



Layered double hydroxides: Emerging sorbent materials for analytical extractions



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ABSTRACT

Layered double hydroxides (LDHs) comprise a category of inorganic materials with highly tunable composition and structures. These materials have shown exciting properties such as high surface area, two-dimensional structures, high thermal stability, and excellent anion-exchange capabilities. To date, these materials have been mostly used in catalysis, flame retardants, drug delivery, super capacitors, polyelectrolyte fuel cells, electrochemical sensors, and biosensors, and removal of organic and inorganic pollutants from different media. However, in recent times, there is an emerging trend in their application in analytical extractions such as solid-phase extraction (SPE), solid-phase microextraction (SPME), and dispersive SPE (DSPE). Hence, this review aims to provide a brief overview of this new trend to the analytical community.

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1. Introduction

Layered double hydroxides (LDHs) represent a fascinating class of inorganic materials with variable chemical composition and structures. They are also known as hydrotalcites or anionic clays. Typically, LDHs are two-dimensional nanostructured materials consisting of positively charged layers of metal hydroxides with charge-balancing

Abbreviations: CNTs, carbon nanotubes; DS, dodecyl sulfate; DSPE, dispersive solid-phase extraction; DSPME, dispersive solid-phase microextraction; FID, flame ionization detector; GC-MS, gas chromatography–mass spectrometry; HG-AAS, hydride generation atomic absorption spectroscopy; HPLC, high-performance liquid chromatography; HS-SPME, headspace solid-phase microextraction; MP, methyl parathion; NanoPt, nano-sized platinum; NPs, nanoparticles; PAHs, polycyclic aromatic hydrocarbons; SDBS, sodium dodecyl benzene sulfonate; SWV, squarewave voltammetry; TDH, three dimensionally honeycomb.

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anions and some water molecules located in between the layers. LDHs are denoted by the general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot nH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal cations and A^{n-} is the interlayer guest ion with n- valence. The values of x vary between 0.22 and 0.33 [1]. LDHs have structural similarity with brucite, $Mg(OH)_2$, where Mg^{2+} is surrounded by six OH^- ions and the resulting octahedral structures are connected to each other to form an infinite two-dimensional layer. Replacement of some divalent ions with trivalent ions results in the formation of a positive charge on brucite-like layers. This positive charge can be balanced by localizing anions in the interlayer spaces. Water molecules are also present in the interlayer spaces stabilizing the structure, and the resulting structures are known as LDHs. (Structure of brucite and hydrotalcites is given in Fig. 1.) [2] The electrostatic interaction and hydrogen bonding between the layer and interlayer contents hold the structure in place. Different divalent and trivalent ions can be used in the formation of LDHs provided that their radii are not significantly different from those of Mg^{2+} and Al^{3+} [3].

The properties which make LDHs useful materials are their low cost, two-dimensional structure, high surface area, positive charge

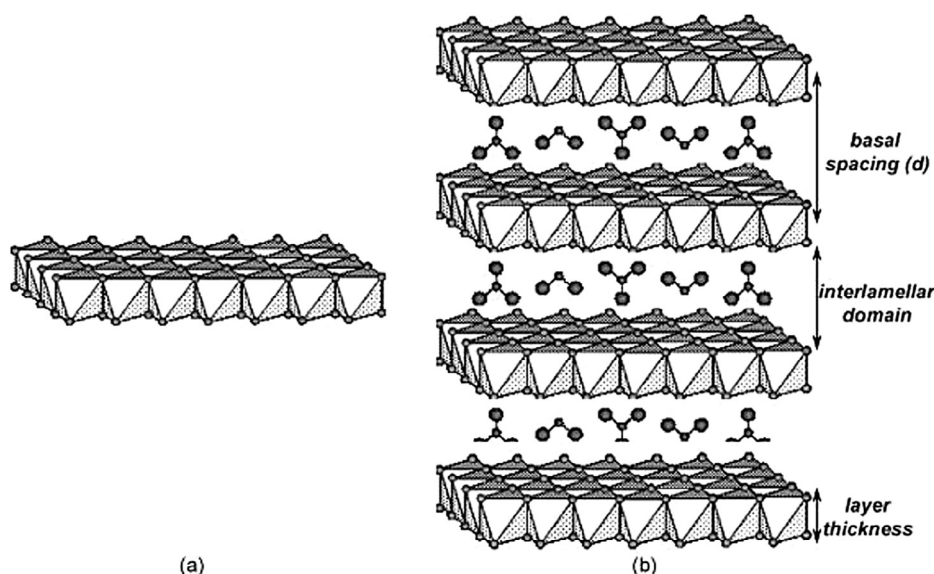


Fig. 1. Schematic structural representation: (a) brucite; (b) hydrotalcite. Reproduced with permission from [2]. Copyright 2007 Elsevier.

