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Chapter 2

LAYERED DOUBLE HYDROXIDES APPLICATIONS AS SORBENTS FOR ENVIRONMENTAL REMEDIATION

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ABSTRACT

The development of new techniques for pollution remediation is an area of high priority due to the increasing contamination of water and soils and the consequent risks to both human health and environmental equilibrium. The pollution causes are extremely diverse and, consequently, the chemicals object of remediation range from inorganic, (heavy metals, arseniate, chromate, cyanide, fluoride, etc.) to organic (petroleum by-products, pesticides, surfactants, among others). Different remediation procedures, involving chemical, biochemical or physicochemical technologies are employed according to the pollutant and the characteristics of the polluted media. One of the most widely studied is the removal or immobilization of the contaminant using sorbents such as active carbon, zeolites, ion exchange resins and layered double hydroxides (LDHs).

LDHs are mineral and synthetic compounds formed by brucite ($\text{Mg}(\text{OH})_2$)-like layers with partial isomorphic substitution by trivalent cations. This replacement leads to a positive charge excess compensated by anions weakly bonded by electrostatic forces and placed in the interlayer space. LDHs present an huge customization capacity: a wide range of metal ions, either divalent (Mg^{2+} , Ca^{2+} , Ni^{2+} , Fe^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , ...) or trivalent (Al^{3+} , Fe^{3+} , Cr^{3+} , ...) can be arranged in the layers. Different anions (from simple and small inorganic anions such as chloride, nitrate or carbonate, to large organic and biological anions such as surfactants, pharmaceutical drugs, and even biomolecules) can also be included due to these solids capacity to expand the interlayer distance.

The main features of these solids are a high anion exchange capacity (around 3 meq/g), the layers instability at low pHs and the capacity to reconstruct its lamellar structure from the oxides obtained by their calcination. Due to their anion exchange properties, LDHs are studied as sorbents for a wide variety of water pollutants either

inorganic (arseniate, chromate) or organic (pesticides, dyes) anions. The contaminant uptake during the reconstruction process of calcined LDHs has also been extensively studied and the acid base buffering properties of LDHs produce heavy metal ions precipitation as hydroxides, either as part of the hydroxylated layers or in a separate hydroxide phase. Also, due to their customization capacity, the environmental applications of LDHs can be extended: modification of LDHs with organic anions allows adsorption of neutral or even positively charged apolar species in the interlayer or in the surface of the solids and the intercalation of polydentate ligands such as citrate, malate and ethylenediaminetetraacetate (EDTA) modifies the metal ions uptake capacity of the hydroxylated layers. In this chapter, the LDHs properties will be described and their uptake mechanisms analyzed. On this base, their applications as pollutant scavengers will be reviewed and analyzed, highlighting the factors that affect the sorbents behavior and the customization strategies used to obtain an optimal performance.

1. INTRODUCTION

Environmental pollution, originated either by human activity or natural sources, is an important issue of public health. The increasing industrialization and population contribute to the rising pollution of water and surrounding soils that affect the aquatic life and causes a shortage of fresh and clean drinking water [1]. A wide range of remediation techniques are necessary to cover the increasingly restrictive regulations, the large number and wide variety of pollutants, media and conditions of application, and the complex chemistry involved in natural media. Ion exchange, adsorption, membrane filtration, coagulation, filtration, solvent extraction, adsorption, electrolysis and microbial biodegradation are some of the techniques for wastewater remediation. Among them, the use of sorbents is quite extended because of their effectiveness, easy operation and simple design. Activated carbon is the most common sorbent for the removal of diverse types of pollutants, however, its widespread use is restricted due to its high operational cost. Other sorbents, such as activated alumina [2], zeolites [3], clays [4], and agricultural products and by-products [1] are increasingly studied in remediation systems by both industry and academia. Layered double hydroxides (LDHs) are lamellar compounds that present structural positive charges, leading to anion intercalation and exchange properties attractive for environmental applications [5,6,7]. LDHs offer other features that extend their environmental applications, such as acid-base buffering capacity, catalytic activity and reconstruction reactions. LDHs also exhibit variable composition, allowing an easy optimization of their physicochemical properties and additional functionalization. In this chapter, the LDHs physicochemical properties are described and their uptake mechanisms analyzed. On this basis, their applications as pollutant scavengers will be reviewed, highlighting the factors that affect the sorbents behavior and the customization strategies used to obtain an optimal performance.

1.1. LDHs Structure

LDHs present a two-dimensional structure derived from that of brucite ($\text{Mg}(\text{OH})_2$), which can be described as a close compact packing of hydroxyl anions with half octahedral sites occupied by divalent cations, leading to edge-sharing octahedrae layers.

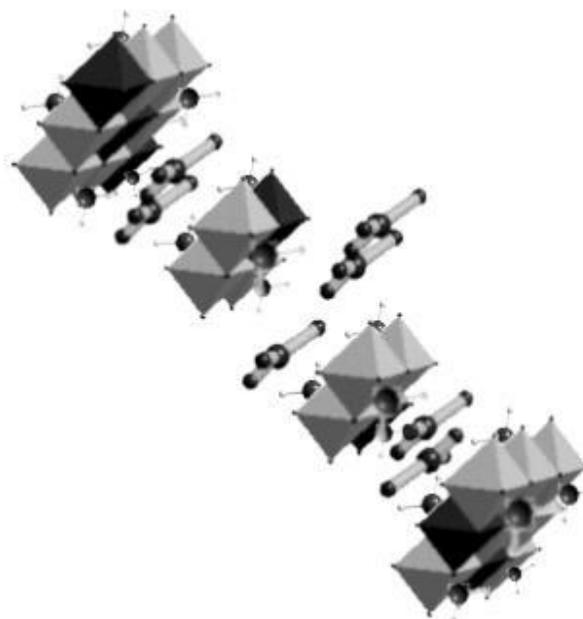


Figure 1. Structure of a carbonate intercalated LDH.

LDHs structure derives from isomorphic substitution by trivalent cations, which produce an overall positive charge in the layers. This charge is balanced by the introduction of anions in the space between the layers where water molecules are also placed (Figure 1). The general formula of LDHs is $[M_{1-x}^{II}M_x^{III}(OH)_2]A_{x/n}^{n-} \cdot mH_2O$, where M^{II} and M^{III} represent the divalent and trivalent metal ions and A^{n-} is the interlayer anion. The identity of M^{II} ($=Mg^{2+}$, Ca^{2+} , Ni^{2+} , Fe^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , ...), M^{III} ($=Al^{3+}$, Fe^{3+} , Cr^{3+} , ...) and A^{n-} (from simple and small inorganic anions such as chloride, nitrate or carbonate, to large organic and biological anions such as surfactants, pharmaceutical drugs, and even biomolecules) is quite variable, and the charge density and anion exchange capacity of LDHs are also adjusted by the x ($=M^{III}/(M^{II} + M^{III})$ atomic ratio) parameter.

1.2. Synthesis of LDHs

LDHs can be found in nature as minerals such as hydrotalcite and manassite (Mg-Al LDH), pyroaurite (Mg-Fe LDH), takovite (Ni-Al LDH), etc, whose interlayer anion is most of times carbonate, although chloride and sulfate are sometimes present [8,9]. LDHs are also synthesized quite easily at laboratory scale, but appropriate synthesis routes and conditions are needed to obtain complex LDH phases with a fine tuning of their properties, with special effect in particle crystallinity and size [10]. Coprecipitation is one of the more usual synthesis methods for its simplicity, flexibility and capacity to obtain solids with different compositions and physicochemical properties [11,12]. It involves the mixture of solutions of the metal ions and the hydroxyl anions that constitute the layers in the presence of a salt of the interlayer

anion. This method is performed at constant pH [13] (or low supersaturation conditions) when the metal ions and the base solutions are slowly and simultaneously added to a solution containing the interlayer anion, their addition rate being controlled to maintain a constant pH. Conversely, it is performed at variable pH [14] (or high supersaturation conditions) when either the base or the metal ions are dissolved with the interlayer anion, and the remaining reactive is added without any pH control. In all cases nitrogen purging is necessary if carbonate intercalation is not desired. Coprecipitation at constant pH generally produces more crystalline particles and larger than those at variable pH. Aging stages, either at room temperature and pressure or at hydrothermal conditions in an autoclave, can be added if higher crystallinity is required.

Variations of the coprecipitation method include homogeneous precipitation by urea hydrolysis [15,16] and fast coprecipitation followed by phase separation and hydrothermal treatment in pure water [17,18], obtaining samples with very large and small particles, respectively. If the interlayer anion of choice can not be incorporated by the coprecipitation method, the anion exchange capacity of the solids and their reconstruction reactions (see below) can be used to replace the interlayer anion of a LDH intercalated with chloride, nitrate, carbonate, etc.

Other synthesis methods include salt-oxide and sol-gel reactions, formation at metal hydroxide particle surfaces, etc. [10] and new synthesis routes are continuously proposed. Thus, Valente et al [19,20] recently proposed a variation of the salt-oxide method as a environmentally friendly synthesis route to obtain LDHs in industrial scale. In addition, Zhou et al [21] recently reported the synthesis of Zn-Al-NO₃ LDHs, controlled to obtain hollow microspheres with enhanced phosphate uptake capacity.

Layered double hydroxides are also produced by the neutralization of red mud, a bauxite refinery by-product. This residue consists primarily of iron, aluminum, silica and titanium oxides; and traces of heavy metals, and its disposal involves a serious environmental and economic problem. Seawater neutralization reduces both pH and dissolved metal concentration of the residue, through the precipitation of magnesium, calcium, aluminum hydroxides and carbonate phases with LDH structure [22]. These neutralized red muds are studied as sorbents or stabilizers of heavy metal cations or oxyanions [23], the LDH presence being essential to understand their behavior.

2. LDHS PROPERTIES AND REACTIVITY

The LDH properties and derived reactivity are of primary importance to understand the removal mechanisms, highlight their advantages as pollutant sorbents and optimize their behavior. These solids present interesting bulk properties: 1) anion exchange due to their structural charge and swellable interlayer space, 2) acid-base dissolution reactions of the hydroxylated layers and 3) reconstruction, the ability of the mixed oxides obtained by LDH calcination to recover their layered structure. The surface properties of these solids (particle charge [24], hydrophobic/hydrophilic character [25]) are also key factors to optimize their adsorptive properties [26]; and the interlayer anion also extends the properties and functionalities of LDHs. Next, an analysis of the main LDHs features relevant to pollutant removal applications is included.

2.1. Anion Exchange

For both cationic clays and polymer resins, the ion exchange process is described as a partial or total substitution of movable ions electrostatically attached to a structure with opposite charges. Consequently, these solids are considered as a solid solution phase where the ions are attached to equivalent binding sites and the solid structure remains unaffected [27]. For LDHs, anion exchange properties arise from the permanent charge of the layers, produced by the introduction of trivalent ions. The interlayer anion is attached to the solid by generally weak electrostatic forces that allow anion exchange. In previous works [28], a model for the LDHs reactivity was proposed where the structural charge is considered placed in an internal plane of the solid and compensated by neutral X sites that undergo anion binding reactions:



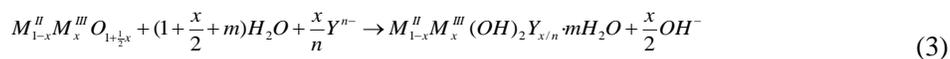
where X represents neutral, unoccupied sites, XA^- negatively charged, occupied sites, and A^- anions in solution. Ion exchange reactions were then written as follows:



LDHs anion exchange capacity (AEC) is easily calculated from the number of trivalent cations per formula unit and the formula weight of the corresponding solid. Typical AEC values range from 2 to 4 meq g^{-1} , much higher than those of clays such as montmorillonite (around 1 meq/g). Anion exchange is greatly influenced by outgoing interlayer anion: small, highly charged anions establish stronger electrostatic bonding with the layers than large, monovalent anions, the former being more difficult to exchange [29, 30, 31]. Additional stabilization is also produced by hydrogen bonding between the interlayer anion and the hydroxylated layers [32]. This effect is illustrated by the strong uptake capacity decrease with increasing M^{II}/M^{III} ratio obtained by Prasanna et al [33] for iodide sorption by Mg-Al- NO_3 LDHs (see section 3.1). Anion exchange is also greatly influenced by the pH of the polluted media. Extreme alkaline conditions imply competition either by hydroxyl or carbonate anions. Furthermore, deprotonation reactions of hydroxyl groups of the layers are also produced with increasing pH, leading to layer charge compensation and decrease in AEC [28]. At low pH conditions, LDH weathering reactions reduce their effectiveness but, in some cases. Acidic media lead to protonation of interlayer anions such as carbonate, which is more easily detached at pH values below 5, easing the scavenging of fluoride (see section 3.1).

2.2. Reconstruction

LDH calcination produce a solid solution of the corresponding metal oxides ($M_{1-x}^{II}M_x^{III}O_{1+\frac{1}{2}x}$) with strong Lewis basic character and large specific surface area. The calcined solids recover the original layered structure when dispersed in aqueous solutions and pollutants can be incorporated as charge-balancing anions in the reconstruction reaction:



Hydroxide anions are produced during the reconstruction reaction, the equilibrium being shifted to products in acid media [34]. Similarly to anion exchange, the incoming anions are considered attached by electrostatic interactions to equivalent binding sites. Reconstruction presents advantages compared to anion exchange [35,36]: 1) absence of interlayer anion, avoiding its competition for anion binding sites; 2) easy sorbent recycling, by removal of volatile or reducing pollutants during the calcination process; 3) enhanced access to active sites as a result of the high surface area and microporosity of the calcined products; 4) improved sorbent stabilization in acid media due to the proton-consumption during the reconstruction process.

