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Selenium removal from drinking water by adsorption to chitosan–clay composites and oxides: Batch and columns tests

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ABSTRACT

Polymer–clay composites were designed to adsorb selenium from water. The highest adsorption efficiency was obtained for chitosan–montmorillonite composites. These composites were characterized by XRD, zeta potential, and FTIR measurements. Adsorption isotherms of selenate on the composite, on Al-oxide and on Fe-oxide were in good agreement with the Langmuir model, yielding a somewhat higher capacity for the composite, 18.4, 17.2 and 8.2 mg/g, respectively. In addition, adsorption by the composite was not pH dependent while its adsorption by the oxides decreased at high pH. Selenium removal from well water (closed due to high selenium concentrations, 0.1 mg/L) by the composite, brought levels to below the WHO limit (0.01 mg/L) and was selective for selenium even in the presence of sulfur (13 mg/L). Selenium adsorption by the composite was higher than by the Al-oxide due to high adsorption of sulfur by the later. Unlike employment in batch Al-oxide is more suitable for employment in filtration columns due to its high hydraulic conductivity. A semi-pilot columns experiment demonstrated selenium removal from the well water below the recommended limit (first 400 pore volumes) by Al-oxide columns. Regeneration of Al-oxide and of the composite was studied and readsorption of selenium was demonstrated.

1. Introduction

Selenium is a natural trace element found in bedrock, but it is also introduced into the environment by anthropogenic activities, such as mining and combustion of fossil fuels [1,2]. At low concentrations, selenium is an essential micronutrient for mammals, but consumption of quantities exceeding daily recommendations can cause health problems. Its toxicity [3] led the World Health Organization (WHO) and the EU to recommend a maximum selenium concentration in drinking water of 10 ppb, while the EPA sets a limit of 50 ppb.

The technology recommended by the EPA for selenium removal (in its soluble forms as selenite and selenate) is precipitation with ferrihydrite [4]. However, this method is not economical for selenium removal to a level below 50 ppb. Other commonly applied treatments are membrane filtration, microbial reduction and anion exchange. Membrane filtration is expensive, due to low selectivity and fouling problems [5–7]. Microbial treatment, based on reduction to elementary selenium [8,9], is sensitive to oxygen and nitrate and high carbon concentrations are required [10,11]. Ion-exchange resins show selectivity for selenate or selenite [6], but sulfate reduces removal and its precipitation with barium prior to filtration is therefore recommended [12].

The adsorption of selenium by oxides has been studied as a function of pH [13,14], adsorbent surface [13], density of adsorption sites [15,16], adsorbent/selenium concentration [17], ionic strength [14] and competing anions [2,15,18]. The potential of other minerals, such as layered double hydroxides [19] and clays [1,20,21], has been explored as well. Compared to the wide range of studies on selenium adsorption by oxides in suspension including recent ones [22], reports on employing these sorbents in filtration columns are scarce.

In the last few years, polymer–clay nanocomposites have received a great deal of attention, including studies on developing the composites as sorbents for non-ionic and anionic pollutants [23], organic pollutants [5], an anionic herbicide [24] and atrazine [25]. Chitosan–montmorillonite composites have been well characterized [26–28] and the adsorption of anionic pollutants by these composites has been investigated [29,30].

In this study, we designed and characterized chitosan–clay composites and analyzed their efficiency in adsorbing selenium. The kinetics of selenium adsorption and adsorption at equilibrium on the composite, on Fe-oxide and on Al-oxide were studied. The removal of selenium from a well that had been closed due to high selenium concentrations was examined by employing the composite and the Al-oxide in batch and by columns filtration, respectively.

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Regeneration of Al-oxide and of the composite was studied and readsorption of selenium was demonstrated.

