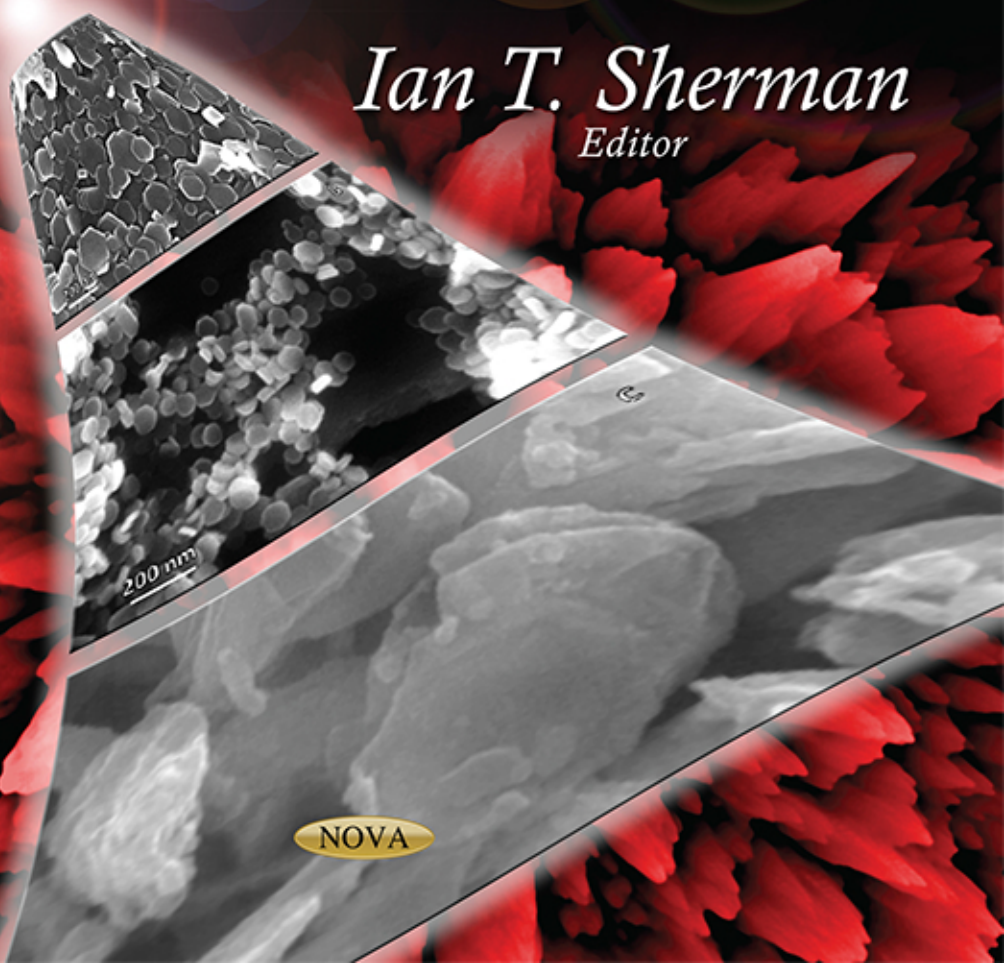


MATERIALS SCIENCE AND TECHNOLOGIES

# Layered Double Hydroxides (LDHs)

Synthesis, Characterization and Applications

*Ian T. Sherman*  
Editor



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## **SYNTHESIS, CHARACTERIZATION AND APPLICATIONS**

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# **LAYERED DOUBLE HYDROXIDES (LDHs)**

## **SYNTHESIS, CHARACTERIZATION AND APPLICATIONS**

**IAN T. SHERMAN**  
**EDITOR**



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## PREFACE

The crystal structure of layered double hydroxides is based on positive charged brucite-like mainlayers and balanced by reversible exchangeable interlayer anions, additional cations and water molecules. Due to their negligible toxicity and buffering properties, LDHs are commercially employed as antacids and they are increasingly studied as vehicles in drug and gene delivery systems. This book discusses the synthesis, characterization and applications of layered double hydroxides.

Chapter 1 - Layered double hydroxides (LDHs) are clay-type materials with extraordinary properties, whose structure is composed of stacked inorganic metal oxide layers built by connected sheets. These layers hold usually charge deficiency which is balanced by the presence of anions (anionic clays) at the interlayer spacing. By taking advantage of this relevant property, many works across several fields have been dedicated to explore this by introducing anions inside the interlayer spacing of the clays. This includes exchange from simple anions to complex structures such as large polyoxoions or even metal complexes. The resulting tuned materials find wide use in several catalytic applications with the advantage that in some cases the heterogeneous process overcomes the homogeneous one.

Important chemical reactions such as the Suzuki and Heck coupling reactions or other such as water splitting can be successfully catalyzed by such materials. Oxidation reactions including epoxidation of olefins and oxidation of alcohols to carbonyl compounds are also important chemical processes where layered double hydroxides can be efficient catalysts.

From the economical point of view such catalysts feature high synthetic flexibility, tunable acid-base properties and ease of set-up and work-up, among others. These properties lead to the development of more efficient catalytic systems with improved yields and selectivity, which are valuable achievements in the present days by contributing towards the establishment of environmentally friendly technologies.