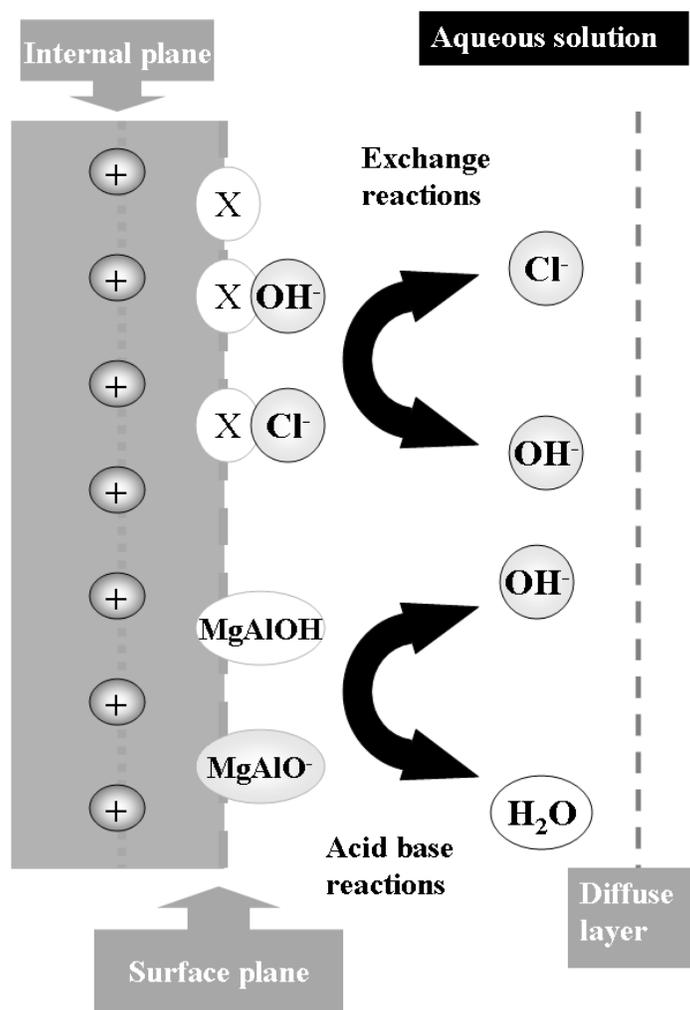
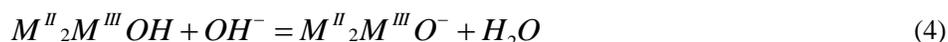


Figure 2. Schematic drawing of the LDH/solution interface including permanent and variable (hydroxyl anions adsorption) charges.

2.3. Adsorption

The term adsorption refers to the accumulation of a substance at the interface between two phases such as solid and liquid or solid and gas. In this chapter, it will be considered to involve binding at the LDH-water interface by other chemical forces besides electrostatic interactions, in order to distinguish adsorption from anion exchange reactions produced at the LDH surface. It is common to use physical adsorption models (Langmuir, Freundlich) to represent the equilibrium between the LDH surface and the adsorbate and even its anion exchange behavior. These models assume the presence of only one type of surface sites where the adsorbate can be attached, these sites being invariable with factors such as pH or particle charge. In the case of LDHs, as with other metal (hydr)oxides [37,38], the application of surface complexation models is more accurate since they describe the adsorption behavior as a function of pH; and the effect of particle charge is included by the introduction of an electric double layer model. In previous works [28, 39], a model for the LDH/aqueous solution interface has been proposed, where the LDH particle surface is described by two kinds of binding sites: exchange sites due to the permanent, structural charges (X sites, previously described) and sites produced by specific interactions between the anions and the particle surface (exemplified in Figure 2 for the case of hydroxyl anions adsorption). This model allowed explaining the reactivity and surface charging behavior of LDHs. Due to the structural charge of the layers, LDH particles show an overall positive charge in aqueous dispersions when anions only interacting by electrostatic forces are placed at its surface. Contrarily, adsorption produces a decrease in surface charge and even negatively charged particles. The interactions between the surface and the adsorbate are quite diverse, leading to different binding sites:

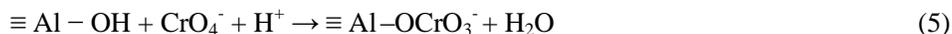
- Hydroxyl anions produce deprotonation reactions, which can be written as follows:



where $M^{II}_2M^{III}OH$ and $M^{II}_2M^{III}O^-$ represent protonated (neutral) and deprotonated (negatively charged) sites, respectively. As pH increases, $M^{II}_2M^{III}OH$ groups become deprotonated, inducing anion detachment from X sites to compensate the negative charge introduced and a particle charge and zeta potential reversal at extreme pH values [40].

- Surfactants are adsorbed due to lateral interactions between their aliphatic tails. They are first bonded by electrostatic interactions, lying flat on the particle surface but, when the surface anion concentration is high enough, lateral interactions rise and a monolayer arrangement is produced, the polar groups of the anions pointing to the particle surface. Once the charge of the surface is fully compensated, additional surfactants units are disposed in a bilayer arrangement, their polar groups pointing to the aqueous side of the interface, leading to negatively charged particles [41].
- Inorganic oxyanions, such as CrO_4^{2-} , HVO_4^{2-} and SO_4^{2-} , also present a chemical affinity for LDHs. Uptake capacities higher than the AEC and displacements of the isoelectric point (pH where positive and negative charges are compensated) were observed by Chatelet and coworkers [42] for chromate and sulfate uptake by calcined

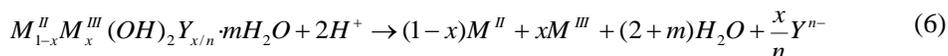
LDHs. These results were explained by the presence of adsorption sites at the surface of LDHs. More recently, Goh et al [43] proposed, for the uptake of these oxyanions, a ligand exchange mechanism, responsible for the high sorption capacity of Mg-Al LDHs. For chromate anions these reactions can be written as follows:



The replacement of the hydroxyl group oxyanion partially compensated the oxyanion charge, increasing the uptake capacity beyond the AEC, while the metal-oxyanion bonding increases the oxyanion affinity, explaining the isoelectric point shift.

2.4. Weathering

As other metal hydroxides, LDHs undergo weathering reactions in acid media that can be written as follows:



Weathering reactions present great importance for their applications as sorbents. It produces a pH increase that leads to heavy metal removal by precipitation of their hydroxides, either as part of LDHs structure or as a separate phase [44] while the release of metal ions also produce coagulation of anionic pollutants such as phosphate [45] or humic acids [46]. On the other hand, LDH weathering leads to a decrease in the amount of sorbent dispersed in the polluted media, decreasing its effectiveness as anion exchanger [47]. LDH weathering extent and rate increase with decreasing pH [48]; it is also affected by the metal ions that constitute their layers [49].

2.5. LDHs Functionalization

The interlayer anion also gives an additional functionality to both the interlayer and the surface of LDHs. Thus, the intercalation of organic anions with large hydrocarbon chains produces an expansion of the interlayer space and imparts hydrophobic properties to the interlayer and the surface of the LDH particles. Many organic anions have been used to alter the adsorption properties of LDHs, however, the most common are dodecylsulfate (DDS⁻) and dodecylbenzylsulfonate (DBS⁻). In these solids, the organic anions are disposed with their polar group (-COO⁻, -SO₃⁻, PO₃⁻, etc.) pointing to the hydroxylated layers while the hydrophobic section dispose vertical or tilted, minimizing the free energy of the solid. These anions are generally disposed in monolayers but, depending on the charge density of the layers and the anion size, bilayer or intertwined structures are also possible (Figure 3). Finally, organic anions with two opposite anionic groups bridge consecutive layers in monolayer arrangements. Neutral, apolar species can then be sorpted by these organic-LDHs either by partition [50] between the aqueous phase and the hydrophobized interlayer or by adsorption at the particle surface [26, 39].

A maximum hydrophobization not always results in an optimized uptake capacity of hydrophobic compounds: clogging of the interlayer space as a result of inclusion of large organic anions or high anion concentration may produce a sorption decrease. Dutta and Robins [51] concluded that pyrene affinity for Li-Al LDH hybrids with mystiric, hexanoic and succinic acids was mainly determined by the anion arrangement, rigidly or tightly packed structures leading to low partition coefficients.

In this way, Zhao and Nagy [52] reported that the maximum affinity of tri- and tetrachloroethylene for dodecylsulfate intercalated Mg-Al LDHs was obtained for a $M^{II}/M^{III}=3$ solid, which presented a loose, intertwined bilayer structure. These authors also indicated that decreasing the Mg/Al ratio increased the DDS^- density, while higher ratios led to a more closely packed monolayer arrangement. The interlayer anion arrangement also depends on the length of its hydrocarbon chains and its structure. Chuang et al [53], reported a higher naphthalene affinity for a rhamnolipid intercalated than for a DDS^- containing 2:1 Mg-Al LDHs, assigned to the more open structure of the former. The intercalation of cyclodextrins, on the other hand, is an example of LDHs acting exclusively as a matrix that supports the interlayer anion, which presents capacity to encapsulate hydrophobic substances such as trichloroethylene, tetrachloroethylene, toluene [54], phenol, nitrobenzene [55], etc. The intercalation of polydentate ligands such as citrate, malate [56], tartrate or ethylenediaminetetraacetate (EDTA) [44] also imparts heavy metal cations chelation properties to LDHs.

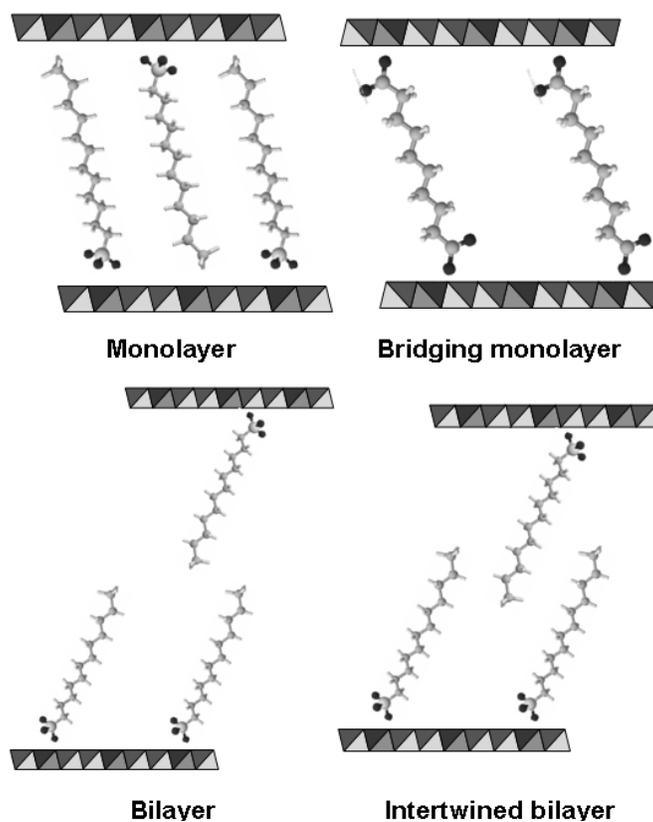


Figure 3. Representation of different organic anions arrangements between LDH layers.

LDH properties are also extended by formation of composites with other materials such as polymers and biopolymers [57,58,59], or active carbon [60], etc. In this way, the combination of LDHs with polyacrylamide to form beads allows its use in fixed-bed filters [57,58] as filter blockages are produced due to the reduced size of pure, powdered LDH particles. Mg-Al-CO₃ LDHs composites with polymerin, a humic acid-like fraction naturally occurring in olive oil mill waste waters, produced simultaneous removal of anions (arsenate) and cations (Zn²⁺). The sorbent also presented increased stability and easier sorbent recovery compared with pure LDH and polymerin, respectively [61].

3. SORPTION OF INORGANIC POLLUTANTS

Inorganic pollutants are naturally found in the environment but, due to human development, they are often concentrated and released, being toxic to humans and the natural world. Since the affinity sequence for simple inorganic anions was established [29], numerous studies on LDH uptake of halides (F⁻, Cl⁻, Br⁻, I⁻) and oxyanions (NO₃⁻, SO₄²⁻, PO₄³⁻, AsO₄³⁻, etc) [62] have been performed. Halides are almost exclusively attached by electrostatic interactions, being incorporated by anion exchange and reconstruction reactions. Oxyanions establish, besides electrostatic interactions, chemical bonds with the layers, leading to adsorption processes. In some cases, inorganic anions can also be removed by the dissolution of the inorganic matrix and the precipitation of insoluble salts of the corresponding pollutant with the layer constituting cations. The study was afterwards extended to heavy metal ions, their removal being produced either by hydroxide precipitation or by chelation with polydentate ligands intercalated between the LDH layers.

3.1. Halides

Halides are constituents of all natural waters and only at high concentrations are considered as pollutants. Fluoride present human health benefits, but causes acute poisoning at high concentrations; its recommended concentration for human is 1-1.5 mg/L according to the World Health Organization (WHO) [71]. High chloride concentrations are delivered by wastewaters of canning and tanning industries, with negative impact on the environmental equilibrium due to water salinity alteration [72]. Bromide oxidizes to bromate, which is a suspected human carcinogen. Finally, iodine radioactive isotopes, produced in nuclear energy plants and medical research and applications, are strictly regulated due to their risks to both human health and environment.

Monovalent anions as halides generally present weak electrostatic interactions with LDH layers. They can be easily displaced by anion exchange from LDH layers by carbonate, phosphate or sulfate. Conversely, they hardly displace these anions from the interlayer, which is an important obstacle for their uptake. The affinity sequence for monovalent anions (F⁻ > Cl⁻ > Br⁻ > NO₂⁻ > NO₃⁻ > I⁻) [29, 73] is explained by their different size and ability to establish hydrogen bonding. Nevertheless, halide uptake by LDHs can be produced by either anion exchange or reconstruction (Table 1).