2. Materials and methods

2.1. Materials

The clay used in the composite was Na–montmorillonite, SWy-2, from the Clay Mineral Society. Poly(4-vinylpyridine-co-styrene) (PVP-co-S; MW 105k), polydiallyldimethylammonium chloride (PDADMAC; MW 400–500k), [2-amino-2-deoxy-(1-4)-D-glucopyranan] chitosan of medium viscosity (MW 400,000 g/mol, 80% deacetylation; CAS 9012-76-4), iron oxide powder (<5 μm, 99%) and selenic acid (99.95% metal basis) in a 40% (w/w) water solution were purchased from Sigma–Aldrich (Stenheim, Germany). Aluminum-oxide 90 active neutral, 0.063–0.2 mm, was purchased from Merck (Darmstadt, Germany). A Spectro "ARCOS" inductively coupled plasma-atomic emission spectrometer (ICP-AES) (EOP-end on plasma) was used, as well as a CHNSO analyzer (Fisons, EA 1108). Shimron-Israel well water contained 0.09–0.11 mg/L selenium and 12–13 mg/L sulfur equivalent to 0.18–0.22 mg/L selenate and to 36–39 mg/L sulfate (measured by ICP).

2.2. Polycation adsorption on montmorillonite – composite preparation

The composites were prepared by applying batch experiments in polycarbonate Oak Ridge centrifuge tubes. The co-polymer PVP-co-S (1:9 styrene:pyridine) was positively charged and dissolved by adding stoichiometric concentrations of H_2SO_4 and mixing for 1 day. Chitosan was dissolved in an acidified solution (2%, v/v, acetic acid). PDADMAC, chitosan or PVP-co-S solutions (10 mL) were added to a clay suspension of montmorillonite (5 mL), to a final concentration of 0–7 g/L polycation and a suspension of 0.167% clay. The clay–polycation suspensions were agitated for 2 h (to reach equilibrium) on a shaker. Suspensions were centrifuged (10,000 rpm for 20 min) and the supernatant removed; the precipitate was washed with distilled water, recentrifuged and the supernatant removed. The precipitates were freeze-dried, percent carbon was measured using a CHNSO analyzer and the amount of adsorbed polymer was calculated accordingly. Experiments were performed in triplicate.

2.3. Selenate removal by polycation–montmorillonite composites

A selenate solution (10 mL of 1.28 mg/L equivalent to 0.64 mg/L) was added to 0.05 g dried composites in a centrifuge tube reaching a final concentration of 5 g/L. The tube was agitated for 24 h and centrifuged. The supernatant was filtered through a 0.45-μm pore size filter and selenium concentration in the supernatant was measured by ICP. Selenate adsorption on the composites was calculated. Experiments were performed in triplicate.

2.4. Zeta potential

The mobilities (converted to zeta potentials) of montmorillonite and chitosan–montmorillonite composites (0–0.3 g polymer/g clay) were measured using a Zetasizer Nanosystem (Malvern Instruments, Southborough, MA). The clay and clay composites were measured in a dilute suspension (∼0.05% clay).

2.5. X-ray diffraction (XRD)

The basal XRD spacing of montmorillonite and chitosan–montmorillonite composites (0–0.3 g polymer/g clay) were measured. The suspension (1–2 mL) was placed on a ground-glass slide and left to sediment and air-dry for 1 day. The basal spacing was measured using an X-ray diffractometer (Philips PW1830/3710/3020) with Cu Kα radiation, λ = 1.542.

2.6. Fourier transform infrared (FTIR) spectroscopy measurements

FTIR spectroscopy was used to determine the effect of interactions of chitosan on its functional groups and on the clay surface (0.024 and 0.3 g polymer/g clay). Infrared spectra were obtained from composite mixed with KBr pellets, using an FTIR spectrometer (Nicolet Magna-IR-550, Madison, WI). The FTIR spectra were recorded in the range of 600–4000 cm^{-1}.

2.7. Selenate adsorption on composite and on oxide sorbents

The kinetics of selenate (0.22 mg/L) adsorption to the chitosan–montmorillonite composite (0.3 g/g, 0.5 g/L), Al-oxide (0.5 g/L) or Fe-oxide (1 g/L) was studied by adding 0.01 g composite or Al-oxide or 0.02 g Fe-oxide to 20 mL of a selenate solution. Selenate (pH adjusted to 4.5) was added to the sorbents in centrifuge tubes which were agitated for 15–240 min. Selenate adsorption (0.22–20 mg/L) to these sorbents was measured at equilibrium (24 h). Selenium adsorption was calculated as described above. Experiments were performed in triplicate.