Chapter 2 - The crystal structure of layered double hydroxides (LDHs) with the formula  $[\text{Zn}_2\text{Al}(\text{OH})_6]^+[\text{A} \cdot n\text{H}_2\text{O}]^-$  is based on positive charged brucite-like mainlayers and balanced by reversible exchangeable interlayer anions, additional cations and water molecules. The interlayer space can be modified by incorporation of complex large organic anions, depending on size and position of the host molecules in the interlayer. Due to their variable chemical composition and the ability of permanent anion-exchange capacity, LDHs are recently used as adsorber, catalytic materials and antacid drugs.

Substitution of amino acid anions was performed by indirect anion-exchange. LDH precursor phases with the formula  $[\text{Zn}_2\text{Al}(\text{OH})_6]^+[\text{NO}_3 \cdot 1.9\text{H}_2\text{O}]^-$  were synthesized at pH

7.4 and 45°C using the co-precipitation method. Anion-exchange reactions were executed by addition of an aqueous solution of amino acids in excess in a pH-range of 10-11 to the precursor suspension with subsequently aging at 45°C for 3-7 days. All synthesis and washing procedures were performed under constant inert atmosphere to prevent the incorporation of carbonate in the interlayer of LDHs. The synthesized compounds were analyzed by in situ X-ray diffraction measurements, thermal analysis (TG), infrared absorption spectra, SEM and chemical analysis, controlling also different relative humidities.

ZnAl-LDHs with amino acid anions form generally small, well-crystallized laminated crystals with pseudo-hexagonal shape. XRD analyses of wet samples (94% r.h.) display sharp basal reflexes with up to 5 orders along the stacking direction. The interlayer space varies between 0.75-1.92 nm, whereas the orientation of the guest anions shows a mixture of preferred perpendicular and subordinate parallel orientated molecules. All intercalated organic anions form mono-molecular layers in the interlayer space, except glycine and isoleucine anions, which are orientated in a bi-molecular arrangement. Depending on type of interlayer anion some reorientation takes place during heating process. Thermal analysis shows a three-step degradation mechanism, related to the removal of interlayer water (< 170°C) followed by de-hydroxylation of mainlayers with subsequent decomposition of interlayer anions.

Chapter 3 - Manganese containing LDH's were synthesized and the optimal conditions for the precipitation determined. Crystallization, dehydration and incorporation of inorganic and organic anions are monitored using X-ray diffraction (XRD). LDH's  $[\text{Me}^{2+}_{1-x}\text{Me}^{3+}_x(\text{OH})_2]^{x+}[\text{A}^{r-}_{x/r}\cdot n\text{H}_2\text{O}]^{x-}$  with  $\text{Me}^{2+} = \text{Mn}$ ;  $\text{Me}^{3+} = \text{Al, Fe, Cr}$  and  $\text{A}^{r-} = \text{carboxylic acid, dicarboxylic acid and sulfonic acid molecules as well as several inorganic anions were synthesized.}$

The basal spacing between the layers depends on the implemented chain length and the type of the anion. The inclination of the organic chains in the interlayer was calculated.

Manganese containing LHD's with aliphatic sulfonic acids molecules show a linear increase in basal spacing from short to long molecules whereas the interlayer distances of compounds with aliphatic carboxylic acids molecules increase much stronger for long molecules compared to short chains, proving a bimolecular arrangement of the anionic molecules.

All synthesized manganese containing LDH's consist of hexagonal shaped lamellar aggregates of some  $\mu\text{m}$  size. Compounds with inorganic sulphate or selenate molecules in the interlayer (shigaite-type structures) need an additionally single charged cation such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Li}^+$ ,  $\text{NH}_4^+$  for charge compensation.

Thermal treatment caused a loss of interlayer water resulting in changes of the c lattice parameter. Non ambient XRD experiments in combination with statistical data evaluation (principal component analysis, PCA) describes the thermal behaviour (dehydration, dehydroxylation, decomposition) of the components.

Characterization of the crystal morphology, size and shape of the synthesized LDHs was monitored with Cryo-SEM, enabling the analysis of water containing components that are not stable under ambient vacuum conditions.

Chapter 4 - A new treatment method for  $\text{SO}_x$  has been examined using a slurry of Mg-Al oxide in  $\text{H}_2\text{O}$ . Dissolution of  $\text{SO}_x$  in the slurry produces  $\text{SO}_x\cdot\text{Mg-Al}$  LDH, which can be calcined to yield sulfuric acid, MgO, and  $\text{MgAl}_2\text{O}_4$ . In addition, the treatment of  $\text{H}_2\text{SO}_4$  with Mg-Al oxide was examined in terms of kinetics and equilibrium studies in order to clarify the

nature of the reaction between the Mg–Al oxide slurry and  $\text{SO}_x$ . The authors also examined this Mg–Al oxide treatment method for  $\text{NO}_x$ . The  $\text{NO}_x$  dissolves in the Mg–Al oxide slurry and produces  $\text{NO}_x$ –Mg–Al LDH. The isolated  $\text{NO}_x$ –Mg–Al LDH can also be calcined, yielding in this case, nitric acid and the reconstituted Mg–Al oxide. In addition, the treatment of  $\text{HNO}_3$  with Mg–Al oxide was examined with respect to kinetics and equilibrium studies in order to clarify the nature of the interaction between the Mg–Al oxide and  $\text{NO}_x$ . Finally, the authors demonstrated the simultaneous removal of  $\text{SO}_2$  and  $\text{NO}_2$  from a mixed gas stream using the Mg–Al oxide slurry treatment.