Table 1. Mechanisms proposed and maximum uptake capacity (C_m) obtained for halide removal by LDHs

Metal ions	M^{II}/M^{III}	Anion	Pollutant	Removal mechanism	C_m (mg/g)	Ref.
Mg-Al	2:1	CO_3^{2-}	F^-	Anion exchange	320	63
Mg-Al	2:1	CO_3^{2-}	F^-	Reconstruction	213	64
Zn-Al	-	Cl^-	F^-	Anion exchange	14	65
Zn-Al	2:1	NO_3^-	Cl^-	Anion exchange	108	66
Mg-Al	2:1	CO_3^{2-}	Cl^-	Reconstruction	150	67
Mg-Al	2:1	CO_3^{2-}	Br^-	Reconstruction	362	68
Mg-Al	2:1	CO_3^{2-}	I^-	Reconstruction	376	69
Mg-Al	2:1	Cl^-	I^-	Anion exchange	308	32
Mg-Al	3:1	Cl^-	I^-	Anion exchange	408	32
Mg-Al	2:1	NO_3^-	I^-	Anion exchange	472	32
Mg-Al	3:1	NO_3^-	I^-	Anion exchange	165	32
Zn-Al	2:1	$S_2O_3^{2-}$	I^-	Reduction	97	70

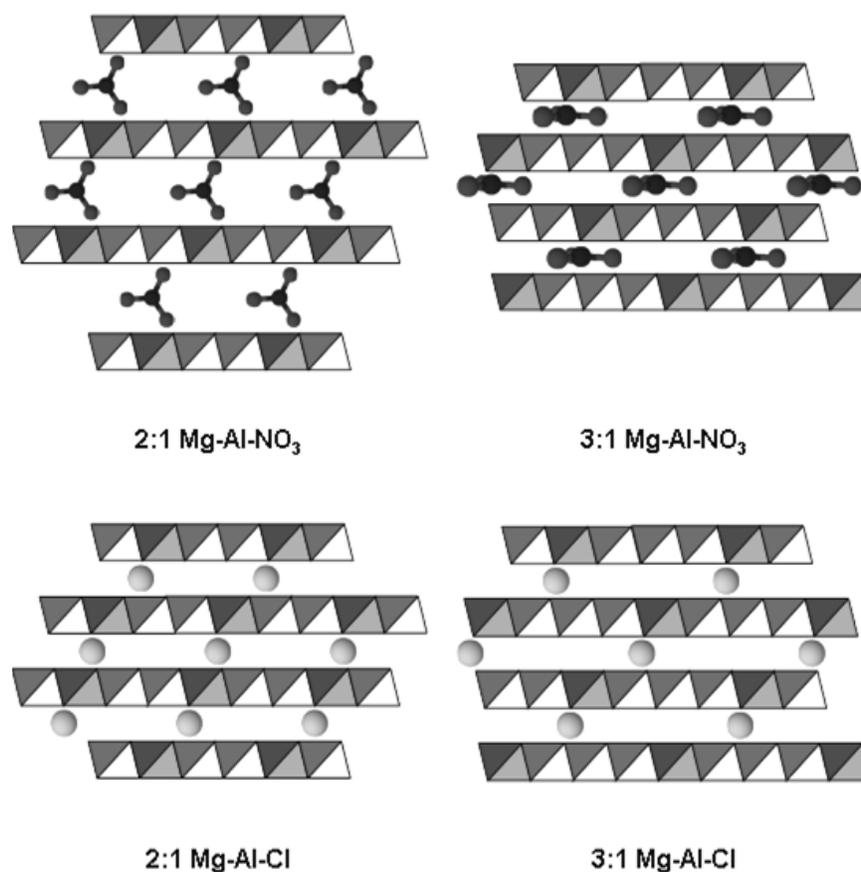
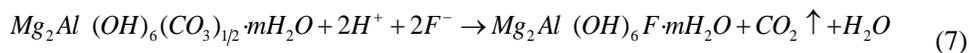


Figure 4. Representation of chloride and nitrate disposal in Mg-Al LDHs with different M^{II}/M^{III} ratio according to that reported by Prasanna et al [32].

Thus, Lu and coworkers [63, 64] studied fluoride removal by carbonate intercalated LDHs in acid media. These conditions led to carbonate protonation and detachment from the layers according to the following reaction:



Fluoride removal was produced in two steps, corresponding to the exchange of surface and interlayer carbonate anions, respectively. The kinetics of both steps increased with decreasing pH, which was ascribed to an increase in carbonate protonation. Nevertheless, increasing weathering and decreasing effectiveness of the sorbent was observed at pH values lower than 5 and the uptake was also diminished by competition of anions such as $H_2PO_4^-$, SO_4^{2-} or even Cl^- . Fluoride uptake by calcined LDHs was also favored by acid media, as reconstruction reactions are proton-consuming (equation 3) and a decrease in uptake capacity with competing anions concentration was also observed, the fluoride removal percentage increasing in the order: $PO_4^{3-} < Cl^- \approx SO_4^{2-} < Br^- < NO_3^-$. In addition, the uptake capacity was dependent on layer composition: calcined Mg-Al LDHs showed higher capacities than Zn-Al and Ni-Al LDHs.

For both ion exchange and reconstruction, sorbent regeneration can be easily produced by fluoride exchange with carbonate anions. Due to fluoride high affinity, and LDHs uptake capacity and recyclability, these sorbents are promising in acidic media, the main disadvantage being the decrease in uptake capacity caused by competing anions. The study was extended to the uptake of chloride [67], bromide [68], and iodide [69], which presented decreasing affinity for LDHs. Both reconstruction and anion exchange were possible for all of them, a more complex behavior being obtained for the latter because of the interlayer anion presence. Thus, high iodide concentrations were necessary to produce a complete exchange in nitrate and chloride intercalated Mg-Al LDHs, according to Prasanna et al [32]. Due to the weak interactions between iodide and the LDH layers, subtle variations in the electrostatic interactions or the hydrogen bonding of the outgoing anion produced an important impact on the uptake capacity of the samples. Thus, iodide uptake capacity by chloride intercalated LDHs increased with decreasing M^{II}/M^{III} ratio due to a decrease in the electrostatic binding strength. Contrarily, for nitrate intercalated samples, the uptake capacity and affinity increased with increasing M^{II}/M^{III} ratio due to a change in the arrangement of nitrate anions that increased electrostatic and hydrogen bonding (Figure 4).

Alternative strategies for the removal of halides by LDHs have been proposed to improve their capacity and/or affinity. The uptake of dry gaseous hydrogen chloride by a carbonate intercalated Mg-Al-LDH was tested by Kameda et al [74], reaching high removal (99%) with increasing sorbent dose. A removal mechanism involving a reaction similar to that in equation (7) was proposed; as the chloride uptake was larger than the sorbent AEC, the concurrence of adsorption processes was considered.

The removal of fluoride by a cellulose/ZnAl-Cl LDH composite has also been studied. The sorption capacity was 4 times higher than for the unsupported LDH (only 4 mg/g), ascribed to an increase in the exposed surface area due to a better sorbent dispersion when formed on the cellulose surface. Finally, thiosulphate intercalated LDHs were studied as iodide (I_2) scavengers, the uptake mechanism being based on the reduction of I_2 to I^- :



According to the charge balance of the reaction, I^- anions should remain in the interlayer to compensate the layers charge. As a consequence, I_2 presented high affinity for the sorbent, being completely removed from 0.33 g/L solutions.

3.2. Oxyanions

Oxyanions are typically mobile in soils and groundwater since most natural minerals have net negative surface charges. Some of them (chromate, arsenate, molybdate, selenite and selenate, etc.) are toxic to humans and wildlife at $\mu\text{g/L}$ to mg/L concentrations. Owing to their high affinity for LDH positively charged layers, the uptake of nitrate, arsenite, arsenate, chromate, phosphate, selenite, selenate, molybdate and vanadate, etc. has been studied. Goh and coworkers [47] have recently reviewed LDH applications for oxyanion removal, discussing the key factors, mechanisms, advantages and disadvantages of their use.

A distinction can be made between oxyanions with one (monovalent) and more than one (multivalent) negative charges. In the first case, the uptake is produced only by anion exchange or reconstruction and LDHs present a behavior similar to that summarized above for halides. Their low affinity for LDH exchange sites hinders uptake, as demonstrated by the partial anion exchange produced by borate, bromate, chlorate, iodate and perchlorate in nitrate intercalated Mg-Al LDHs [89] but higher removal capacities are achieved by the reconstruction mechanism as a result of the absence of competition by the interlayer anion and their higher surface area [76,81]. Among monovalent oxyanions, nitrate has been extensively studied due to its impact on algal growth and water eutrophication as well as to its potential risk to public health [71]. Chloride intercalated Mg-Al [77] and Zn-Al [78] LDHs presented low nitrate uptake capacities and strong interferences by competing anions and pH, demonstrating the inefficiency of anion exchange to produce nitrate removal. On the other hand, Kameda et al [79] reported high HNO_3 uptake capacity for calcined LDHs, the sorption process being enhanced by the acid media and proton-consumption during reconstruction reactions. In good accord, Socías-Viciana et al [80], obtained a lower uptake capacity of nitrate by reconstruction in neutral solutions (Table 2), improved with increasing calcination and sorption temperature during the processes, reaching nitrate removal percentages above 99%. The recyclability of nitrate intercalated LDHs resulting from the uptake process makes promising the application of these solids for nitrate remediation. Multivalent oxyanion removal is also produced by either anion exchange or reconstruction but additional uptake is eventually produced by adsorption as a result of ligand exchange reactions between the oxyanion and hydroxyl groups of the layers and inner sphere complexes formation [89]. Due to their importance as pollutants, arsenate, phosphate and chromate are the most studied among multivalent oxyanions. Increasing concentrations of arsenate and arsenite in natural water have been reported in many areas all over the world, proving a serious environmental issue. Due to the risk of these anions to human health (peripheral neuropathy, skin, bladder and lung cancer, etc.), the WHO has recommended a $10 \mu\text{g/L}$ maximum arsenic level for drinking water. Phosphate is an essential nutrient for human, plant and microorganisms, however, high phosphate concentrations, mainly caused by the agrochemical industries and household products, lead to algae proliferation and eutrophication of lakes and rivers.

Table 2. Mechanisms proposed and maximum uptake capacity (C_m) obtained for oxyanion removal by LDHs

Metal ions	M ^{II} / M ^{III}	Anion	Pollutant	Removal mechanism	C_m (mg/g)	Ref.
Mg-Al	2:1	NO ₃ ⁻	BO ₃ ⁻	Anion exchange, adsorption	40	75
Mg-Al	3:1	Cl ⁻	BrO ₃ ⁻	Reconstruction	112	76
Mg-Al	3:1	Cl ⁻	NO ₃ ⁻	Anion exchange	42	77
Zn-Al	3:1	Cl ⁻	NO ₃ ⁻	Anion exchange	40	78
Mg-Al	4:1	NO ₃ ⁻	NO ₃ ⁻	Reconstruction	236	79
Mg-Al	2:1	CO ₃ ²⁻	NO ₃ ⁻	Reconstruction	147	80
Mg-Al	2:1	CO ₃ ²⁻	ClO ₄ ⁻	Reconstruction	97	81
Mg-Al	3:1	CO ₃ ²⁻	AsO ₄ ³⁻	Adsorption	7	82
Mg-Al	2:1	NO ₃ ⁻	AsO ₄ ³⁻	Anion exchange, adsorption	31	82
Mg-Al	2:1	CO ₃ ²⁻	AsO ₄ ³⁻	Reconstruction, adsorption	116	82
Mg-Al	2:1	NO ₃ ⁻	AsO ₄ ³⁻	Anion exchange, adsorption	170	82
Mg-Fe	2:1	Cl ⁻	AsO ₄ ³⁻	Anion exchange	373	83
Mg-Al	2:1	Cl ⁻	AsO ₄ ³⁻	Anion exchange	222	83
Mg-Al	2:1	CO ₃ ²⁻	AsO ₄ ³⁻	Anion exchange	277	61
Mg-Al	2:1	CO ₃ ²⁻	CrO ₄ ²⁻	Reconstruction	276	42
Mg-Al	2:1	CO ₃ ²⁻	CrO ₄ ²⁻	Reconstruction	280	84
Mg-Al	5:1	CO ₃ ²⁻	CrO ₄ ²⁻	Reconstruction	248	84
Ni-Al, Zn- Cr	2:1	CO ₃ ²⁻	CrO ₄ ²⁻	Reconstruction	86	84
Mg-Al	2:1	Cl ⁻	CrO ₄ ²⁻	Anion exchange	145	32
Mg-Al	3:1	Cl ⁻	CrO ₄ ²⁻	Anion exchange	174	32
Mg-Al	2:1	NO ₃ ⁻	CrO ₄ ²⁻	Anion exchange	177	33
Mg-Al	3:1	NO ₃ ⁻	CrO ₄ ²⁻	Anion exchange	78	33
Zn-Al	2:1	CO ₃ ²⁻	PO ₄ ³⁻	Anion exchange	232	21
Mg-Al	2:1	CO ₃ ²⁻	PO ₄ ³⁻	Reconstruction	44	85
Zn-(Al,Zr)	2:1	CO ₃ ²⁻	PO ₄ ³⁻	Weathering/Precipitation	75	86
Zn-(Al,Zr)	3:1	CO ₃ ²⁻	PO ₄ ³⁻	Weathering/Precipitation	189	86
Zn-(Al,Zr)	4:1	CO ₃ ²⁻	PO ₄ ³⁻	Weathering/Precipitation	273	86
Mg-Fe	2:1	Cl ⁻	P ₃ O ₁₀ ⁵⁻	Anion exchange	33	87
Ca-Fe	2:1	Cl ⁻	P ₃ O ₁₀ ⁵⁻	Weathering/Precipitation	168	87
(Mg,Ca)-Fe	2:1	Cl ⁻	P ₃ O ₁₀ ⁵⁻	Weathering/Precipitation	252	87
Mg-Al	2:1	Cl ⁻	SO ₂ ²⁻	Anion exchange	193	88
Zn-Al	2:1	Cl ⁻	SO ₂ ²⁻	Anion exchange	158	88
Mg-Al	2:1	Cl ⁻	SO ₃ ²⁻	Anion exchange	489	88
Mg-Al	3:1	Cl ⁻	SO ₃ ²⁻	Anion exchange	410	88
Mg-Al	4:1	Cl ⁻	SO ₃ ²⁻	Anion exchange	306	88
Zn-Al	2:1	Cl ⁻	SO ₃ ²⁻	Anion exchange	444	88
Mg-Al	2:1	NO ₃ ⁻	VO ₄ ³⁻	Anion exchange, adsorption	70	89

Finally, chromium oxometalates are present in high concentrations in industrial effluents such as tanning and mining. Both chromate and dichromate (predominant at high and low pH values, respectively) show a high toxicity, causing lung cancer and liver damage.

