Electronic Supporting Information

Sorption Performances of TiO(OH)(H$_2$PO$_4$)•H$_2$O in Synthetic and Mine Waters

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Content:

Potentiometric titrations

Figure S1. Direct titration curve of H-TiP1 in the presence of 0.1 M NaCl (♦) and the first derivative of the pH titration curve (---).
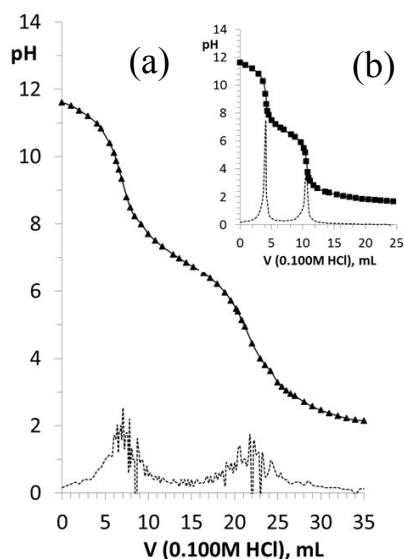
Figure S2. Indirect titration curves of TiP1. (**a**) Suspension composed of 30 mL NaOH solution and TiP1, (**b**) 20 mL filtrated solution above the suspension. The dash lines (---) represent the corresponding first derivatives of the curves.

The indirect potentiometric titration data of TiP1 (in Na^+ form) suspension with 0.100 M HCl are shown in Figure S1. Using these titration curves, the dissociation constants of the first (pKa_1) and second (pKa_2) protons were determined. The pKa_1 was found to be equal to 2.7 for the suspension (Figure S1a) and 2.9 for the filtrated solution (Figure S1b); both values are close to some extent to the pKa_1 for H_3PO_4 of 2.2. As for pKa_2, 7.1 (Figure S1a) and 7.2 (Figure S1b) were estimated for the suspension and the filtrated solution, respectively, which is in good agreement with the pKa_2 of H_3PO_4 being 7.2.

