Design of Mg-Al-CO_3 layered double hydroxides (LDHs) which are capable to remove aqueous selenate (SeO_4^{2-}) and selenite ($HSeO_3^-$) via direct exchange of the interlayer anions

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Abstract* – *In this work we present the knowledge-based preparation method of Mg-Al layered double hydroxides with predefined properties, purely inorganic synthesis with a step of sol-gel routes. Difference in sorption mechanisms of Se(VI) and Se(IV) was revealed by XPS, EXAFS, FTIR. The removal efficiency was confirmed under static and dynamic conditions.

Keywords – layered double hydroxides (LDHs), fine inorganic synthesis, sol-gel routes, selenate, selenite, batch sorption, column sorption experiments, x-ray photoelectron spectroscopy (XPS), extended x-ray absorption fine structure (EXAFS), Fourier transform-infrared (FTIR) spectroscopy.

Introduction

After arrival of the first commercial inorganic anion exchanger based on (individual) metal oxide (Activated Alumina-AA) for the removal of toxic arsenic species in the beginning of the 21st century, material scientists focus on development of next generations of such inorganic sorbents in order to improve their uptake performance and to broader their sorption applicability. Layered double hydroxides (LDHs) have a greater potential to remove anionic species from water than any bulk structure material of the same chemical nature. Advantage of LDHs consists in existence of the interlayer space which is expected to host aqueous anions, extracted from water solutions. However, despite the well-known superiority of LDHs as anion exchangers, these materials have not reached industrial scale application in water treatment since their discovery in 1842. The list of obstacles in this field includes inertness of the interlayer anions (which are unable to directly exchange with aqueous anions) in all LDHs known from the literature as well as their lower stability in this best solvent. The most popular workaround pathway of using LDHs in the removal of anions (called “memory effect”) has been a preliminary ruining of their layered structure followed by further reconstruction of the layered arrangement at contact with water; the latter process results in incorporation of aqueous anions in-between the layers.

In contrast to the “memory effect” approach, the goal of this work was to develop new Mg-Al-CO_3 LDHs which is capable to directly exchange its interlayer anions with aqueous anions, first of all, of tetrahedral geometry, such as arsenate ($H_2AsO_4^-$), phosphate ($H_2PO_4^-$) and selenate (SeO_4^{2-}), avoiding a stage of destruction of the layered structure via the “memory effect” approach. To achieve this goal, the following tasks had to be carried out:

- using purely inorganic raw materials and reagents to develop a new method of Mg-Al-CO_3 LDHs preparation which includes a step of sol-gel routes in the entire synthetic strategy, for application in water treatment;
- to characterize the synthesis products and to test their sorption affinities to the list of anions;
- to investigate the mechanism of SeO_4^{2-} and $HSeO_3^-$ sorption on the obtained Mg-Al-CO_3 LDHs using XPS, EXAFS and FTIR;

- to prove a capability of the developed Mg-Al-CO_3 LDHs to remove Se(VI) and Se(IV) under both static and dynamic sorption conditions.

Methods: material characterization and sorption experiments

The developed materials were characterized by greater than usual number of methods: N_2 sorption/desorption – surface area, x-ray diffraction (XRD), CHNS elemental analysis, nuclear magnetic resonance (NMR), particle size distribution, thermal gravimetric analysis (TGA), potentiometric titration, zeta-potential, see [1-7] for more details.

In particular, FTIR spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrometer within the range of 400 to 4000 cm^{-1} with 32 scans at a resolution of 2 cm^{-1} using the conventional KBr pellet method in transmission mode, see [4].

The Se K-edge EXAFS spectra (12658 eV) were collected in transmission mode at the ambient temperature at DUBBLE (BM26A) at the European Synchrotron Radiation Facilities (ESRF), Grenoble, France. ESRF. The monochromator was calibrated assigning an energy value of 12658 eV to the first inflection point in the absorption edge.

XPS spectra were written on a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al Kα X-ray source (1486.68 eV). Conditions of writing the spectra: An X-ray beam of 400 μm size at 6 mA x 12 kV; constant analyzer energy mode with a pass energy of 200 eV for the survey; a pass energy of 50 eV for narrow regions; the argon partial pressure of 2×10^{-7} mbar in the analysis chamber.

