Sorption-desorption of selenite and selenate on Mg-Al layered double hydroxide in competition with nitrate, sulfate and phosphate

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HIGHLIGHTS

- Calcined hydrotalcite HTC was tested for selenium species sorption-desorption.
- HTC sorption-desorption capacity was analysed in solid phase by EDXRF.
- Mathematical modelling allowed us to estimate selenium mobilization in environment.
- Hysteresis index and mobilization factor were calculated to estimate reversibility.
- HTC desorption capacity was explored for quantitation purposes in aquatic systems.

GRAPHICAL ABSTRACT
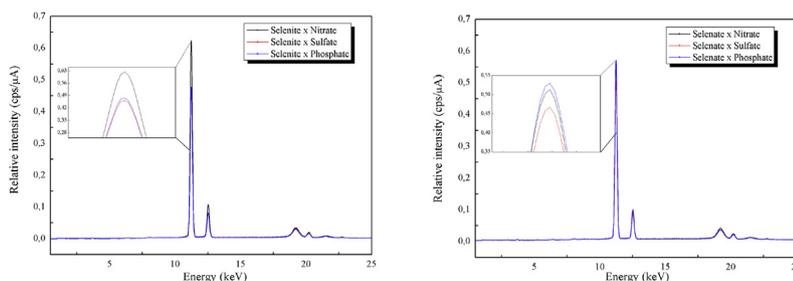
ABSTRACT

Selenate and selenite are considered emerging contaminants and pose a risk to living organisms. Since selenium anion species are at low concentration in aquatic environments, materials for its retention are required to enable monitoring. Herein, hydrotalcite was calcined and characterised to investigate sorption and desorption of selenite and selenate in competition with nitrate, sulfate and phosphate. Sorption experiments were carried out in batch system and desorption by sequential dilution. Selenite and selenate concentration remaining after N desorption steps was determined by mass balance. The isotherms were adjusted to the dual-mode Langmuir-Freundlich model ($R^2 > 0.99$). Maximum sorption capacity ranged from 494 to 563 meq kg^{-1} for selenite and from 609 to 659 meq kg^{-1} for selenate. Sulfate and phosphate ions showed greater competitive effect on the sorption of selenate and selenite, respectively. Low mobilization factors and high sorption efficiency (MF<3%; SE ≈ 100%) indicated that calcined hydrotalcite has the wanted characteristics for retention of relevant selenium anion species in aqueous media.

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1. Introduction

Selenium is a non-metal trace element, essential for plants and animals, which is present in different environmental compartments due to natural and anthropogenic causes (Santos et al., 2015). In high concentrations selenium is considered toxic and its monitoring in aquatic environments has become important in recent years (Hageman et al., 2013; Xie et al., 2015; Garousi et al., 2016). The most important selenium species are selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), the later being more toxic. (Li et al., 2008). The United States Environmental Protection Agency (USEPA) considers that 5.0 µg L^{-1} of selenium can cause chronic effects on aquatic life (USEPA, 2014). However, the World Health Organization (WHO) establishes the limit of 40.0 µg L^{-1} in drinking water and the European Union recommends up to 10.0 µg L^{-1} (Santos et al., 2015).

Selenium is found in low concentrations in aquatic environments and, in this case, pre-concentration methods can be used to enable the quantification of important species. Such methods are directly related to materials with high sorption capacity for selenium species. In this sense, hydrotalcite stands out for sorption potential of anionic species in aqueous solutions, and has been applied to chromate, arsenate, vanadate, phosphate, fluoride, selenate, molybdate and borate, among others (Moujahid et al., 2003; Goh et al., 2008; Ashekuzzaman and Jiang, 2014; Dessalegne et al., 2016; Sani et al., 2016).

Hydrotalcite, a layered double hydroxides (LDH), consists of brucite-like positively charged layers compensated with carbonate anions and water molecules to maintain neutrality (Ulibarri et al., 2001; Li et al., 2006; Vágvolgyi et al., 2008). Calcination or thermal activation increases the surface area and improves the anion sorption capacity (Chatelet et al., 1996; Yang et al., 2005; Li et al., 2006), allowing hydrotalcite to replace carbonate by other anion species. Anions of higher charge density and smaller anionic radii are preferentially intercalated, and divalent species has greater affinity for sorptive sites of calcined hydrotalcite (Miyata, 1980; Sato et al., 1986; Chatelet et al., 1996; Vágvolgyi et al., 2008).

Although aquatic systems have been extensively studied and different mechanisms proposed to describe reactions at solid-liquid interface such as: ion exchange, inner-sphere or outer-sphere complexation, diffusion and precipitation (Goh et al., 2010; Paikaray et al., 2013), the complexity of this environment can modify the sorption behavior (Goh and Lim, 2010; Chubar and Szlachta, 2015; Kyzas et al., 2015). Hence, it is important to investigate competitive effects of major anions with species of interest onto sorbent materials. Therefore, this study was aimed to apply calcined hydrotalcite to study the sorption-desorption processes of selenite and selenate in competition with nitrate, sulfate and phosphate, naturally found in aquatic environments.

