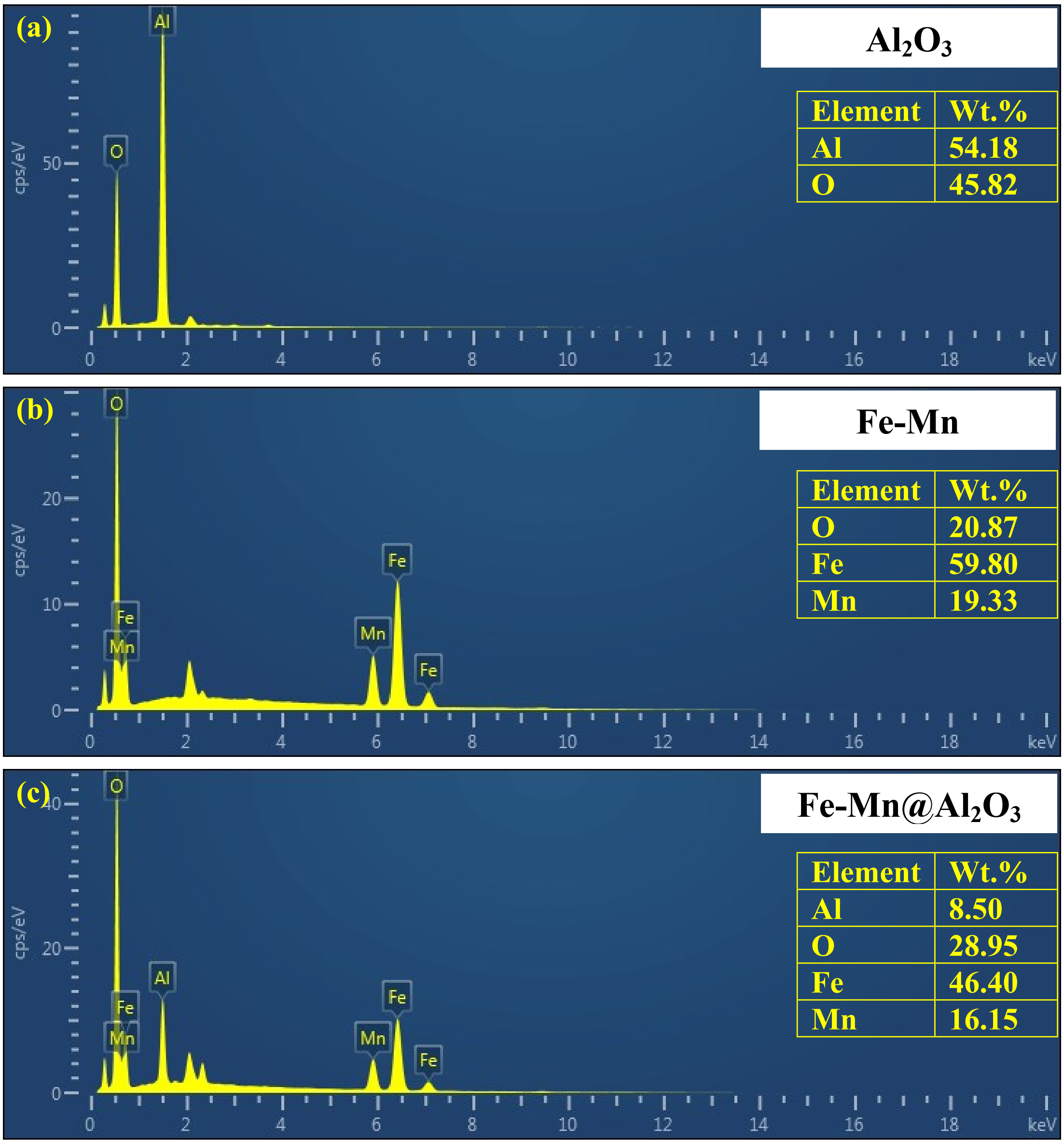
Sample	**Composition (at.%)**				
	Al	**O**	**Fe**	**Mn**	**Sb**
Fe-Mn@Al_2O_3	9.1	65.2	19.6	6.1	0
Sb laden Fe-Mn@Al_2O_3[a] (1 h)	9.2	60.2	19.6	5.6	5.4
Sb laden Fe-Mn@Al_2O_3[a] (4 h)	9.2	59.9	20.0	5.2	5.7
Sb laden Fe-Mn@Al_2O_3[a] (8 h)	9.6	60.1	20.1	4.6	5.5
Sb laden Fe-Mn@Al_2O_3[a] (48 h)	9.7	59.6	20.3	4.2	5.5