Langmuir model　　　　　Temkin model　　　　　Freundlich model

Figure S3. Linear plots of all sorption isotherms for (**a**) Zn^{2+}, (**b**) Cu^{2+}, (**c**) Ni^{2+}, (**d**) Co^{2+} and (**e**) Mn^{2+} ions on TiP1; plotted according to Langmuir (left column), Temkin (middle column) and Freundlich (right column) model parameters used to simulate the actual q_e data in Figure 4 in the main article.
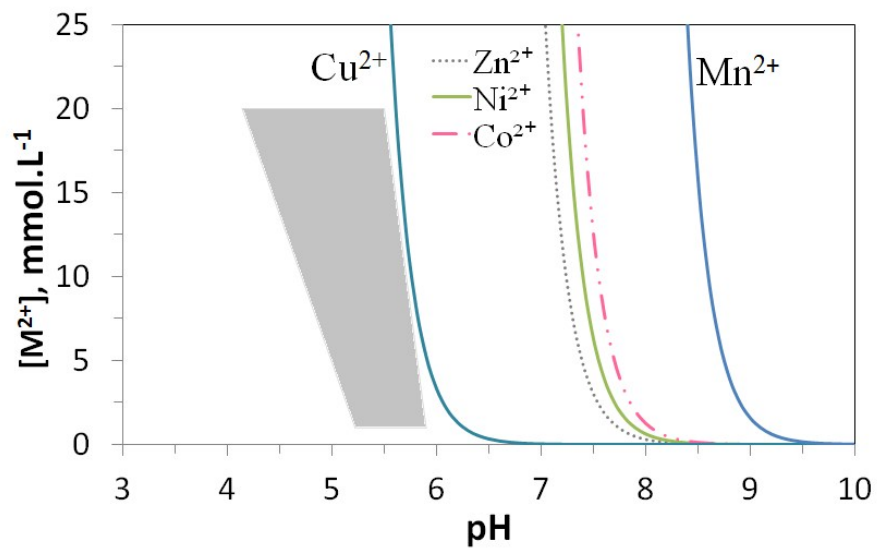
