

Competing sorption of Se(IV) and Se(VI) on schwertmannite

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Supplementary Material

1. Freundlich adsorption isotherms of Se(IV) and Se(VI)

The Freundlich model assumes heterogeneous sorption on the surface sites with different energies and is defined as:

$$C(Se)_{SHM} = K_F * C(Se)_{sol}^n$$

where $C(Se)_{sol}$ is the equilibrium adsorbate concentration in solution (mol/L) and $C(Se)_{SHM}$ is the adsorption capacity onto schwertmannite at equilibrium (mol/g). The parameters n and K_f can be determined from the slope and intercept of the equation, respectively, the value of n generally ranges from 0 to 1 as a measure of adsorption intensity; and K_f ($L^n \cdot mol^{(1-n)} \cdot g^{-1}$) is the Freundlich adsorption coefficient.

The data used for the isotherm model were obtained within 48 h, the parameters of the Freundlich equation were obtained through non-linear parameter optimisation using the Microsoft Excel Solver tool.

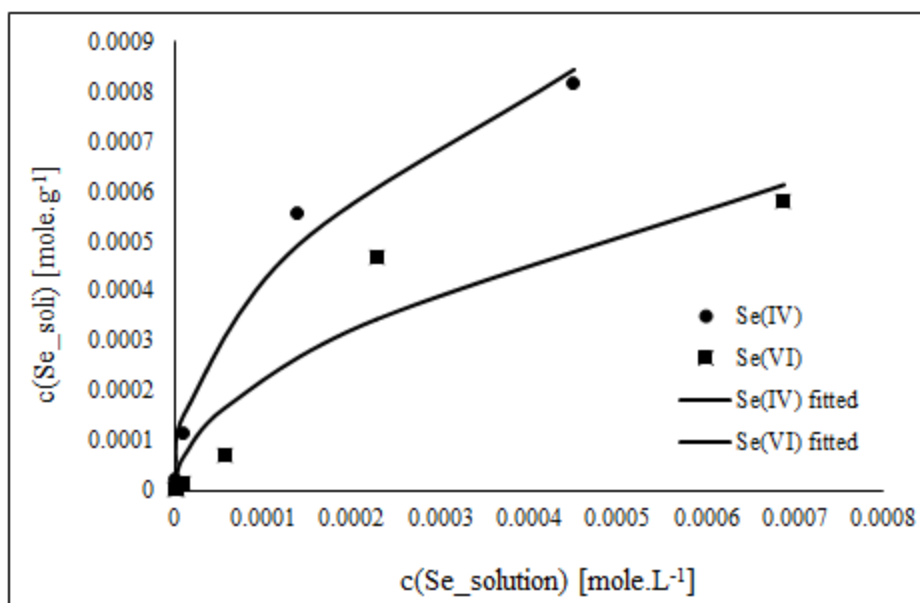


Figure S1. Freundlich isotherms of Se(IV) and Se(VI) onto schwertmannite (SorbS). Black lines represent the fitted values using the Solver tool.

Table S1. Freundlich isotherm parameters for Se(IV) and Se(VI) adsorption

Model	Freundlich	
Parameters	K_f	n
	$(L^n \cdot mol^{(1-n)} \cdot g^{-1})$	
Se(IV)	0.029	0.46
Se(VI)	0.028	0.53

2. Se k-edge XAS analyses

Selenium K-edge (12 658 eV) X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure spectra were collected at the Hard X-ray MicroAnalysis (HXMA) Beamline at the Canadian Light Source (Saskatoon, Canada). During the experiment, the CLS storage ring was under 250 mA operation mode with HXMA superconducting wiggler running at 2.2T. At HXMA beamline, a double crystal Si(111) monochromator was used to provide the monochromatic X-ray for the experiment. The monochromator second crystal was detuned by 50% at the end of the XAFS scan to reduce the high harmonic components in the X-ray beam. The monochromator energy was initially calibrated by using the Se K edge signal from an elemental Se reference foil from the EXAFS Materials Inc., and was further in-step calibrated for each individual XAFS scan by the same Se foil set downstream to the samples. The beamline was configured in its focused mode with Rh mirrors (collimating and focusing mirrors) in the X-ray beam path. The experiment was performed in fluorescence mode by using a Canberra 32 element Ge array detector, equipped with Soller slits, arsenic filters (3 absorption length), and 12 layers of aluminum foil. The latter was used to reduce the effect from the strong Fe fluorescence signal from the sample. Preliminary experiments showed that when sample contain Se(VI) species (either as a single species or in a mixture with Se(IV)), the samples undergo X-ray beam damage if they were under X-ray for too long, and Se(IV) is reduced to Se(0) and Se(VI) is reduced to Se(IV) species at least partially. To avoid this problem, we had to change the X-ray detecting positions for the corresponding samples when a 2nd scan or more scan was necessary. During the experiment, all of the three Oxford ionization chamber detectors were filled with 100% of helium gas. The scan steps for the pre-edge, XANES, and EXAFS regions were 10 eV/step, 0.25 eV/step, and 0.05 Å⁻¹/step, respectively.