Batch experiments of Se(VI) and Se(IV) removal included: obtaining equilibrium sorption isotherms, kinetics of sorption at Se concentration levels of mg/L and μg/L, effects of adsorbent doze and competing ions, as well as mathematical modeling of some data. Major experimental conditions were: solid-liquid ratio (adsorbent doze) = 2 g_{dw}/L, background electrolyte = 0.01 NaCl, ambient temperature = 22±2 °C. Adsorption was calculated using the well-known equation (1):

$$q = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where q (mg/g_{dw}) is the amount of selenium sorbed per gram of dry weight of the adsorbent, C_o (mg/L) is the initial concentration of Se, C_{eq} (mg/L) is the final (or equilibrium) concentration of the anion in solution, V (L) the volume of solution, and m (g_{dw}) is the dry mass of the adsorbent.

Dynamic sorption studies (fixed bed columns) were performed in a glass column with inner diameter of 1.1 cm and height of 29.55 cm which was loaded with the previously soaked Mg-Al LDH. Influent water was passed through the columns in a down flow mode with the rate of 1 mL/min, controlled with a Masterflex peristaltic pump (Cole-Parmer, USA) at a constant temperature of 22±2 °C until reaching full saturation of the adsorbent with adsorbate. More details can be seen in [5]. Conditions: Se(VI)/Se(IV) initial concentration was ~50 μg [Se]/L; background electrolyte = 0.01 N NaCl in absence or presence of competing ions, PO_4^{2-} and SO_4^{2-}. The breakthrough capacity (q_b, μg/g) of the columns was calculated by the following expression (2):

$$q = \frac{\int_{V=0}^{V=V} (C_0 - C)\, dV}{m} \qquad (2)$$

where C_0 (μg/L) is the initial adsorbate concentration; C (μg/L) is the anion concentration in the effluent; m (g) is the amount of the adsorbent packed in the column; and V (L) is the volume of water that passes through the column. In the q_b case, $V = V_b$, or the volume passing through until the breakthrough moment, and in the q_s case, $V = V_s$, or the volume of total saturation.

The adsorbent exhaustion rate, AER (the mass of adsorbent used per volume of liquid treated at breakthrough), was estimated using the following formula (3):

$$AER = \frac{m}{V} \qquad (3)$$

where m (g) is mass of adsorbent in the column, and V (L) is the volume of treated water solution until breakthrough.

Chemical analysis: Se concentration (as well as of competing ions) was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The synthetic strategy for preparation of Mg-Al-CO_3 LDHs for water treatment

To produce an inorganic anion exchanger with wanted properties, the following basic principles (background starting points) had to be taken into account:

---The material shall be a layered structure double hydrous oxides with CO_3^- in the interlayer space;

--- The entire preparation approach must be a fine inorganic synthesis which avoids using toxic and expensive alkoxides as raw materials, as well as any other organic reagents including neutralizers, additives and background electrolytes;

--- The synthetic strategy shall include a step of purely inorganic sol-gel transformations, using only inorganic raw precursors and neutralizers;

--- The methodology must have a stage of thermal treatment to guarantee a stability of anion exchanger in water;

--- The temperature of thermal treatment shall not be too high to avoid minimization (elimination) of surface OH^- groups (which initiates anion exchange with aqueous anions);

---The temperature of 300 ^oC, if applied to the final product, is too high and can ruin the layered structure (based on an occurrence of the interlayer CO_3^{2-}) resulting in release of $CO_2\uparrow$; thus, the sense of synthesis would be lost;

--- The synthetic method shall provide high hydration to the final material as it always correlates with considerable anion exchange capacity realized via exchange of surface OH^-.

Application of conventional approaches to preparation of inorganic anion exchangers based on metal oxides does not allow to take into account all the conditions mentioned above. In this work we discovered untraditional compromise ways of Mg-Al LDHs preparation which will be presented at the conference.

The synthesis was carried out in two stages, general scheme of which is shown in Fig. 1. This method was described in details in [1]. Briefly: the stage 1 was a gentle preparation of hydrogel; the stage 2 was a careful search for the best pathways for treatment of hydrogel or xerogel. Any tiny violence/inaccuracy could spoil the entire production and may result in a low-quality anion exchanger which would not be an advantageous material compared with commercial analogues. Dozens of ways of hydrogel/xerogel treatments were tested, nine of which are shown in Fig. 1. Depending on small details of the materials chemistry, hydrogel can differ from transparent homogeneous (A) to porous (C-E) as shown in Fig. 2, so differ the properties.

To select the samples for the next stage investigations we assessed their anion removal performance to many anions [1-2]. The materials which demonstrated a promising sorption of several anions were further characterized for their structural properties, stability in water, XRD-based phase composition and surface chemistry, see [1]. The best pathway(s) for production of Mg-Al-CO_3 LDHs was selected based on combination of the above properties.