2. Materials and methods

2.1. Materials, chemicals and standards

Hydrotalcite (HT) was acquired from Sigma-Aldrich (St. Louis, MO, USA) and calcined at 500 °C for 4 h. The resulting solid was named HTC (Ulibarri et al., 2006; Li et al., 2006; Lim et al., 2009).

Selenite and selenate (Na_2SeO_3 and Na_2SeO_4), both from Sigma-Aldrich (St. Louis, MO, USA) were used for sorption and desorption steps. Solutions of 0.01 mol L^{-1} NaNO$_3$, Na$_2$SO$_4$ and Na$_3$PO$_4$ (p.a. grade, purity $\geq$ 99%, Merck, Darmstadt-Germany) were employed as background electrolyte. Milli-Q water (Millipore, Billerica, MA, USA) was used for all solutions and dilutions. All glassware was soaked in 10% HNO$_3$ (Anidrol, Diadema, Brazil) for 24 h and rinsed with ultrapure water.

2.2. Characterization of the material

HT and HTC were analysed by ICP-MS after treatment with 1.0 mol L^{-1} HNO$_3$ for 24 h at 20 $\pm$ 2 °C to quantify acid-extractable elements from the material (Anjos et al., 2014). The point-of-zero charge (pH$_{PZC}$) for LDH from HTC in aqueous solution was found as an pH intersection point for pH titration curves at three different ionic strengths (0.1, 0.001 and 0.01 mol L^{-1} KCl; Longisland Biotec, Shanghai, China) (Embrapa, 2011). The specific surface area and pore diameter were determined by BET method. For this, the calcined material was dried for 21 h at 110 °C and analysed in an Quantachrome Instruments NOVA1200e.

Infrared spectra (IR) were recorded on a *Prestige-21* spectrophotometer (Shimadzu, Kyoto, Japan), with resolution of 2 cm^{-1} and 20 accumulation scans in the range of 4000–400 cm^{-1}. Samples were analysed as KBr discs with a 1% mass loading.

Thermogravimetric analysis (TGA) was carried out on a TGA-50 Thermogravimetric Analyser (Shimadzu, Kyoto, Japan) with temperature programming from 25 to 600 °C at a heating rate of 10 °C min^{-1}, in air atmosphere.

X-ray powder diffraction (XRD) patterns were collected on a X'Pert PRO MPD (PANalytical, Almelo, The Netherlands) with radiation of copper Kα (λ = 1.5418 Å), tension of 40 kV and current of 30 mA, in the 2θ range from 5° to 80° at the scanning speed of 0.031° min^{-1}. The diffraction patterns were acquired with the software *X'Pert HighScore*.

Energy dispersive X-Ray fluorescence (EDXRF) were carried out in a EDX-720 spectrometer (Shimadzu, Kyoto, Japan) with a Rh anode X-ray tube and a Si(Li) detector. Thin-film sample supports of polyester with 2.5″ and diameter of 63.5 mm (Chemplex, Palm City, USA) were used. The measurement were performed in two channels, Ti–U at 50 kV, 13 µA with excitation time of 100 s and Na–Sc at 15 kV, 202 µA for 100 s. The incident beam had 10 mm collimation.

2.3. Sorption and desorption experiments

Batch sorption tests were carried out in triplicate using 10 mL of Na_2SeO_3 or Na_2SeO_4 solutions (0.1–10.0 meq L^{-1}) and 0.200 g of HTC, in 10.0 meq L^{-1} of nitrate, sulfate and phosphate solution, equilibrated by end-over-end shaking at 30 rpm for 24 h (20 $\pm$ 2 °C) (Sato et al., 1986; Chatelet et al., 1996; Lim et al., 2009). Before the tests, the initial pH was measured. The suspensions were centrifuged at 3000 rpm (1607.9 $\times$ g) for 10 min using a DCS-16-RV device (Presvac, Brazil) and filtered through cellulose ester membranes with pore size equal to 0.22 µm (Millipore, Billerica, MA). The supernatants were collected in polyethylene bottles and the post-sorption pH was measured. The solid was dried at 40 °C and analysed by EDXRF.

Desorption tests were carried out from the highest initial sorption concentration (10.0 meq L^{-1}) by ten sequential dilutions with equilibration time of 24 h. At each desorption step, 5.0 mL of the liquid phase were removed for quantitation of selenite and selenate, and the removed aliquot was replaced with 100 meq L^{-1} NO$_3^-$, SO$_4^{2-}$ or PO$_4^{3-}$.

The concentration of selenium was determined by inductively coupled plasma mass spectrometry (ICP-MS) using a Varian instrument model 820-MS (Palo Alto, CA, USA) and the ICP-MS Expert Software (version v2.0 b87). The experimental conditions are presented in Table 1 of Supplementary Material (SM).

Selenite and selenate in initial solutions (C_i, meq L^{-1}) as well as in supernatants at equilibrium after the sorption and sequential desorption experiments (C_{eq} e $C_{eq,D}$, meq L^{-1}) were quantified by ICP-MS. Sorption efficiency (SE, %) was estimated by the difference between the initial and at equilibrium concentrations in relation to the initial concentration.