

Sorption of Se (IV) and (VI) oxyanions from aqueous solutions

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ABSTRACT

Different types of sorbents were tested to selectively remove oxyanions of Se^{IV} and Se^{VI} from model solutions containing various accompanying anions (chlorides, nitrates, sulphates) that simulate real conditions and may affect the sorption of selenium oxyanions. In addition to the optimization of sorption conditions.

The best results of selenite sorption were achieved with sorbent GEH (hydrated iron oxide sorbent) and selenate sorption with Purolite S110 (*N*-methylglucamine functional group). The optimal pH for sorption of Se^{IV} using GEH was found to be 3 and for sorption of Se^{VI} it was pH 4.

Keywords: selenium; removal of selenium; aqueous solutions; sorption; treatment; sorbents; ion exchange

INTRODUCTION

Selenium occurs naturally in the environment. Erosion of rocks and soils may cause a low concentration of selenium in water. Into the air could be selenium released by volcanic eruptions, burning coal or oil. Selenium is an essential trace element of the human body, but it is also toxic in high concentration. In the European Union¹, the selenium limit in drinking water is established to $10 \mu\text{g}\cdot\text{L}^{-1}$.

Selenium is removed from aqueous solutions by such methods as chemical reduction, coagulation-based processes, biological methods, membrane separation, ion exchange, adsorption, etc².

Sorption of selenium was studied at the aluminum oxide/water interface³ and on granular activated carbon⁴ (GAC) and powdered activated carbon (PAC).

For selective removal of inorganic selenium⁵ were used anion-exchange resin and functionalized cellulose sorbent Cellex T. It could be also used phase extraction on Dowex1X2 resin⁶.

Removal by mesoporous activated alumina was studied and the optimal pH for different types of this alumina was found⁷. For example, by using Al-modified bentonite is for sorption of selenite optimal pH 3. Goethite which is also alumina in different form is good for removal of selenite and selenite using pH 4.

It was found that selenate could be adsorbed from water by chitosan-clay polymer and the adsorption is increased with polymer loading on clay⁸.

For selenate removal was also used a chelating resin⁹ (polyamine-type weakly basic ion exchange, prepared from styrene-divinylbenzene copolymer beads immobilizer) which is designed for adsorbing Cr^{VI} .

EXPERIMENTAL

Sorbents used for removal of selenium oxyanions:

- 1) Lewatit MP500- macroporous strongly basic (type I) anion exchanger with trimethylammonium functional groups
- 2) Purolite A 520E- macroporous strongly basic (type I) anion exchanger with

triethylammonium functional groups; is selective for nitrate removal

- 3) GEH- Hydrated iron oxide sorbent; modified $\text{Fe}(\text{OH})_3$
- 4) Purolite S110- macroporous polystyrene based resin with *N*-methylglucamine functional groups; it is designed for the selective removal of boron
- 5) Arsen Xnp- composite sorbent containing 42 % of Fe_2O_3

Lewatit MP500 and Purolite A 520E were converted into chloride (by 5 BV of 1M NaCl) and sulfate (by 10 BV of 1M Na_2SO_4) forms. Purolite S110 was converted into chloride form (by 10 BV of 1M HCl) and hydroxide form (by 10 BV of 1M NaOH). All forms were tested separately. The inorganic sorbents GEH and Arsen Xnp were used in their pure form.

The input solution was prepared from demineralized water, Se^{IV} or Se^{VI} ($0.2 \text{ mmol} \cdot \text{L}^{-1}$), and accompanying ions such chlorides ($1 \text{ mmol} \cdot \text{L}^{-1}$), nitrates ($1 \text{ mmol} \cdot \text{L}^{-1}$) and sulfates ($0.5 \text{ mmol} \cdot \text{L}^{-1}$). Selenite solution was prepared from Na_2SeO_3 and selenite from Na_2SeO_4 . Solution of accompanying ions was prepared from their sodium salts. Input solution had pH 5-6.

All experiments were carried out by batch experiments using a platform shaker (Unimax1010 from Heidolph Instrument GmbH), 500 mL of input solution, and 1 mL of sorbent. Concentrations of selenium were analyzed by ICP-OES technique (CAP 7000 Series ICP-OES by Thermo Fisher Scientific).

The amount of captured selenium in sorbent phase q were calculated according to equation (1), respectively:

$$q = \frac{(c_i - c_e)V}{m_s} \quad (1)$$

Where:

- c_i concentration of ion in the input solution [$\text{g} \cdot \text{L}^{-1}$]
- c_e concentration of ion in the output solution [$\text{g} \cdot \text{L}^{-1}$]
- V volume of the solution [L]
- m_s mass of the sorbent [L]
- q amount of captured ion in sorbent [$\text{g} \cdot \text{L}^{-1}$]

RESULTS AND DISCUSSION

Comparison of sorbents for selenite removal

Batch equilibrium experiments were carried out with different sorbents in various forms. Sorption of Se^{IV} oxyanions by inorganic

sorbent GEH (Figure 1) was very fast than the others, especially exchange resins. The equilibrium was reached after 48 hours where was captured 97 % of Se^{IV} oxyanions (9.2 g for 1 L of sorbent). Arsen Xnp captured lower amount of selenite than GEH, after 6 hours, it reached equilibrium, and the maximum removal of Se^{IV} was $4.9 \text{ g} \cdot \text{L}^{-1}$, from the input solution was captured 53.3 %. Lewatit MP500 reached after 2 hours its maximum sorption of selenite ($4.56 \text{ g} \cdot \text{L}^{-1}$), it was captured 48.67 %. Sorption process of Purolite S110 in OH^- form was as fast as using GEH, but the maximum captured amount of selenite was only 41.42 %. Ion exchange resins in other forms did not even capture 20 % of selenite oxyanions.

