



Applications versus properties of Mg–Al layered double hydroxides provided by their syntheses methods: Alkoxide and alkoxide-free sol–gel syntheses and hydrothermal precipitation



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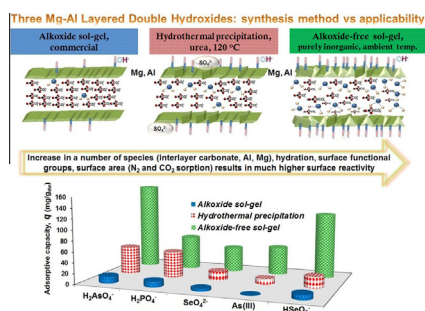
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HIGHLIGHTS

- Mg–Al Layered Double Hydroxides (LDH) structure and reactivity depends on speciation.
- Removal of five toxic anions (arsenic and selenium species, phosphate) was studied.
- Alkoxide sol–gel LDH had a very low adsorptive performance.
- Hydrothermally precipitated LDH demonstrated average adsorptive capacities.
- Alkoxide-free sol–gel generated LDH showed outstanding removal capabilities.

GRAPHICAL ABSTRACT



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ABSTRACT

A tremendous number of studies have examined layered double hydroxides (LDH) for their technological applications in the ion exchange removal of toxic ions, recovery of valuable substances, catalysis, CO₂ capture, as a layered host for storage/delivery of biologically active molecules, additives to plastics and building materials, and other functions. Numerous publications always conclude that the materials (prepared, as a rule, using the oldest synthesis method) are very promising for each investigated application; however, the main chemical industries producing these materials advertise them mainly (or only) as plastic additives. The authors performed extensive research using many of the appropriate methods to compare the structure, surface and adsorptive properties of three Mg–Al LDHs produced by advanced synthesis methods. One industrial sample (by Sasol, Germany) prepared by the alkoxide sol–gel method and two novel Mg–Al LDHs synthesised in-house by alkoxide-free sol–gel and hydrothermal precipitation approaches were investigated. Reasons for the very different adsorptive selectivity of the three LDHs towards arsenate, selenate, phosphate, arsenite and selenite have been provided, highlighting the role of speciation of the interlayer carbonate, aluminium, magnesium, interlayer hydration and moisture content in the adsorptive selectivity towards each toxic anion. This work is the first report presenting the

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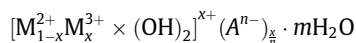
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regularities of the LDHs structure, surface and anion exchange properties as a function of their syntheses method. It establishes the links to potential technological applications of each investigated LDH and explains the necessary properties required to make the technological application cost-effective and efficient. The paper might accelerate industrial applications of these advanced materials.

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1. Introduction

Layered double hydroxides (LDH), also called hydrotalcites (HTs) or, due to their layered structure, anionic clays, are white hydrous minerals with a rhombohedral crystalline system, a low hardness (2.00) and a low density (2.06 g/cm³), which are rare in nature and often associated with serpentine and calcite [1]. The general formula of these substances is



where M²⁺ usually represents metallic divalent cations, such as Mg, Fe(II), Co(II), Zn, Mn(II) and M³⁺ typically represents trivalent cations such as Al or Fe(III). The layered structure was also obtained when a tetravalent metal (instead of trivalent) was used in the composition (such as Zr(IV), Ce(IV), and Sn(IV)) and when the ratio between the divalent and trivalent metals differed from 2:1 [2]. In the last decade, LDHs have been under the focus of material scientists and engineers due to the variety of possible applications, which include (but are not limited to) ion exchange adsorption (mainly the removal of toxic anionic or polar organic species), solid base catalysis (in various processes including biodiesel production), CO₂ capture, heat stabilisation in PVC or as flame retardant additives in plastics, carrier of bioactive molecules in medicine and pigments in cosmetics and other possible applications [1]. The reason for this great focus on these materials is their complex layered structure, wide range of chemical compositions, variable layered charge density, high ion exchange capacity, reactive surface and the interlayer space as well as the possibility to control/change their chemical composition and surface chemistry.