2.8. Selenium removal from well water by clay composites–batch experiment

Chitosan–montmorillonite composites (0.019–0.43 g/g) were added to centrifuge tubes with selenate (0.22 mg/L equivalent to 0.11 mg/L selenium), a solution containing selenate (0.22 mg/L) and sulfate (39 mg/L equivalent to 13 mg/L sulfur), or Shimron well water (0.11 mg/L selenium and 13 mg/L sulfur) to a final concentration of 5 g/L (0.05 g composite 10 mL) or in the case of the well water, 10 g/L. Selenium adsorption was calculated as described above (Section 2.3).

2.9. Selenium removal from well water – column experiments

A column filter experiment was performed with Shimron well water in glass columns of 25 cm length and 1.6 cm diameter. The columns were filled with 2 g Al-oxide or composite mixed with 38 g of crushed basalt (inert medium to increase hydraulic conductivity). The experiment was performed in duplicate. Polypropylene geotextile filters were placed on both ends of the column. Prior to filtration, the column was connected to a peristaltic pump and saturated from the bottom with distilled water (3 mL/min). The pH of the Shimron well water was adjusted to 4 with 2 M HCl. The well water (1500 mL) was passed through each column at a rate of 3 mL/min. Eluting water (20 mL) was collected every 400–800 mL for ICP analysis.

A semi-pilot columns experiment was performed with Shimron well water in glass columns of 50 cm length and 5 cm diameter filled with 800 g Al-oxide (pore volume 700 mL). Columns were prepared as described above. The pH of the Shimron well water was adjusted to 4 with 2 M HCl. The well water (400 L) was passed through each column at a flow rate of 40 mL/min, which is equivalent to 1.25 m/h. Eluting water (20 mL) was collected every 30 L for ICP analysis.

2.10. Regeneration of sorbents

Regeneration of the saturated composite (with sulfur and selenium) was performed by rinsing the composite (0.05 g) with NaCl (2 M) or NaOH (pH 10) solutions (10 mL) in centrifuge tubes. The

tube was agitated for 3 h and centrifuged. The supernatant was filtered through a 0.45-μm pore size filter. The concentration of sulfur and selenium in the eluting water was measured by ICP to determine anion desorption. Readsorption was tested by adding 10 mL of well water to the regenerated composite, agitating for 24 h and adsorption was calculated as described (Section 2.3).

Regeneration of the Al-oxide columns (25 cm long) saturated with sulfur and selenium following the filtration experiment was examined. The columns were washed with 5.5 L of NaCl (2 M) or NaOH (pH 10) at a rate of 3 mL/min. The concentration of sulfur and selenium in the eluting water was measured by ICP to determine anion desorption.

The performance of the regenerated filters was examined after rinsing them with 1.5 L distilled water; 70 L of well water was filtered through the column at a rate of 1.25 m/h. Sulfur and selenium concentrations in the filtered water were measured.

3. Results and discussion

3.1. Selenate adsorption by polymer–clay composites

Three polycations–chitosan, PDADMAC and PVP-co-S, were adsorbed at an identical loading of 0.23 g/g on montmorillonite. Selenate (1.28 mg/L) (equal to 0.64 mg/L of Se) showed the lowest affinity to the PVP-co-S composite (82% removal), high affinity to the PDADMAC composite (94%), and the highest affinity to the chitosan composite (99%), which reduced selenate to below the recommended limit (0.01 mg/L).

Electrostatic interactions between selenate and the positively charged composites can account for its removal. We hypothesized that the extremely high removal by the chitosan composite and relatively high removal by the PDADMAC composite may be attributed to the additional anion-exchange sites formed (not only on the external surface) by the intercalation of more than one polymer layer in the clay. Correspondingly, we observed lower selenate removal by PVP-co-S composites in which only one layer of polymer is intercalated [25].

To confirm the intercalation of more than one polymer layer (at high polymer loadings on the clay) and the consequent formation of additional anion-exchange sites, adsorption isotherms of chitosan on montmorillonite were obtained and three analytical methods were applied: zeta potential, XRD and FTIR.