Note: Sb-laden Fe-Mn@Al_2O_3 were prepared under the following experimental conditions: Fe-Mn@Al_2O_3 = 100 mg/L, Sb(III) concentration = 5 mg/L, pH = 6.4, and reaction time = 1 h, 4 h, 8 h, and 48 h, respectively.

Table S7 Concentrations of different Sb species on Fe-Mn@Al_2O_3 and in aqueous phase at different time intervals.[a]

Time (h)	$S_{Sb(total)}$[a] (μg/L)	$S_{Sb(III)}$[a] (μg/L)	$S_{Sb(V)}$[a] (μg/L)	$C_{Mn(II)}$[b] (μg/L)	$C_{Sb(total)}$[b] (μg/L)	$C_{Sb(III)}$[b] (μg/L)	$C_{Sb(V)}$[b] (μg/L)
0		-	-	-	5006.7	4954.0	-
1	2465.1	522.4	1942.7	536.3	2461.9	1925.0	536.9
4	3389.6	442.7	2966.9	979.1	1558.6	768.8	789.8
8	3315.0	406.8	2908.2	1181.8	1593.1	506.9	1086.2
48	2833.5	235.1	2598.4	1456.8	2045.4	242.4	1803.0

[a] Sb-laden Fe-Mn@Al_2O_3 at different time were dissolved in 50 mL 9.6 mol/L HCl solution and analyzed for aqueous Sb species. [b] $S_{Sb(total)}$, $S_{Sb(III)}$, and $S_{Sb(V)}$ are contents of Sb adsorbed onto Fe-Mn@Al_2O_3. [c] $C_{Mn(II)}$, $C_{Sb(total)}$, $C_{Sb(III)}$, and $C_{Sb(V)}$ are concentrations of Mn(II), total Sb, Sb(III), and Sb(V) in aqueous phase at different reaction times , respectively.



Al_2O_3

Element	Wt.%
Al	54.18
O	45.82

Fe-Mn

Element	Wt.%
O	20.87
Fe	59.80
Mn	19.33

Fe-Mn@Al_2O_3

Element	Wt.%
Al	8.50
O	28.95
Fe	46.40
Mn	16.15

Fig. S1 SEM-EDS spectra of (a) Al_2O_3, (b) Fe-Mn, and (c) Fe-Mn@Al_2O_3 (a Fe:Al_2O_3 molar ratio = 1:2).