Figure S4. pH influence on solubility/precipitation of metal hydroxides. The grey area represents the range of experimental data throughout the sorption and kinetics studies.
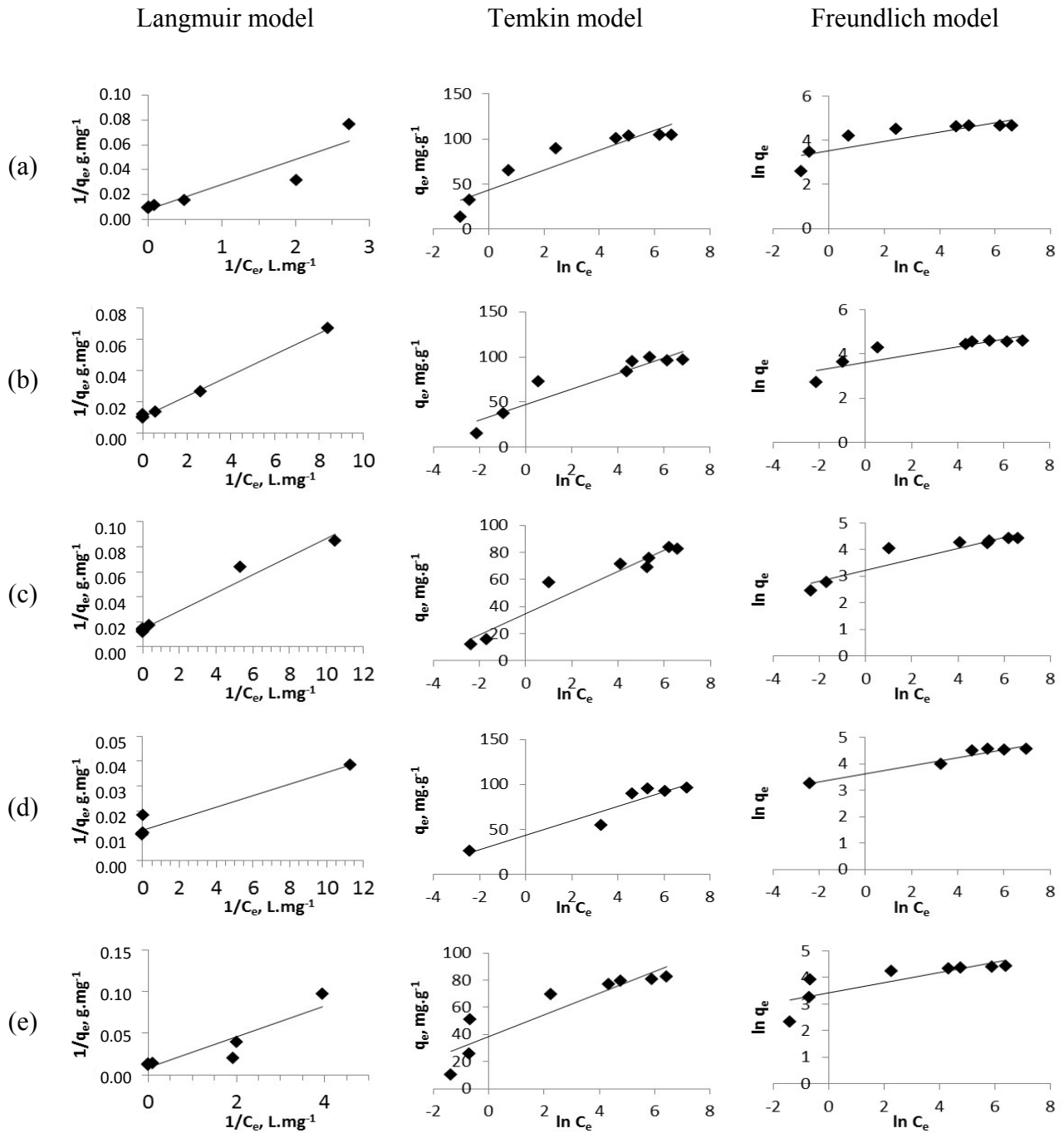
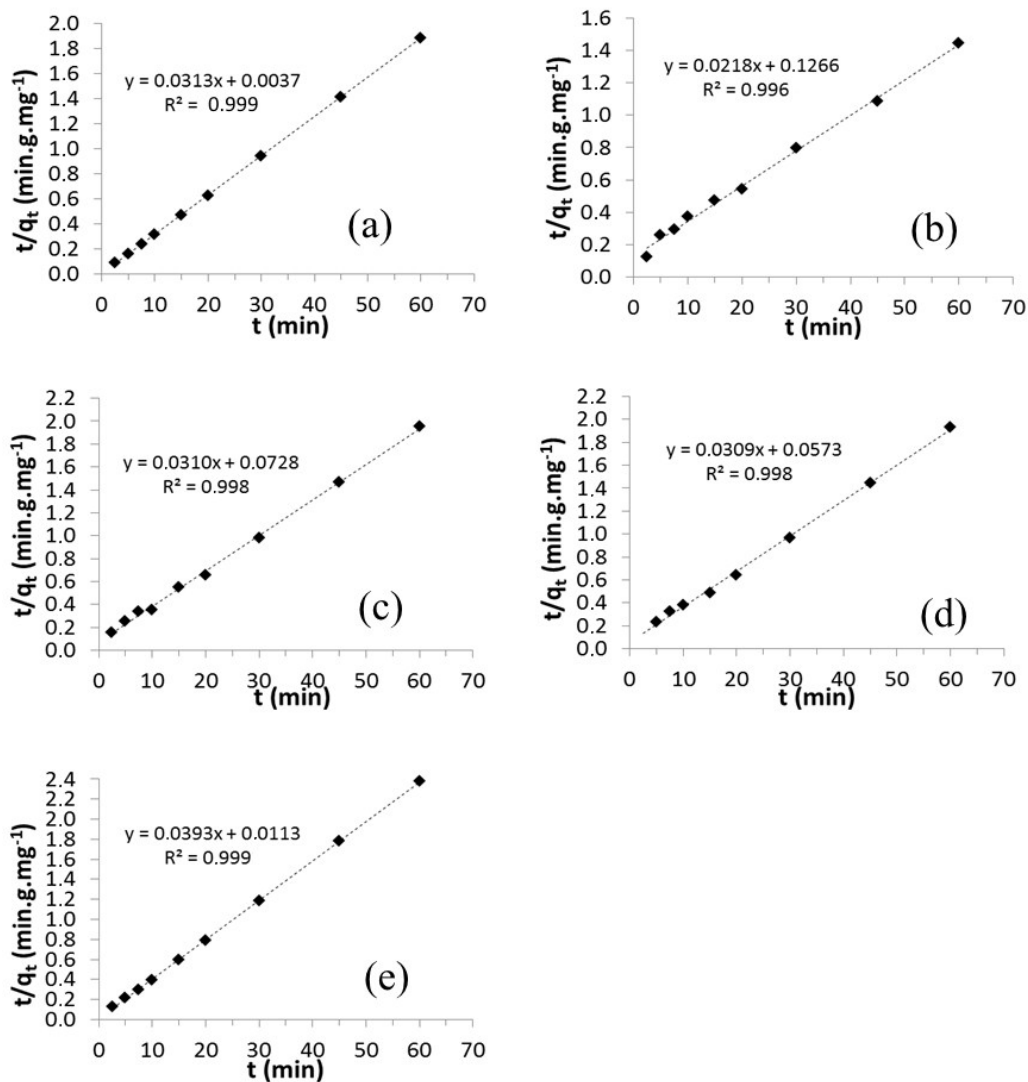**Figure S5.** Linear plots of all kinetic data for (a) Zn^{2+}, (b) Cu^{2+}, (c) Ni^{2+}, (d) Co^{2+} and (e) Mn^{2+} ions on TiP1; plotted according to the pseudo-second order model parameters used to simulate the data in Figure 7 in the main article.