3.2. Characterizing chitosan–clay composites

Chitosan adsorption on montmorillonite does not reach a plateau beyond charge reversal, as reported by [31]; rather, it increases gradually upon addition of high polycation concentrations, reaching a maximum adsorption of 0.3 g/g (1.73 mmol/g) (Fig. 1), similar to previous studies [31]. Zeta potential ranged from −40 mV for the bare clay, to 30 mV upon adsorption of 0.3 g polymer/g clay (Fig. 1). The clay's zeta potential reached zero at a loading which was approximately the calculated loading (0.17 g polymer/g clay) required to neutralize the clay's CEC (0.76 mmol/g). Calculated neutralization was based on stoichiometric adsorption of the positively charged monomers (80% deacetylation). Composites with a loading higher than 0.17 g/g were positively charged indicating that anion (selenate) adsorption may be promoted.

The XRD patterns of montmorillonite and of the chitosan–montmorillonite composites (0–0.3 g/g) are shown in Fig. 2. Montmorillonite gave the expected basal spacing of 1.22 nm, with additional 0.1-nm spacing due to illite impurities. The basal spacing of the chitosan composites at low polymer loadings (0.024–0.154 g/g) increased to 1.46 nm, indicating the intercalation of one polymer layer. However, at the higher polymer
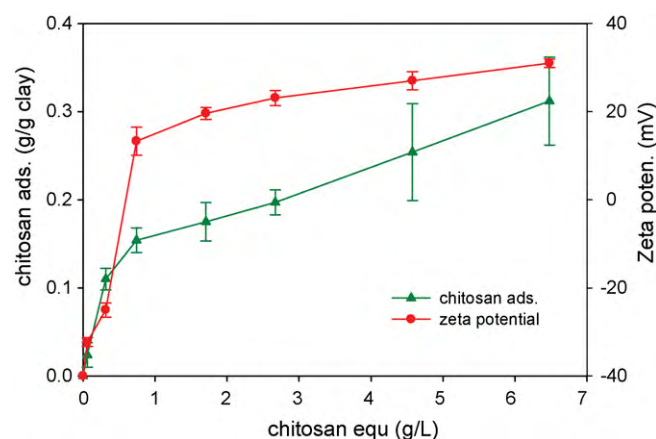

Fig. 1. Adsorption isotherm of chitosan (0–7 g/L) on montmorillonite (1.67 g/L) and zeta potentials of the composites.

loading of 0.23 g/g, the spacings were 1.46 and 2.18 nm, which could be due to the penetration of an additional polymer layer. At even higher chitosan loadings (0.3 g/g), the 1.46-nm spacing appeared but additional spacing was observed at extremely low angles (too low to recorded), which may be due to partial exfoliation. Full intercalation or full exfoliation are not often seen in nanocomposites; most are a mixture of intercalation and exfoliation [32,33].

Intercalation of two PDADMAC [24] and chitosan [26,31] layers at high polymer loadings has been reported. Darder et al. [26] reported a spacing of 2 nm when the clay chitosan ratio was 5:1, similar to the spacing we report for a ratio of 4:1. They showed that an anion-exchange composite can be formed when the chitosan intercalates as a bilayer since the excess –NH$_3^+$ groups, which do not interact electrostatically with the clay, are balanced by the acetate counterions. XRD evidence for an 8.3 nm spacing when the clay chitosan ratio was 12:1 is reported [34].
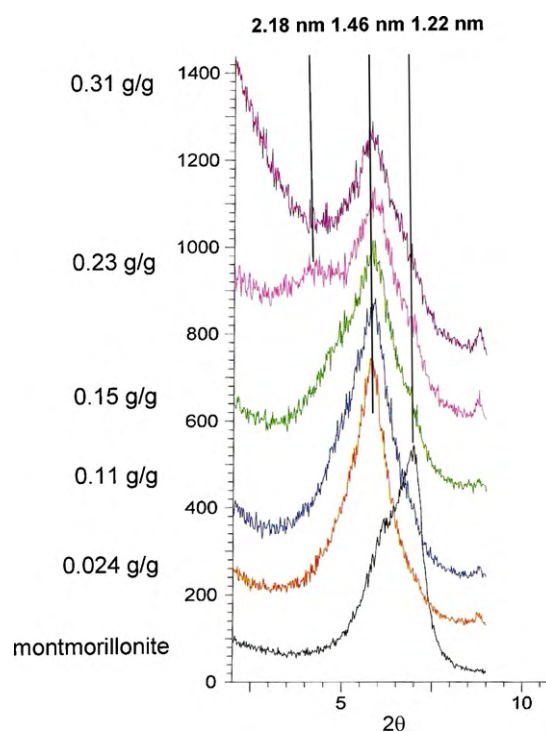