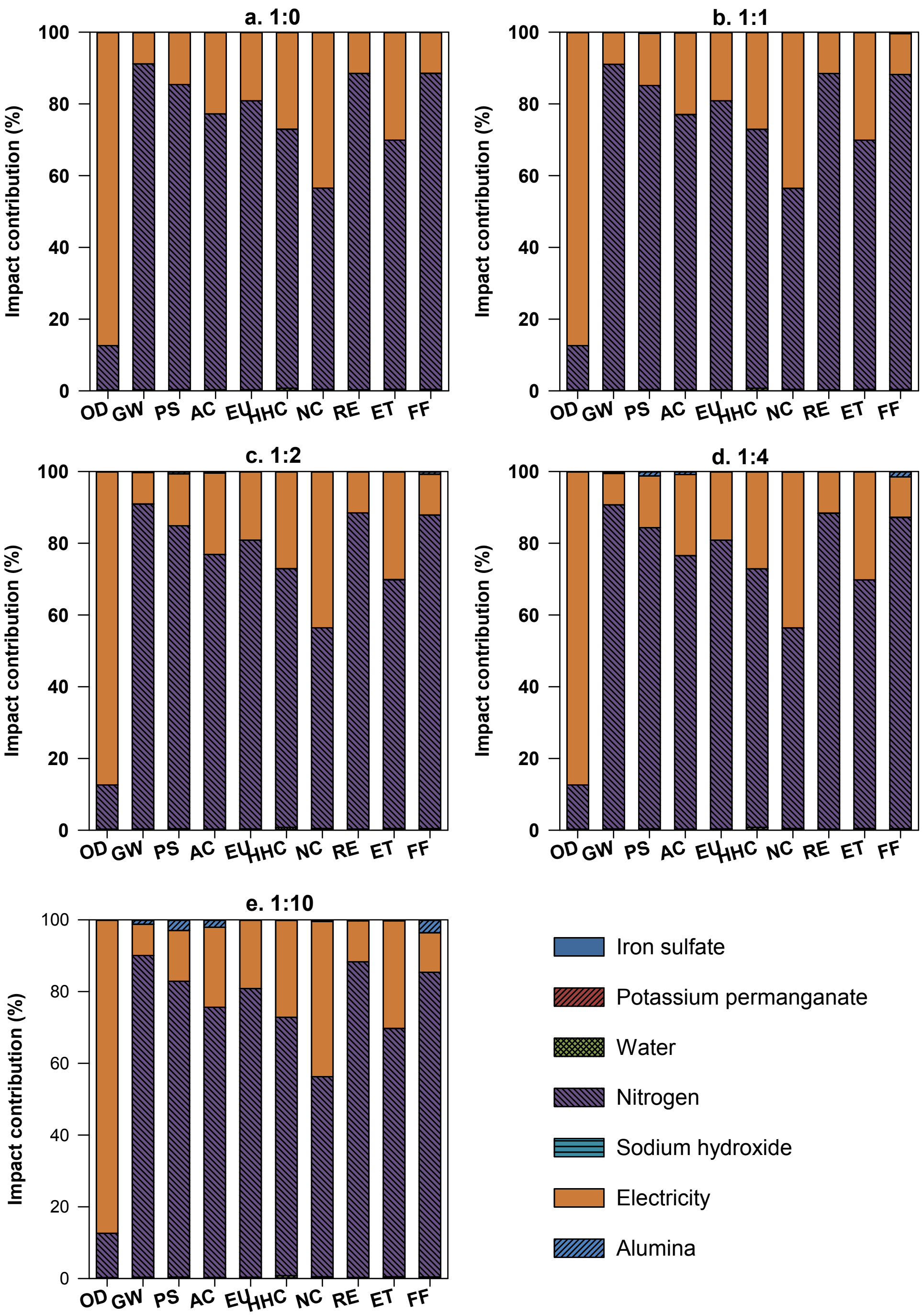


Fig. S2 The environmental impact contributions of all materials and energy inputs for Fe-Mn@Al_2O_3 with various Fe:Al_2O_3 molar ratios: (a) 1:0, (b) 1:1, (c) 1:2, (d) 1:4, and (e) 1:10. Potential impact categories are ozone depletion (OD), global warming (GW), smog (PS), acidification (AC), eutrophication (EU), carcinogenic (HHC), noncarcinogenic (NC), respiratory effects (RE), ecotoxicity (ET), and fossil fuel depletion (FF).

