Selenium adsorption and speciation with Mg–FeCO₃ layered double hydroxides loaded cellulose fibre

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ABSTRACT

A novel adsorbent was developed by coating Mg–FeCO₃ layered double hydroxides (LDHs) on cellulose fibre. The LDHs take up significant amount of selenite and selenate in a wide pH range with similar sorption capacities (pH 3.8–8.0 for selenite and pH 5.8–7.0 for selenate). A mini-column packed with Mg–FeCO₃ LDHs layer coated cellulose fibre particles was incorporated into a sequential injection system for uptake of selenite at pH 6.0. The retained selenite was afterwards collected with 70 μL of 0.8%(m/v) NaOH as eluent, followed by hydride generation and atomic fluorescence spectrometric detection. Total inorganic selenium was adsorbed at pH 6.0 by the LDHs-cellulose fibre mini-column after selenate was pre-reduced to selenite by 2.0 mol L^{-1} HCl at 80 °C, and selenium speciation was performed by difference. With a sample volume of 1.0 mL, an enrichment factor of 13.3 was derived with a detection limit of 11 ng L^{-1} within a linear range of 0.04–4.0 μg L^{-1}. A relative standard deviation (RSD) of 3.3% (0.5 μg L^{-1}, n = 11) was achieved. The procedure was validated by analyzing selenium in a certified reference material GBW 10010 (rice), and speciation of inorganic selenium in natural water samples.

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1. Introduction

Layered double hydroxides (LDHs) are a class of nanostructured anionic clays. They have a general formula of $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} is the divalent cation such as Mg, Cu, Co and Ni, M^{3+} is the trivalent cation such as Al, Fe and Cr, X is the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$, and A is the interlayer anion. LDHs are consisted of positively charged brucite-like sheets which are balanced by intercalation of anions in the hydrated interlayer regions. The LDHs generally have very large surface area and anionic exchange capacity [1–3], their potential applications for the removal of oxyanions from contaminated waters, e.g., arsenate, chromate, borate, phosphate and nitrate have been reported [4–10]. The interactions between oxyanions and the LDHs include surface adsorption, interlayer anionic exchange and memory effect [1].

Selenium is an essential trace nutrient. The level of selenium is of considerable interest because of its dual role as an essential nutrient at low concentrations and as a toxic substance at higher levels. In the natural biota, the toxic effect of selenate is generally considered to be less than selenite because of its strong adsorption onto soil sand particles which lowers its chance of ending up in civil water systems. The concentrations of selenium species in natural waters are in the μg L^{-1} range or lower, thus, it is of great importance to develop sensitive and reliable analytical procedures for the detection of selenium species and their speciation [11–13].

The most common analytical approach toward selenium speciation is the hyphenation of a powerful separation technique, e.g., hydride generation (HG) [14–17], solid phase extraction (SPE) [18–22], ion exchange [23,24], capillary electrophoresis [25] and high-performance liquid chromatography (HPLC) [26,27], with a sensitive and selective detection technique. Among those sample pretreatment methodologies, SPE is applied widely for the preconcentration and separation of selenium species and their speciation. Numerous substances have been used as adsorbent for solid phase extraction of selenium species [20,21]. Solid phase extraction procedures based on precipitation and coprecipitatiion are very useful for selenium. However in many cases such approaches may increase the salt concentration in the final effluent. In practice, the introduction of excessive amount of coexisting foreign species into a limited volume of effluent is mostly disadvantageous for trace level of target analytes. Therefore the potential interfering effects or some additional adverse effects arisen from the adsorbents on the final quantification of the analytes should be carefully evaluated.

Layered double hydroxides (LDHs) have been reported as an adsorbent for the adsorption of metal species, including selenite

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Table 1
The summary of AFS operating parameters.

Parameters	Settings
Lamp current	80 mA
Atomizer height	8 mm
Integration time	2 s
Time delay	7 s
Negative high voltage of PMT	370 V
Carrier argon flow	400 mL min^{-1}
Shield argon flow	900 mL min^{-1}
Reading mode	Peak area

[28,29]. However, difficulties are often encountered when used in dynamic systems, because the very small size of the LDHs, ranging from nanometer to micrometer, tends to cause serious flow resistance. In this respect, the immobilization of LDHs on a suitable solid support could solve this problem by making the sorbent ease of operation in a dynamic system. In addition, when alkaline stripping reagents are used for the recovery of the adsorbed analytes, the dissolution of sorbent medium, e.g., LDHs, will be avoided and thus providing a clear effluent after stripping with minimized interfering effects to the analytes. For the purpose of immobilization, cellulose fibre particles have been proven to be a green medium. In the present work, we investigated the coating of a thin layer of Mg–FeCO$_3$ LDHs precipitate on the surface of cellulose fibre particles. The coated material provides a green adsorbent for the adsorption of inorganic selenium species via co-precipitation with the Mg–FeCO$_3$ LDHs layer.

