



Static and dynamic adsorptive removal of selenite and selenate by alkoxide-free sol-gel-generated Mg–Al–CO₃ layered double hydroxide: Effect of competing ions

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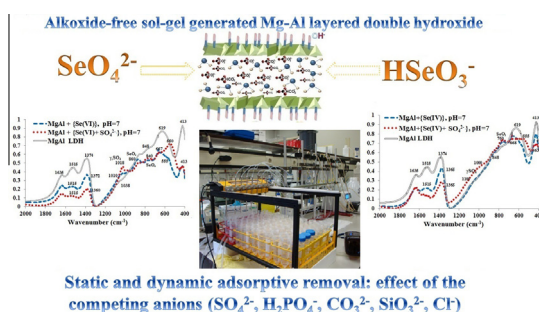
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HIGHLIGHTS

- Mg–Al LDH efficiently removes selenate and selenite from multicomponent solutions.
- It was extensively examined under static and dynamic adsorption conditions.
- Phosphate and sulphate had no influence on the dynamic adsorption of selenite.
- Sulphate reduced the time of selenate removal till break-through.
- Phosphate had no influence on the dynamic adsorption of selenate.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption/ion exchange is a major separation approach capable of recovering the valuable Se component from various multicomponent solutions or to reduce its concentration. In this study, we report a method for selenite and selenate adsorptive removal based on the application of Mg–Al–CO₃ layered double hydroxide (LDH) generated via an alkoxide-free sol-gel synthesis method developed by the authors. The selenite and selenate removal capability of Mg–Al LDH was examined under static and dynamic adsorption conditions, focusing on the influence of the competing anions (phosphate, sulphate, carbonate, silicate, chloride). The adsorption capacities of Mg–Al LDH for selenite and selenate obtained from the equilibrium isotherms were not influenced by the presence of the competing sulphate, retaining the highest values of 168 and 103 mg [Se]/g_{dwt} for Se(IV) and Se(VI) at pH 5, respectively. This inorganic ion exchanger is capable of functioning across the broad range of pH values from 5 to 9. Mg–Al LDH could purify 16,200 and 4200 bed volumes (BVs) of the selenite/selenate-containing solutions (~50 μg [Se]/L initial concentration), respectively, until reaching a selenium concentration of zero in the effluents. The presence of phosphate and a 74-times higher concentration of sulphate compared with selenate or selenite in the adsorbate showed nearly no influence on the dynamic adsorptive performance of Mg–Al LDH for selenite. An equivalent concentration of phosphate did not influence the dynamic adsorptive removal of selenate. Markedly higher concentrations of sulphate, however, decreased the time to break-through for selenate but did not affect the quality of its removal. Mg–Al LDH is a promising inorganic ion exchanger for the removal of both of the aqueous selenium species and will be tested on industrial scales.

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1. Introduction

The chemical element selenium, discovered by Swedish chemist Jöns Jacob Berzelius in 1817, was initially thought to be a toxin. However, in 1950, researchers demonstrated that selenium is a nutritionally essential mineral for living organisms. Selenium deficiency is associated with a number of health conditions, such as fatigue, dry skin, dandruff, cataract development, Keshan disease, increased risks of tumours, heart and thyroid diseases, mental retardation, and cognitive decline [1]. Recent studies also suggested that selenium deficiency might result in visual disturbance and myelopathy [2,3]. Currently, selenium is a constituent of many food supplements provided by most suppliers.

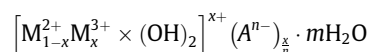
However, the number of articles resulting from the investigation of selenium toxicity is as great as the number of publications demonstrating negative effects of selenium deficiency. Excess doses of selenium might result in a disease called selenosis (reflected in symptoms such as headache, loss of hair, deformation and loss of nails, skin rash, malodorous (garlic) breath and skin, excessive tooth decay and discoloration, numbness, paralysis and hemiplegia) [4,5]. In 2014, the European Food Safety Authority (EFSA) published a scientific opinion on dietary reference values for selenium [6]. The EFSA panel recommended the generation of more research to better understand the health influence of selenium, including the influence of selenium concentration, genotypes and the effect of various selenium substances and their combinations. A Society of Environmental Chemistry and Toxicology (SETAC) meeting was organised to discuss selenium toxicity for the biosphere inhabitants and the Se fate in environmental ecosystems as well as to recognise a lack of knowledge in the areas of environmental selenium [7]. There are two thermodynamically stable selenium water species, selenite (HSeO_3^-) and selenate (SeO_4^{2-}). Selenate is the predominant selenium species under ordinary alkaline and oxidised conditions.