Depending on the pathway of hydrogel treatment (see Fig. 1), the material can be a pure layered double hydroxides, an inorganic composite with LDHs or even an amorphous sample. The paths 3a and 4a allow preparation of pure phase Mg-Al-CO_3 LDHs, however the material prepared via 4a was found to be stronger anion remover [1], therefore the pathway-4a-generated LDHs was used in all next investigations shown in [2-7]. The 4a-synthetic procedure was reproduced >60 times which resulted in Mg-Al-CO_3 LDHs with the same structural and sorption properties.

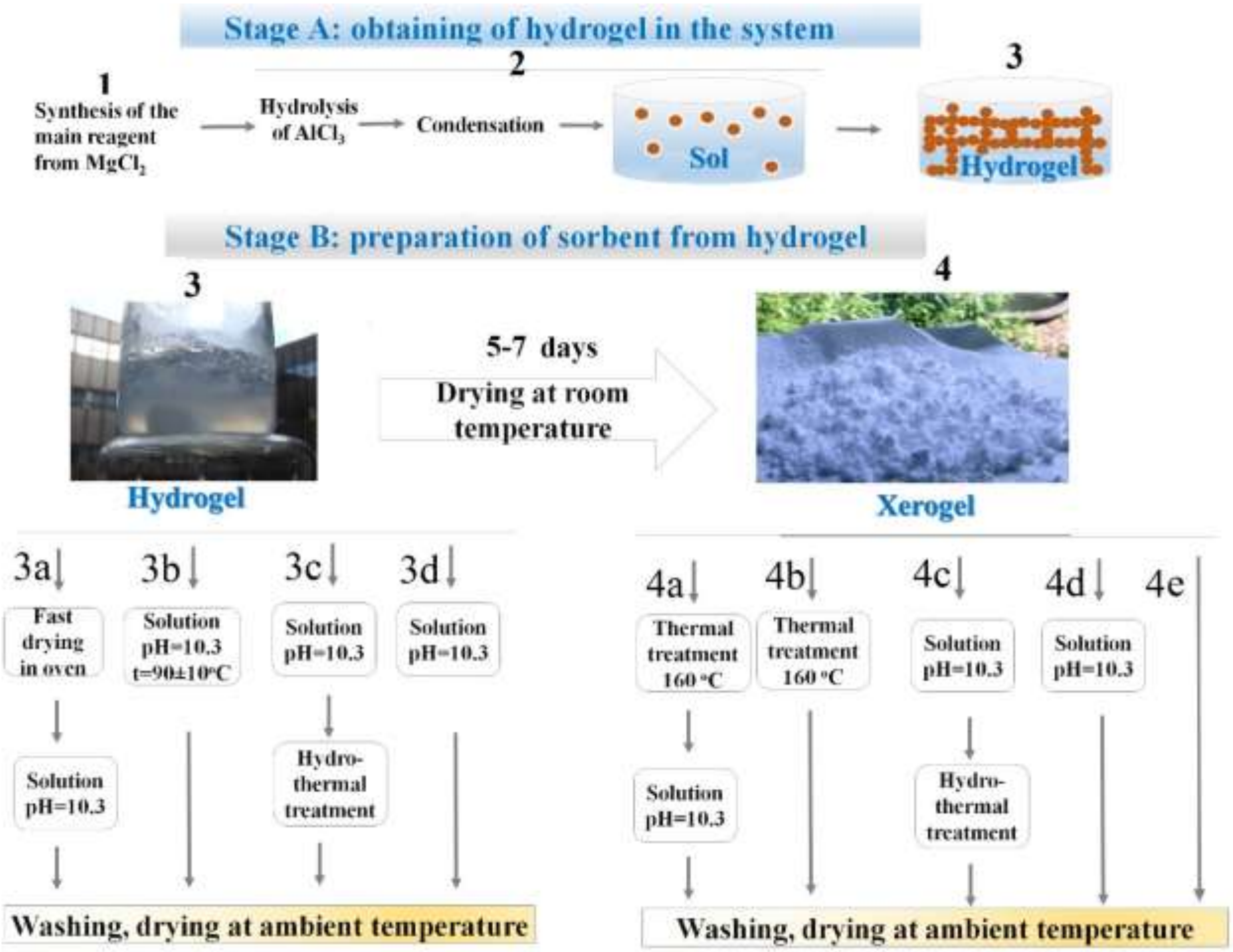

Figure 1. The scheme of preparation of Mg-Al-CO_3 LDHs via a step of alkoxide-free sol-gel routes.