Removal of toxic anions (such as arsenic, selenium, fluoride, and bromate) is an urgent drinking water treatment task recently lowered by World Health Organisation (see the website of WHO). In order to meet the increasingly stronger drinking (and surface/ground) water standards (<5–10 µg/L) new materials (which must be highly selective) and new technologies are of high demand. At present, there are two main commercial adsorptive materials (inorganic ion exchangers) widely used to reduce, first of all, arsenic concentration till <10 µg/L, AA (activated alumina) and GFO (granular ferric oxide). Scientific community however is working on development of new materials with more complex structure than individual hydroxides. Variety of composite (organic + inorganic), mixed and double hydrous oxides are under focus of the researchers who are also exploring their removal performance towards many toxic anions or/and organic persistent molecules [3,4]. LDHs, due to their double anion removal ability, might be one of the alternatives to the two main commercial inorganic ion exchangers. In addition, they can be defined as sustainable materials due to their multiple applications as reviewed by many researchers [1–4].

Today, due to sustainability requirements, for a new material to be suitable for large-scale applications, their synthesis methods should be cost-effective, environmentally friendly and easy to upscale. The methods must also produce the necessary physico-chemical properties for the materials (such as surface chemistry, structure, adsorptive affinity to definite particles, and catalytic activity), which are very different for each sample depending on the synthesis approach applied. Since 1977, when one of the first methods of hydrotalcites preparation (based on the direct

hydrolysis of inorganic salts with a strong alkali) was developed by Miyata and Okada [3], regular attempts to prepare these class materials by other, more advanced, methods including composite materials have been performed [4].

For the moment, the main chemical industries producing hydrotalcites (Kizuma and Sasol) advertise them mainly as plastic additives, as can be observed on their websites [5,6]. To explain this phenomenon, the authors have performed detailed investigations of the surface chemistry, structure and adsorptive properties of three Mg–Al layered double hydrous oxides produced by different yet advanced syntheses approaches. In addition to the scientific task of extending/deepening the knowledge about LDHs, the main technology-oriented goal of this work has been to speed up the industrial application of these materials by establishing regularities between the synthesis method, surface/structure/properties and potential applications, first of all in water treatment and catalysis.

Three samples of Mg–Al LDHs were used in this study. Two of them are new materials synthesised in-house using a novel alkoxide-free sol–gel synthesis method [7] and hydrothermal precipitation [8]. One industrial sample (by Sasol industry (Germany)) produced by the traditional, yet improved, sol–gel synthesis was also investigated [6]. The authors consider the three synthesis methods used to prepare the three investigated LDHs more advanced comparing to the other ones, first of all, the most widely spread direct precipitation by strong bases (NaOH, Na₂CO₃ or their combination) or any modification of, in principle, the same approach listed in [1–4]. Many appropriate methods were applied to examine the surface, structure and adsorptive removal properties towards the target (for water treatment) anions of these materials.

2. Experimental section: materials and methods

2.1. Synthesis of Mg–Al Double-Layered Hydrous Oxides

2.1.1. Alkoxide sol–gel method (Mg–Al-ASG)

Metal alkoxides are the most popular (and generic) raw materials in sol–gel syntheses [1,2]. The most widely used metal alkoxides are the alkoxy silanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). Industrial production of Mg–Al LDH by the German company Sasol is based on such a synthesis approach (via hydrolysis of heterometallic alcoholates) [6]. The refined synthesis method has been patented. Their material PURAL MG 63 HT (Product No. 595063) was used in this study. In this paper, this material is referred to as Mg–Al-ASG, which means that the Mg–Al layered double hydroxide was produced via the alkoxide sol–gel method.

2.1.2. Alkoxide-free sol–gel synthesis (Mg–Al-AFSG)

The advantages of sol–gel-generated materials encouraged researchers to search for new syntheses routes that were also cost-effective, easier to upscale and environmentally friendly. The main efforts were directed at replacing the metal alkoxides with inorganic salts while still maintaining the sol–gel routes in the system. Recent work in this area performed by the authors resulted in the novel synthesis method of Mg–Al LDH production [7]. The best way of hydrogel treatment (out of 9 chosen ways) was selected and

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