2. Experimental

2.1. Instrumentation

An AFS-920 non-dispersive atomic fluorescence spectrometer (Titan Instruments, Beijing, China) equipped with two ancillary syringe pumps (5.0 mL) and a selection valve was employed for hydride generation and quantification. A high-intensity hollow cathode selenium lamp at 196.0 nm (Beijing General Research Institute for Nonferrous Metals, Beijing, China) was used as a radiation source. The selenium hydride generated was isolated from the reaction mixture in a standard glass gas–liquid separator (Titan Instruments, Beijing, China) and finally swept into the atomizer by using an argon flow.

A FIAlab-3000 sequential injection system (FIAlab instruments, WA, USA) equipped with a 2.5-mL syringe pump and a six-port selection valve was employed for sample pretreatment and fluids delivery.

All the external channels were made of 0.8 mm i.d. PTFE tubing connected to the multi-port selection valve with peek nut/ferules from Upchurch Scientific (OAK HARBOR, WA, USA), except for the reaction coil, i.e., the conduit connecting the separation unit and the four-way connector for facilitating the hydride generation reaction, which was made from 1.0 mm i.d. PTFE tubing. Table 1 summarizes the operating parameters for the AFS instrument.

pH measurements were performed by using an Orion model 868 digital pH meter (Thermo Electrom Co., USA).

2.2. Chemicals

All reagents used were at least of analytical reagent grade and de-ionized water of 18 MΩ cm^{-1} was used throughout. Working standard solutions of selenite and selenate were prepared by stepwise dilution of 1000 mg L^{-1} stock solutions.

NaBH$_4$ solution in 0.5% (m/v) NaOH was prepared daily with 96% sodium tetrahydroborate (Shanghai Chemicals, China). Other chemicals include MgCl$_2$·6H$_2$O, FeCl$_3$·6H$_2$O, Na$_2$CO$_3$·10H$_2$O, nitric

acid (Beijing Chemicals, China), sodium hydroxide (Shanghai Chemicals, China), and hydrochloric acid (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China). De-ionized water was used as carrier solution.

2.3. Sample pretreatment

Certified reference material of rice (GBW 10010): 0.1 g of the certified reference material was taken into a PTFE beaker along with 8 mL of HNO$_3$ (65%) and 2 mL of HClO$_4$ (73%). After soaking for 2 h at room temperature, the mixture was heated on a sand bath at 210 °C until fumes appeared and the solution nearly dried. After cooling, 5.0 mL of hydrochloric acid (37%) was added and the mixture was heated at 180 °C to near dryness. Afterwards, 1 mL of de-ionized water was introduced and heated at 180 °C to near dryness again. The residue in the beaker was finally soaked by using de-ionized water and adjusted to pH 6.0 before transferring into a volumetric flask and diluted to 50 mL.

Water samples: surface water samples (river water, lake water and rain water) were obtained in the campus of Northeastern University (Liaoning province, China). When measuring selenite, the water samples were adjusted to pH 6.0 and directly processed by following the procedures given in the ensuing sections, after filtration using a filter membrane with a pore size of 0.22 μm. When performing selenium speciation, the concentration of selenate was obtained by difference after preduction of selenate to selenite at 80 °C as detailed elsewhere [18] and quantifying the total selenium content by adjusting the sample solution to pH 6.0.

In order to control the potential sample contamination, sample blanks were also prepared at this stage.

2.4. Preparation of Mg–FeCO$_3$ LDHs coated cellulose and column packing

The Mg–FeCO$_3$ LDHs utilized in the experiments (with a Mg/Fe molar ratio of 3:1) was prepared by the co-precipitation method. First, 4.06 g of MgCl$_2$·6H$_2$O and 1.89 g of FeCl$_3$·6H$_2$O were dissolved in 100 mL of water while the solution was stirred (solution 1). Next, 1.73 g of NaOH and 4.0 g of Na$_2$CO$_3$·10H$_2$O were dissolved into 100 mL of water with 2.0 g of cellulose fibre (solution 2). Solution 1 was added slowly into solution 2 while vigorously stirring. The co-precipitation reaction was performed at 50 °C and pH 11.5 adjusted by diluted NaOH and HCl (0.1 mol L^{-1}). The mixed suspension was centrifuged at 1300 rpm for 2 h to collect the cellulose fibre with LDHs coating. The supernatant was removed and the residue was rinsed with water to completely remove chloride ion. The product was finally collected by filtration and dried in an oven for 20 h at 60 °C.