Figure 2. Photographs of hydrogels as a function of small changes in the preparation conditions.

Results and Discussion: material characterization and sorption studies

The developed Mg-Al-CO_3 LDHs demonstrated exceptional or very competitive sorption of many anions ($H_2AsO_4^-$, SeO_4^{2-}, $H_2PO_4^-$, $HSeO_3^-$, As(III), F^-, Br^-, BrO_3^-, H_3BO_3), see [1-7]. However, because the World water authorities considered selenium, especially selenate (SeO_4^{2-}), as anions which cannot be treated by sorption approach, we began investigating the removal of selenium species (Se(VI) and Se(IV)), see [4,5,7]. Fig. 3 presents sorption capacities of Mg-Al-CO_3 LDHs in comparison with other sorbents.

Many experimental and theoretical studies were carried out to explain the exceptional anion exchange capabilities of the 4a-generated Mg-Al-CO_3 LDHs (Fig. 1) and the removal mechanisms, see [2-7]. Comparison of Mg-Al-CO_3 LDHs with LDHs of the same composition produced by the authors [3] using different methods, as well as the review of all available literature [6], revealed a list of properties which distinguish this material from all other LDHs. They are: rich speciation of the chemical elements (Mg, Al, O), phases, interlayer carbonate and high hydration, which altogether provide developed surface area (enriched with OH^{-}) and heterogeneity which result in capability to directly exchange their interlayer CO_3^{2-} with aqueous anions (in contrast to the “memory effect”).

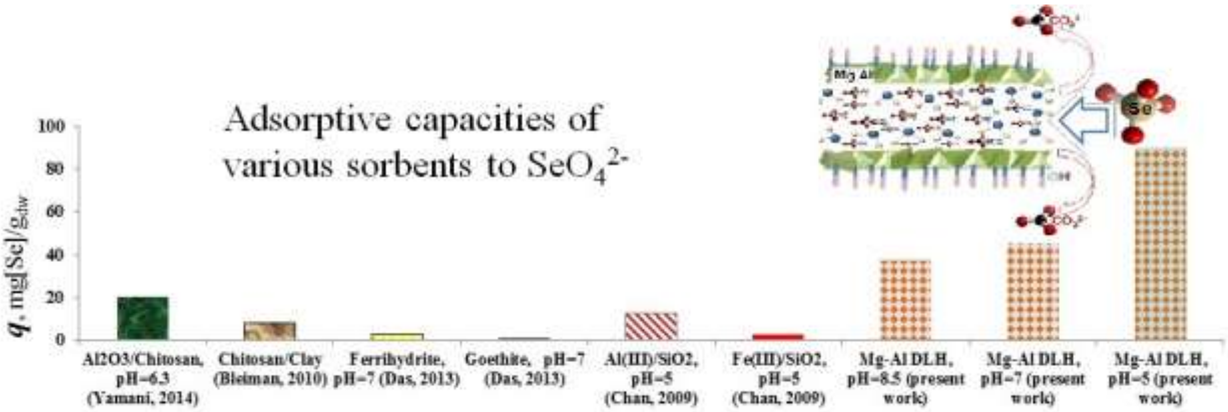

Figure 3. Sorptive removal of Mg-Al-CO_3 LDHs in comparison with other materials [4].

During investigation of the molecular-level mechanism of Se(VI)/Se(IV) sorption [4], for the first time, a theoretical explanation of the unsatisfactory sorption properties of tetrahedral selenium species (SeO_4^{2-}) was found. Due to using EXAFS/FTIR/XRD, it was shown that inner-sphere complexation (chemisorption) of selenate is impossible uptake mechanism on highly hydrated surfaces of Mg and Al oxides, in contrast to $HSeO_3^{-}$. SeO_4^{2-} is removed by Mg-Al-CO_3 LDHs exclusively via anion exchange of surface OH^{-} and interlayer CO_3^{2-}, with further localization in the interlayer space of this material [4]. The reason for stronger affinity of selenite (compared with selenate) to Mg-Al-CO_3 LDHs is a stage of chemisorption in the entire removal process which played a greater role in the uptake of Se(IV) from aqueous solutions than an exchange with the interlayer carbonate, see Fig. 4.