Arsenate removal is mainly produced by either anion exchange or reconstruction, but adsorption is also produced, leading to formation of monodentate mononuclear inner-sphere complexes with the $M^{III}\text{-OH}$ groups. The importance of the different mechanisms depends on the LDH considered. According to Goh et al [82] Mg-Al- CO_3 LDHs presented the lower uptake capacity (7 mg/g), indicating that CO_3^{2-} was not displaced from the interlayer. With the addition of bulk processes, the sorption capacity increased to 31 mg/g and 116 mg/g for Mg-Al- NO_3 and calcined Mg-Al-LDHs, respectively. Moreover, decreasing the average particle size of nitrate intercalated LDHs to 122 nm, an increase in uptake capacity to 170 mg/g, related to a surface area and adsorption increase, was observed. The pH increase during the uptake process, and the presence of arsenate anions more strongly attached to LDH layers, confirmed the importance of the adsorption reactions. The removal kinetics showed two steps: surface anion exchange and adsorption caused a fast initial removal, whose extent increased with decreasing particle size, while anion exchange/reconstruction in the bulk of the particle led to a slower process. A higher sorption rate was obtained in the second step for calcined samples because of the absence of interlayer anion and the higher surface area of the sorbent.

Arsenate sorption was also dependent on media conditions such as pH or competing anion concentration. Thus, LDH uptake capacity slowly decreased with pH in the 5-9.5 range, which can be ascribed to an adsorption equilibrium shift to reactive (equation 5). Nevertheless, the most important effect found was on arsenate speciation [82]: the uptake capacity decreased steeply above 9.5 due to H_2AsO_4^- anion deprotonation to HAsO_4^{2-} , compensating two layer charges and decreasing the theoretical uptake capacity. Conversely, arsenite sorption increased in the same pH range as a result of H_3AsO_3 deprotonation to the H_2AsO_3^- , able to undergo exchange reactions. Competition by coexisting anions also reduced the arsenate uptake: although the effect of nitrate was almost negligible, multivalent oxyanions competed in the following order: silica \leq sulfate < carbonate < phosphate [43]. The presence of organic matter (humic and fulvic acids) also caused a decrease in removal capacity ascribed to its adsorption at the LDH particle surface, avoiding arsenate attachment at adsorption sites and physically blocking arsenate access to the interlayer. This effect was more noticeable at alkaline pH values, as the organic matter increased its negative charge and affinity for the LDH surface. Finally, the influence of the layers composition was reported by Caporale et al [83], which found a higher uptake capacity and affinity for Mg-Fe than for Mg-Al LDHs and assigned this result to a higher capacity of AsO_4^{3-} to form inner sphere complexes with the former. Accordingly, a greater portion of arsenate anions were not easily desorbed from Fe^{3+} containing LDHs.

Chromate uptake is produced by similar mechanisms, pH being the main factor in determining the effectiveness of the different removal mechanism. Goswamee et al [84] explored dichromate sorption by calcined and uncalcined Mg-Al- CO_3 , Ni-Al- CO_3 and Zn-Cr- CO_3 LDHs at low pHs. Calcined LDHs showed larger and faster dichromate sorption than uncalcined samples, the uptake being higher than the AEC in some cases. Furthermore, the uptake capacity decrease with decreasing Al^{3+} content was smaller than the decrease in AEC. These results confirmed that adsorption was concurrent with reconstruction, the former mechanism remaining unaffected by the layer charge. The layer composition also showed a

marked effect on the uptake capacity of the calcined samples, being higher for Mg-Al LDHs than for Ni-Al, or Zn-Cr. On the other hand, Carriazo et al [90] studied chromate sorption in alkaline media using chloride intercalated and calcined LDHs with diverse layers composition. They observed a faster and larger chromate uptake for uncalcined samples, as reconstruction was hindered by the alkaline media. The chromate sorption was always lower than the AEC, indicating that no adsorption reaction was produced.

Phosphate removal by anion exchange or reconstruction has been studied for LDHs with different composition, presenting a sorption behavior similar to that found for chromate or arsenate [85]. Thus, Caporale et al [83] reported a phosphate uptake behavior similar to that found for arsenate (increasing uptake capacity and adsorption importance for Fe^{3+} LDHs, dependence with pH and competing anions). Nevertheless, phosphate presented a slightly higher affinity, which resulted in a higher uptake capacity and the interference with arsenate uptake. Besides, phosphate uptake by LDH dissolution and pollutant precipitation was extensively studied in the last years. Seida and coworkers [45] showed that M^{II} ions release and pH increase during the dissolution of Mg-Fe and Ca-Fe LDHs lead to precipitation of phosphate salts; they reported an uptake increase with Ca^{2+} containing LDHs and acid media. In addition, for phosphate uptake by a ternary Zn-(Al,Zr)- NO_3 LDH, Koilraj and Kannan [86] observed an increase in phosphate sorption with decreasing sorbent crystallinity and media pH. They proposed a surface precipitation mechanism where phosphate anions are first incorporated to positively charged sites at the sorbent particle surface and, afterwards, Zn^{2+} cation release by LDH partial dissolution induced the precipitation of hopeite ($\text{Zn}_3(\text{PO}_4)_2$) above the layer of X-PO_4^{3-} sites. The presence of Zn^{2+} and Pb^{2+} enhanced the precipitate formation, indicating the sorbent potential application for the simultaneous removal of phosphate and heavy metals. This mechanism is dependent on the pH and the buffering capacity of the media, as it controlled the extent of LDH weathering. The layer composition also determines the stability of the sorbent and the solubility of the pollutant salt. Hence, Zhou et al studied removal of triphosphate by chloride intercalated (Mg,Ca)-Fe LDHs with different Ca/Mg ratio. A low sorption capacity was obtained for Mg-Fe-LDH by the surface exchange and adsorption mechanisms. The higher uptake capacity was produced for Ca-Fe LDHs due to sorbent dissolution and precipitation of a calcium triphosphate precipitate. Furthermore, combination of both processes yielded the highest uptake capacity for a $(\text{Mg}_{0.5},\text{Ca}_{1.5})\text{-Fe}$ LDH.

All these mechanisms are able to explain the LDH uptake behavior of other oxyanions (Table 2). You et al studied the uptake of selenite and selenate by Mg-Al and Zn-Al LDHs, which presented an anion exchange mechanism, the uptake dependence with $\text{M}^{\text{II}}/\text{M}^{\text{III}}$ ratio and competing anions being quite similar to that for arsenate or chromate. On the other hand a weathering/precipitation mechanism was reported for the uptake of antimonite anions by calcined Mg-Al- CO_3 , ascribed to the formation of a magnesium antimony hydrate hydroxide ($\text{MgSb}_2(\text{OH})_{12}\cdot 6\text{H}_2\text{O}$) due to the release of Mg^{2+} during the calcined products dissolution [91].

3.3. Heavy Metals

Heavy metals are produced by both natural processes and human activities. They are more persistent than organic contaminants such as pesticides and petroleum by-products and

exhibit high toxicity. In natural environments, LDH minerals are important to determine the fate of heavy metal ions. Aluminum (hydr)oxide minerals uptake of divalent heavy metal cations lead to formation of hydrotalcite-like minerals, such as takovite (Ni-Al LDH). This process reduces heavy metal concentration in aquifers, and subsequent migration and bioavailability [98,99]. One of the most extensively used techniques for heavy metal remediation is its chemical precipitation as sulphides or hydroxides [100]. pH values higher than 8 greatly reduce the solubility of different heavy metals hydroxides, which are afterwards removed from wastewaters by filtration or flocculation. A variety of hydroxides have been used to increase the pH of the media but lime is the most common due to its easy handling and low cost. Seed material, such as fly ash, is used to improve particle size and hydroxides separation, increasing the efficiency of heavy metal removal [101]. LDHs find applications in heavy metal remediation as a result of their weathering reactions, which leads to pH increase and chemical precipitation of heavy metal hydroxides. These weathering reactions are partial at mildly acidic media, the divalent cations being selectively dissolved by reason of the lower solubility of trivalent cation (usually Al^{3+} or Fe^{3+}) hydroxides. Heavy metal precipitation can be produced either as part of LDHs structure or in a separate phase. Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} uptake by Mg-Al LDHs was produced by substitution of the M^{II} cations of the layers [102] and Zn^{2+} ions were also removed from aqueous solutions by Ca-Al LDHs, leading to formation of Zn-Al LDH [92].

Table 3. Mechanisms proposed and maximum uptake capacity (C_m) obtained for heavy metal removal by LDHs

Metal ions	$\text{M}^{\text{II}}/\text{M}^{\text{III}}$	Anion	Pollutant	Removal mechanism	C_m (mg/g)	Ref.
Ca-Al	2:1	Cl^-	Zn^{2+}	Weathering/precipitation	458	92
Mg-Al	3:1	CO_3^{2-}	Pb^{2+}	Weathering/precipitation	1800	93
Mg-Al	3:1	CO_3^{2-}	Cu^{2+}	Weathering/precipitation	318	93
Mg-Al	2:1	CO_3^{2-}	Ni^{2+}	Weathering/precipitation*	104	94
Mg-Al	2:1	CO_3^{2-}	Pb^{2+}	Weathering/precipitation*	91	94
Mg-Al	2:1	CO_3^{2-}	Cd^{2+}	Weathering/precipitation*	71	94
Mg-Al	2:1	ms	Hg^{2+}	Chelation	99	95
Mg-Al	2:1	ms	Cu^{2+} , Pb^{2+}	Chelation	< 5	95
Zn-Al	1.2:1	dtpa	Cu^{2+}	Chelation	51	96
Zn-Al	1.2:1	dtpa	Pb^{2+}	Chelation	145	96
Zn-Al	1.2:1	dtpa	Cd^{2+}	Chelation	45	96
Zn-Al	1.3:1	dmsa	Cu^{2+}	Chelation	63	96
Zn-Al	1.3:1	dmsa	Pb^{2+}	Chelation	393	96
Zn-Al	1.3:1	dmsa	Cd^{2+}	Chelation	101	96
Zn-Al	1:1	edta	Cu^{2+}	Chelation	70	97
Zn-Al	1:1	edta	Pb^{2+}	Chelation	207	97
Zn-Al	1:1	edta	Cd^{2+}	Chelation	90	97

*, calcined LDHs.

ms, mercaptosuccinate; dtpa, diethylenetriaminepentaacetate; dmsa, meso-(2,3)-dimercaptosuccinate; edta, ethylenediaminetetraacetate.

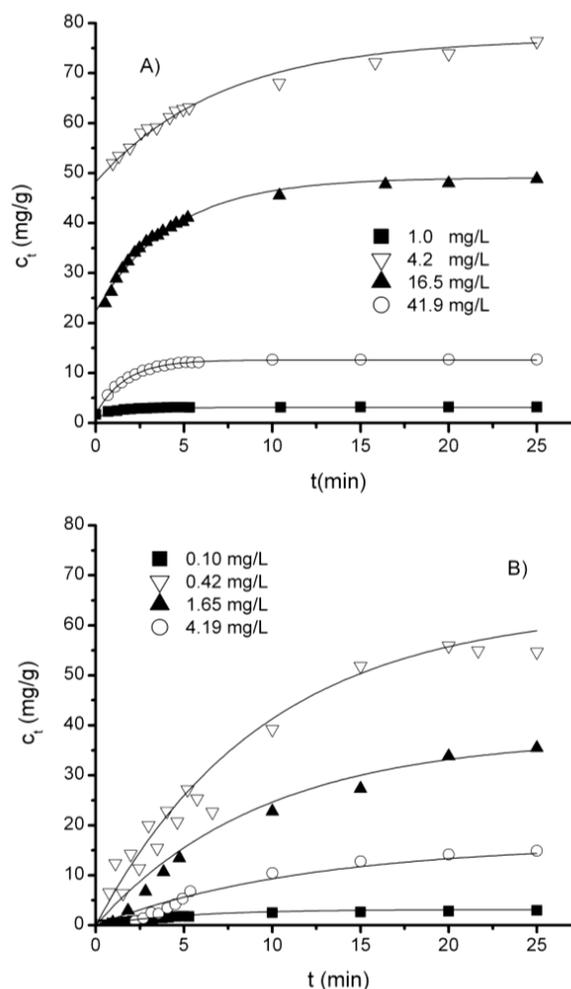


Figure 5. Copper uptake (q_t) kinetics for a Zn-Al LDH intercalated with ethylenediaminetetraacetate (edta) at different sorbent doses (a, 0.01 g; b, 0.001 g) and initial copper concentrations.

Contrarily, Pb^{2+} uptake by a Mg-Al- CO_3 LDH led to the precipitation of Pb^{2+} salts such as carbonate chloride ($PbCO_3PbCl_2$) and hydroxide chloride ($Pb(OH)Cl$) [93]. The weathering/precipitation mechanism is affected by: 1) pH of the media and its buffering capacity [103]; 2) layers composition, which determines the stability of the sorbent [104]; 3) the solubility constant of the heavy metal hydroxide; 4) the coexisting species, which may lead to precipitation of insoluble salts or hydroxide salts [93] or a sorbent stability increase [92, 103], causing an increase or decrease in uptake capacity, respectively. Calcined LDHs can also be used to produce heavy metal precipitation, being even more effective due to the proton consumption during the reconstruction process [94]. Heavy metal removal can also be produced by direct precipitation of a LDH phase. Zhou et al [105] achieved 99% removal of Ni^{2+} , Zn^{2+} , Cr^{3+} from electroplating waste waters by carbonation and alkalization of the effluent, leading to the synthesis of a (Zn,Ni)-Cr- CO_3 LDH. Furthermore, the solid obtained was used to remove acid brilliant scarlet GR (an azoic dye), showing the potential applications of the solid obtained.