3. XRD analyses

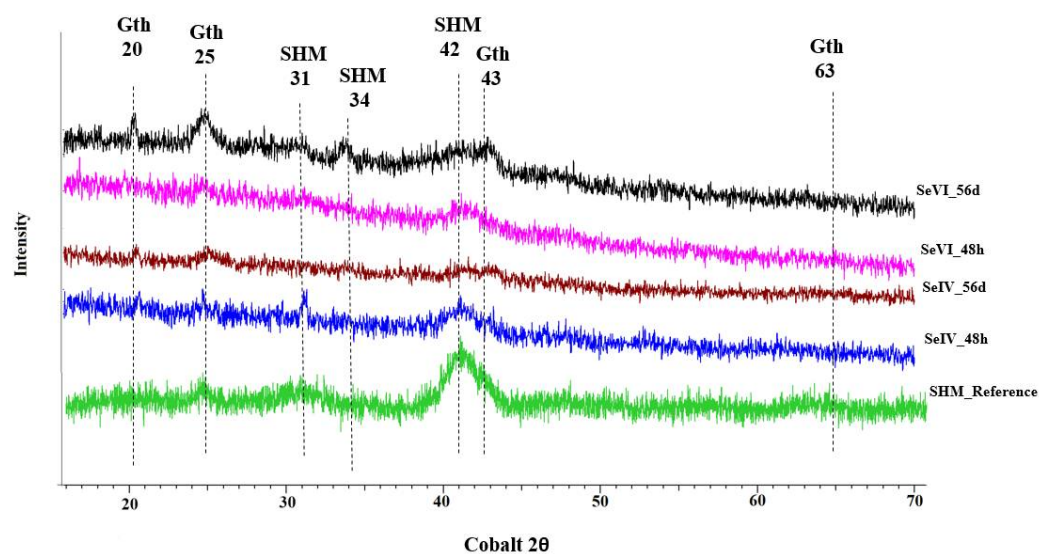


Figure S2. X-Ray diffractograms of SHM samples after 48 h and 56 d sorption reaction.