Kinetic experiments – Mathematical models

- Pseudo-first order

The pseudo-first order model developed by Lagergren [S1] can be described using the following linearized equation [S1]:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \tag{S1}$$

with q_e and q_t the amount of metal ion adsorbed at equilibrium and at time t, respectively (mg.g^{-1}) and k_1 the rate constant of the pseudo-first order (min^{-1}). The constant k_1 can be determined from the plot of $\ln(q_e - q_t)$ versus t.

- Liquid film diffusion

The equation rate of the liquid film diffusion was proposed by Boyd *et al*. and the resulting equation can be expressed as [S2]:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_3 t \tag{S2}$$

where k_3 (min^{-1}) is liquid film diffusion constant. The plot of $\ln(1-q_t/q_e)$ versus t *is* a straight line with a slope $-k_3$ when the film diffusion is the rate limiting step.

- Intraparticle diffusion

Weber and Morris have developed the intraparticle model which is based on a linear variation of the solute uptake with $t^{0.5}$ rather than t. The model can be described by equation (S3) [S3]:

$$q_t = k_4 t^{0.5} \tag{S3}$$

where k_4 (mg.g^{-1}.min$^{-0.5}$) is the rate constant of the intraparticle diffusion model. The plot of $\ln(q_t)$ versus $t^{0.5}$ gives a straight line passing through the origin where the slope corresponds to k_4 when the intraparticle diffusion is the rate limiting step.
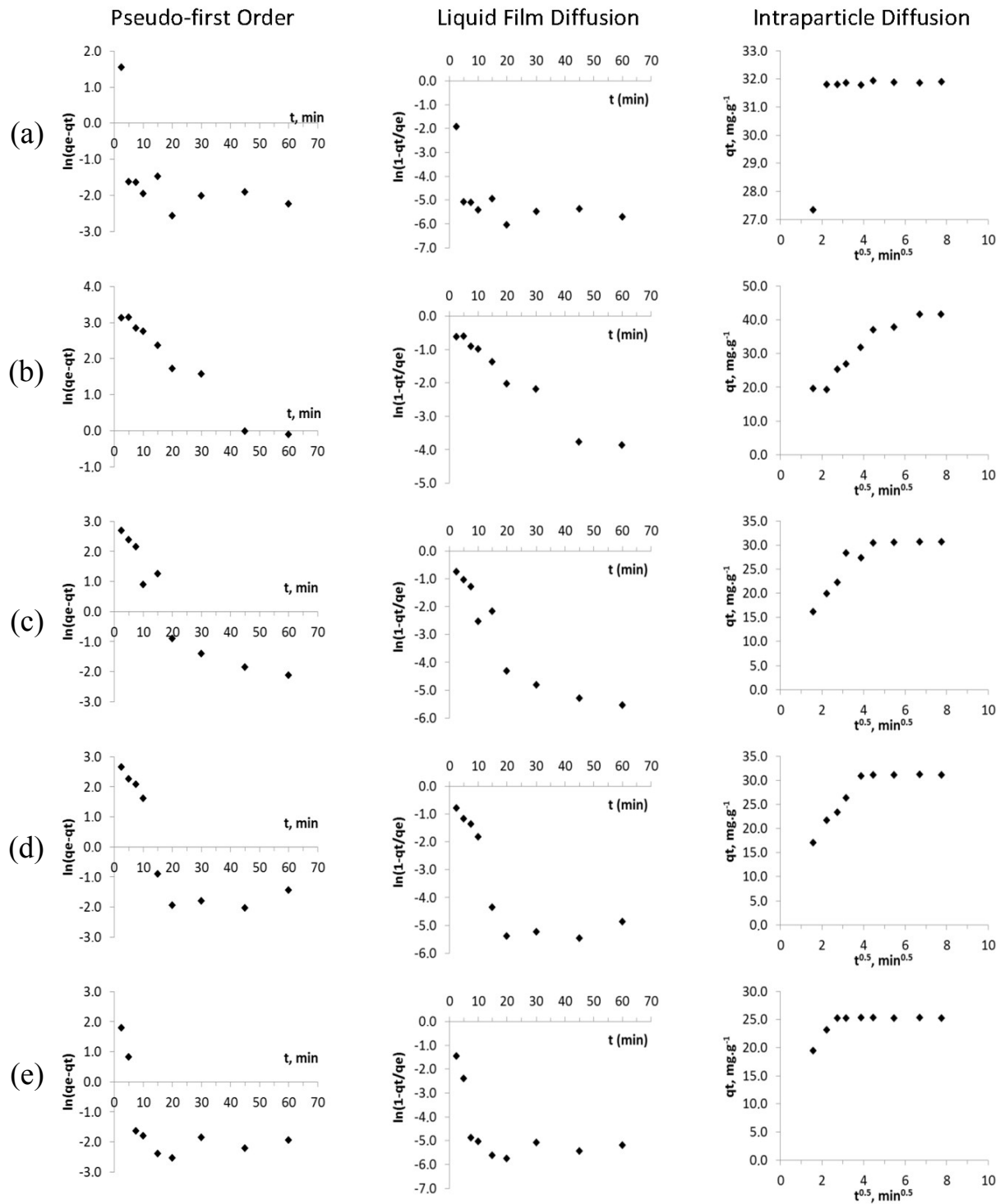
Pseudo-first Order | Liquid Film Diffusion | Intraparticle Diffusion

Figure S6. Linear plots of all kinetic data for (**a**) Zn^{2+}, (**b**) Cu^{2+}, (**c**) Ni^{2+}, (**d**) Co^{2+} and (**e**) Mn^{2+} ions on TiP1; plotted according to pseudo-first order (left column), liquid film diffusion (middle column) and intraparticle diffusion (right column) model parameters.