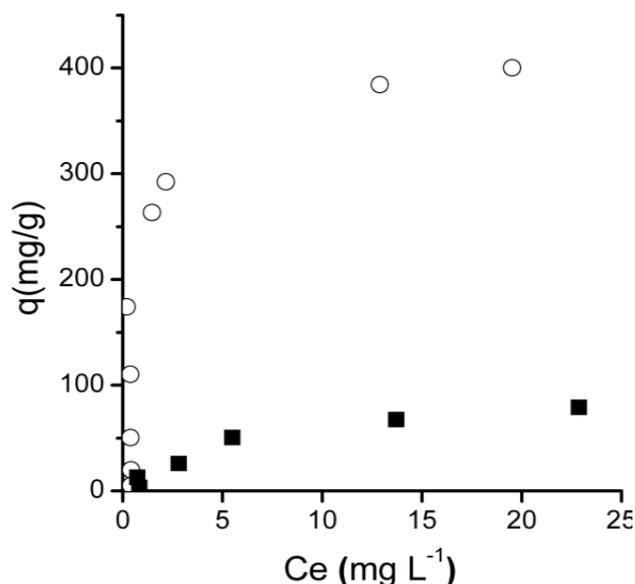


Figure 6. Sorption isotherms of Cu^{2+} for $[\text{Zn}(\text{edta})]^{2-}$ intercalated Zn-Al (squares) and $[\text{Ca}(\text{edta})]^{2-}$ intercalated Ca-Al (circles) layered double hydroxides.

LDHs can be also functionalized with the intercalation of ligands such as citrate, malate and tartrate [56,106], edta [97,107], diethylenetriaminepentaacetate, meso-(2,3)-dimercaptosuccinate [96], etc. The solids obtained showed uptake capacity for heavy metal cations such as Ni^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Sc^{3+} or La^{3+} . The uptake mechanism proposed is the formation of ligand-metal complexes in the interlayer; the heavy metal affinity for the sorbent is determined by the formation constant of the corresponding complex [56]. Consequently, the uptake can be quite selective to specific metal ions: mercaptocarboxylate intercalated LDHs presented specific activity towards mercury ions (Table 3), assigned to the formation of disulfide bridges with high affinity for Hg^{2+} ions.

This mechanism is quite independent of pH, being only affected at very low pHs by weathering and the consequent ligand/complex release. Similarly, coexisting anion may also produce anion exchange with the intercalated ligand, decreasing the uptake capacity. Also, the competition by coexisting cations and the concurrence of the weathering/precipitation mechanism should be considered. The study of Cu^{2+} removal by edta modified Zn-Al LDHs [44] indicated that the sorbent was not intercalated by edtaH_2^{2-} ligand, as previously proposed [97]. The polydentate ligand produced partial erosion of the layers during the exchange process, causing the intercalation of $[\text{Zn}(\text{edta})]^{2-}$ complex instead of the ligand and, consequently, Cu^{2+} uptake was produced by an exchange reaction with Zn^{2+} cations. Also, additional Cu^{2+} removal was produced at high sorbent dose and Cu^{2+} concentrations by LDH weathering and $\text{Cu}(\text{OH})_2$ precipitation. Both mechanisms were clearly identified in the uptake kinetics shown in Figure 5: most of q_t vs. time curves converged to the origin and presented a similar profile, with the equilibrium removal increasing with the initial Cu^{2+} concentration, reaching a maximum value of 54 mg/g. The curves were adjusted to a pseudo first-order kinetics, indicating that the rate-determining step was the exchange reaction between Zn^{2+} and Cu^{2+} cations. However, the curves did not converge to origin at high sorbent dose and Cu^{2+} concentrations, indicating that another mechanism was taking place concomitant to Cu^{2+}

uptake at interlayer $[\text{Zn}(\text{edta})]^{2-}$ complexes. This fast mechanism was associated with copper hydroxide precipitation and increased the overall Cu^{2+} uptake up to 72 mg/g. These results highlighted the importance of layer composition, as its constituting cations competed with the heavy metals for the sorption sites. The study was afterwards extended to $[\text{Ca}(\text{edta})]^{2-}$ intercalated Ca-Al LDHs due to the lower formation constant of $[\text{Ca}(\text{edta})]^{2-}$ complexes, the high solubility of $\text{Ca}(\text{OH})_2$ and the negligible toxicity of Ca^{2+} ion. This solid showed higher Cu^{2+} removal capacity (Figure 6), due to the complete replacement of Ca^{2+} ions placed in the layer and the interlayer of the sorbent.

4. ORGANIC POLLUTANTS ADSORPTION

Industrial and sewage effluents present an increasing number of hazardous organic compounds that must be degraded or detoxified by physical, chemical and/or biological treatments. Among these pollutants, phenols, pesticides and dyes receive great attention because of their extreme toxicity and/or persistency in the environment. LDHs scavenging mechanisms for organic pollutants depend on the latter charge and hydrophobic character. For anionic compounds, anion exchange and reconstruction are the main uptake mechanisms, resulting in pollutant/LDH hybrids where the pollutants adopt arrangements as those described in section 2.5 and represented in Figure 3. In the case of neutral pollutants, hydrophobic interactions replace electrostatic binding. The sorption is then only possible in LDHs intercalated with organic anions, the main uptake mechanisms being surface adsorption and/or partition. Finally, cationic pollutants with an important hydrophobic segment can be adsorbed over LDHs with hydrophobic and negatively charged surfaces, as we will be seen in following sections.

4.1. Phenols

Phenols present industrial applications in pesticide and disinfectant production, wood and plastics processing, etc. Their widespread use leads to environmental pollution and health risks as a result of their carcinogen action. They are quite soluble in water, either in neutral form or as phenolates, their pK_a being quite variable according to their substituents. Phenol uptake was extensively studied by Ulibarri, Hermosin, and coworkers [108,109,113], testing the sorption of 2,4,5 trichlorophenol (TCP, $\text{pK}_a=6.92$) and 2,4,6 trinitrophenol (TNP, $\text{pK}_a=0.38$) by calcined and uncalcined LDHs (Table 4). Uptake capacities for TNP were higher than for TCP at every pH value and for both LDH types assigned to the lower pK_a of the former. In alkaline and neutral media, TNP only displaced carbonate anions from the particle surface of uncalcined LDHs. On the contrary, intercalation was also produced at low pH values, as demonstrated by the increased interlayer distance after TNP uptake. Replacing carbonate by chloride enhanced anion exchange in neutral media, reaching 100 % AEC. Total occupancy of anion binding sites is also obtained by the reconstruction mechanism, although hydrothermal treatment during the synthesis of the LDH was required to obtain an optimal performance.

Table 4. Mechanisms proposed and maximum uptake capacity (C_m) obtained for phenols removal by LDHs

Metal ions	M ^{II} /M ^{III}	Anion	Pollutant	Removal mechanism	C_m (mg/g)	Ref
Mg-Al	3:1	CO ₃ ²⁻	TNP	Anion exchange	183	108
Mg-Al	3:1	Cl ⁻	TNP	Anion exchange	744	108
Mg-Al	3:1	CO ₃ ²⁻	TNP	Reconstruction	1330	108
Mg-Al	3:1	CO ₃ ²⁻	TCP	Anion exchange	2	109
Mg-Al	3:1	CO ₃ ²⁻	TCP	Reconstruction	8	109
Mg-Al	3:1	NO ₃ ⁻	2-CP	Anion exchange	21	110
Mg-Al	3:1	DDS ⁻	2-CP	Partition	18	110
Mg-Al	3:1	CO ₃ ²⁻	4-NP	Reconstruction	368	111
Mg-Al	3:1	CO ₃ ²⁻	Phenol	Reconstruction	47	111
Mg-Al	3:1	Cl ⁻	DNP	Anion exchange	900	112
Mg-Al	4:1	Cl ⁻	DNP	Anion exchange	714	112
Mg-Al	3:1	Cl ⁻	DNOP	Anion exchange	503	112
Mg-Al	4:1	Cl ⁻	DNOP	Anion exchange	440	112

DDS⁻, dodecylsulfate; TNP, trinitrophenol; TCP, trichlorophenol; 2-CP, 2-dichlorophenol; 4-NP, 4-nitrophenol; DNP, 2,4-dinitrophenol; DNOP, 2-methyl-4,6-dinitrophenol.

Contrarily to that proposed by Ulibarri and coworkers, Chen et al [110] assigned the higher uptake capacity of 4-nitrophenol (4-NP, $pK_a=7.2$) than phenol ($pK_a=9.8$) by reconstruction of calcined Mg-Al LDHs to interactions between the layers and the -NO₂ group of 4-NP, which was intercalated between the layers while phenol was only incorporated at the sorbent surface (Table 4). Chaara et al [112] also studied 2,4-dinitrophenol (DNP, $pK_a=4.02$) and 2-methyl-4,6-dinitrophenol (DNOC, $pK_a=4.42$) sorption by calcined and uncalcined Mg-Al LDHs. Both DNP and DNOC were sorpted with high affinity, in good accord with the presence of a -NO₂ group in para- position and the low pK_a . Furthermore, DNP uptake capacity by Mg-Al-Cl LDH was larger than its AEC, which was assigned to additional adsorption as a result of π - π stacking interactions. These authors also reported a higher uptake capacity for 3:1 than for 2:1 LDHs, which was ascribed to steric hindrance. The uptake of non-ionized phenols was also produced by a partition mechanism. Chuang et al [110] studied the removal of 2-chlorophenol (2-CP, $pK_a=8.56$) by nitrate and dodecylsulfate intercalated LDHs. At $pH > pK_a$, 2-CP was sorpted by anion exchange, the nitrate intercalated sample showing higher uptake capacity. Conversely, partition was predominant at $pH < pK_a$, being the DDS⁻ intercalated sample the best sorbent in this pH range.

4.2. Pesticides

Groundwater and soils are increasingly polluted with pesticides as a result of their importance in the optimization of agricultural activities and the control of pest such as mosquitoes, wasps, etc. A recent article by Cornejo et al [4] reviewed the applications of clays and LDHs as pesticides sorbents. LDHs were first investigated as sorbents of acid

pesticides that produce anions in neutral and basic media [122]. According to the pesticide affinity, sorption is produced exclusively at the surface or also in the interlayer space. In this last case, two-step kinetics were usually found, the pesticides being first incorporated at the particle surface. The uptake capacity dependence with solution pH, nature of the competing anions and M^{II}/M^{III} ratio was quite similar to that above mentioned for halides or oxyanions. Anion exchange was explored for the removal of pesticides such as 4-chloro-2-methylphenoxyacetate (MCPA), 2,4-dichlorophenoxyacetate (2,4-D), 4-chlorophenoxyacetate and 2,4,5-trichlorophenoxyacetate [26, 114, 115, 123, 124]. Chao et al [115,124] studied 2,4-D uptake by Mg-Al-NO₃ LDHs, reporting a C_m dependence with the M^{II}/M^{III} ratio (Table 5), varying from 10 % AEC to 70 % AEC for 4:1 and 2:1 samples, respectively. These results were explained by different arrangements of nitrate anions in the interlayer (Figure 4). The influence of the pollutant extended chemical formula (Figure 7) is exemplified by the opposite behavior of glyphosate and imazamox. Glyphosate, which present two negatively charged groups [125], produced partial substitution of carbonate in the interlayer space of a Mg-Al LDH and ligand exchange reactions with hydroxyl anions of the layers. Contrarily, imazamox [126] sorption by carbonate or DDS⁻ intercalated LDHs was negligible, which can be explained by its single negative charge and the large hydrophobic section, whose disposal around the polar group increases steric hindrance.

Table 5. Mechanisms proposed and maximum uptake capacity (C_m) obtained for pesticide removal by LDHs

Metal ions	M^{II}/M^{III}	Anion	Pollutant	Removal mechanism	C_m (mg/g)	Ref.
Mg-Al	3:1	Cl ⁻	MCPA	Anion exchange	100	114
Mg-Al	3:1	NO ₃ ⁻	MCPA	Anion exchange	242	114
Mg-Al	3:1	CO ₃ ²⁻	MCPA	Anion exchange	16	114
Mg-Al	2:1	NO ₃ ⁻	2,4-D	Anion exchange	561	115
Mg-Al	3:1	NO ₃ ⁻	2,4-D	Anion exchange	306	115
Mg-Al	4:1	NO ₃ ⁻	2,4-D	Anion exchange	67	115
Mg-Al	3:1	CO ₃ ²⁻	2,4-D	Reconstruction	166	116
Mg-Al	3:1	CO ₃ ²⁻	Clopyralid	Reconstruction	492	116
Mg-Al	3:1	CO ₃ ²⁻	Picloram	Reconstruction	283	116
Mg-Al	3:1	CO ₃ ²⁻	Dicamba	Reconstruction	298	117
Mg-Al	2:1	CO ₃ ²⁻	2,4-D	Reconstruction	1111	118
Mg-Al	2:1	CO ₃ ²⁻	MCPA	Reconstruction	938	118
Mg-Al	2:1	CO ₃ ²⁻	Picloram	Reconstruction	793	118
Zn-(Al,Zr)	3:(0.67,0.33)	CO ₃ ²⁻	2,4-D	Reconstruction	1300	119
Mg-Al	3:1	DDS ⁻	Carbetamide	Adsorption/Partition	212	120
Mg-Al	3:1	DDS ⁻	Metamitron	Adsorption/Partition	93	120
Mg-Al	3:1	DDS ⁻	Alachlor	Adsorption/Partition	130	121
Mg-Al	2:1	SEB ²⁻	Alachlor	Adsorption/Partition	122	121
Mg-Al	3:1	DDS ⁻	Metolachlor	Adsorption/Partition	256	121
Mg-Al	2:1	SEB ²⁻	Metolachlor	Adsorption/Partition	77	121

DDS⁻, dodecylsulfate; MCPA, 4-chloro-2-methylphenoxyacetate; 2,4-D, 2,4-dichlorophenoxyacetate.