4. Sulfate release

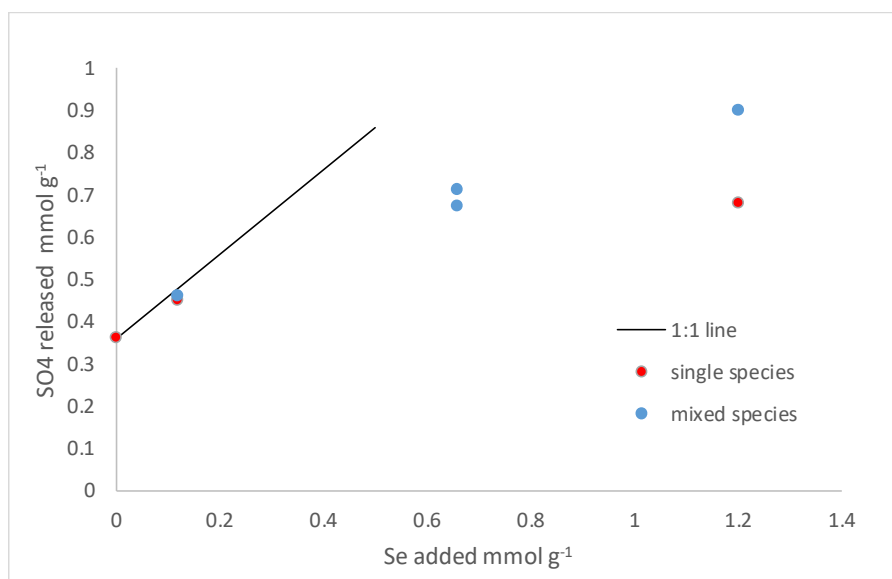


Figure S3. Fraction of SO_4^{2-} (mM) released from SorbS after 48 h at different Se concentration in single-species and mixed-species and in control experiment. Single-species measurements were identical for both, Se(IV) and Se(VI). The straight line indicates the 1:1 ratio of SO_4^{2-} replacement by Se species.

5. Se k-edge XANES and EXAFS

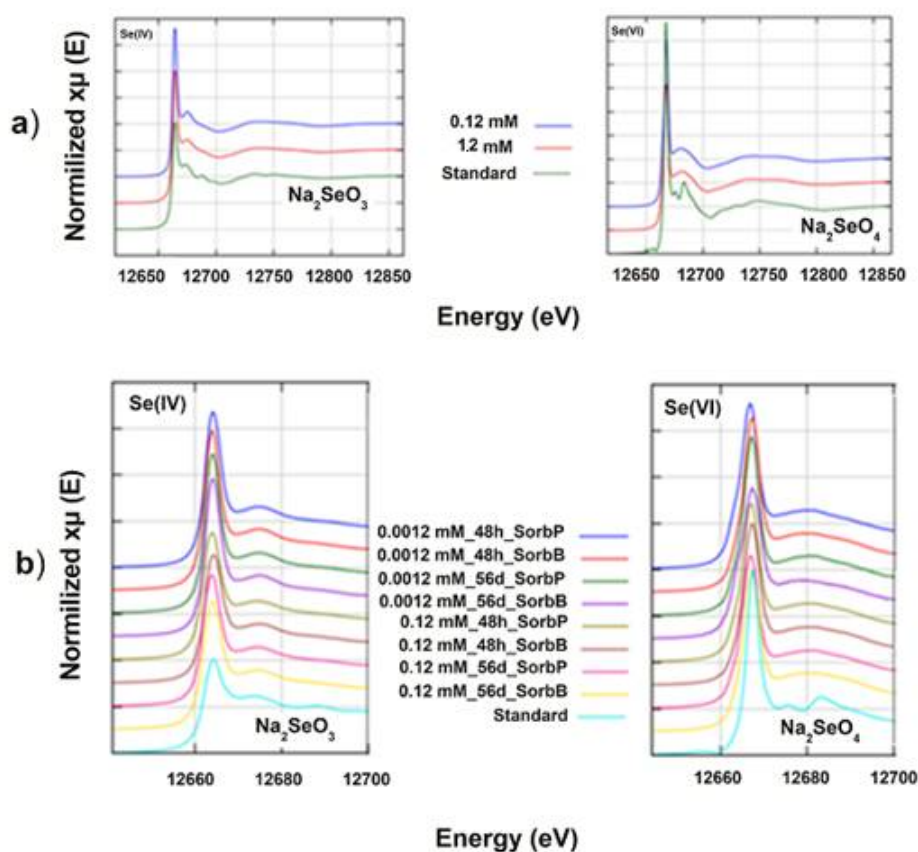


Figure S4. Se K-edge XANES of Se(IV) and Se(VI) adsorbed onto (a) SorbS (1 g/L) at Se loading concentration (0.12 and 1.2 mM) after 48 h and (b) SorbB and SorbP (1 g/L) at Se loading concentration (0.0012 and 0.12 mM) after 48 h and 56 d at pH 3 as well as Na_2SeO_3 and Na_2SeO_4 as references.