5 mg of the Mg–FeCO$_3$ LDHs coated cellulose fibre was used to pack a mini-column into a piece of PTFE tubing (2.0 mm i.d/3.2 mm o.d) blocked at both ends by a small amount of glass wool. Before use, the mini-column was rinsed thoroughly by pumping 1.0 mL of de-ionized water and 0.5 mL of conditioning solution (blank solution with identical pH value as that of the sample solution) through it and finally evacuated by an air flow.

2.5. Analytical procedure

Fig. 1 illustrated the flow manifold of the sequential injection system incorporating a mini-column packed with Mg–FeCO$_3$ LDHs coated cellulose fibre for selenite separation and preconcentration. The entire operating process includes the following steps:

System conditioning: 100 μL of the carrier solution was first aspirated into the syringe pump, 200 μL of air and 200 μL of conditioning solution were subsequently aspirated from port 2 and port
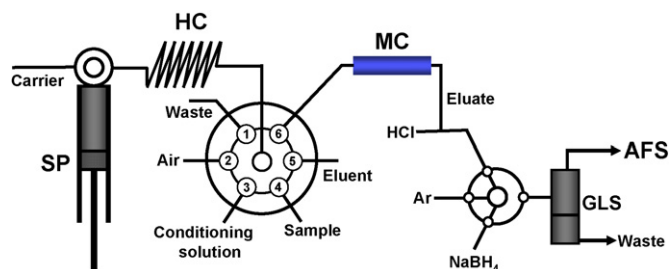
Fig. 1. The flow manifold for selenium uptake in a mini-column of cellulose fibre coated with Mg–FeCO$_3$ LDHs layer. HC, holding coil; MC, mini-column packed with LDHs-cellulose fibre particles; GLS, gas–liquid separator.

3 into the holding coil, which were afterwards dispensed through port 6 to flush the mini-column at a flow rate of 10 µL s^{-1}.

Sorption and de-sorption: 1000 µL of sample solution was aspirated into holding coil from port 4 and directed to flow through the mini-column at a flow rate of 10.0 µL s^{-1} to facilitate the sorption and preconcentration of selenium; then 50 µL of air was introduced to evacuate the mini-column. Thereafter, 200 µL of air and 70 µL of 0.8% NaOH solution were sequentially aspirated into the holding coil, which were afterwards dispensed to flow through the mini-column at 5.0 µL s^{-1}. The NaOH solution zone was used to elute the retained selenium while the air zone was used to transport the eluate into the HG-AFS system for quantification.

Mini-column refreshing: before starting the next operation cycle, 200 µL of air, 100 µL of 1.0% (m/v) NaOH solution and 300 µL of the conditioning solution were aspirated sequentially into the holding coil followed by directing them to flow through the mini-column to eliminate any potential residues on the surface of the Mg–FeCO$_3$ LDHs coating layer.

3. Results and discussion

3.1. Characterization of the adsorbent

XRD patterns of the LDHs, pure cellulose and cellulose fibre coated with LDHs are shown in Fig. 2A. The diffraction peaks for the Mg–FeCO$_3$ LDHs correspond to 0 0 3, 0 0 6, 0 1 2, 0 1 5, 0 1 8 and 1 1 0 at 2θ positions of 11.4, 22.8, 34.2, 38.6, 46.0 and 59.6. This well demonstrated that the LDHs obtained in the present study have a typical layered structure as reported in previous literatures [1,8,10]. It is obvious that the above peaks were clearly identified from the XRD pattern of the LDHs coated cellulose fibre, except for the 0 0 6 peak which was merged into the intensive peak of the cellulose fibre. This illustrates successful coating of Mg–FeCO$_3$ LDHs layer on the cellulose fibre.

FT-IR spectra in Fig. 2B illustrated that the absorptions at 3500–3650 cm^{-1} were assigned to the H-bonding stretching vibrations of OH group in the brucite-like layer. The bending vibration of the interlayer water (δ_{H_2O}) occurs at ca. 1650 cm^{-1}. The absorption bands at ca. 1380 cm^{-1}, ca. 860 cm^{-1} and ca. 670 cm^{-1} were ascribed to the vibration of CO$_3{}^{2-}$ [1]. The bands in the range of ca. 560 cm^{-1} are attributed to metal–oxygen–metal stretching. The morphology of the cellulose fibre surfaces before and after coating of Mg–FeCO$_3$ LDHs were illustrated by the SEM images in Fig. 2C and D. It is clearly demonstrated that after coating the cellulose surface was covered by a thin layer of precipitate.