Chapter 5 - Due to their negligible toxicity and buffering properties, layered double hydroxides (LDHs) are commercially employed as antacids and they are increasingly studied as vehicles in drug and gene delivery systems. The bioactive compounds (drugs, biomolecules) are incorporated by intercalation or adsorption and released under appropriate conditions by anion exchange, desorption and LDH layers dissolution. More recently, their application as nanovehicles for cellular delivery has been developed based on their synthesis in the nanometer scale. LDH nanoparticles are obtained by different synthesis routes, but the more extended involves coprecipitation at either constant or variable pH followed by hydrothermal aging in pure water. LDH based nanocarriers present several advantages as drug and gene nanovehicles when compared to other inorganic nanoparticles. First, LDH nanovehicles interact with the negatively charged cell membrane due to the positive charge and the hydrophilic character of the nanoparticles and their transfection is mainly produced by clathrin-mediated endocytosis. Secondly, LDH nanovehicles are dissolved in mildly acid media into non-toxic species, releasing their cargo and preventing the accumulation usually observed with polymers and other inorganic vehicles. Finally, they are expected to avoid renal clearance and to allow long circulation times due to their size. In this chapter, the strategies to obtain LDH nanoparticles as well as the factors that determine the particle size distribution are reviewed with emphasis on their application in drug and gene delivery. Hence, the chapter highlights the physicochemical factors that affect the delivery process and the proposed customization strategies to produce an optimal performance of LDH nanoparticles as drug nanovehicles.

Chapter 6 - Synthetic layered double hydroxides (LDHs) are hydrotalcite-like materials known for their ability to sorb anions from aqueous solutions, such as the chromates, arsenates, reactive azo dyes etc.; the latter will be merely used as remediation examples in the present. Their release into the environment is undesirable and their removal becomes environmentally important. The relative scientific area will be reviewed for the current developments in the literature. Synthesis and characterization aspects of the sorbents will be also commented. The influence of solution pH, conditioning duration, initial chromium concentration, sorbent concentration, sorbent particle size, and temperature was tested at sorption kinetic runs. Desorption experiments showed that the loaded material can be fully regenerated and reused. Thermodynamic analysis revealed that the sorption is spontaneous and endothermic. These materials usually exist in powder form, thereby exhibiting high surface area, especially their calcined compounds, and rapid kinetics for adsorption; but presenting often appreciable problem in the subsequent solid/liquid separation process.



*Chapter 6*

## LAYERED DOUBLE HYDROXIDES AND CERTAIN ENVIRONMENTAL APPLICATIONS (THE CONTRIBUTION OF LGICT)

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### ABSTRACT

Synthetic layered double hydroxides (LDHs) are hydrotalcite-like materials known for their ability to sorb anions from aqueous solutions, such as the chromates, arsenates, reactive azo dyes etc.; the latter will be merely used as remediation examples in the present. Their release into the environment is undesirable and their removal becomes environmentally important. The relative scientific area will be reviewed for the current developments in the literature. Synthesis and characterization aspects of the sorbents will be also commented. The influence of solution pH, conditioning duration, initial chromium concentration, sorbent concentration, sorbent particle size, and temperature was tested at sorption kinetic runs. Desorption experiments showed that the loaded material can be fully regenerated and reused. Thermodynamic analysis revealed that the sorption is spontaneous and endothermic. These materials usually exist in powder form, thereby exhibiting high surface area, especially their calcined compounds, and rapid kinetics for adsorption; but presenting often appreciable problem in the subsequent solid/liquid separation process.

**Keywords:** Layered double hydroxides, dyes, arsenates, chromates, flotation

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## INTRODUCTION

Layered double hydroxides, as a typical example of inorganic ion exchangers aiming priority pollutants, has long been mentioned [1]. LDHs are lamellar mixed hydroxides containing positively charged main layers and undergoing anion exchange chemistry. In recent years, many studies have been devoted to investigating their ability to remove harmful oxyanions from contaminated waters by both surface adsorption and anion exchange of the oxyanions for interlayer anions in the LDH structure [2]. For instance, calcined Fe(III)-substituted LDHs materials were used to sorb phosphate [3]. Earlier, the effect of interlayer anion and crystallinity were investigated [4]. The calcined product can reconstruct its original layer structure with rehydration and sorption of various anions, provided the upper temperature did not exceed 550-600°C [5]. Because of the presence of large interlayer spaces, the presence of a huge number of exchangeable anions (2-5 mmol/g) and their relatively large surface areas (10-120 m<sup>2</sup>/g) LDHs are good ion exchangers/adsorbents for the removal of toxic anions from contaminated waters [6].

Industries engaged in metal production operations or metal finishing use large quantities of contact process water and the spent process streams generally contain moderate concentrations of heavy metal ions. Apart from the toxic metals, synthetic dyes are another application example; many industries like textiles, leather, cosmetics, paper, printing, plastics, etc., use many synthetic dyes to color their products [7]. The foreseeable worldwide limitation of water resources leads to the need for water re-use, which requires treatment of water streams to reduce the amounts of harmful components. The need for fresh sources of drinking water is becoming urgent worldwide, meanwhile looking for sustainability [8].