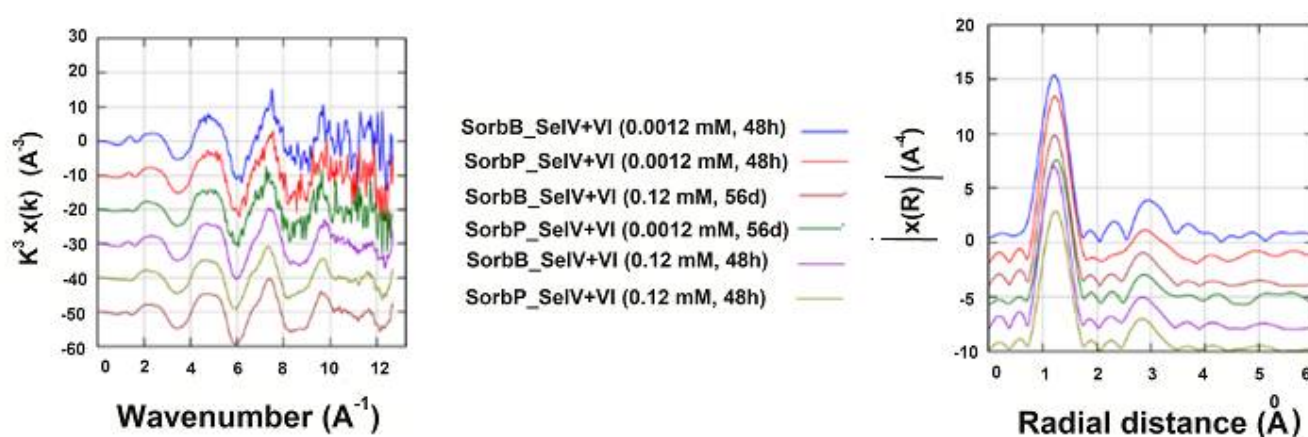


Figure S5. Normalized k_3 -weighted Se K-edge EXAFS spectra (left) and RSF profiles of EXAFS spectra (right) of Se(IV) and Se(VI) in mixture (ratio 1:1) adsorbed onto SorbB and SorbP (1 g/L) at initial Se concentration of 0.0012 and 0.12 mM after 48 h and 56 d at pH 3.

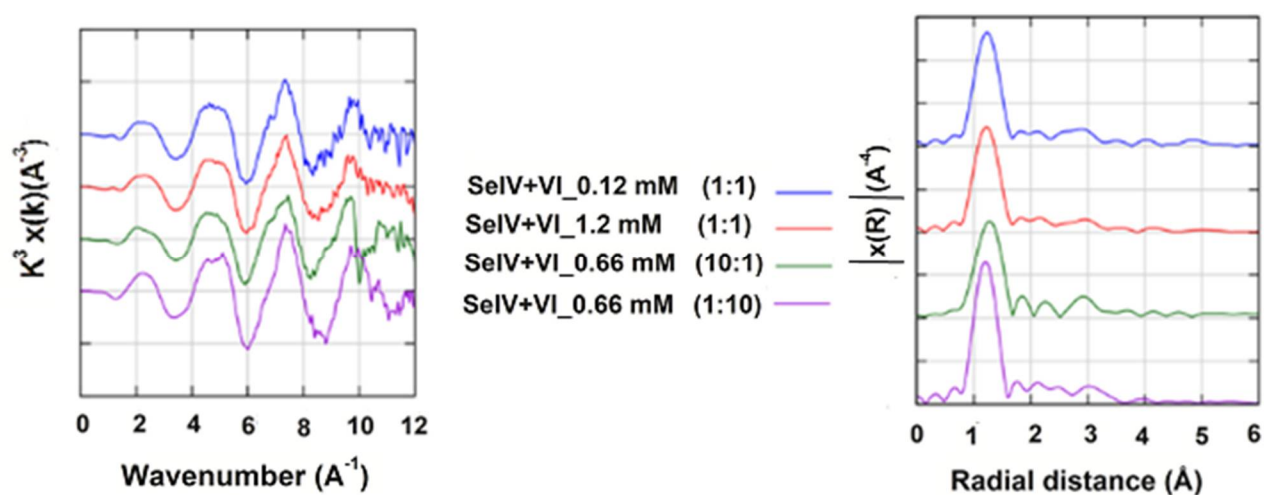


Figure S6. Normalized k^3 -weighted Se K-edge EXAFS spectra (left) and RSF profiles of EXAFS spectra (right) of Se(IV) and Se(VI) in mixture at different ratios (1:1, 10:1 and 1:10) adsorbed onto SorbS (1 g/L) at initial Se concentration of 0.12, 0.66 and 0.12 mM after 48 h at pH 3.