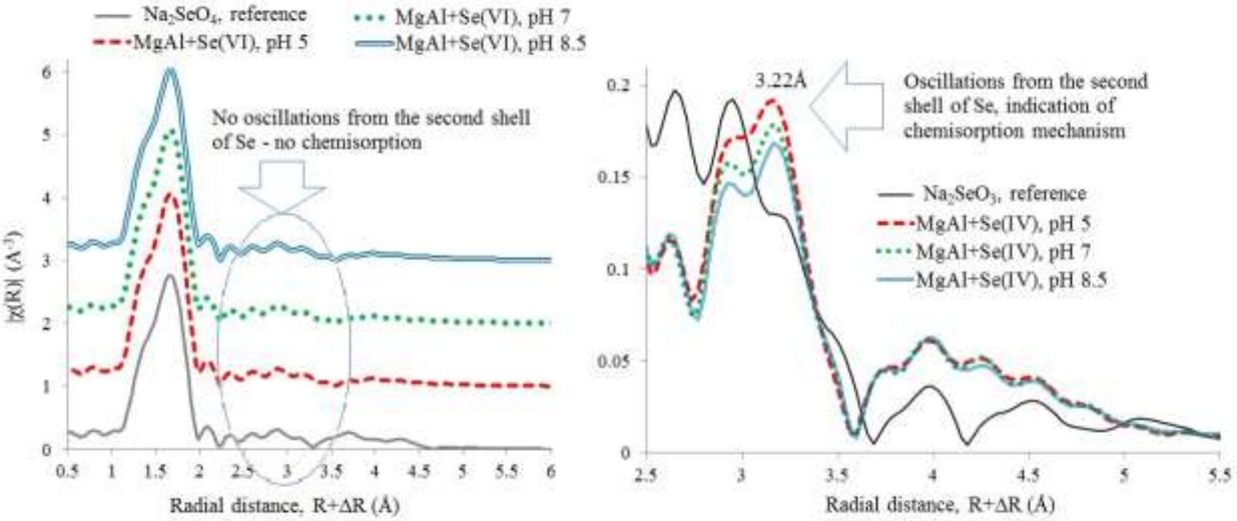

Figure 4. Radial structure around Se (Se(VI)-left and Se(IV)-right) sorbed to Mg-Al-CO_3 LDHs from Fourier transforms of Se K-edge EXAFS oscillations. Modified from [4].

Using XPS analysis, the role of various phases of Mg-Al-CO_3 LDHs in selenate sorption was established as function of two variables: pH (4.5, 7.0 and 8.5) and competing influence of SO_4^{2-}, see [7]. It was shown that among the three major Al-containing phases of Mg-Al-CO_3 LDHs

($Al(OH)_3$, $AlOOH$ i Al_2O_3), $Al(OH)_3$ played predominant role in selenate removal at almost all experimental conditions, see Fig. 5 (a decrease of the respective band). For the first time it was shown that localization of Se(VI) and Se(IV) in the interlayer space of LDHs closes the binding energies of Se 3d in Se(VI)- and Se(IV)-sorbed layered double hydroxides, which allowed to make a contribution to XPS database which had not contained such data yet [7].

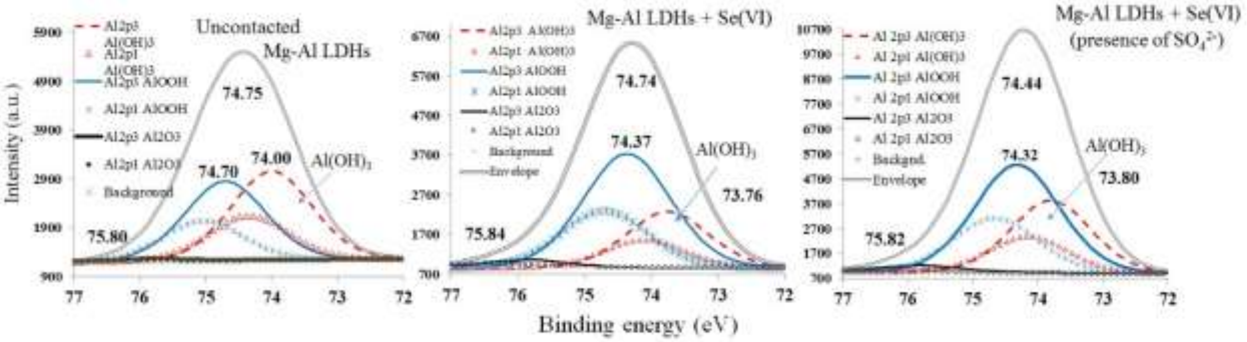

Figure 5. Al 2p XPS spectra in the uncontacted Mg-Al LDHs (left), and after sorption of SeO_4^{2-} in absence (middle) and presence of sulfate (right) at pH=7. Modified from [7].