A whole family of what are frequently termed mixed metal hydroxides, layered double hydroxides or simply hydrotalcites exists, both in nature and as the result of synthesis, in addition to the parent hydrotalcite structure. Hydrotalcite is structurally related to brucite, a layered structure comprising edge-sharing Mg(OH)<sub>6</sub> octahedra, which form two parallel sheets of hydroxyl ions with magnesium cations occupying all the octahedral holes between them, according to Webb [9] - then at Crosfield Ltd. In hydrotalcite, the structure is identical except that there has been stoichiometric replacement of some of the Mg<sup>2+</sup> by Al<sup>3+</sup> cations, the result of which is that the lattice has a net positive charge. This is compensated for by the anions (here, CO<sub>3</sub><sup>2-</sup>) associated with the lattice surface which are mobile and hence exchangeable. The resulting structure comprises hydrotalcite platelets aligning themselves in parallel to form small domains of stacked platelets. Between them are the counter-anions and the water of crystallization. These clay domains are themselves aggregated in a typical product particle and micro/mesopores exist between them [10].

Recently, the adequacy of synthetic Zn-Al-sulphate LDHs to remove arsenic from aqueous systems was tested through sorption experiments, together with other anions to assess their competition influence on the As removing process [11]. Complexation reactions of environmentally important inorganic anions on the surface of hydrotalcite-like compounds were investigated to understand their role in the immobilization of hazardous anions in an alkaline environment [12]. The structural and adsorptive characterization of a Zn-Al-type layered double hydroxide, used for the retention of chromate ions, were elsewhere examined [13]. A kinetic analysis of the process, among others, was performed [14]. The sorption mechanisms were also studied of various Mg/Al LDHs [15-16]. In the former, it was pointed

out that the main chemical industries producing these materials advertise them mainly (or only) as plastic additives.

Certainly, a quite large number of papers have examined LDHs for their technological application to the removal of toxic ions, recovery of valuable substances, catalysis etc. Main focus of this paper was to present an overview of the research related to the effective removal (by sorption and/or flotation) of pollutants onto LDHs from aqueous effluents, as exerted in depth at the Laboratory of General & Inorganic Chemical Technology (denoted as LGICT) during the last years.

## DYES REMOVAL

Amongst various methods for dye removal, sorption and/or biosorption is the procedure of choice, as it can be used to remove different types of coloring materials and can be effective even at very low concentrations of dye (ppm or ppb) in the waste waters to be treated [17-18]. The industrial dyestuff effluents are highly colored and their disposal into receiving waters causes damage to the environment as they may significantly affect photosynthetic activity in aquatic life due to reduced light penetration and also may be toxic to some aquatic life, in the case they contain metals, chlorides, etc. The application of layered double hydroxides to the removal of dyes has been reported: indigo carmine dye [19], acid dyes like Green Bezanyl-F2B [20], Evans Blue [21], C.I. Acid Blue 9 [22], benzopurpurine 4B [23], or a basic dye [20]. The azo-reactive dyes (as the Remazol Red 3BS) are used extensively in textile industries owing to their favorable characteristics of bright color, water-fast and simple application techniques with low energy consumption.

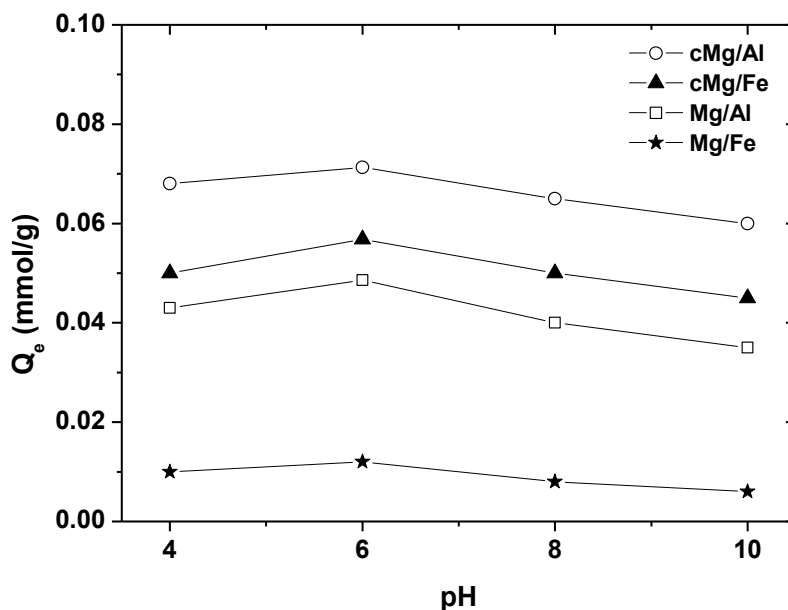


Figure 1. Effect of pH on dye uptake by various LDHs; where c stands for the calcined material. Reprinted with permission; copyright Wiley [24].

Figure 1 presents a part of our work. In general, it did not seem that pH had any significant impact on adsorption. In this publication [24], hydrotalcite-like materials  $\text{Mg}/\text{M}^{3+}$  (where  $\text{M} = \text{Al}^{3+}, \text{Fe}^{3+}$ ) have been synthesized using a simple co-precipitation method and were subsequently calcined in air at 450 °C. Both as-synthesized and calcined materials were characterized by means of X-ray diffraction,  $\text{N}_2$  porosimetry, scanning electron microscopy. The order of dye loading between these mesoporous sorbents was:  $\text{cMg}/\text{Al} > \text{cMg}/\text{Fe} > \text{Mg}/\text{Al} > \text{Mg}/\text{Fe}$ . The resulting by calcination material is an atomic mixture of metal oxides. This hydrotalcite is able to reform the original layered structure when it is exposed to water and anions. This property, termed “memory effect”, makes it possible to intercalate in the interlayer space  $\text{OH}^-$  anions as well as specific anions, leading to applications as anion scavengers in water detoxification [25].