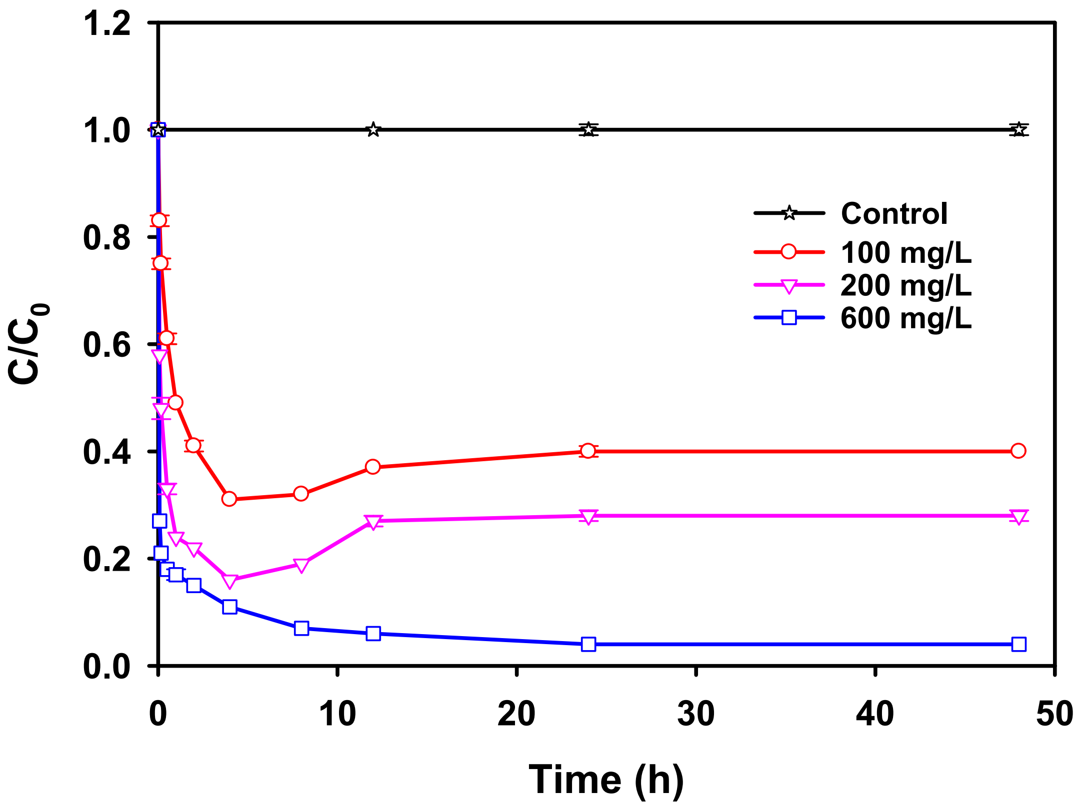


Fig. S3 Effects of Fe-Mn@Al_2O_3 dosage on total Sb removal from simulated surface water. Experimental conditions: Initial Sb(III) concentration = 5 mg/L, Fe-Mn@Al_2O_3 (Fe:Al_2O_3 molar ratio = 1:2) = 100 mg/L, 200 mg/L, and 600 mg/L, reaction volume = 50 mL, pH = 6.4, and equilibrium time = 48 h. Data plotted as mean of triplicates and error bars (calculated as standard deviation) indicate data reproducibility.