Selenium deficiency and toxicity are popular research topics relevant to human health and ecosystems. Recent studies demonstrated that depending on the Se concentration and speciation, this chemical element might be either a UVA-photoprotector or a causative factor of toxic effects in human fibroblasts [8]. The key aspect of Se toxicity and deficiency is the narrow range between its dietary essentiality and toxicity. For either of these aspects, it is necessary to develop the separation tools (or to update a suitable separation system) to extract this valuable element from multi-component solutions for its removal from water or for control of its content in effluents. The drinking water standard for selenium (any species) in many countries, including EU countries, Canada and several US States, is $10 \mu\text{g} [\text{Se}]/\text{L}$ [9].

However, application of selenium is not limited by using its compounds as food supplements. This chemical element plays an increasingly important role in organic synthesis and other technologies such as catalysis. The first catalytic *syn*-stereospecific dichlorination of alkenes using selenium-containing catalyst has been recently reported [10]. Organoselenium was found to be the best pre-catalyst for Baeyer–Villiger oxidation of (E)- α,β -unsaturated ketones with the green oxidant hydrogen peroxide at room temperature [11].

Adsorption and ion exchange are promising methods for selenium removal; however, the existing commercial adsorptive materials have low removal capacity for both of the aqueous selenium species (selenite and selenate), and their removal performance for selenate is often (nearly) zero. Currently, scientists are searching for the new technological solutions for selenium removal [12,13] including those approaches based on the reduction of the main selenium water species, selenate, to selenite [14]. In parallel, research focused on the development of new adsorption media

capable of removing selenium species resulted in the cost-effective promising adsorbent [15] and the complex oxide capable of removal both aqueous selenium species [16]. Hydrotalcites (HT) (or layered double hydroxides (LDH)) are promising inorganic anion exchangers that might become a new generation of inorganic adsorbents, replacing the current commercial materials of the same chemical nature, AA (activated alumina) and GFH (granulated ferric hydroxide). LDHs are amazing layered materials that are naturally tailored to be perfect anion exchange adsorbents and basic catalysts. The general formula of these materials is as follows:



where M^{2+} typically represents metallic divalent cations, such as Mg, Fe(II), Co(II), Zn and Mn(II), and M^{3+} typically represents trivalent cations, such as Al and Fe(III). However, to date, HTs have not found an industrial application in adsorption and catalysis because the HT synthetic methods used in industries do not provide the surface/structure properties necessary for excellent adsorbents and catalysts, which was demonstrated by the authors who compared the surface and adsorptive properties of the three Mg–Al– CO_3 LDHs synthesised by different methods [17].

The authors developed a cost-effective and easy-to-upscale synthetic method for Mg–Al– CO_3 LDH preparation [18] that produces this material with exceptionally high removal capacities for aqueous selenium species, selenite and selenate. The reason for the high removal efficiency of Mg–Al LDH for selenite and selenate has been explained using extended X-ray absorption fine structure (EXAFS) and FTIR spectroscopy [19]. The main goal of this study was to examine the applicability of Mg–Al– CO_3 LDH in water treatment for the removal of both of the aqueous selenium species. Consequently, the tasks were as follows: (1) to test selenium behaviour under dynamic (column) adsorption conditions at low ($\sim 50 \mu\text{g} [\text{Se}]/\text{L}$) initial concentrations of selenite and selenate; (2) to study the influence of the competing ions (phosphate, sulphate, silicate, carbonate, chloride) on selenite and selenate removal by Mg–Al– CO_3 LDH in static (batch) and dynamic (column) adsorption experiments; (3) to quantitatively characterise additional factors influencing anion exchange adsorption selectivity (pH, anion loading, adsorbent dose, and kinetics of uptake), and (4) to investigate the mechanism of selenite and selenate adsorption by FTIR and mathematical modelling of the experimental adsorption data.

2. Materials and methods

2.1. Materials

The inorganic adsorbent used for this study is Mg–Al– CO_3 layered double hydroxide synthesised via the non-traditional (alkoxide-free) sol–gel synthesis method. The synthesis method was developed specifically to produce an inorganic (an)ion exchanger for the adsorptive removal of the tetrahedral anions, such as arsenate (H_2AsO_4^-) [17]. The idea was based on the HT potential capability to exchange their interlayer anions for aqueous tetrahedral anionic species based on the structural correspondence principle. The interlayer anions were expected to demonstrate a secondary anion removal capacity for surface OH-groups, in addition to the primary and initiating capacity of these groups. However, in many LDHs, the interlayer anions are not involved in the adsorptive removal mechanisms [17]. The synthetic method developed by the authors produces Mg–Al– CO_3 LDH with the highly mobile interlayer ionic carbonate capable of ion exchange with the aqueous selenate [19]. A detailed description of the synthesis approach is shown in [18].

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