To describe the sorption behavior with time several kinetic models were tested. Among them the second-order equation gave the best fit results [26]. The surfactant (by SDS) enhanced regeneration technique was used to remove the adsorbed dye from the calcined LDH material [27]. The recycling use of the adsorbent is likely to be a key factor in improving wastewater process economics. The Langmuir adsorption model was used to describe these adsorption data. Some results of relative adsorption capacities of selected sorbents for the dye, arsenates and also chromates are given in Table 1 [10, 17-18, 24, 28-37], in order to get an idea. Nevertheless, any comparison requires much attention, due to the often different experimental conditions.

**Table 1. Comparison from the literature of adsorption capacities of various selected sorbents for the three studied pollutants**

| Material                            | Capacity (mg/g) | Reference |
|-------------------------------------|-----------------|-----------|
| <b>Dye (Remazol Red 3Bs)</b>        |                 |           |
| Modified mesoporous carbon          | 296             | [17]      |
| Ordered mesoporous silica           | 571             | [18]      |
| Calcined $\text{Mg}/\text{Al}$ LDHs | 134             | [24]      |
| Carbon nanotube                     | 69              | [28]      |
| Silylated palygorskite              | 34              | [29]      |
| <b>Arsenates</b>                    |                 |           |
| $\text{Mg}/\text{Al}$ LDHs          | 33              | [30]      |
| Calcined $\text{Mg}/\text{Al}$ LDHs | 615             | [30]      |
| Modified activated carbon           | 33              | [31]      |
| Zero valent Fe on activated carbon  | 12              | [32]      |
| Fe-containing mesoporous carbon     | 7               | [33]      |
| <b>Chromates</b>                    |                 |           |
| Calcined $\text{Mg}/\text{Al}$ LDHs | 120             | [14]      |
| $\text{Mg}/\text{Al}$ LDHs          | 17              | [10]      |
| Sargassum biomass                   | 60              | [35]      |
| <i>Rhizopus nigricans</i>           | 212             | [36]      |
| Chitin                              | 104             | [37]      |

The adsorption capacity of the sorbent materials was increased with increasing temperature and the required time for the system material-sorbate to reach equilibrium was

decreased [24]. These observations indicate that the nature of the interaction between the sorbate and the sorbent was endothermic. The relative thermodynamic parameters were found in this case; the negative values for the Gibbs free energy ( $\Delta G^0$ ) show that the sorption of dye onto LDH sorbent materials was spontaneous under the experimental conditions, without requiring an induction period. The positive values of standard enthalpy change ( $\Delta H^0$ ) of sorption reflect its endothermic nature. Since this adsorption process is endothermic, the amount sorbed at equilibrium is increased with increasing temperature. The positive values of standard entropy change ( $\Delta S^0$ ) confirm a high preference of Remazol Red molecules for the surface of LDH materials and suggest the possibility of some structural changes or readjustments in the dye-LDH adsorption complex [38]. During adsorption the coordinated water molecules that are displaced by the dye molecules gain more translational entropy than is lost by the dye molecules, resulting in increased randomness in the dye-LDHs interaction [39].

## ARSENATES REMOVAL

Relatively high arsenic levels have been reported to be found in raw water supplies, hence requiring urgent treatment and separation; arsenicosis is called the poisoning of people from arsenic existing in “potable” water, usually from wells [40]. Today, several techniques are available for removing arsenic from aqueous solution, including precipitation, coagulation, ion exchange, adsorption, flotation, reverse osmosis and electrodialysis [41-46]. The influences of common oxyanions (i.e. nitrate, silica, sulfate, carbonate, and phosphate) and natural organic matter on the sorption of toxic oxyanions by nanocrystalline LDH were investigated [2]. It was also demonstrated that surface sites at the edges of hydrotalcite particles are prone to form inner-sphere edge complexes with dissolved anionic ligands [47]. Complexation at edges is a particular case of the widely accepted surface complexation approach, its underlying concepts accounting well for the different affinities of chromate and arsenate; see, for instance, Table 1. Manifestation of chemisorption on edge sites depends not only on affinity, but also on particle size, according to Jobbágy et al. [47].

In the pH range from around 7 to 11.5, it is known that the predominant arsenic species are that of  $\text{AsO}_4^{3-}$ , while in the lower region (pH 3-7) the form of  $\text{HAsO}_4^{2-}$  dominates. Figure 2 presents a part of this work; the  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$  compound, was used. The calcined sample showed better removals; the significant difference in the sorptive behavior among the calcined and the uncalcined material is due to the varying mechanism of the anions removal; the sorption mechanism of the calcined material is mainly due to the intercalation into the positively charged interlayer, while for the uncalcined material is due to the ion exchange of the interlayer anions [48]. Rehydration of the calcined material results in reconstruction of the hydrotalcite structure [49] which incorporates as the interlayer anion the available anions from the rehydrating solution. In the presence of mono- and divalent anions calcined hydrotalcite was also said to behave not only as an anion exchanger but as well as an oxide adsorbent.

The statistic values of  $R^2$  found confirm that the Redlich-Peterson model [50] resulted in the closer prediction of the isotherm as compared to the experimental data. Relatively rapid kinetics of sorption was experienced [30]. Application of this study was proposed to be to

various types of water, in which the presence of toxic metals causes problems as in the (i) production of drinking water from ground water (contaminated with As) and (ii) treatment of mine water and other industrial wastewater effluents.