Figure S7. Linear plots of the first kinetic data points (before the sorption kinetic plateau) for (**a**) Zn^{2+}, (**b**) Cu^{2+}, (**c**) Ni^{2+}, (**d**) Co^{2+} and (**e**) Mn^{2+} ions on TiP1, according to pseudo-first order (left column), liquid film diffusion (middle column) and intraparticle diffusion (right column) model parameters.
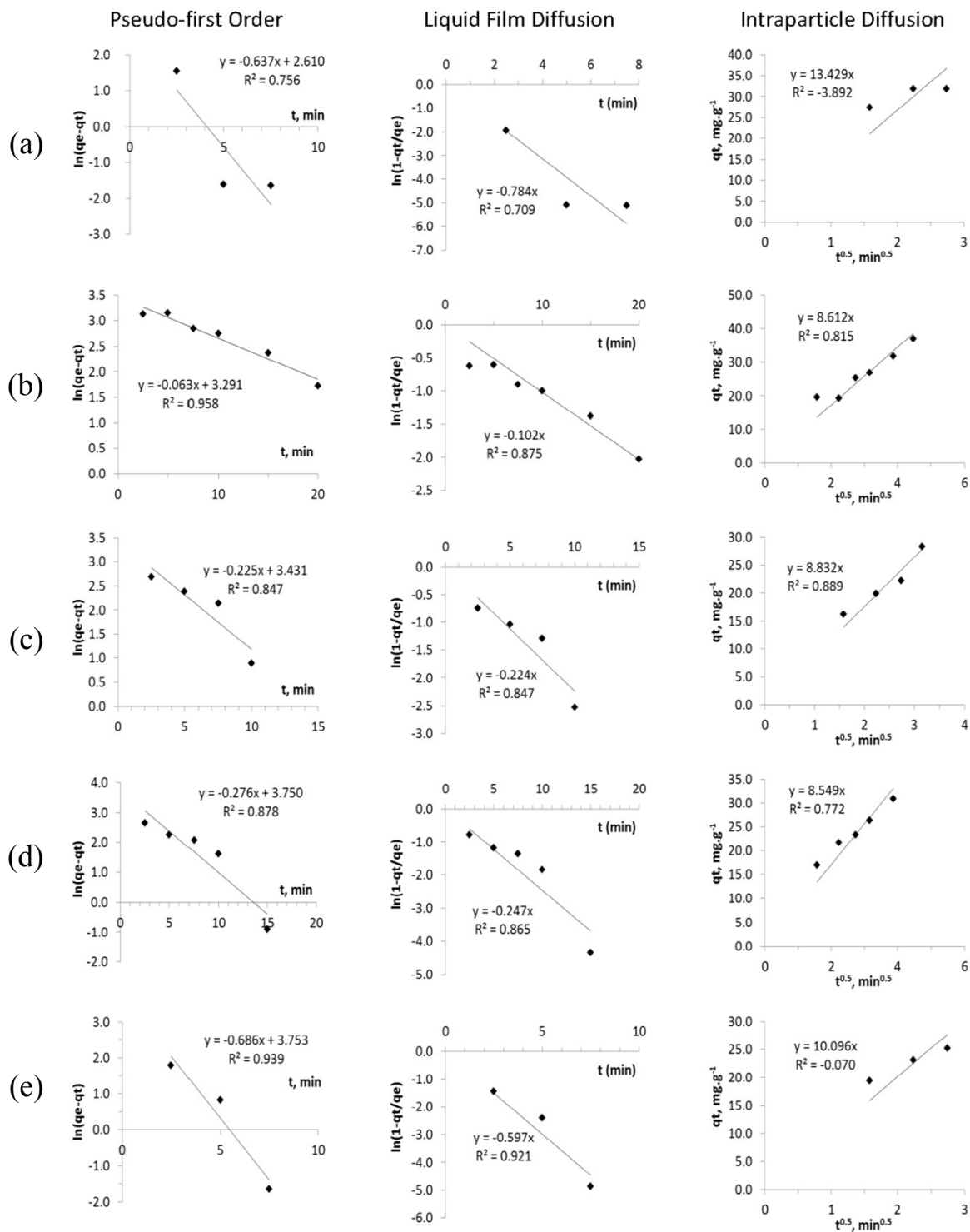
Table S1. Pseudo first-order model parameters for sorption kinetics of Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} ions on TiP1 considering the early steps of the sorption process.

Metal ions	q_e observed from the experimental data	Pseudo first-order model		
	$q_{e, exp}$ (mg/g)	$q_{e, calc}$ (mg/g)	k_1 (min^{-1})	R^2
Zn^{2+}	31.9	13.6	0.637	0.756
Cu^{2+}	41.6	32.2	0.081	0.958
Ni^{2+}	30.7	30.9	0.225	0.847
Co^{2+}	31.1	42.5	0.276	0.878
Mn^{2+}	25.3	42.6	0.686	0.939

Table S2. EDS data (in wt%) for NaTiP in comparison with the calculated values.