Calcined LDHs are generally better sorbents for anionic pesticides due to the absence of interlayer anions and their higher surface area (Table 5). Consequently, the pollutant was incorporated to LDH interlayer in most cases. In addition to some of the pesticides mentioned above, reconstruction processes have been assayed for the uptake of clopyralid, picloram, acephate, dicamba, among others [116,117,126,125]. Cardoso and Valim [118] studied the uptake of 2,4-D, MCPA and picloram on calcined Mg-Al LDHs and obtained high uptake capacities and interlayer distance variations that confirmed their incorporation in the sorbent interlayer space. The affinity of the pesticide for the interlayer space of LDHs is eventually increased by lateral interactions. Thus, dicamba sorption by calcined Mg-Al-CO₃ [117] was produced in two stages: in the first stage, the pesticide is incorporated exclusively by electrostatic interactions, the affinity for the sorbent increasing in a second stage due to hydrophobic interactions. Enhanced uptake capacity towards 2,4 D was also obtained by Chaparadza and Hossenlopp [119] for a calcined Zn-(Al,Zr) LDH due to a higher layer charge by the introduction of Zr⁴⁺ ions, optimal at a 0.08 Zr⁴⁺/(Zn²⁺+Al³⁺+Zr⁴⁺) ratio. The sorbent presented optimal sorption capacity in the pH range between 2 and 9 and high recyclation capacity and high recyclability, losing only 6% of its uptake capacity after six sorption/desorption cycles.

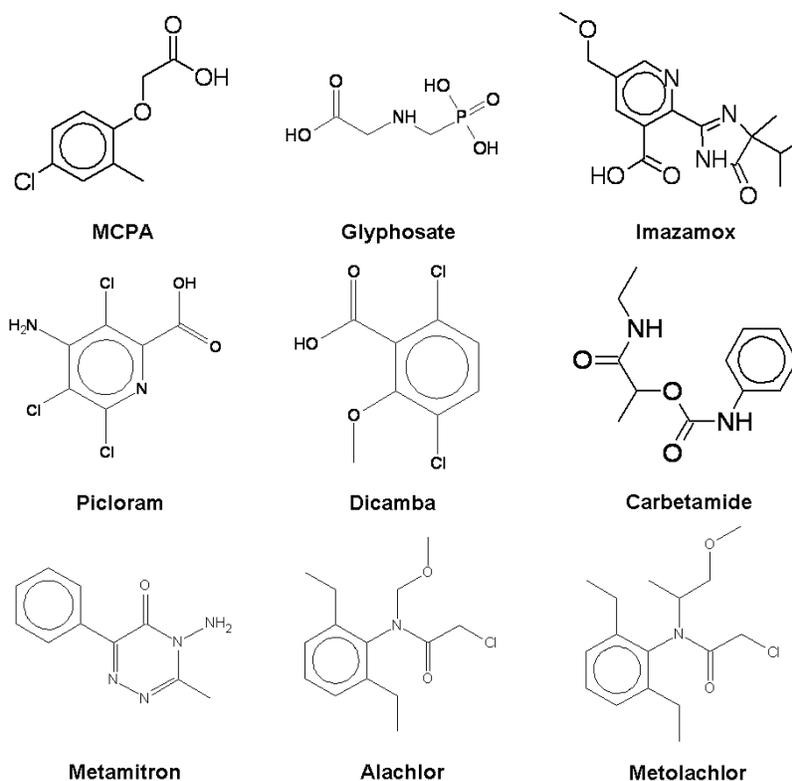


Figure 7. Extended chemical formula of representative pesticides.

Hydrophobic pesticides present low affinity for hydrophilic LDHs but are incorporated into hydrophobized LDH hybrids by partition or adsorption. The pesticide affinity for the sorbent is defined by the former hydrophobicity and size, as well as by the hydrocarbon chain length, concentration and arrangement of the interlayer anion. Linuron, atrazine and diazinon presented high affinity for the interlayer of DDS^- and DBS^- intercalated Mg-Al LDHs [126]. Their partition coefficients between the intercalated organic mass and water were similar to those of octanol/water systems, which highlights pollutant hydrophobicity influence. Bruna et al [120] reported an increasing carbetamide and metamitron uptake with increasing DDS^- intercalation for a 3:1 Mg-Al LDH, which increases the hydrophobicity of the solid. The results obtained also highlighted the relation between the pesticide extended chemical formula (Figure 7) and its adsorption behavior. A 100% DDS^- intercalated sorbent showed higher sorption capacity for metamitron than for carbetamide ascribed to hydrogen bonding between the NH_2 of the former and the LDH surface. The adsorbate was easily removed by simple dispersion in ethanol from the organo-LDH hybrid, its sorptive properties maintained almost unaltered. Similarly, Chaara et al [121] reported, for a DDS^- intercalated LDH, a higher uptake capacity of metachlor than of alachlor, assigned to stronger hydrophobic interactions for the former herbicide. Contrarily, a higher alachlor uptake capacity was obtained for sebacate intercalated LDHs, assigned to the lower size of this pollutant that eases its introduction between the layers. Accordingly, incorporation of either pesticide to DDS^- intercalated samples did not expand the interlayer space of the solids while, for the sebacate intercalated, a noticeable increase in interlayer distance was registered.

4.3. Dyes

The effluents from textile industries contain high levels of diverse dyes that produce appearance issues, heavy metals complexation and solubilization, and an increase of the organic fraction of large water bodies [138]. Currently, a combination of biological treatment and adsorption is used to remove dyes from wastewater. Although commercial activated carbon is a preferred sorbent for dye removal, its high cost restricts widespread use. Layered double hydroxides present sorption capacity for anionic dyes, which are incorporated by ion exchange and reconstruction processes, although adsorption can also be concurrent. As can be observed in Table 6, the uptake capacity is quite variable as, depending on the dye structure (Figure 8) and the outgoing anion, uptake is produced exclusively at the particle surface or also in the particle bulk of LDHs.

Anionic dyes such as acid blue 29, Eosin B [127] and Yellow LS-R [132] were incorporated into Mg-Al- CO_3 LDHs by surface anion exchange and adsorption processes. Similar results were obtained for the removal of Brilliant Blue R (BBR^{2-}) by calcined Mg-Al- CO_3 LDHs, which presented high uptake effectiveness due to BBR^{2-} charge. The sorpted amount was less than 20% of the AEC, and a small or negligible interlayer distance increase was registered, indicating that the dye was almost exclusively placed at the particle surface. BBR^{2-} polar groups are placed in nearby positions, which hinders a bridging disposal between LDH layers and, consequently, its intercalation.

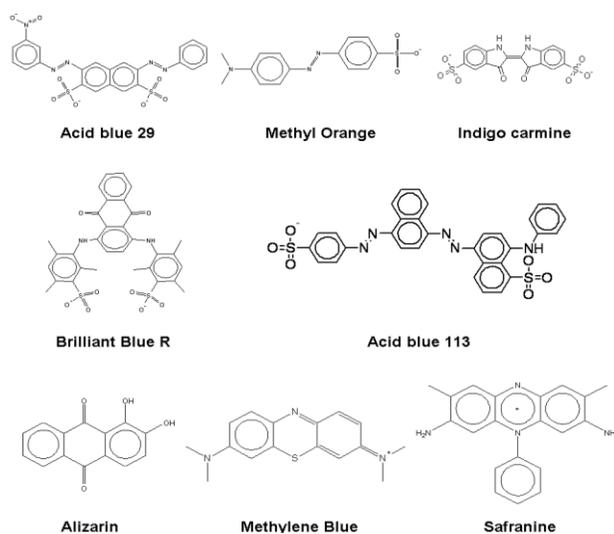


Figure 8. Extended chemical formula of representative dyes.

Table 6. Mechanisms proposed and maximum uptake capacity (C_m) obtained for dyes removal by LDHs.

Metal ions	M ^{II} /M ^{III}	Anion	Pollutant	Removal mechanism	C_m (mg/g)	Ref.
Mg-Al	3:1	CO ₃ ²⁻	AB29 ²⁻	Anion exchange	33	127
Zn-Al	3:1	CO ₃ ²⁻	MO ⁻	Reconstruction	182	128
Mg-Al	2:1	CO ₃ ²⁻	BBR ²⁻	Reconstruction	613	129
Mg-Al	2:1	CO ₃ ²⁻	BBR ²⁻	Anion exchange	55	129
Mg-Al	2:1	CO ₃ ²⁻	IC ²⁻	Reconstruction	1800	130
Mg-Al	2:1	CO ₃ ²⁻	AB113 ²⁻	Anion exchange	47	131
Mg-Al	2:1	CO ₃ ²⁻	AB113 ²⁻	Reconstruction	2544	131
Mg-Al	-	CO ₃ ²⁻	YLS-R	Anion exchange	80	132
Zn-Al	2:1	Cl ⁻	MO ⁻	Anion exchange	820	133
Zn-Al	2:1	ClO ₄ ⁻	Fluorescein	Anion exchange	276	134
Mg-Al	2:1	NO ₃ ⁻	OII ⁻	Anion exchange	1181	135
Mg-Al	3:1	NO ₃ ⁻	OII ⁻	Anion exchange	1121	135
Mg-Al	4:1	NO ₃ ⁻	OII ⁻	Anion exchange	953	135
Mg-Al	2:1	DDS ⁻	Safranin	Adsorption	83	136
Mg ²⁺ , Al ³⁺	2:1	-	DGLN ⁵⁻	LDH synthesis	524	137
Mg-Al	2:1	D-GLN	VBB ⁺	Adsorption	1064	137

AB29²⁻, acid Blue 29; MO⁻, methyl orange; BBR²⁻, brilliant blue R; IC²⁻, indigo carmine; AB113²⁻, acid blue 113; YLS-R, yellow LS-R; OII⁻, orange II; DGLN⁵⁻, direct blending scarlet D-GLN; VBB⁺, victoria blue B.

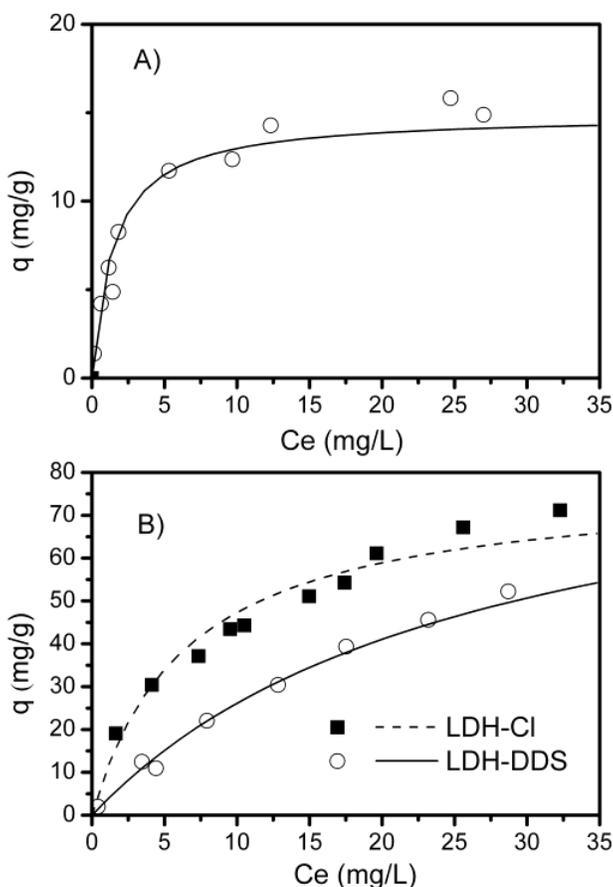


Figure 9. Sorption isotherms of methylene blue (A) and alizarin (B) on Mg-Al LDHs intercalated with chloride (squares) and dodecylsulfate (DDS⁻, circles).

On the other hand, Constantino et al reported the intercalation of methyl orange [133] and fluorescein [134] in the interlayer of Zn-Al LDHs by anion exchange, partial in the last case. The interaction between dyes and LDH structure is mainly electrostatic, but an additional stabilization is produced by hydrogen bonding and π - π stacking interactions [134]. Thus, Bouhent et al [135] studied orange II uptake by a nitrate intercalated Mg-Al LDH and reported an increase of both uptake capacity and affinity with decreasing M^{II}/M^{III} ratio, leading in some cases to uptake capacities above AEC. Indigo carmine (IC²⁻) removal by a calcined Mg-Al-CO₃ LDH also led to an almost complete occupation of the anion binding sites and an interlayer distance increase to 2.1 nm, which evidenced the dye intercalation between the inorganic layers. IC²⁻ presents two SO₃⁻ groups at opposite extremes and disposes as bridges between consecutive layers, maximizing electrostatic interactions and hydrogen bonding. As a result, IC²⁻ uptake was independent of the media pH, showing a fast and efficient removal behavior even in alkaline media. Similarly, Bascialla and Regazzoni [131] reported Acid Blue 113 (AB113²⁻) uptake by calcined Mg-Al LDHs, which presented high sorption capacities in alkaline media. Nevertheless, the dye affinity was not enough to produce anion exchange in the interlayer of the uncalcined, carbonate intercalated LDH, displacing only loosely bound anions at the particle surface.