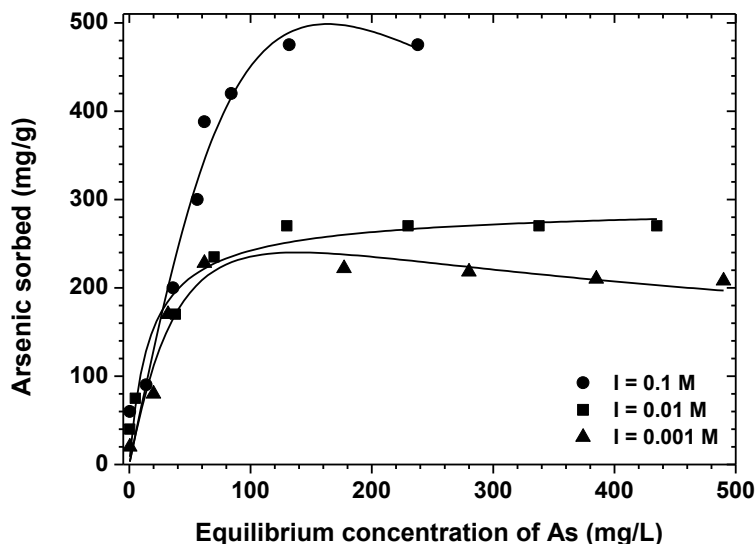


Figure 2. Arsenate sorption isotherms by calcined LDH, at varying ionic strength and natural pH. Reprinted with permission; copyright Elsevier [30].

The sorbent was prepared in the laboratory by coprecipitating mixed metal solutions of magnesium and aluminum nitrates [ $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ] by raising the solution pH with the addition of sodium hydroxide and sodium carbonate solutions under intense mixing for 4 h at 35°C, heating (at ~65 °C for 18 h) to crystallize, then filtering and washing with water to remove sodium below 0.1% level on a dry weight basis. The filter cake was dried, pulverized in a ball mill and sieved to various particle sizes, in case the effect of the latter was sought. Hence, the LDHs are simple to synthesize in the laboratory.

The aforementioned paper [30] concluded also that the combined process of sorptive flotation provided promising results for arsenic removal and a relative flowsheet of this process was presented; the calcined metal-loaded hydrotalcite revealed high hydrophilicity, as could be expected from its structure. Noting that previously, flotation was also examined for metal-loaded resins [51] – to be further commented in the following. The impact of chemical speciation on any similar process investigated including flotation is important [52]. The coexistence of adsorption and coagulation processes was elsewhere described [53].

## CHROMATES REMOVAL

The removal of chromate oxyanions was selected as a typical example of anionic pollutants for another investigation [54]. Results from a variety of separation techniques have been published in the literature for chromium removal from aqueous solution; ranging from applying as adsorbents solid wastes [55] or industrial by-products [56]. Hexavalent chromium

is the form of chromium commonly found at contaminated sites [57]. Cr(VI) is also the more toxic and the more mobile form. Major sources of Cr contamination include releases from electroplating processes and the disposal of chromium containing wastes. Chromium can be transported by surface run-off to surface waters in solution or in precipitated form. A thermodynamic equilibrium diagram was calculated and presented for the different chemical species of the studied metal [58]. Under the experimental conditions used and at pH values greater than around 7 (the natural solution pH with hydrotalcite), the main species existing in solution was  $\text{CrO}_4^{2-}$ . Figures 3 and 4 show some of our results in this area. In the latter, the Freundlich isotherm was used, in this case, to best fit the equilibrium experiments. A different behavior of arsenates and chromates towards the ionic strength was observed during their removal onto LDH. Four kinetic models have been also evaluated, including two ion-exchange models [10].

The main issue when searching for an appropriate sorption mechanism is to select a mathematical model that not only fits the data with satisfactory accuracy but also complies with a reasonable sorption mechanism. Generally, several steps are involved during the sorption process by porous sorbent particles: (i) bulk diffusion; (ii) external mass transfer (boundary layer or film diffusion), between the external surface of the sorbent particles and the surrounding fluid phase; (iii) intraparticle transport within the particle; and (iv) reaction kinetics at phase boundaries. In the case of chemisorption, the rate of sorption is generally controlled by the kinetics of bond formation [26].

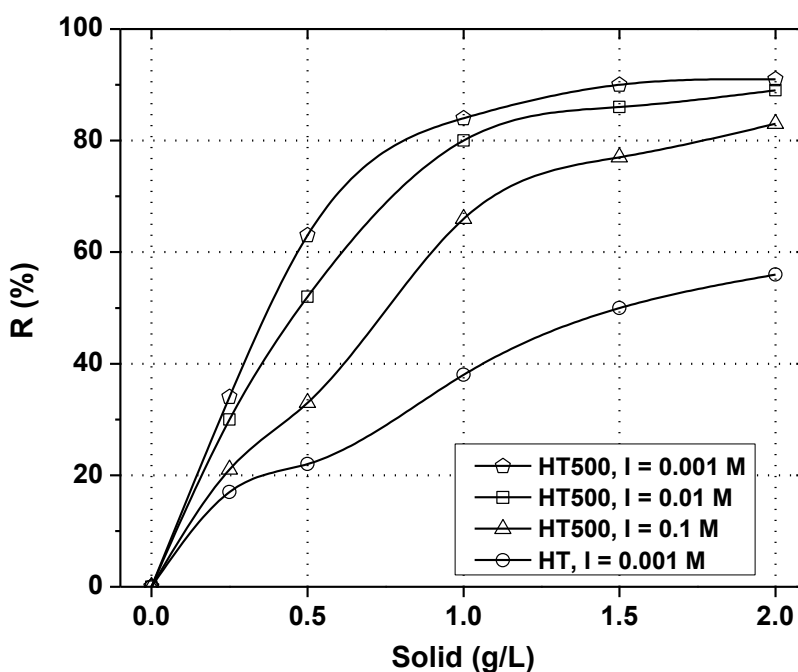


Figure 3. Influence of LDH type and added concentrations on chromate removals. Reprinted with permission; copyright Elsevier [54].