Fig. 2. XRD of montmorillonite and of chitosan–montmorillonite composites (0–0.3 g/g).
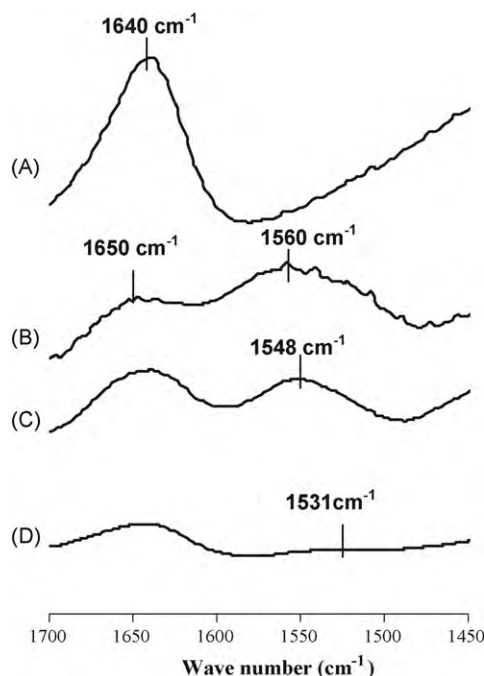
Fig. 3. FTIR spectra (1700–1450 cm^{-1}) of (A) Na–montmorillonite, (B) the chitosan film, and the chitosan–montmorillonite composites with (C) 0.3 g polymer/g clay and (D) 0.024 g polymer/g clay.

FTIR spectroscopy (Fig. 3) showed a shift from 1560 to 1531 cm^{-1} in the –NH$_3^+$ vibration upon interaction of the polycation with the clay. The intensity of the –NH$_3^+$ band increased with increasing chitosan loading on the clay (0.024–0.3 g/g). For the composites with the highest loading (0.3 g/g), in which bilayer composites and partial clay exfoliation were observed, a wave number value (1550 cm^{-1}) that tended toward that observed in the films of pure chitosan was obtained. This band is attributed to the –NH$_3^+$ groups that do not interact with the clay and are available for selenate binding. Similar results were reported for chitosan [26] and for PDADMAC [24]. The CO band of the chitosan at 1650 cm^{-1} overlapped with that of the water in the clay.

Since the chitosan–montmorillonite composite which is derived from a natural polymer removed selenate with the highest affinity, we further explored this composite for the removal of selenium.