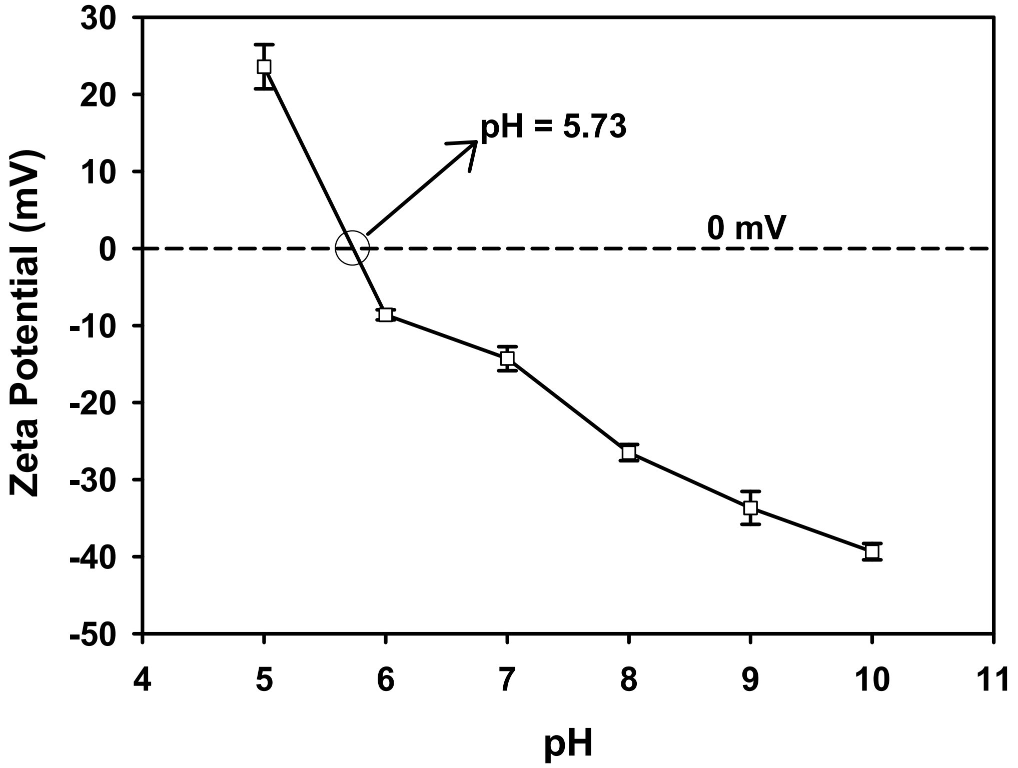


Fig. S4 Net electric charges of Fe-Mn@Al_2O_3 as a function of pH. Experimental conditions: Fe-Mn@Al_2O_3 (Fe:Al_2O_3 molar ratio = 1:2) = 100 mg/L, reaction volume = 50 mL, pH = 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0. Data plotted as mean of triplicates and error bars (calculated as standard deviation) indicate data reproducibility.

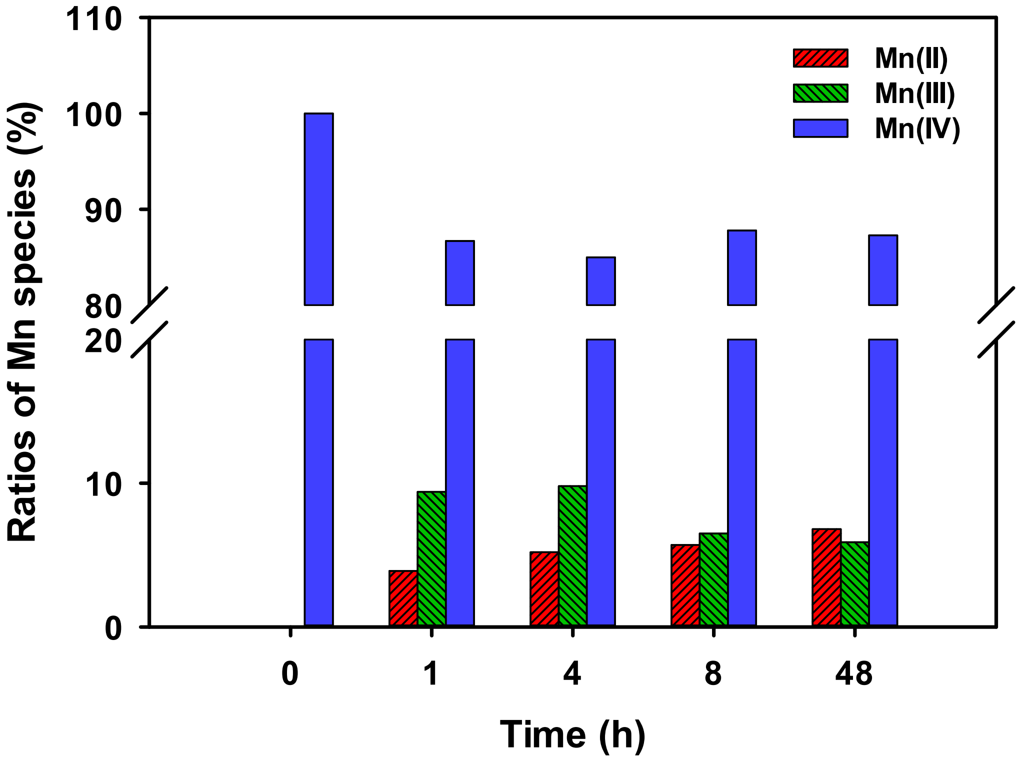


Fig. S5 The ratios of Mn species (Mn(II), Mn(III), and Mn(IV)) to total Mn over reaction.

Notes and references

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