Desorption experiments also showed that the loaded material could be fully regenerated by a dilute eluant (0.001 mol/L  $\text{Na}_2\text{CO}_3$ ) in a short time (~20 min). LDH performance during

10 complete cycles (sorption-desorption) was consistently stable, presenting the same sorption capacity.

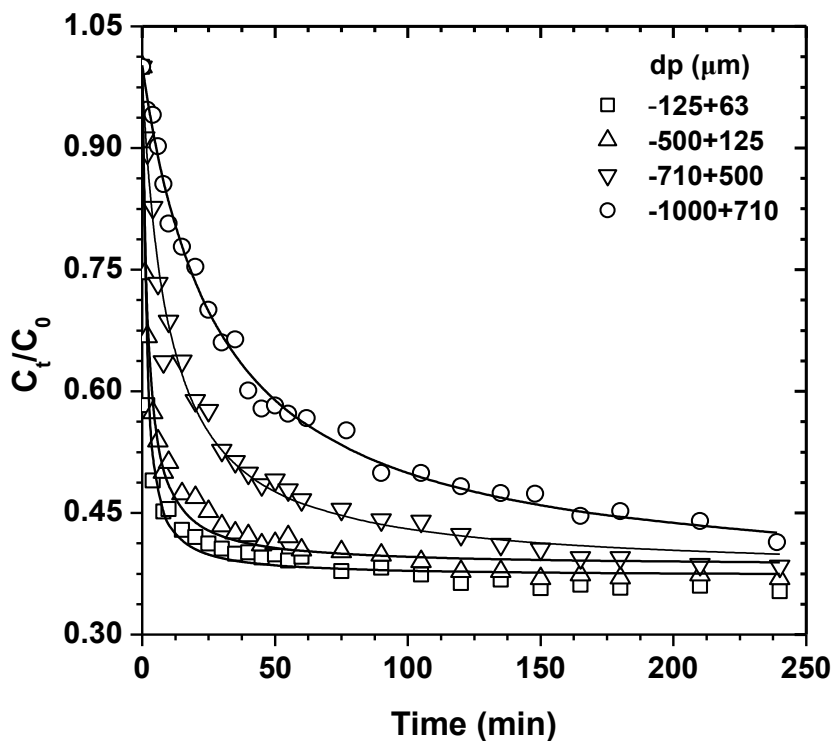


Figure 4. Adsorption kinetics; time variation of dimensionless Cr(VI) bulk concentration: with different uncalcined sorbent particle sizes. Reprinted with permission; copyright ACS Publisher [10].

## FLOTATION SEPARATION

As it was shown in Figure 4, the adsorbent particle size had significant effect on the kinetics of adsorption, due to the change of easily available adsorption sites. LDH sorbents usually exist in powder form, i.e. presenting appreciable problems in the subsequent solid/liquid separation. Almost complete removals were obtained in this paper, from batchwise dispersed-air flotation [54]. A few continuous-flow laboratory runs certified also the effectiveness of this process; with the application of a suitable surfactant (as collector, i.e. lauryl-pyridinium chloride), plus a commercial flocculant (a very high molecular weight anionic polyacrylamide) for the calcined LDH. The reactions of organic anions and anionic surfactants with hydroxy double salts were studied [59]. The uncalcined sample was much easier to float, due to the less surface area (from 72 increased by calcinations to 256 m<sup>2</sup>/g) and significantly smaller pore volume (from 0.27 to 0.86 cm<sup>3</sup>/g [24]). There is no other application of flotation to LDHs, to our knowledge, with which to have some meaningful comparison, perhaps because the process has been mainly known from minerals beneficiation



[60]. May be flotation, a gravity separation process, constitutes a promising innovative treatment technology for this scope.

Sorptive flotation has been earlier extensively reviewed [61]. This method involves the preliminary abstraction or scavenging of metal ions using proper "sorbents", which exist at the fine or ultrafine particle-size range, followed by a subsequent flotation stage for the separation of metal-loaded sorbent particles from the treated (cleaned) solution. The main flotation techniques for the generation of the necessary bubbles (dissolved-air, dispersed, and electrolytic) were applied effectively. Dissolved-air flotation, which is the established technique in water treatment, is quite different from the dispersed-air flotation, as showed [62]. The examined sorbents for the initial stage of the process could be of either inorganic nature, conventional (powdered activated carbon and zeolites) or industrial solid byproducts originated in the mineral industry, or of a biological nature (biosorbents), such as those produced during fermentations, etc. As a result of the process application, purified water is produced (underflow) as well as a foam concentrate; the recovery and recycling of removed species is also possible from the latter, leading to an overall clean technology.

## CONCLUSION

Synthetic LDHs were in-depth studied in the present work, applied to adsorb effectively the chromates, arsenates and reactive azo-dyes from aqueous solutions. Their possible solid/liquid separation downstream by flotation was also commented.