3.3. Selenate adsorption by a chitosan–clay composite and oxide sorbents

The removal of selenate (0.22 mg/L equivalent to 0.11 mg/L Se) by the Al-oxide as well as by the composite was relatively fast (nearly complete, within detection limits, 15 min), whereas removal by the Fe-oxide was very slow (Fig. 4A). The adsorption isotherms (Fig. 4B) were in good agreement with the Langmuir equation ($R^2 = 0.97$–0.98). The binding coefficient of the composite was (0.7 L/mg) in comparison with those of the Fe-oxide (1.04 L/mg) and the Al-oxide (1.2 L/mg). The calculated parameters indicated a lower capacity of the Fe-oxide, 8.2 ± 0.04 mg selenate/g, in comparison with those of Al-oxide and the composite, which were 17.2 ± 0.06 and 18.4 ± 0.04 mg/g, respectively. In addition, the adsorption of selenate by the composite was not pH dependent, whereas the adsorption by the Al-oxide decreased at high pHs as reported by other studies [14,16,17]. For example, upon adding 0.22 mg/L selenate at pHs 4 and 7 the adsorption by the composite (0.31 g/g) was approximately complete at both pHs but the adsorption by the Al-oxide decreased from 100% at pH 4 to 40% at pH 7.
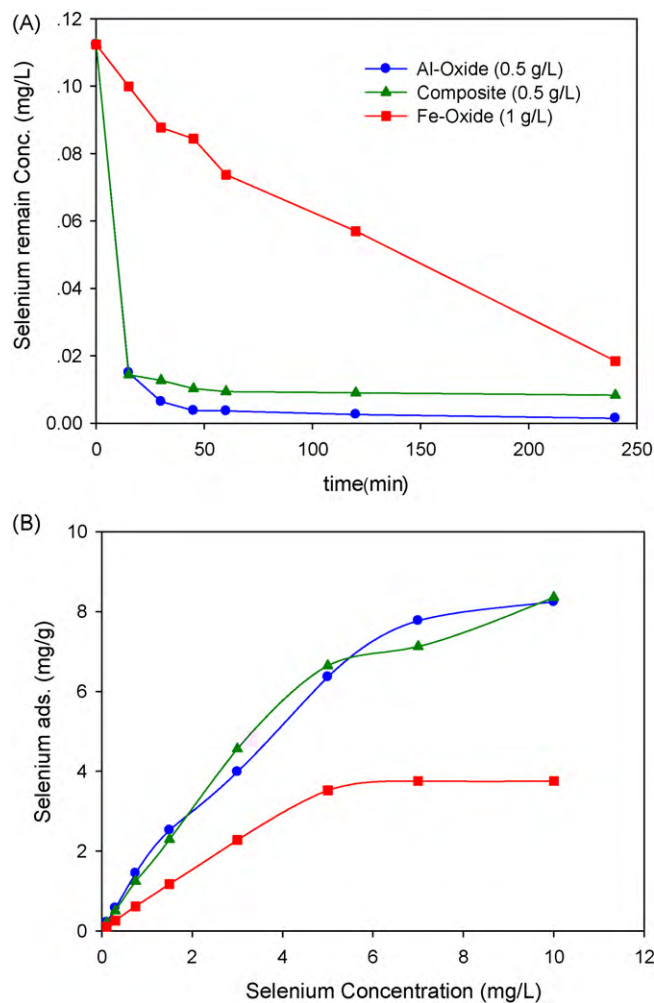

Fig. 4. (A) Kinetics of selenate (0.11 mg/L) binding to chitosan–montmorillonite composites (0.5 g/L), Al-oxide (0.5 g/L) and Fe-oxide (1 g/L). (B) Adsorption isotherm of selenium (0.11–10 mg/L) on chitosan–montmorillonite composite (0.3 g/g) (0.5 g/L), Al-oxide (0.5 g/L) and Fe-oxide (1 g/L). Errors within limitation of measurement ±0.002 mg/L.

The capacities obtained for selenate adsorption on the composite and on the Al-oxide in this study were higher than those reported for the adsorption of selenate on Fe- or Al-oxide mixed with SiO$_2$ (2.4 and 11.3 mg/g, respectively) [35] and on hematite (0.52 mg/g base on SSA indicated by the investigators) [16].

Based on these results we further explored the removal of selenium from well water (pH 7.6) (closed due to high selenium concentrations) employing the composite in suspension without adjusting the pH.