It has been reported that hydroxyl, ether and some other functional groups in the framework of cellulose are effective for binding specific species [30,31], especially metal cations, while no obvious retention of anionic groups was observed. On the other hand, metal hydroxide or oxide is able to adsorb anionic groups because of their positive core [19]. In the present case, the hydroxyl and other functional groups on the cellulose surface is covered by the Mg–FeCO$_3$ LDHs precipitate layer, therefore the newly formed
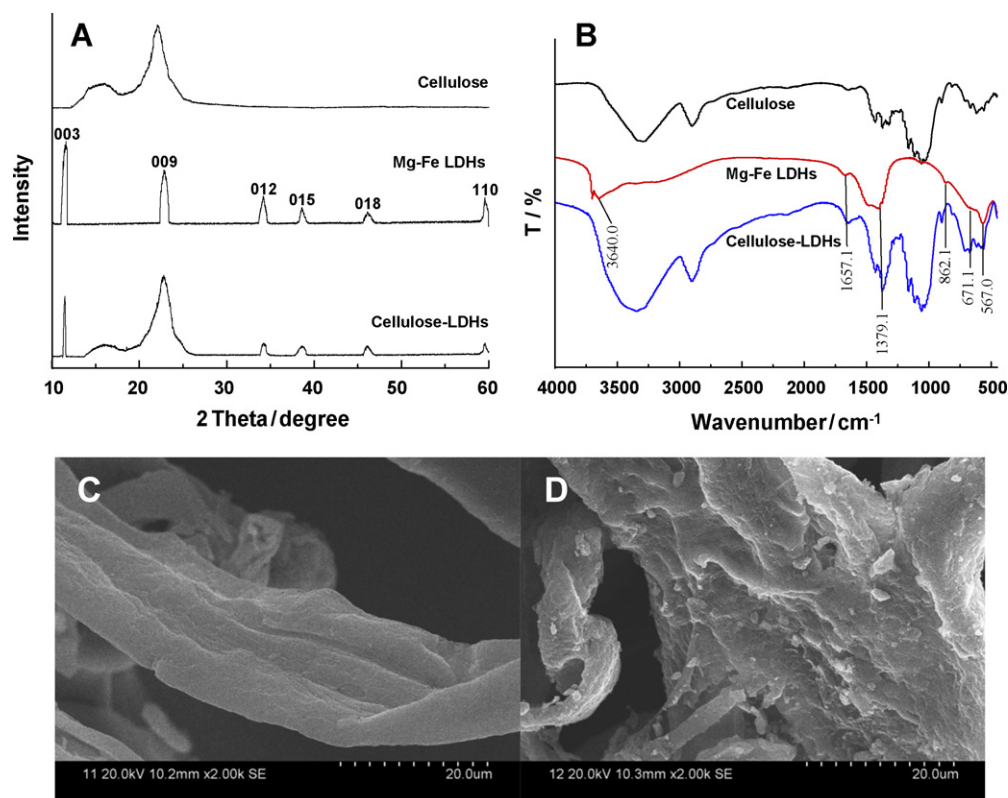

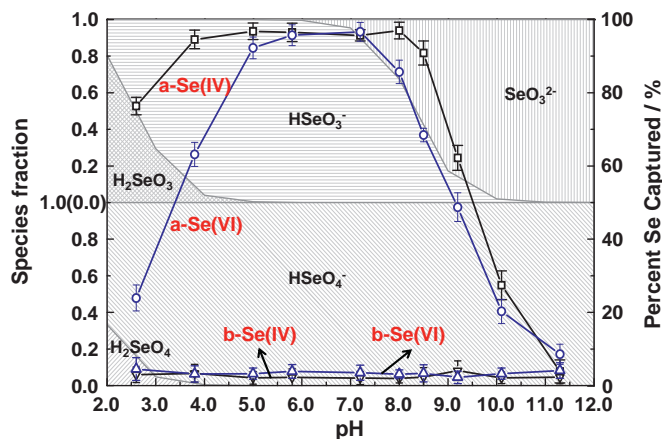**Fig. 2.** (A) XRD patterns; (B) FI-IR spectra; (C) and (D) SEM images of cellulose fibre before and after coated with Mg–FeCO$_3$ LDHs.

