SELENITE REMOVAL FROM WATER USING A POLYMER/HYDRATED IRON OXIDE COMPOSITES

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The removal of selenite (SeO_3^{2-}) was investigated using a new polymer/ hydrated iron oxide composites. These composites may have potential applications in reducing or entirely eliminating selenite from contaminated drinking water or industrial wastewaters, especially those from flue gas desulphurization. Commercially available ion exchange resins were irreversibly impregnated by hydrated iron oxide to increase selenite removal from model water solutions simulated contaminated drinking water containing various accompanying anions such as nitrates and sulfates, that may affect the sorption of selenite. By batch experiments the effect of the accompanying ions and pH of the input model water solutions on the selenite removal was investigated. The results of the measurements show that the most suitable sorbents for the removal of selenite from aqueous solutions are macroporous sorbents, which contained more hydrated iron oxide in their structure and thus showed higher selenite removal efficiency than gelular composites. It was found that the prepared composites achieved the highest efficiency of removed selenite at low pH, whereas the optimum pH for commercially available sorbents was in the neutral range. Reduced selenite removal efficiencies from the solution were primarily observed for macroporous composites in the presence of sulfates, either alone or when mixed with nitrates.

Key words: Removal, selenite, ion exchange, composite, adsorption

Received 21. 3. 2025, Accepted 26. 3. 2025

1. Introduction

Selenium occurs naturally in five oxidation states: (–II), (–I), (0), (IV), and (VI), with the (IV) and (VI) oxidation states known as soluble oxoanions. Among these, (IV) is more toxic than (VI) [1]. Erosion of rocks and soils may cause a low concentration of selenium in water. The anthropological release of selenium into the environment occurs during coal mining and its subsequent processing, possibly via fly ash from combustion processes [2]. The selenium concentration in fly ash ranges from 0-49.5 mg·kg^{-1}, in bottom ash 0.007–9 mg·kg^{-1}, in slag 0.1–14 mg·kg^{-1}, and in materials from flue gas desulphurization 0.015–162 mg·kg^{-1} [3].

The ash is then mixed with water and discharged as sludge into ponds, lagoons or the ocean [4]. In its dry form, ash is disposed of in landfill by mixing it with waste gypsum from desulfurization [5]. High concentrations of selenium can subsequently occur in soil and water, which can cause leaching and subsequent contamination of water sources intended for drinking purposes.

Due to selenium toxicity in high concentration, the WHO [6] proposed a strict drinking water limit of 40 µg·L^{-1} and in the Czech Republic [7], the selenium limit concentration in drinking water is established to 10 µg·L^{-1}. The maximum permissible concentrations of selenium in wastewater have been set at 100 µg·L^{-1} according to a Czech government regulation [8]. Selenite removal can be done by many known methods such as chemical reduction [9], coagulation [10], biological methods [11], adsorption, and ion exchange technology [12]. The preparation of composite sorbent by impregnation with hydrated iron oxide has already been done in other study but with different polymer matrix [13]. The effect of sulfates on the removal of selenite from wastewater after flue gas desulfurization in a coal-fired power plant was also investigated using commercial iron oxide impregnated strong base anion exchange resin [14].

Based on the results of a previous study, high selenite removal efficiency was found for sorbents with iron content in their structure [15]. On a strong base anion exchange resin, oxoanions of selenite are removed through a pure ion exchange mechanism. In the case of the chelating sorbent in its free base form, cyclic complexes are formed between the diol groups and the oxoanions [16]. When the chelating sorbent is in the hydrochloride form, complex formation occurs alongside classical ion exchange at the protonated nitrogen. For inorganic sorbents based on hydrated iron oxides, selenite removal begins with interaction between the charged surface of the oxide, leading to the formation of inner-sphere complexes [17, 18]. The removal mechanism of selenite by composites depends on the original matrix as described above. In the case of a chelating sorbent composite, the mechanism combines ion exchange and complex formation with both the resin’s functional group and the hydrated oxide surface. If the composite consists of an anion exchange resin matrix, the sorption mechanism combines ion exchange and complex formation with the hydrated oxide [19, 20].

