ESRF

ESRF	**Experiment title:** Mechanism of selenate and selenite adsorption on schwertmannite: effect of sulphate and kinetics	**Experiment number**:
Beamline:	**Date of experiment**: from: 07/12/2018 to: 10/12/2018	**Date of report**:
Shifts:	**Local contact(s)**: Dr. Dipanjan Banerjee (BM26)	*Received at ESRF:*

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Report:

Background and objectives

The scientific project studied removal of selenite and selenate species on *schwertmannite*, a nano-crystalline Fe^{III}oxyhydroxy sulfate mineral with a variable composition, typically represented as $Fe_8O_8(OH)_{8-2x}(SO_4)_x$. The substrate showed to be an excellent adsorbent to selectively remove selenium in the presence of high sulphate concentrations. In order to understand the involved mechanisms in the immobilization reaction, XANES and EXAFS was performed at BM26A – DUBBLE at ESRF. In particular, interest lies in unravelling the local structure of selenium oxyanion complexes during the adsorption reaction and verify if chemical changes, such as reduction, oxidation or binding reactions are involved. Finally, fundamental insights gain motivation for maximizing the capacity or achieving low discharge concentrations of selenium, highly beneficial for *e.g.* the aquatic environment to which such waste waters are discharged.

Research outcomes

Transmission mode XAS evaluated the Fe-K (7.112 keV, Figure 1) and Se-K (12.658 keV, Figure 2) absorption edges of (i) *schwertmannite*, (ii) selenium species in solution and (iii) selenium that was adsorbed on the surface of *schwertmannite*. XAFS analysis of *ex-situ* samples, that have reached full chemical equilibrium, confirmed no structural changes of the iron-based structure (Figure 1). The observed stability also correspond to the spectra obtained by XRD and FT-IR, following adsorption of selenium species.

In addition, despite differences in oxidation state of the target metalloid - Se^{IV} versus Se^{VI} – binding to schwertmannite follows a similar mechanism. No redox reactions are involved during the immobilization

(Figure 2), suggesting ionic interactions are a main driver. This preserves the adsorbent to its original state and means saturation is likely due to occupation of active binding sites, alligning with the behaviour from isotherms.

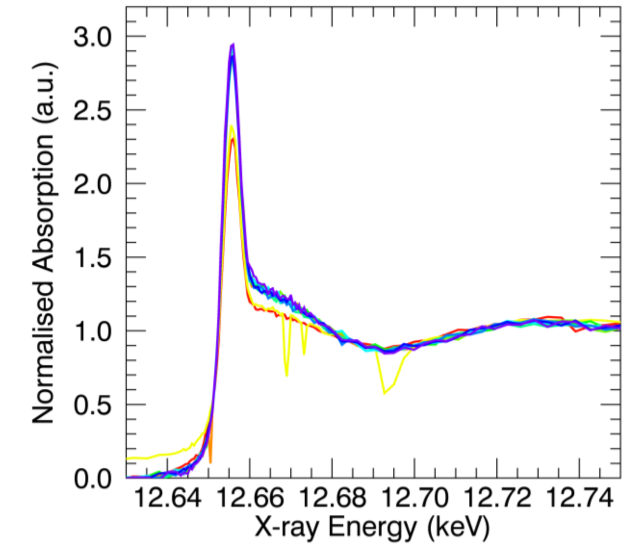

Figure 1. Fe-XANES spectrum of *schwertmannite* prior and after adsorption of Se^{IV} and Se^{VI} from synthetic waste water: no change was seen over time, confirming the *schwertmannite* stability over time.

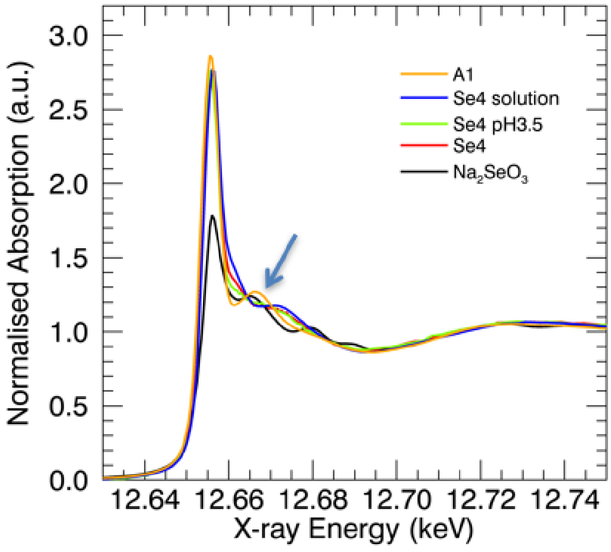

Figure 2. Comparison of Se-XANES spectrum prior and after adsorption of Se^{IV} and Se^{VI} from synthetic waste water. Although no formal change in oxidation potential is observed, adsorption slightly alters the chemical surrounding of Se^{IV} ions.

Short-term Se-XANES spectra were collected (Figure 3) from the *in-situ* measurement right after dosing Se^{IV} and Se^{VI} to a suspension of the *schwertmannite* adsorbent. Constant absorption energies, corresponding also to *ex-situ*, confirmed the preservation of oxidation state during selenium immobilization. The obtained characterization, along with experimental data, provides insights to design a new removal technique that is suitable for hazardous concentrations of selenium in the presence of sulphate ions.

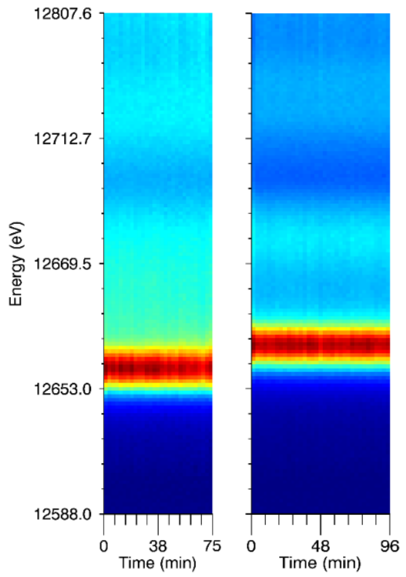

Figure 3. *In-situ* monitoring of X-ray energy absorption (XANES) during adsorption of Se^{IV} (left) and Se^{VI} (right) from synthetic waste water on *schwertmannite*. The constant K_α ‘white’ line suggests that no redox reaction occur during the immobilization.