Fig. 3. The uptake of selenite and selenate by Mg–FeCO$_3$ LDHs coated cellulose fibre and pure cellulose as a function of pH. (a) On the Mg–FeCO$_3$ LDHs coated cellulose fibre, (b) on the pure cellulose fibre. Sample volume: 1000 μL, 10 μg L^{-1} Se(IV) or Se(VI); sample loading flow rate: 10 μL s^{-1}. The species distribution of Se(IV) or Se(VI) are shown in the background, right ordinate.

positively charged surface of the precipitate facilitates the retention of certain anionic species [32,33].

3.2. pH dependent adsorption of selenite and selenate

pH is one of the most important factors affecting the adsorption of metal species. Fig. 3a shown that the adsorption of selenite and selenate by the LDHs coated cellulose fibre is highly pH dependent. The quantitative adsorption of selenite and selenate was achieved at pH 3.8–8.0 and pH 5.8–7.0 respectively, and significant drop on the adsorption of both species was observed outside these pH ranges. These results were attributed probably to the fact that the sorption of selenite and selenate are closely related to the distribution of the chemical forms of selenium and the surface properties of the sorbent.

The impact of pH can be explained by taking into account the different species of selenium in aqueous solution as a function of pH. H$_2$SeO$_3$ is weak acid, dissociating into HSeO$_3^-$ and SeO$_3^{2-}$ in aqueous solution, while H$_2$SeO$_4$ is a strong acid and give rise to SeO$_4^{2-}$ on dissociation. The surface of Mg–FeCO$_3$ LDHs is positively charged when pH < pH$_{pzc}$ (point of zero charge of Mg–FeCO$_3$ LDHs. pH$_{pzc}$ = 8.78 [34,35]), facilitating the adsorption of oxyanions. However, the stability of the LDHs is decreased at a very low pH, i.e., pH $\ll$ pH$_{pzc}$, which impaired the adsorption of oxyanions. At pH > pH$_{pzc}$, the LDHs surface is negatively charged, which repelled the oxyanions and thus offering low adsorption. At pH $\gg$ pH$_{pzc}$, the OH$^-$ starts to compete with the adsorption of oxyanions, and thus the sorption of both selenium species are minimal.

Fig. 3b indicated that when a solution containing 10.0 μg L^{-1} selenite and selenate pass through the mini-column, no selenite and selenate was found in the effluent, demonstrating that no sorption of selenium oxyanions occurred in the pure cellulose fibre. Previously, the adsorption of metal cations has been reported by cellulose fibre [36], but the sorption of anionic species, i.e., selenite and selenate in this particular case, has never been reported attributed to the surface property of the cellulose fibre.

It can be seen from the above discussions that the adsorption of selenite can be obtained within a wide range of pH 3.8–8.0, and meanwhile certain amount of selenate was also retained by the LDHs. In the ensuing hydride generation process, however, the conversion of selenate into hydride was not observed. Thus, selective quantification of selenite is achieved. The total amount of inorganic selenium can be obtained by pre-reduction of selenate into selenite by following the same procedure, and speciation could be

performed by difference. For the ensuing experiments, the adsorption of selenite is conducted at pH 6.0.

3.3. Sample loading flow rate

In the flow system, the effect of sample loading flow rate on the sorption of selenite was investigated within a range of 5–30 μL s^{-1}. A decline of the retention efficiency of selenite with the increase of flow rate was observed. A retention efficiency of >95% was obtained within a flow rate of 5–15 μL s^{-1}, while a sharp drop to ca. 74% was observed when further increasing the flow rate to 30 μL s^{-1}. This result is associated with the adsorption kinetics of selenite by the Mg–FeCO$_3$ LDHs coated cellulose fibre. A reasonable length of contacting time is required to facilitate the sorption process. As a compromise between the retention efficiency and the analysis frequency, a sample loading flow rate of 10 μL s^{-1} was employed. In practice, the sorption or uptake capacity of selenite is an important factor to evaluate the sorbent efficiency. To quantify the uptake capacity of the Mg–Fe CO$_3$LDHs coated cellulose fibre, 2 mL of sample solution with various selenite was adjusted to pH 4–8, and then processed according to the proposed procedure. A sorption capacity of 3.84 mg g^{-1} was obtained by plotting the amount of selenite taken up versus the amount of selenite retained per gram Mg–FeCO$_3$ LDHs coated cellulose.