As previously said, cationic dye removal is also produced due to adsorption on modified LDH surfaces. In a previous work [39], the uptake of alizarin (AZ^-) and methylene blue (MB^+) by chloride and dodecylsulfate (DDS^-) intercalated Mg-Al LDHs was studied (Figure 9). The surfaces of these solids were quite different: hydrophilic, positively charged for the former, hydrophobic and negatively charged for DDS^- . AZ^- interacted with both sorbents, the maximum uptake being around 84 mg/g, equivalent to 10-15 % of the AEC in both cases. AZ^- was incorporated at exchange and adsorption sites on the sorbent surface (Figure 9B), leading to negatively charged particles for both DDS^- and chloride intercalated LDHs [28]. The affinity was higher for Cl^- than for DDS^- intercalated samples, as corresponds to the latter stronger binding. On the other hand, MB^+ adsorption only occurred on LDH- DDS^- particles (Figure 9A). The maximum uptake (around 20 mg/g) was about 3% of the sample AEC, indicating that MB^+ adsorption was produced above the layer of DDS^- anions placed at the particle surface due to both electrostatic and hydrophobic interactions.

Although the uptake capacity is quite low, the high affinity of cationic dyes for the sorbent surface is attractive for the removal dyes at low concentrations. Thus, safranin removal by dodecylsulfate and dodecylbenzylsulfonate intercalated LDHs has been studied [136], obtaining a low but pH-independent uptake capacity. The sorbent recovered its sorption capacity in acetone even after several sorption/desorption cycles. This mechanism has also been proposed to obtain cooperative removal of anionic and cationic dyes by Wei et al [137]. The synthesis of a Mg-Al-LDH in the presence of multivalent anionic dye (direct blending scarlet D-GLN) produced a dye/LDH hybrid that presented uptake capacity towards cationic dyes, such as victoria blue B (VBB^+). The sorption capacity was almost independent of pH but a slight increase with NaCl concentration was registered, which can be related to screening of the surface charge generated by adsorption. The resulting sludge was reutilized as filler in polymer materials that presented enhanced resistance to bleeding and fire.

4.4. Other Organic Pollutants

Humic substances represent an important fraction of the organic matter of water. They are natural polymers that present variable molecular weight and a large concentration of polar groups, leading to high water solubility and heavy metal complexation capacity. Humic substances can be adsorbed in the surface of a wide variety of inorganic solids, such as clays and goethite [139], reducing their activity of sorbents in water purification processes. According to Amin and Jayson [140], nitrate, chloride or carbonate Mg-Al LDHs presented high affinity for humic substances, reaching uptake capacities above 1000 mg/g by anion exchange and adsorption. Similarly, Vreisen et al [46] proposed surface anion exchange and adsorption as main uptake mechanisms of NO_3^- and Cl^- intercalated Mg-Al LDHs. The intercalation of humic substances was considered unlikely, only small portions being introduced in the interlayer. The preference observed for humic substances with low molecular weight was assigned to their easier diffusion at interparticle mesopores of the sorbent while the decrease in uptake with increasing ion strength was assigned to competition by the electrolyte anions. On the other hand, Seida and coworkers [141] reported an increasing uptake with increasing M^{II}/M^{III} ratio and decreasing media pH for humic acids sorption by Mg-Fe and Ca-Fe LDHs. These results were explained with a mechanism involving partial LDHs weathering and humic acids precipitation at the surface of the

remaining solid. In contrast to that observed by Vreisen et al, the uptake capacity was enhanced by increasing ionic strength, due to a salting-out effect. LDHs has also been proposed as effective material for the removal of the carboxylated hydrocarbons resulting from carbon nanotube manufacture, due to this residue similarity with humic acids [142].

As seen in section 2.5, the uptake of aliphatic and aromatic hydrocarbons such as pyrene, trichloroethylene, etc by LDHs can be produced due to partition and adsorption processes. In this way, Kameda et al have studied the uptake of bisphenol A and benzene derivatives with Mg-Al LDHs intercalated with DDS^- and aromatic anions. In the case of DDS^- intercalated sorbents, their affinity for bisphenol A was explained by hydrophobic interactions between both compounds, leading to partition processes. The pollutant was easily recovered by dispersion in ethanol, the sorbent maintaining its uptake capacity [143]. In the case of benzene derivatives (nitrobenzene, benzaldehyde, anisole, etc.), the uptake was produced by π - π stacking interactions with the aromatic interlayer anions (2,7-naphthalenedisulphonate, 2-naphthalenesulphonate, etc.). The authors affirmed that the uptake affinity was dependent on the electronic state of the aromatic compounds, both interlayer anion and sorbate. As the interlayer anion presented weak electron-withdrawing groups, the sorption of compounds with electron-donor substituents was enhanced [144,145].

CONCLUSION

Layered double hydroxides are convenient pollutant sorbents for pollutants ranging from halides and oxyanions to pesticides and dyes. These solids display variable composition and multiple uptake mechanisms, including anion exchange, reconstruction, weathering/precipitation, adsorption and partition. According to the uptake mechanism, different factors are important to predict their behavior: for example, the media pH and the competing anions rule anion exchange and reconstruction, the nature of the pollutant is determining in the concurrence of adsorption processes, the composition of the sorbent layers control the weathering/precipitation mechanism and the hydrophobicity, concentration and arrangement of the interlayer anions are an important factor in partition processes. Removal by LDHs present as main advantages economical synthesis, short equilibration times, large uptake capacities and easy recyclability. Yet, a long way is still to go on large scale synthesis optimization, sorbent testing in actual conditions and matrixes, sorption behavior and recycling optimization, and integration with other sorbents and/or remediation techniques. The promising applications exposed and the increasing literature on the subject indicates that, in a not so distant future, the application of LDHs to pollutant elimination or stabilization will compete in some cases with established sorbents such as activated carbon, ion exchange resins or iron hydroxides.

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REFERENCES

- [1] Bhatnagar, A.; Sillanpää, M.; *Chem. Engineer. J.* 2010; 157; 277-296.
- [2] Kasprzyk-Hordern, B.; *Adv. Colloid Interface Sci.* 2004; 110; 19-48
- [3] Misaelides, P.; *Microp. Mesop. Mater.* 2011; 144; 15-18.
- [4] Cornejo, J.; Celi, R.; Pavlovic, I.; Ulibarri, M. A.; *Clay Miner.* 2008; 43; 155-176.
- [5] Evans, D. G.; Slade, R. C. T. In *Layered Double hydroxides*, Duan, X.; Evans, D.G.; Ed.; Structure and Bonding, Springer: Berlin, 2005; 119, pp. 1-88.
- [6] Ulibarri, M. A.; Hermosin, M. C.; in *Layered Double Hydroxides: Present and Future*, Rives, V.; Ed.; Nova Science Publishers, New York, 2001, pp. 251-284.
- [7] Forano, C.; in *Clay Surfaces: Fundamentals and Applications*, Wyppych, F., Satyanarayana, K. G. Eds.; Elsevier: Amsterdam, 2004, pp. 425-458.
- [8] De Roy, A.; Forano, C.; Besse, J. P. in *Layered Double Hydroxides: Present and Future*, Rives, V.; Ed.; Nova Science Publishers, New York, 2001, pp. 1-38.
- [9] Bookin, A. S.; Drits, V. A.; *Clays Clay Miner.* 1993; 41; 551-557.
- [10] He, J.; Wei, M.; Li, B., Kang, Y.; Evans, D.G.; Duan, X. In *Layered Double hydroxides*, Duan, X.; Evans, D.G.; Ed.; Structure and Bonding, Springer, Berlin, 2005; 119, pp. 89-119.
- [11] Cavani, F.; Trifiró, F.; Vaccari, A. *Catal. Today* 1991; 11; 173-301.
- [12] Olf, H. W.; Torres-Dorante, L. O.; Eckelt, R.; Kosslick, H. *Appl. Clay Sci.* 2009; 43; 459-464.
- [13] Seftel, E. M.; Popovici, E.; Mertens, M.; De Witte, K.; Van Tendeloo, G.; Cool, P.; Vansant, E. F. *Micropor. Mesopor. Mater.* 2008; 113; 296-304.
- [14] Valente, J. S.; Hernandez-Cortez, J.; Sánchez-Cantú, M.; Ferrat, G.; Lopez-Salinas, E. *Catal. Today* 2010; 150; 340-345.
- [15] Arai, Y.; Ogawa, M. *Appl. Clay Sci.* 2009; 42; 601-604.
- [16] Adachi-Pagano, M.; Forano, C.; Besse, J.-P.; *J. Mater. Chem.* 2003; 13; 1988-1993.
- [17] Xu, Z.P.; Stevenson, G. S.; Lu, C.Q.; Lu, G.Q. *J. Phys. Chem. B* 2006; 110; 16923-16929.
- [18] Xu, Z.P.; Stevenson, G. S.; Lu, C.Q.; Lu, G.Q.M.; Bartlett, P.F.; Gray, P.P. *J. Am. Chem. Soc.* 2006; 128; 36-37.
- [19] Valente, J. S.; Sánchez-Cantú, M.; Figueras, F. *Chem. Mater.* 2008; 20; 1230-1232.
- [20] Valente, J. S.; Sánchez-Cantú, M.; Lima, E.; Figueras, F. *Chem. Mater.* 2009; 21; 5809-5818.
- [21] Zhou, J.; Yang, S.; Yu, J.; Shu, Z. *J. Hazard. Mater.* 2011; 192; 1114-1121.
- [22] Palmer, S. J.; Nothling, M.; Bakon, K.H.; Frost, R. L. *J. Colloid Interf. Sci.* 2010; 342; 147-154.
- [23] Liu, Y.; Naidu, R.; Ming, R. *Geoderma* 2011; 163; 1-12.
- [24] Xu, Z. P.; Jin, Y.; Liu, S.; Hao, Z. P.; Lu, G. Q. *J. Colloid Interface Sci.* 2008; 326; 522-529.
- [25] Wang, J.; Yang, F.; Liu, S.; Sun D. *Langmuir* 2008; 24; 10054-10061.
- [26] Bruna, F.; Celis, R.; Pavlovic, I.; Barriga, C.; Cornejo, J.; Ulibarri, M. A. *J. Hazard. Mater.* 2009; 168; 1476-1481.
- [27] MacBride, M. B. *Environmental chemistry of solids*; Oxford University Press: Oxford, 1994.

- [28] Rojas, R.; Arandigoyen, M.; De Pauli, C.; Ulibarri, M. A.; Avena, M. J. *J. Colloid Interface Sci.* 2004; 80; 431–441.
- [29] Miyata, S., *Clays Clay Miner.* 1983; 3; 305-311.
- [30] Israeli, Y.; Gueho, C. T.; Besse, J. P.; Morel, J. P.; Desrosiers, N. M. J. *Chem. Soc., Dalton Trans.*; 2000, 791-796.
- [31] Goh, K.-H.; Lim, T.-T. *J. Hazard. Mater.* 2010; 180; 401-408.
- [32] Prasanna, S. V.; Vishnu Kamath, P. *Ind. Eng. Chem. Res.* 2009; 48; 6315–6320.
- [33] Prasanna, S. V.; Vishnu Kamath, P. *Solid State Sci.* 2008; 10; 260-266.
- [34] Sato, T.; Wakabayashi, T.; Simada, M. *Ind. Eng. Chem. Prod. Res. Dev.* 25 (1986) 89-92.
- [35] Carja, G.; Nakamura, R.; Niiyama, H. *Micropor. Mesopor. Mater.* 2005; 83; 94–100.
- [36] Yang, L.; Shahrivari, Z.; Liu, P. K. T.; Sahimi, M.; Tsotsis, T. T. *Ind. Eng. Chem. Res.* 2005; 44; 6804–6815.
- [37] Novack, B.; Sigg, L.; *J. Colloid Interf. Sci.* 1996; 177; 106-121.
- [38] Avena, M. J. in *Encyclopedia of Surface and Colloid Science*; Hubbard, A.; Ed., Dekker: New York, 2002; pp. 37-63.
- [39] Rojas, R.; Bruna, F.; de Pauli, C. P.; Ulibarrim M. A.; Giacomelli, C. E. *J. Colloid Interface Sci.* 2011; 359; 136-141.
- [40] Jiao, J. N.; Hou, W. G. *Colloids Surf. A* 2007; 296; 62-66.
- [41] Pavan, P. C.; Crepaldi, E. L.; Gomes, G. A.; Valim, J. B. *Colloids Surf. A* 1999; 154; 399-410.
- [42] Châtelet, L.; Bottero, J. V.; Yvon, J., Boulaghem, A. *Colloids Surf. A* 1996, 111, 167-175.
- [43] Goh, K.-H.; Lim, T.-T. *J. Hazard. Mater.* 2010; 180; 818-827.
- [44] Rojas, R.; Pérez, M. R.; Erro, E. M.; Ortiz, P. I.; Ulibarri, M. A.; Giacomelli, C. E. *J. Colloid Interf. Sci.* 2009; 331; 425-431.
- [45] Seida, Y.; Nakano, Y. *Water Res.* 2002; 36; 1306–1312.
- [46] Vreysen, S.; Maes, A. *Applied Clay Sci.* 2008; 38; 237-249.
- [47] Goh, K. H.; Lim, T. T.; Dong, Z. *Water Res.* 2008; 42; 1343-1368.
- [48] Rojas, R.; Parello, M. L.; Giacomelli, C. E. *J. Colloid Interface Sci.* 2010; 351; 134-139.
- [49] Ferreira, O. P.; de Moraes, S. G.; Duran, N.; Cornejo, L.; Alves, O. L. *Chemosphere* 2006; 62; 80–88.
- [50] Jobbágy, M.; Regazzoni, A. E. *Chem. Phys. Lett.* 2006; 433; 62-66.
- [51] Dutta, P.; Robins, D. S. *Langmuir* 1994; 10; 1851-1856.
- [52] Zhao, H.; Nagy, K. J. *Colloid Interf. Sci.* 2004; 274; 613-624.
- [53] Chuang, Y.-H.; Liu, C.-H.; Tzou, Y.-M.; Chang, J.-S.; Chiang, P.-N.; Wang, M.-K. *Colloids Surf. A* 2010; 366; 170-177.
- [54] Zhao, H.; Vance, G. F. *Clays Clay Miner.* 1998; 46; 712-718.
- [55] Jin, L.; He, D.; Wei, M. *Chem. Engineer. Technol.* 2011; 34; 1559-1566.
- [56] Kameda, T.; Takeuchi, H.; Yoshioka, T. *Separ. Purif. Technol.* 2008; 62; 330-336.
- [57] Gillman, G.P. *Sci. Total Environ.* 2006; 366; 926–931.
- [58] Kuzawa, K.; Jung, Y. J.; Kiso, Y.; Yamada, T.; Nagai, M.; Lee, T. G. *Chemosphere* 2006; 62; 45–52.
- [59] Guo, X.; Zhang, F.; Peng, Q.; Xu, S.; Lei, X.; Evans, D. G.; Duan, X. *Chem. Engineer. J.* 2011; 166; 81-87.