DOI: 10.35933/paliva.2025.01.02

2. Experimental part

2.1. Materials

The commercially available ion exchange resins used as matrixes for preparing composites:

- Lewatit MonoPlus M 600

Monodisperse strongly basic, gelular anion exchange resin (type II) based on styrene-divinylbenzene copolymer with quaternary ammonium functional group. Total capacity is min. 1.3 eq·L–1 and mean bead size is 0.62 (±0.05) mm. [21]

- Purolite S110

Chelating macroporous polystyrene based resin with N-methylglucamine functional groups; it was designed for the selective removal of boron. Total capacity is min. 0.8 eq·L–1 and mean bead size is 0.30–0.85 mm. [22]

- Lewatit MonoPlus M 800

Monodisperse strongly basic, gelular anion exchange resin (type I) based on styrene-divinylbenzene copolymer with quaternary amine functional group. Total capacity is min. 1.4 eq·L–1 and mean bead size is 0.59 (±0.05) mm. [23]

- Lewatit MonoPlus MP 800

Monodisperse strongly basic, macroporous anion exchange resin (type I) based on styrene-divinylbenzene copolymer with quaternary ammonium functional group. Total capacity is min. 1.0 eq·L–1 and mean bead size is 0.62 (±0.05) mm. [24]

The commercially available composites used for comparing:

- Arsen X^{np}

Macroporous composite sorbent based on styrene-divinylbenzene copolymer containing 42 % of Fe_2O_3 for arsenic removal. The mean bead size is 0.3–1.2 mm. [25]

- Lewatit FO 36

Macroporous, monodisperse composite based on styrene-divinylbenzene copolymer, doped with a nano-scale iron oxide film (15 % Fe) covering the inner surfaces of the pores of the polymer bead. This composite is designed for the selective adsorption of oxoanions, such as arsenate or arsenite ions. The mean bead size is 0.34–0.38 mm. [26]

The input solutions (see Table 1) were prepared from demineralized water containing selenite and accompanying anions (sulfates and nitrates). Selenite solution was prepared from Na_2SeO_3 and solutions of accompanying anions were prepared from their sodium salts.

Tab. 1 Concentration of selenite and accompanying anions in the initial solution

	c [mmol·L^{-1}]	q [mg·L^{-1}]
Selenite	0.2– 0.24	18.16– 18.95
Sulfates	0.16– 0.20	15.36– 19.20
Nitrates	0.34– 0.40	21.07– 24.79

2.2. Preparation and characterization of the composites

The composites were prepared following a patented method for composite preparation [27], utilizing various matrixes of Lewatit MonoPlus M 800, Lewatit M 600, Lewatit MonoPlus MP 800, and Purolite S110. Initially, the sorbents were dried in chloride or hydrochloride form, then mixed in a 20% ferric chloride solution dissolved in ethanol. After filtration and drying, the saturated beads were placed in a 25% ammonia solution and stirred for one hour. The resulting composite beads were then washed with demineralized water to eliminate excess ammonia. Each composite was conditioned in a column by recirculating demineralized water acidified with hydrochloric acid until the pH at the column outlet stabilized at 4. Concurrently, the composites were transformed to the chloride or hydrochloride form. The amount of incorporated hydrated iron oxide was determined by decomposition according to the US patent [28].

Macro photographs of the prepared composites were taken by image analysis using a Canon EOS 500D camera (15.1 MPix) with a Canon MP-E 65 mm macro lens. The distribution of beads was determined in the NIS-Elements Advanced Research 3.0 program.

The specific surface area and the pore volume of the prepared composites were determined from equilibrium adsorption isotherms of nitrogen at 77 K using a Micrometrics TriFlex analyzer static volumetric adsorption system. The sorbents were incubated at 50 °C for 48 h under vacuum prior to the adsorption measurements.

The pressure drop was measured using a column (inner diameter 1.3 cm) and a height of the composite bed of 3 cm. The result of the measurement is the dependence of pressure drop (normalized per 1 m of bed height) on the flow rate.

2.3. Batch experiments

The experiments were performed by mixing 0.5 mL of composite with 500 mL of a solution containing only selenite or selenite with accompanying anions. The mixture was shaken at 270 rpm using platform shaker.

The concentrations of selenium were measured by an optical emission spectrometer with inductively coupled plasma ICP-OES (CAP 7000 Series ICP-OES by Thermo Fisher Scientific) with wavelength of 196.09 nm. The concentrations of accompanying anions were measured on an ion chromatograph (ICS 1000, Dionex by Thermo Fisher Scientific).

3. Results and discussion

3.1. Characterization of composites

The prepared composites retained their spherical geometry (see Fig 1), and due to the incorporation of hydrated iron oxide, the Lewatit M 600 (KM600) and Lewatit MonoPlus M 800 (KM800) composites turned dark brown, and the Purolite S110 (KS110) and Lewatit MonoPlus MP 800 (KMP800) composites turned brown-orange.