3.4. The elution process

Fig. 3a indicated that no adsorption of selenite was observed at high pH. For this reason, alkaline medium should be a suitable eluent for the recovery of the adsorbed selenite from the LDHs-cellulose fibre. NaOH is thus employed for this purpose and the effect of its concentration, volume and elution flow rate on the recovery of selenite was investigated in a concentration range of 0.4–1.4% (m/v) by using a volume of 30–100 μL and a flow rate of 5–15 μL s^{-1}. The results showed that an increase of the elution efficiency was observed with the increase of NaOH concentration and volume, while the increase of flow rate gives rise to decline of selenite recovery. After careful scrutiny, a recovery of >92% of selenite is achieved by using >60 μL of 0.8–1.0% (m/v) NaOH as eluent at a flow rate of 10 μL s^{-1}. For further studies, 70 μL of 0.8% NaOH solution is used for elution at 10 μL s^{-1}.

3.5. Interferences

In order to evaluate the practical applicability of the present procedure for the determination of selenium species in real samples, the potential interferences of foreign species on the preconcentration and determination were tested. For this purpose, a selenite solution of 0.5 μg L^{-1} with various amount of the foreign species was tested within an error range of ±5%. It indicated that 100 mg L^{-1} alkali, 50 mg L^{-1} alkaline earth metal ions and 150 mg L^{-1} Cl$^-$ do not interfere with the determination.

Effects of some frequently encountered heavy metals were also investigated. 5 mg L^{-1} Mn^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Pb^{2+}, Ni^{2+} and 1 mg L^{-1} Cu^{2+}, Al^{3+}, Fe^{3+} pose no interferences on the quantification of selenium (no tests were made for higher concentration levels). For common biological and environmental samples, the contents of the above metals in sample digests or after appropriate dilution will not exceed the tolerant concentration levels, therefore the present procedure can be directly employed, and no further treatment or masking reagents are need.

3.6. Analytical applications

Under the optimal conditions, the calibration curve for selenite was linear up to 5.0 μg L^{-1} with a correlation coefficient of

Table 2
Determination of selenium species in natural water samples.

Sample	Spiked ($\mu g\,L^{-1}$)		Found ($\mu g\,L^{-1}$)		Recovery (%)	
	Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)
River water	0	0	0.31 ± 0.02	0.39 ± 0.03		
	0.2	0.2	0.50 ± 0.03	0.61 ± 0.04	96	106
Lake water	0	0	0.38 ± 0.02	0.56 ± 0.03		
	0.2	0.2	0.57 ± 0.03	0.77 ± 0.04	95	102
Rain water	0	0	0.18 ± 0.02	0.42 ± 0.03		
	0.2	0.2	0.37 ± 0.03	0.63 ± 0.04	96	103

0.9989. The regression equation is $A = 252.95\,C_{Se} + 46.439$. The detection limit, calculated as the ratio of three times of the standard deviation for 11 replicate measurements of the blank signals and the slope of the calibration curve, is $22\,ng\,L^{-1}$ for selenite, and the relative standard deviation (RSD) was 3.3% ($0.5\,\mu g\,L^{-1}$, $n = 11$).

The method is validated by analyzing selenium content in a certified reference material of rice (GBW 10010). A good agreement was achieved between the certified value ($61 \pm 15\,ng\,g^{-1}$) and the found value ($65 \pm 10\,ng\,g^{-1}$), showing acceptable reliability of the present system for selenite uptake by using the Mg–FeCO$_3$ LDHs layer coated cellulose fibre as sorption medium.

For the purpose of inorganic selenium speciation, selenite was first quantified by following the procedures reported herein. Afterwards, selenate was converted to selenite as detailed in our previous work [18] and then the total amount of inorganic selenium was determined. Finally the amount of selenate was obtained by difference. This method was applied to the speciation of inorganic selenium species in river water, lake water and rain water samples collected in Shenyang, China. Spiking recoveries for selenite and selenate at the concentration level of $0.2\,\mu g\,L^{-1}$ were carried out respectively, and it can be seen that reasonable recoveries were obtained as given in Table 2.

4. Conclusions

Layered double hydroxides (LDHs) were used for the selective uptake of selenite, and the coating of LDHs on cellulose fibre provides a novel green adsorbent. An on-line solid-phase extraction procedure for the preconcentration of selenite by using Mg–FeCO$_3$ LDHs coated cellulose fibre has been demonstrated to be feasible for selenium speciation with detection by hydride generation atomic fluorescence spectrometry.

Acknowledgments

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