	wt% *	wt% (EDS)
Na	12.2	11.0
P	13.3	13.2
Ti	21.5	20.7

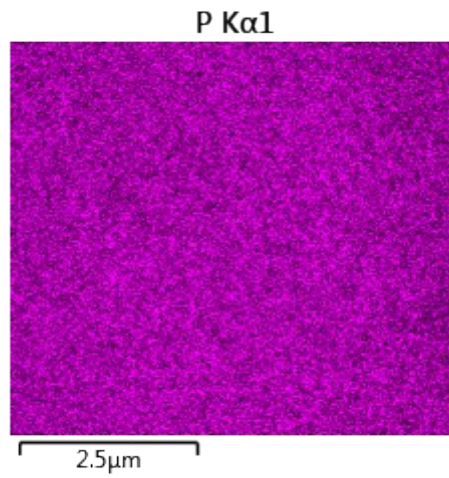* calculated based on the Na$^+$ uptake by TiP1 of 6.3 meq.g^{-1} (see section 3.2 in the main article).
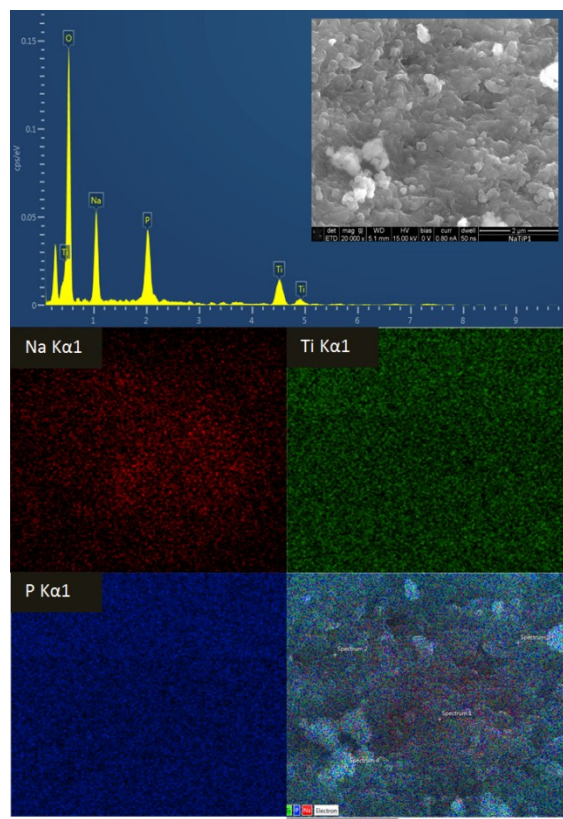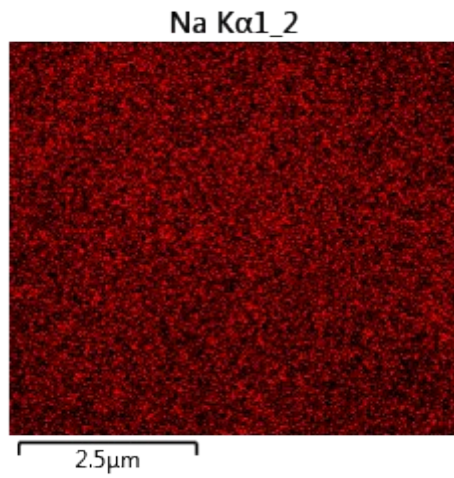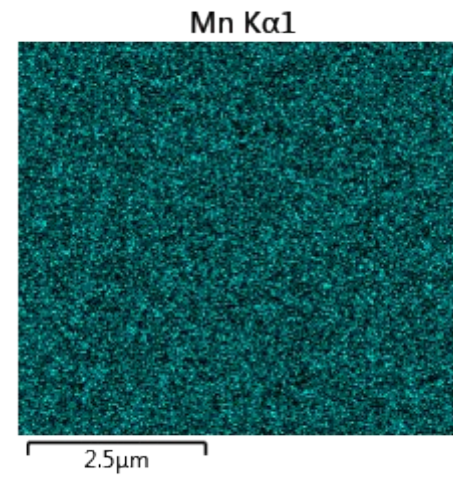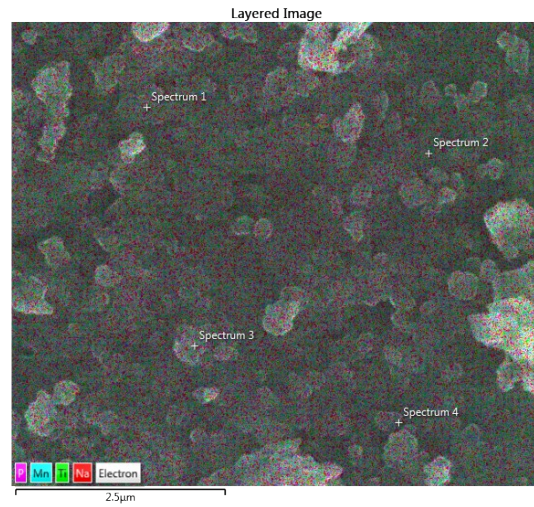

Figure S8. A SEM image and EDS Mapping of NaTiP1 sorbent before sorption experiment.