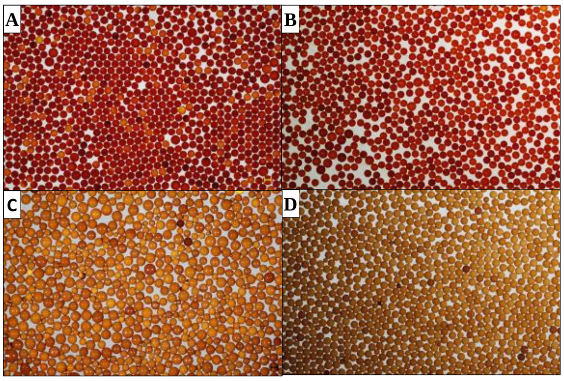

Fig. 1 Photographs of composites with scale of 500 µm. A. KM600; B. KM800; C. KS100; D. KMP800

The specific surface area and pore volume of the gelular composites could not be evaluated because of the small pore size in the dried state and the failure to achieve nitrogen adsorption equilibrium despite vacuum pretreatment. In contrast, the values were measured for macroporous composites, with the composite KMP800 showing lower values than the composite KS110 (see Table 2). This difference could be due to the degree of shrinkage of the composite beads during the drying process. Additionally, the pore volume is likely influenced by the amount of hydrated iron oxide bound to the composite- higher amounts of hydrated iron oxide result in more pore closure, leading to a smaller pore volume in the beads.

Tab. 2 Properties of prepared composites

Sorbent	KM600	KM800	KS110	KMP800
Matrix structure	Poly (styrene-divinylbenzene)			
Type	Gelular		Macroporous	
Mean bead size [mm]	0.54–0.83	0.44–0.79	0.37–1.14	0.35–0.71
Incorporated Fe [%]	2.65	3.48	9.81	14.61
BET surface area [m2·g–1]	–	–	26.85	3.01
Pore volume [cm3·g–1]	–	–	0.10	0.01

3.2. Pressure drop measurements

The pressure drops of commercially available composites and prepared composites were compared. From Fig 2 is seen that the pressure drop of the Lewatit FO 36 composite was up to 2.3 times higher than the pressure drop of the prepared composites. At speeds above 122 $m \cdot h^{-1}$, the pressure drop was so high that it could not be measured. This problem was caused by the very low mean bead size of the composite. On the other hand, the lowest pressure drop was for the composite Arsen X^{np}, which had a larger mean bead size.

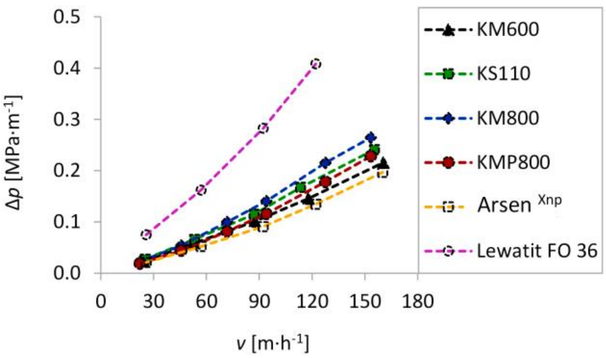

Fig. 2 Comparison of pressure drops of the composites

3.3. Removal of selenite by batch experiments

The optimal pH value was established for selenite removal in the presence of the accompanying anions (nitrates and sulfates). Subsequently, the effect of the accompanying anions on selenite removal was measured at these optimum pH values.

3.3.1 Effect of pH value

The pH values were measured in the range 3-9. The prepared composites showed the highest selenite removal efficiency at the low pH (Fig 3). In contrast, commercially available composites Arsen X^{np} and Lewatit FO 36 showed the highest selenite removal efficiency at neutral pH.

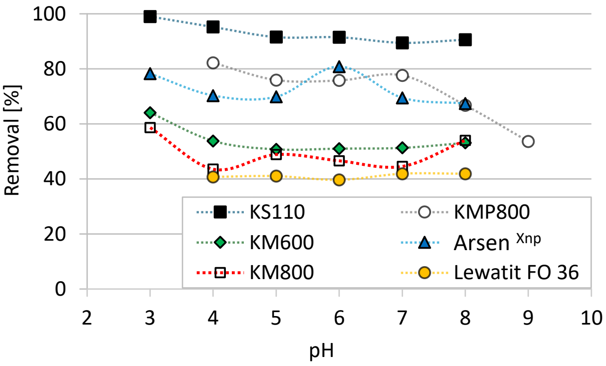

Fig. 3 Removal of selenite in presence of accompanying anions using composites at different initial solution pH, after 144 hours of sorption

The highest selenite removal efficiency was measured for KS110 composite, where a selenite removal efficiency of 99 % was achieved at pH 3, and 88.2 % was achieved for composite KMP800 at pH 4. The two remaining prepared composites had lower selenite removal efficiencies, KM600 composite 64.1 % at pH 4 and KM800 composite 58.7 % at pH 3.