3.4. Selenium removal from well water by composites – batch experiments

The removal of selenium (0.11 mg/L) from well water by chitosan–montmorillonite composites was measured as a function of polymer loading and compared to the removal of selenate (0.11 mg/L of Se) and of selenate in the presence of sulfate (40 mg/L equivalent to 13 mg/L of S) (Fig. 5). In all cases, an increase in selenium removal was obtained for the composites in which two polymer layers were intercalated and partial clay exfoliation was observed (0.23–0.4 g/g) supporting our hypothesis that under these condition selenium removal would be promoted. This trend was most pronounced for the removal of selenium from well water at composite concentrations of 10 g/L. In this case selenium removal
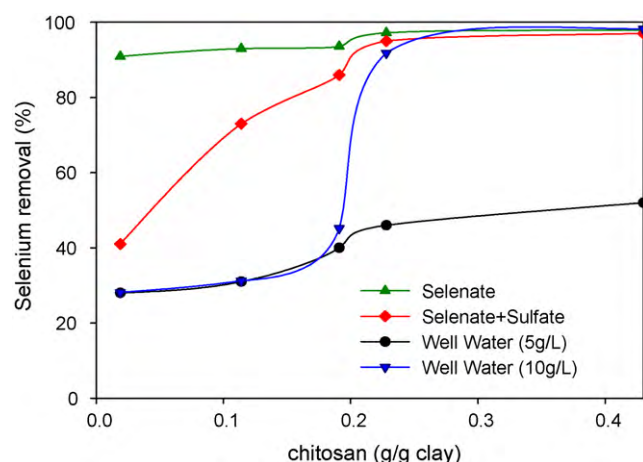
Fig. 5. Selenium removal by chitosan–montmorillonite composites (0.019–0.43 g/g, 5 g/L) from a selenate solution (0.22 mg/L), a selenate (0.22 mg/L) and sulfate (39 mg/L) solution, and Shimron well water (5 and 10 g/L composite). Error within limitation of measurement ±0.002 mg/L.

Table 1
Selenium (Se; 0.09 mg/L) and sulfur (S; 13 mg/L) removal by chitosan–clay composites (10 g/L) from the well water.

S removal (%)	Se removal (%)	S in solution (mg/L)	Se in solution (mg/L)	Composite (g/g clay)
11	28	11.52	0.067	0.02
–	31	13.112	0.064	0.11
35	45	8.488	0.051	0.15
82	92	2.352	0.008	0.23
89	98	1.396	0.002	0.43

by composites with polymer loading above 0.23 g/g was below the recommended limit (0.01 mg/g) and demonstrated selectivity towards selenate over sulfate (Table 1). For example, selenium binding by the 0.43 g/g composite reached 98%, whereas sulfur removal was 89%.

3.5. Selenium removal from well water: column experiments

To examine selenium removal from well water by filtration through composite columns the composite was mixed with inert crush basalt due to the low hydraulic mobility of the composite. For the sake of comparison the Al-oxide was mixed with the basalt as well and the water pH was adjusted to 4. Selenium removal was not efficient (mainly due to the low percent of active ingredient in the column) but higher adsorption of selenium by the composite was demonstrated (Table 2). The lower adsorption by the Al-oxide may be explained by the high adsorption of sulfate to this sorbent. The advantage of the composite would be more pronounced if the water was not acidified.

Despite the advantages of the composites, due to the composite's low hydraulic conductivity, Al-oxide is more suitable for employment in filtration columns, since it has a higher hydraulic mobility. Therefore, the removal of selenium from the well water by

Table 2
Selenium and sulfur removal from Shimron well water by applying filtration columns of Al-oxide or composite (0.3 g/g clay) mixed with basalt (1:20).

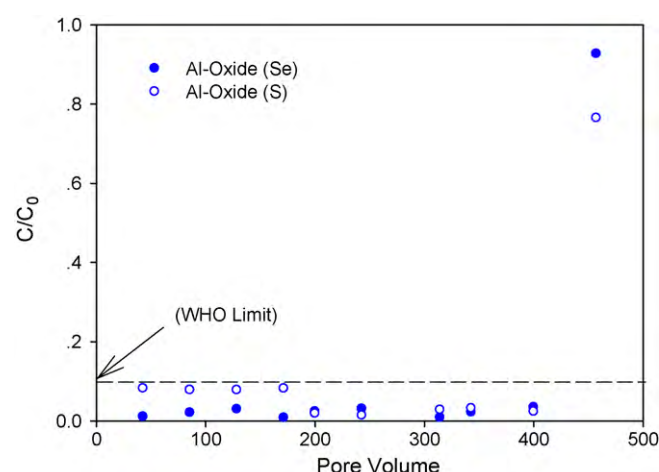| Basalt–comp. S removal (%)	Basalt–comp. Se removal (%)	Basalt–Al-oxide S removal (%)	Basalt–Al-oxide Se removal (%)	Volume (mL)
41	56	51	39	300
12	24	29	17	800
10	19	19	15	1200