Figure S9. EDS mapping for M-TiP1 samples with adsorbed M = Cu^{2+}, Mn^{2+} and Ni^{2+} ions.
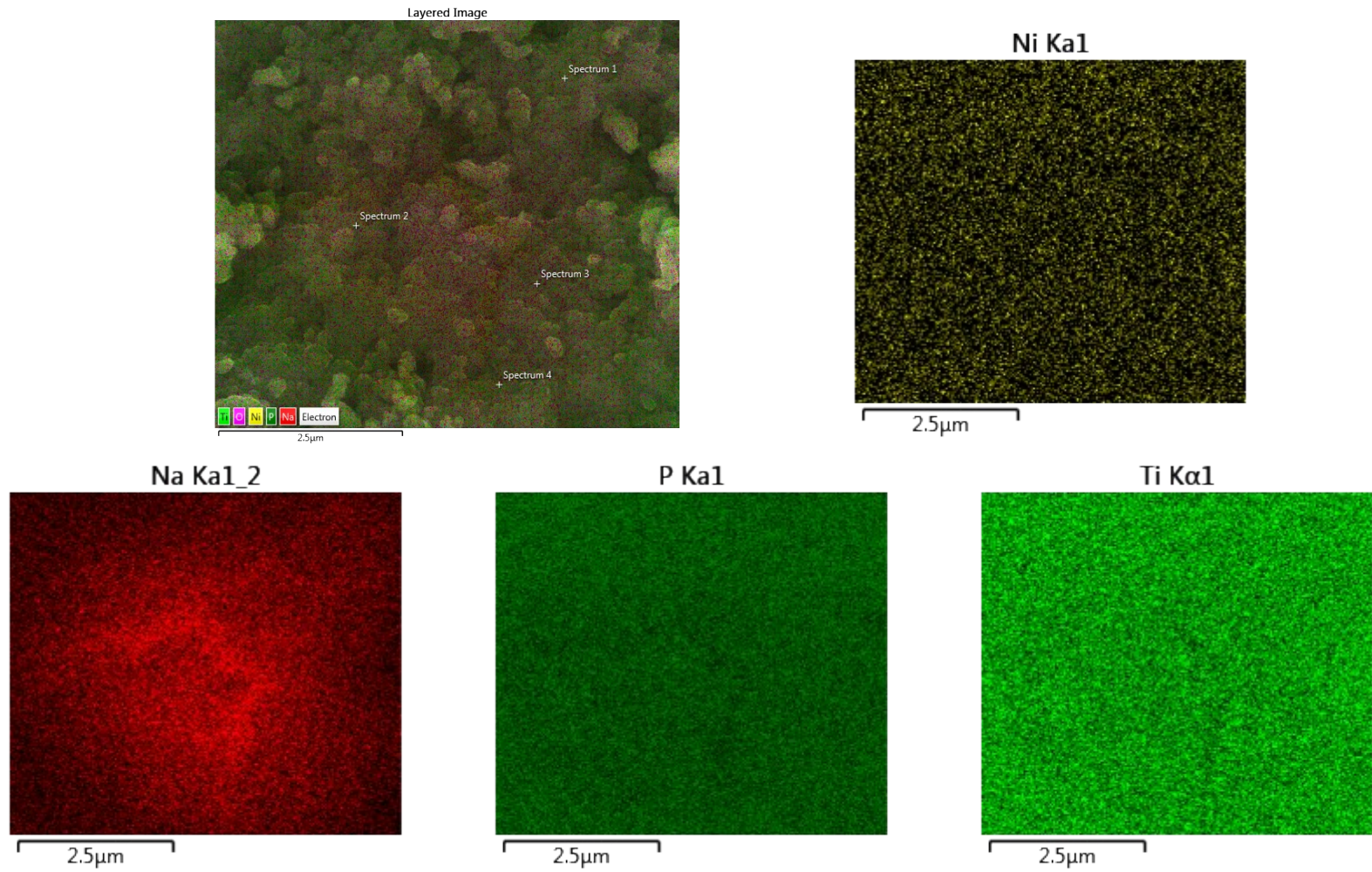
EDS mapping for NaTIP1-Cu Sample
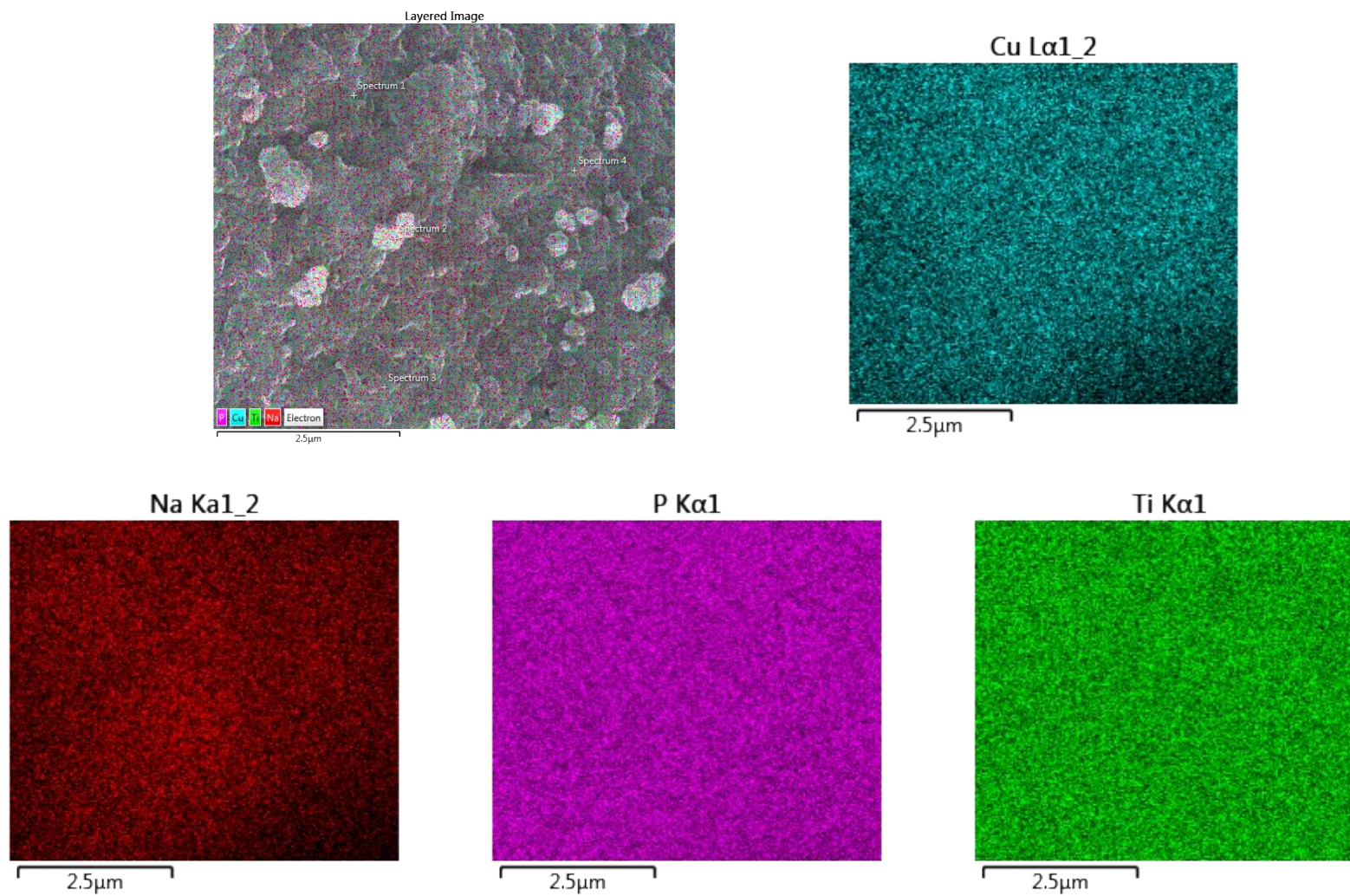
EDS mapping for NaTIP1-Mn Sample
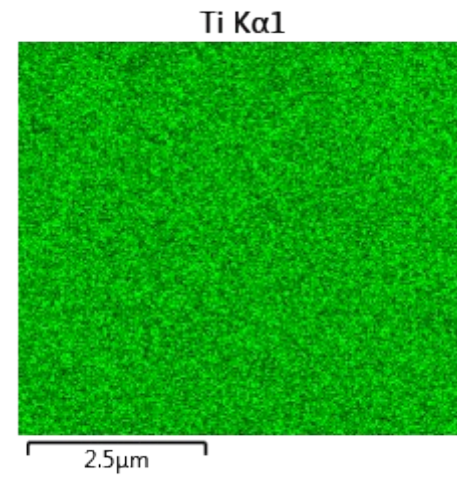
EDS mapping for NaTIP1-Ni Sample

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S1   S. Y. Lagergren, *Zur Theorie Der Sogenannten Adsorption Gelöster Stoffe*, 1898.

S2   G. E. Boyd, A. W. Adamson and L. S. Myers, *J. Am. Chem. Soc.*, 1947, **69**, 2836–2848.

S3   W. J. Weber and J. C. Morris, *J. Sanit. Eng. Div. ASCE*, 1963, **89**, 31–60.