The commercially available sorbent Arsen Xnp also showed a higher selenite removal efficiency of over 80 % at pH 6. Selenite removal was lowest with the composite Lewatit FO 36, which had a removal efficiency of 41.9 % at pH 7.

3.3.2 Effect of accompanying anions

From experiments carried out with accompanying anions, it was found that sulfates, either alone or in mixture with nitrates, had the greatest effect on the removal of selenite (see Fig 4).

Removal of selenite alone was 98.4 % efficient using composite KS110. After adding sulfates to the solution, the removal efficiency decreased by 9.6 %. From the results, it was found that sulfates were removed from the solution as efficiently as selenite, with 96.6 % efficiency. In the mixture of sulfates and nitrates, removal efficiency of selenite was 91.2 %.

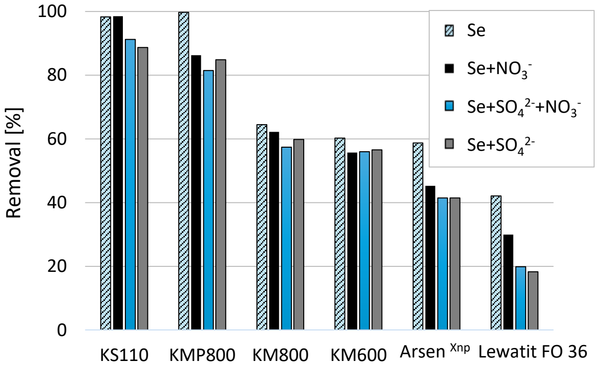

Fig. 4 Selenite removal efficiency in % after 144 hours of sorption in combination with accompanying anions

The composite KMP800 removed over 99 % of the selenite from the solution. However, due to sulfates and nitrates, the selenite removal efficiency decreased by 27.9 %. When only sulfates were presented in the solution, the selenite removal efficiency was 84.9 % and sulfates removal efficiency was almost identical to the KS110 composite.

The remaining prepared gelular composites were not as effective as the macroporous composites in removing selenite. Composite KM800 and KM600 had selenite removal efficiencies from solution of 64.5 % and 60.3 %, respectively. For composite KM800, the highest effect on the selenite removal efficiency was again due to sulfates in the mixture with nitrates, where the selenite removal efficiency decreased to 57.4 %. The selenite removal efficiency of the composite KM600 decreased to 56 % in the presence of nitrate, as well as when both nitrate and sulfate were combined.

The commercially available composites Arsen X^{np} and Lewatit FO 36 showed selenite removal efficiencies of 58.7 % and 42.1 %, respectively. In the presence of sulfates alone, the selenite removal efficiency decreased by 17.3 % for Arsen X^{np} and 23.8 % for Lewatit FO 36. Sulfates removal efficiency was 53.1 % for Arsen X^{np} and 39.6 % for Lewatit FO 36.

4. Conclusions

In this study, polymer/hydrated iron oxide composites were developed. It was observed that macroporous composites (KS110 and KMP800) were more effective for selenite removal compared to gelular composites, likely because they contained a greater quantity of hydrated iron oxide integrated into the polymer matrix. Specifically, the amount of bound hydrated iron oxide was 14.6 % for the composite KMP800 and 9.8 % for the composite KS110.

The prepared macroporous composites showed the highest efficiency of selenite removal from the solution containing the accompanying ions in the acidic pH range. The composite KS110 reached a removal efficiency of just over 99 % at pH 3, while the composite KMP800 achieved 88.2 % at pH 4.

The main factor affecting the efficiency of removal of selenite from the solution was the presence of sulfates, either alone or in a mixture with nitrates. For the composite KS110, selenite removal efficiency was reduced by 9.6 % when sulfates were present alone. In contrast, for the composite KMP800, there was a significant reduction of 27.9 % when both sulfates and nitrates were present together.

The batch experiments revealed that the most effective composites for removing selenite from water are the macroporous composites KS110 and KMP800. However, when higher concentrations of accompanying anions are present in the contaminated water, the composite KS110 proves to be the most suitable choice for selenite removal.

Acknowledgments

This work was supported from the grant of Specific university research– grant No A1_FTOP_2025_001. Additional thanks belong to Associate Professor Miloslav Lhotka for his collaboration on this paper.

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