Fig. 6. Selenium and sulfur removal from Shimron well water by applying filtration column of Al-oxide. Selenium and sulfur removal (C/Co) as a function of pore volumes.

filtration was explored applying Al-oxide in filtration columns and adjusting the water to pH 4. We point out though, that granulation of the composite can make it advantageous in future column tests. The efficiency of the composite is not affected by pH and therefore in this case the filtration can be performed without adjusting the pH to 4. However, in the case of the Al-oxide in which the pH is adjusted, following filtration the pH will be raised back to 7.

To examine the performance of Al-oxide columns to remove selenium from the well water a semi-pilot filtration experiment was conducted. Selenium removal to below the recommended limit (0.01 mg/L) was achieved for the first 400 pore volumes (equivalent to 280 L and to 294 bed volumes) (Fig. 6). Sharp breakthroughs in emerging selenium (and sulfur) concentrations were observed at 450 L.

3.6. Regeneration

The composite saturated with selenium and sulfate was rinsed (in suspension) with NaCl or NaOH to release the adsorbed sulfate and selenium in order to regenerate the columns. Increasing the pH (rinsing with NaOH) released 65 and 44% of the adsorbed sulfur and selenium, respectively. Desorption by rinsing with NaCl was lower reaching 42 and 11% for sulfur and selenium, respectively. The performance of the composite to readsorb selenium was tested on a composite rinsed with NaOH. The regenerated composite readsorbed 50% selenium more than its released amount. The amount of sulfur readsorbed by the regenerated composite increased by only 10%.

The Al-oxide columns from the semi-pilot filtration experiment were washed with NaOH or NaCl to release the adsorbed sulfate and selenium in order to regenerate the columns. The NaOH solution did not promote anion desorption from the filters. Passing NaCl solution (1 L) desorbed 15 and 33% of the selenium and sulfur, respectively. To test the regenerated material, well water was filtered through the regenerated column until Se concentrations exceeded the recommended limit (70 L). The regenerated filter readsorbed more than twice the amount of selenium released (2.45 mg released vs. 5.7 mg readsorbed). Nearly the same amounts of sulfur were released by the salt and readsorbed by the regenerated filter, i.e. 770 and 830 mg, respectively.

These preliminary results indicate that the regeneration improved selenium removal by the composite and by the Al-oxide.

4. Conclusions

Selenate adsorption to chitosan–clay composites increased with polymer loading on the clay. Zeta potential, XRD and FTIR measurements indicated that at such high loadings the composites are positively charged and that a bilayer and partial clay exfoliation structures are formed. Such structures can account for high selenate adsorption due to internal anion-exchange sites.

Adsorption isotherms of selenate on the composite, Al-oxide and Fe-oxide were in good agreement with the Langmuir model, yielding a somewhat higher capacity for the composite. In addition, adsorption by the composite was not pH dependent while its adsorption by the oxides decreased at high pHs.

Employing the composite in suspension for selenium removal from well water brought Se levels to below the WHO limit and was selective for selenium in the presence of sulfur. Employing the composite in columns required mixing it with an inert media due to the composite's low hydraulic conductivity. However, the column experiment demonstrated that selenium adsorption by the composite was higher than by Al-oxide due to high adsorption of sulfur by the oxide. Unlike employment in batch Al-oxide is currently more suitable for employment in filtration columns due to its high hydraulic conductivity. A semi-pilot columns experiment demonstrated selenium removal from the well water by Al-oxide columns below the recommended limit. Regeneration of Al-oxide and of the composite was studied and readsorption of selenium was demonstrated.

To conclude, the composite is an innovative sorbent that in suspension efficiently removed selenium from well water with high selenium concentrations. On the other hand the Al-oxide efficiently removed selenium from the well water when employed in filtration columns.

Acknowledgment

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