Possibility of industrial (water treatment) application of Mg-Al-CO_3 LDHs, produced by the developed inorganic (sol-gel) synthesis, has been proved under both static and dynamic sorption experiments, see [5]. This material is capable to extract the low (ppb levels) concentrations of both selenium species (SeO_4^{2-}/$HSeO_3^{-}$) in dynamic sorption conditions in the presence of the main competing anions ($H_2PO_4^{-}$/SO_4^{2-}).

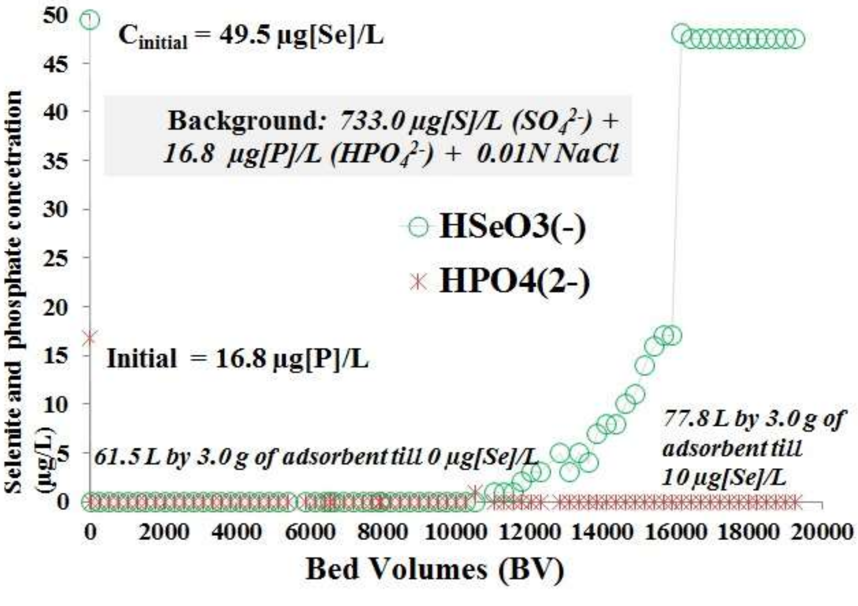

Figure 6. Breakthrough curve of selenite sorption in the presence of phosphate (16.8 µg/L) and sulphate (733.0 µg/L) by Mg-Al LDHs. Experimental conditions: initial concentration of $HSeO_3^-$ = 49.5 µg/L; background electrolyte=0.01N NaCl; mass of adsorbent=3.0 g; bed height=5.6 cm.

A unique property of Mg-Al-CO_3 LDHs to preserve its layered structure at thermal treatment up to 600°C has been discovered [6]. Such resistance to high temperatures principally distinguishes this material from all other LDHs (fabricated by different synthetic methods) which lose their layered arrangement at 300°C transubstantiating into double oxides of bulk (not layered) structure. This property allows to use the thermally treated sample in dynamic sorption (in contrast to all other LDHs) which will extend the list of water purification tasks to be solved by inorganic anion exchangers.

Conclusions

New (fine inorganic with a stage of alkoxide-free sol-gel routes) method of synthesis, which creates complex hydroxides of the layered structure Mg-Al-CO_3 LDHs with unique structural properties and sorptive characteristics to tetrahedral anions, has been discovered. The synthetic method is in principle new approach for production of layered double hydroxides, the strategy of which was based on the final purpose, its application as anion exchanger in water treatment. It is a foundation for elaboration of a new technology for production of layered double hydroxides Mg-Al-CO_3 LDHs aiming for their utilization in both water purification and other industries.

Trying to proper characterize the developed Mg-Al LDHs and to explain its properties, several theoretical elaborations have been made which greatly contributed to advancement of the entire research areas (inorganic anion exchangers and layered double hydroxides).

Acknowledgments

The authors gratefully acknowledge: King Abdullah University of Science and Technology (KAUST) (Saudi Arabia) which funded this research via GCR program (award № KUK-C1-017-12); the Netherlands Organization for Scientific Research (NWO) (The Netherlands) for EXAFS/ XANES studies at Dutch-Belgian Beamline (DUBBLE) at ESRF (France), and grant VEGA 02/0010/18 (Slovak Republic) for XPS analysis.

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