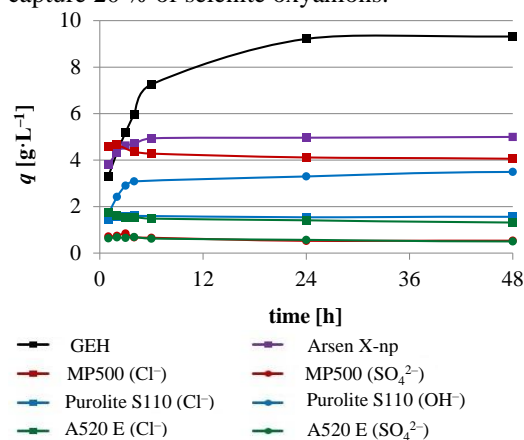


Figure 1 Amount of captured Se^{IV} into 1 L of different sorbents

The GEH was chosen for the next batch experiments which were based on previous experiments. The input solutions had different pH values and were tested to increase the sorption efficiency. After 24 hours, the lowest concentration was measured in the experiment using pH 3 (Table I), it was captured $7.28 \text{ g} \cdot \text{L}^{-1}$ (removed 99.2 %) of Se^{IV} in contrast to the previous experiment where $9.21 \text{ g} \cdot \text{L}^{-1}$ was captured (removed 96.85 %).

Table I Concentration of Se^{IV} during sorption by GEH, using different pH of input model solutions

Time [h]	pH 3	pH 4	pH 6	pH 8
	$c [\text{mg} \cdot \text{L}^{-1}]$			
0	14.68	14.41	14.71	14.67
1	2.29	3.55	4.76	6.83
2	0.76	2.15	3.01	5.72
3	0.48	1.42	2.05	4.48
24	0.12	0.29	0.29	0.45

Comparison of sorbents for selenate removal

For the experiments were used same sorbents and conditions like for selenite oxyanions removal.

Results shows that effective sorbents for the removal of selenate were resins in chloride form (Figure 2). Maximum removal of Se^{VI} oxyanions was reached by resin with *N*-methylglucamine functional groups Purolite S110 and strongly basic (type I) anion exchanger Lewatit MP500, both in chloride form. Sorption by Lewatit MP500 in chloride form was very fast, equilibrium was reached after 2 hours of sorption, where the maximum removal of Se^{VI} oxyanions was 89% (the amount of captured selenate was $8.4 \text{ g} \cdot \text{L}^{-1}$). The equilibrium gradually stabilized using Purolite S110 in chloride form. It reached its maximum removal after 4 hours of sorption where the amount of captured selenate was $7.8 \text{ g} \cdot \text{L}^{-1}$. The maximum removal of Se^{VI} oxyanions after 4 hours was 6 % higher than using Lewatit MP500 at the same time.

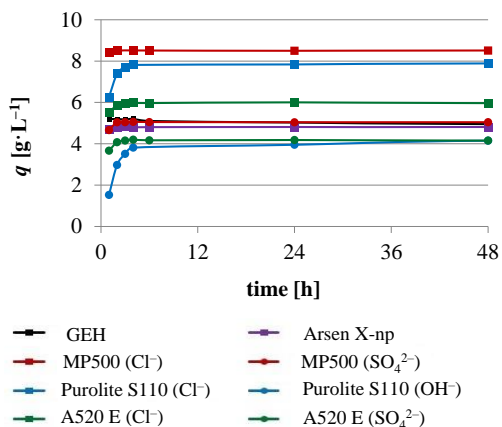


Figure 2 Amount of captured Se^{VI} into 1 L of different sorbents

Purolite S110 and Lewatit MP500 were same effective sorbents for the selenate removal but for next experiments was chosen Purolite S110 because its long sorption process (after 144 hours the concentration on the output was still decreasing). The optimal pH of the input solution was tested.

Experiments with different pH values of the input solution were carried out (Table II). The output concentration of selenate was similar using pH 3, 4 and 5. The maximum removal was reached after 24 hours with pH 4. It was removed 97 % of Se^{VI} oxyanions (the amount of captured selenate was $8.15 \text{ g} \cdot \text{L}^{-1}$).

Table II Concentration of Se^{VI} during sorption by Purolite S110, using different pH of input solutions

Time [h]	pH 2	pH 3	pH 4	pH 5
	<i>c</i> [$\text{mg} \cdot \text{L}^{-1}$]			
0	16.39	16.47	16.80	16.74
1	6.37	3.52	2.80	3.37
2	4.82	1.76	1.23	1.67
3	4.04	1.09	0.76	1.02
24	3.31	0.69	0.50	0.69

CONCLUSIONS

Batch equilibrium experiments have shown that GEH is most suitable for the removal of Se^{IV} oxyanions. The sorption efficiency was increased by 2.35 % after using the input solution with pH 3 compared to experiments using pH 5-6.

Effective sorbents for the removal of selenate were resins in chloride form such a Purolite S110 and Lewatit MP500. Purolite S110 because its long sorption process was tested using input solution with pH 4. The sorption efficiency using pH 4 increased by 1.4 % in contrast to the previous experiment with pH 5-6.

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