on the surface, high anion-exchange capacities, tunable interior architecture, and resistant to changes upon heating. Significant number of reports can be found on the applications of LDHs in catalysis [4,5], flame retardants [6], adsorption [7,8], drug delivery [9–11], super capacitors [12,13], fuel cells [14], electrochemical sensors [15], and biosensors [16,17], and many other fields. Most notable, however, is their potential as adsorbents. LDHs have excellent adsorbing properties because of three major reasons:

- (i) large interlayer spaces (high porosity)
- (ii) huge number of exchangeable anions in between the positively charged layers
- (iii) water-resistant structure.

LDHs have shown considerable applications as anion exchangers. Their high anion uptakes can be attributed to large surface area, high anion-exchange capacities, and highly tunable and flexible interlayer spaces. LDHs can adsorb anions via direct adsorption or anion exchange or by hydration of calcined LDH in an anion-containing aqueous solution [8]. This hydration of calcined LDH signifies their fascinating property of “memory effect.” [18] During calcination at high temperatures, interlayer anions and water molecules of LDHs are eliminated and they transform into a mixture of oxides. When such mixtures are rehydrated in anionic solutions, it leads to reconstruction of the structure of LDHs with intercalated anions. As LDHs have the ability to reform their structure, they can be easily recycled and reused which is a desirable property in any good adsorbent material [8]. Anion-exchange capacities of LDHs are, however, affected by the nature of intercalated anions present initially and layer charge density (ratio of M^{2+}/M^{3+}).

Although LDHs have exchangeable anions which can be easily replaced by other inorganic anions, their highly tunable structure also allows replacing the interlayer anions with organic anions. These organic anion-intercalated LDHs show hydrophobic character and high affinity toward organic molecules. LDHs can be categorized into four types:

- (i) Parent LDH crystallites (Original LDH with interlayered inorganic anions): they are hydrophilic in nature. Such LDHs are excellent anion exchangers, and interlayer spaces of these LDHs are accessible not only to anions but also to polar molecules.
- (ii) Calcined LDHs: The interlayer inorganic anions and water molecules are removed by thermal treatment. The obtained material can retake anions and water into the interlayer spaces upon treatment with an anionic solution. Hence, calcined LDHs are added to the solution of anions of interest and they can take new anions into their interlayer spaces as a result of “memory effect.” Pictorial representation of “memory effect” is given in Fig. 2. Such LDHs can take inorganic or organic anions and can adsorb organic molecules such as phenols [19].
- (iii) Organically modified LDH structures: The interlayer inorganic anions are replaced by organic anions, or organic anions are introduced during synthesis. These LDHs are hydrophobic in nature and show special affinity toward the organic target molecule [20]. A range of organic anions can be intercalated inside the interlayer spaces [21]. Possibly, sorption capacity of LDHs for nonionic organic pollutants can be enhanced by the intercalation of organic anions such as surfactants into the interlayer spaces of LDH. Such intercalation

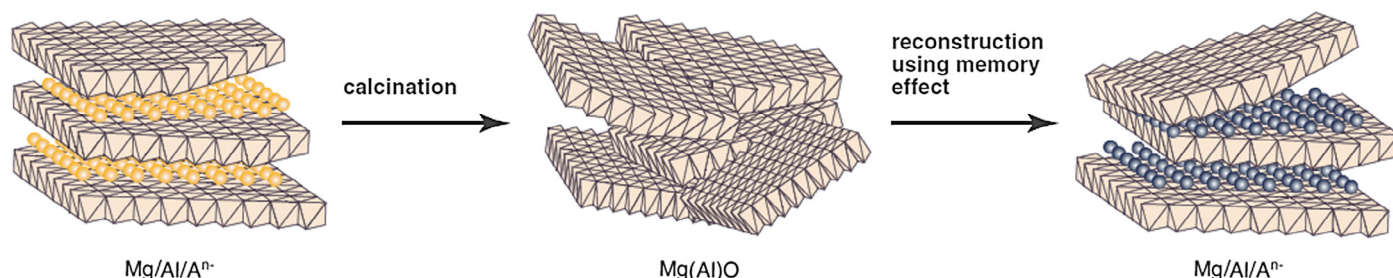


Fig. 2. Pictorial representation of memory effect. Reproduced with permission from [56]. Copyright 2003 Springer-Verlag Wien.

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