- [60] Gong, J.; Liu, T.; Wang, X.; Hu, X.; Zhang, L. *Environ. Sci. Technol.* 2011; 45; 6181-6187.
- [61] Iorio, M.; De Martino, A.; Violante, A.; Pigna, M.; Capasso, R. *J. Agric. Food Chem.* 5523-5530.
- [62] Hourri, B.; Legrouri, A.; Barroug, A.; Forano, C.; Besse, J. P. *J. Chim. Phys.* 1999; 96; 455-463.
- [63] Lu, L.; He, J.; Evans, D. G.; Zhou, Z. *Water Res.* 2007; 41; 1534-1542.
- [64] Lu, L.; He, J.; Wei, M.; Evans, D. G.; Duan, X. *J. Hazard. Mater. B* 2006; 133; 119-128.
- [65] Mandal, S.; Mayadevi, S. *Chemosphere* 2008; 72; 995-998.
- [66] Lu, L.; Sun, P.; Gu, Z.; Du, H.; Pang, X.; Tao, X.; Xu, R.; Xu, L. *J. Hazard. Mater.* 2009; 161; 1444-1449.
- [67] Lu, L.; He, J.; Wei, M.; Evans, D. G.; Duan, X. *Water. Res.* 2006; 40; 735-743.
- [68] Lu, L.; Wang, Y.; Wei, M.; Cheng, J. *J. Hazard. Mater.* 2008; 152; 1130-1137.
- [69] Lu, L.; Li, L. *J. Radioanal. Nucl. Chem.* 2007; 273; 221-226.
- [70] Thomas, N.; Rajamathi, M. *Langmuir* 2009; 25; 2212-2216.
- [71] WHO, World Health Organization. Organization, Guidelines for Drinking Water Quality (3rd Ed.); World Health Organization: Geneva, Switzerland, 2008.
- [72] Lefebvre, O.; Moletta, R. *Water. Res.* 2006; 40; 3671-3682.
- [73] Prasad, B. E.; Vishnu Kamath, P.; Vijayamohanan, K. *Langmuir* 2011; 27; 13539-13543.
- [74] Kameda, T.; Uchiyama, N.; Yoshioka, T. *Chemosphere* 2010; 81; 658-662.
- [75] Kentjono, L.; Liu, J. C.; Chang, W. C. *Desalination* 2010; 262; 280-283.
- [76] Chitrakar, R.; Sonoda, A.; Makita, Y.; Hirotsu, T. *Ind. Eng. Chem. Res.* 2011; 50; 9280-9285.
- [77] Islam, M.; Patel, R. *J. Hazard. Mater.* 2009; 169; 524-529.
- [78] Islam, M.; Patel, R. *J. Desalination.* 2010; 256; 120-128.
- [79] Kameda, T.; Fubasami, Y.; Yoshioka, T. *J. Colloid Interf. Sci.* 2011; 362; 497-502.
- [80] Socías-Viciano, M. M.; Ureña-Amate, M. D.; González-Pradas, E.; García-Cortés, M. J.; López-Teruel, C. *Clays Clay Miner.* 2008; 56; 2-9.
- [81] Wu, X.; Wang, Y.; Xu, L.; Lu, L. *Desalination* 2010; 256; 136-140.
- [82] Goh, K.-H.; Lim, T.-T.; Dong, Z. *Environ. Sci. Technol.* 2009; 43; 2537-2543.
- [83] Caporale, A. G.; Pigna, M.; Dynes, J. J.; Cozzolino, V.; Zhu, J.; Violante, A. *J. Hazard. Mater.* 2011; 198; 291-298.
- [84] Goswamee, R. L.; Sengupta, P.; Bhattacharyya, K. G.; Dutta, D. K. *Appl. Clay Sci.* 1998; 13; 21-34.
- [85] Das, J.; Patra, B. S.; Baliarsingh, N.; Parida, K. M. *Appl. Clay Sci.* 2006; 32; 252-260.
- [86] Koilraj, P.; Kannan, S. *J. Colloid Interf. Sci.* 2010; 341; 289-297.
- [87] Zhou, J.; Xu, Z. P.; Qiao, S.; Liu, Q.; Xu, Y.; Qian, G. *J. Hazard. Mater* 2011; 189; 586-594.
- [88] You, Y.; Vance, G. F.; Zhao, H. *Appl. Clay Sci.* 2001; 20; 13-25.
- [89] Goh, K. H.; Lim, T. T.; Banas, A.; Dong, Z. *J. Hazard. Mater.* 2010; 179; 818-827.
- [90] Carriazo, D.; del Arco, M.; Martin, C.; Rives, V. *Appl. Clay Sci.* 2007; 37; 231-239.
- [91] Kameda, T.; Honda, M.; Yoshioka, T. *Separ. Purif. Technol.* 2011; 80; 235-239.
- [92] Liu, Q.; Li, Y.; Zhang, J.; Chi, Y.; Ruan, X.; Liu, J.; Qian, G. *Chem. Enc. J.* 2011; 175; 33-38.

- [93] Park, M.; Choi, C. L.; Seo, Y. J.; Yeo, S. K.; Choi, J.; Komarneni, S.; Lee, J. H. *Appl. Clay Sci.* 2007; 37; 143-148.
- [94] Lazaridis, N. K. *Water Air Soil Poll.* 2003; 146; 127-139.
- [95] Nakayama, H.; Hirami, S.; Tshako, M. *J. Colloid Interf. Sci.* 2007; 315; 177-183.
- [96] Pavlovic, I.; Pérez, M. R.; Barriga, C.; Ulibarri, M. A. *Appl. Clay Sci.* 2009; 43; 125-129.
- [97] Pérez, M. R.; Pavlovic, I.; Barriga, C.; Cornejo, J.; Hermosin, M. C.; Ulibarri, M. A. *Appl. Clay Sci.* 2006; 32; 245-251.
- [98] Allada, R. K.; Navrotsky, A.; Berbeco, H. T.; Casey, W. H. *Science* 2002; 296; 721-726.
- [99] Regeling, I. C.; Temminghoff, J. M. *Environ. Pollut.* 2011; 159; 716-721.
- [100] Hashim, M. A.; Mukhopadhyay, S.; Sahu, J. N.; Sengupta, B. *J. Environ. Manage.* 2011; 92; 2355-2388.
- [101] Chen, Q. Y.; Luo, Z.; Hills, C.; Xue, G.; Tyrer, M.; *Water Res.* 2009; 43; 2605-2614.
- [102] Komarneni, S.; Kozai, N.; Roy, R.; *J. Mater. Chem.* 1998; 8; 1329-1331.
- [103] Seida, Y.; Nakano, Y.; Nakamura, Y. *Water Res.* 2001; 35; 2341-2346.
- [104] Bocclair, J. W.; Braterman, P. S. *Chem. Mater.* 1999; 11; 298-302.
- [105] Zhou, J. Z.; Wu, Y. Y.; Liu, C.; Orpe, A.; Liu, Q.; Xu, Z. P.; Qian, G. R.; Qiao, S. Z. *Environ. Sci. Technol.* 2010; 44; 8884-8890.
- [106] Kameda, T.; Takeuchi, H.; Yoshioka, T. *Colloids Surf. A* 2010; 355; 172-177.
- [107] Kameda, T.; Hoshi, K.; Yoshioka, T. *Solid State Sci.* 2011; 13; 366-371.
- [108] Ulibarri, M. A.; Pavlovic, I.; Barriga, C.; Hermosin, M. C.; Cornejo, J. *Appl. Clay Sci.* 2001; 18; 17-27.
- [109] Ulibarri, M. A.; Pavlovic, I.; Hermosin, M. C.; Cornejo, J. *Appl. Clay Sci.* 1995; 10; 131-145.
- [110] Chuang, Y. H.; Tzou, Y. M.; Wang, M. K.; Liu, C. H.; Chiang, P. N. *Ind. Eng. Chem. Res.* 2008; 47; 3813-3819.
- [111] Chen, S.; Xu, Z. P.; Zhang, Q.; Max Lu, G. Q.; Hao, Z. P.; Liu, S. *Sep. Purif. Technol.* 2009; 67; 194-200.
- [112] Chaara, D.; Pavlovic, I.; Bruna, F.; Ulibarri, M. A.; Draoui, K.; Barriga, C. *Appl. Clay Sci.* 2010; 50; 292-298.
- [113] Barriga, C.; Gaitan, M.; Pavlovic, I.; Hermosin, M. C.; Cornejo, J. *J. Mater. Chem.* 2002; 12; 1027.
- [114] Inacio, J.; Taviot-Guého, C.; Forano, C.; Besse, J.-P. *Appl. Clay Sci.* 2001; 18; 255-264.
- [115] Chao, Y. F.; Chen, P. C.; Wang, S. L. *Appl. Clay Sci.* 2008; 40; 193-200.
- [116] Pavlovic, I.; Barriga, C.; Hermosin, M. C.; Cornejo, J.; Ulibarri, M. A. *Appl. Clay Sci.* 2005; 30; 125-133.
- [117] You, Y.; Zhao, H.; Vance, G. F. *Appl. Clay Sci.* 2002; 21; 217-226.
- [118] Cardoso, L. P.; Valim, J. B. *J. Phys. Chem. Solids* 2006; 67; 987-993.
- [119] Chaparadza, A.; Hossenlopp; *J. M. J. Colloid Interf. Sci.* 2011; 363; 92-97.
- [120] Bruna, F.; Pavlovic, I.; Barriga, C.; Cornejo, J.; Ulibarri, M. A. *Appl. Clay Sci.* 2006; 33; 116-124.
- [121] Chaara, D.; Bruna, F.; Ulibarri, M. A.; Draoui, K.; Barriga, C.; Pavlovic, I. *J. Hazard. Mater.* 2011; 196; 350-359.
- [122] Lakraimi, M.; Legrouri, A.; Barroug, A.; de Roy, A.; Besse, J. P. *J. Chim. Phys.* 1999; 96; 470-478.

- [123] Ragavan, A.; Khan, A.; O'Hare, D. *J. Mater. Chem.* 2006; 16; 4155-4159.
- [124] Chao, Y. F.; Chen, P. C.; Wang, S. L. *J. Hazard. Mater.* 2009; 165; 846-852.
- [125] Sánchez-Martin, M.; Villa, M. V.; Sánchez-Camazano, M. *Clays Clay Miner.* 1999; 47; 777-783.
- [126] Villa, M. V.; Sánchez-Martin, M. J.; Sánchez-Camazano, M. *J. Environ. Sci. Health* 1999; B34; 470.
- [127] Orthman, J.; Zhu, H. Y.; Lu, G. Q. *Sep. Purif. Technol.* 2003; 31; 53-59.
- [128] Ni, Z.-M.; Xia, S.-J.; Wang, L.-G.; Xing, F.-F.; Pan, G.-X. *J. Colloid Interf. Sci.* 2007; 316; 284-291.
- [129] Zhu, M.-X.; Li, Y.-P.; Xie, M.; Xin, H.-Z. *J. Hazard. Mater.* 2005; 120; 163-171.
- [130] El Gaini, L.; Lakraimi, M.; Sebbar, E.; Meghea, A.; Bakasse, M. *J. Hazard. Mater.* 2009; 161; 627-632.
- [131] Bascialla, G.; Regazzoni, A. E. *Colloids Surf. A* 2008; 328; 34-39.
- [132] Lazaridis, N. K.; Karapantsios, T. D.; Georgantas, D. *Water Res.* 2003; 37; 3023-3033.
- [133] Constantino, U.; Coletti, N.; Nocchetti, M.; Aloisi, G. G.; Elisei, F. *Langmuir* 1999; 15; 4454-4460.
- [134] Constantino, U.; Coletti, N.; Nocchetti, M.; Aloisi, G. G.; Elisei, F.; Latterini, F. *Langmuir* 2000; 16; 10351-10358.
- [135] Bouhent, M. M.; Derriche, Z.; Denoyel, R.; Prevot, V.; Forano, C. *J. Solid State Chem.* 2011; 184; 1016-1024.
- [136] Bouraada, M.; Lafjah, M.; Ouali, M. S.; de Menorval, L. C. *J. Hazard. Mater.* 2008; 153; 911-918.
- [137] Wei, Y.-P.; Wei, D.-Q.; Gao, H.-W. *Chem. Eng. J.* 2011; 172; 872-878.
- [138] Gupta, V. K.; Suhas. *J. Environ. Manag.* 2009; 90; 2313-2342.
- [139] Bolto, B.; Dixon, D.; Eldridge, R.; King, S.; Linge, K. *Water Res.* 2002; 36; 5057-5065.
- [140] Amin, S.; Jayson, G. G. *Water. Res.* 1992; 30; 299-306.
- [141] Seida, Y.; Nakano, Y. *Water Res.* 2000; 34; 1487-1494..
- [142] Alves, O. L.; Stéfani, D.; Parizotto, N. V.; Souza Filho, A. G. *J. Phys.: Conf. Series* 2011; 304; 012024.
- [143] Kameda, T.; Saito, M.; Umetsu, Y. *J. Alloys Comp.* 2005; 402; 46-52.
- [144] Kameda, T.; Yamazaki, T.; Yoshioka, T. *Chem. Lett.* 2009; 38; 522-523.
- [145] Kameda, T.; Yamazaki, T.; Yoshioka, T. *Mater. Res. Bull.* 2010; 45; 751-753.