## REFERENCES

- [1] Hudson, M. J., Extraction of priority pollutants using inorganic ion exchangers. In *Mineral Processing and the Environment*, Gallios, G. P.; Matis, K. A., Eds. Kluwert: Dordrecht, 1998; pp 225-238.
- [2] Goh, K. H.; Lim, T. T., *J. Hazard. Mater.* 2010, *180* (1-3), 401-408.
- [3] Triantafyllidis, K. S.; Peleka, E. N.; Komvokis, V. G.; Mavros, P. P., *J. Colloid Interface Sci.* 2010, *342* (2), 427-436.
- [4] Cavani, F.; Trifirò, F.; Vaccari, A., *Catal. Today* 1991, *11* (2), 173-301.
- [5] Reichle, W. T.; Kang, S. Y.; Everhardt, D. S., *J. Catal.* 1986, *101* (2), 352-359.
- [6] Ulibarri, M. A.; Pavlovic, I.; Barriga, C.; Hermosín, M. C.; Cornejo, J., *Appl. Clay Sci.* 2001, *18* (1-2), 17-27.
- [7] Kyzas, G.; Fu, J.; Matis, K., *Materials* 2013, *6* (11), 5131-5158.
- [8] Peleka, E. N.; Matis, K. A., *Ind. Eng. Chem. Res.* 2011, *50* (2), 421-430.
- [9] Webb, M., Synthetic clay anion exchangers: their structure, modification and application in removing colour and toxins from textile process waters. In *Ion Exchange Developments and Applications*, Greig, J. A., Ed. Royal Society of Chemistry: London, 1996; pp 135-142.
- [10] Lazaridis, N. K.; Pandi, T. A.; Matis, K. A., *Ind. Eng. Chem. Res.* 2004, *43* (9), 2209-2215.
- [11] Arda, C.; Frau, F.; Lattanzi, P., *Appl. Clay Sci.* 2013, *80-81*, 1-9.

- [12] Morimoto, K.; Anraku, S.; Hoshino, J.; Yoneda, T.; Sato, T., *J. Colloid Interface Sci.* 2012, 384 (1), 99-104.
- [13] Cochechi, L.; Barvinschi, P.; Pode, R.; Seftel, E. M.; Popovici, E., *Adsorpt. Sci. Technol.* 2010, 28 (3), 267-279.
- [14] Lazaridis, N. K.; Karapantsios, T. D.; Georgantas, D., *Water Res.* 2003, 37 (12), 3023-3033.
- [15] Chubar, N.; Gerda, V.; Megantari, O.; Mičušík, M.; Omastova, M.; Heister, K.; Man, P.; Fraissard, J., *Chem. Eng. J.* 2013, 234, 284-299.
- [16] Goh, K. H.; Lim, T. T.; Banas, A.; Dong, Z., *J. Hazard. Mater.* 2010, 179 (1-3), 818-827.
- [17] Asouhidou, D. D.; Triantafyllidis, K. S.; Lazaridis, N. K.; Matis, K. A., *Colloid Surf. A.* 2009, 346 (1-3), 83-90.
- [18] Asouhidou, D. D.; Triantafyllidis, K. S.; Lazaridis, N. K.; Matis, K. A.; Kim, S. S.; Pinnavaia, T. J., *Micropor. Mesopor. Mater.* 2009, 117 (1-2), 257-267.
- [19] El Gaini, L.; Lakraimi, M.; Sebbar, E.; Meghea, A.; Bakasse, M., *J. Hazard. Mater.* 2009, 161 (2-3), 627-632.
- [20] Bouraada, M.; Lafjah, M.; Ouali, M. S.; de Menorval, L. C., *J. Hazard. Mater.* 2008, 153 (3), 911-918.
- [21] Saiah, F. B. D.; Su, B. L.; Bettahar, N., *Macromol. Symp.* 2008, 273 (1), 125-134.
- [22] Auxilio, A. R.; Andrews, P. C.; Junk, P. C.; Spiccia, L., *Dyes Pigm.* 2009, 81 (2), 103-112.
- [23] Drici Setti, N.; Jouini, N.; Derriche, Z., *J. Phys. Chem. Solids* 2010, 71 (4), 556-559.
- [24] Asouhidou, D. D.; Triantafyllidis, K. S.; Lazaridis, N. K.; Matis, K. A., *J. Chem. Technol. Biotechnol.* 2012, 87 (4), 575-582.
- [25] Vaccari, A., *Appl. Clay Sci.* 1999, 14 (4), 161-198.
- [26] Ho, Y. S.; Ng, J. C. Y.; McKay, G., *Sep. Purif. Methods* 2000, 29 (2), 189-232.
- [27] Purkait, M. K.; DasGupta, S.; De, S., *J. Environ. Manage.* 2005, 76 (2), 135-142.
- [28] Wang, J.; Peng, X.; Luan, Z.; Zhao, C., *J. Hazard. Mater.* 2010, 178 (1-3), 1125-1127.
- [29] Xue, A.; Zhou, S.; Zhao, Y.; Lu, X.; Han, P., *Appl. Clay Sci.* 2010, 48 (4), 638-640.
- [30] Lazaridis, N. K.; Hourzemanoglou, A.; Matis, K. A., *Chemosphere* 2002, 47 (3), 319-324.
- [31] Deliyanni, E.; Bandosz, T. J.; Matis, K. A., *J. Chem. Technol. Biotechnol.* 2013, 88 (6), 1058-1066.
- [32] Zhu, H.; Jia, Y.; Wu, X.; Wang, H., *J. Hazard. Mater.* 2009, 172 (2-3), 1591-1596.
- [33] Gu, Z.; Deng, B.; Yang, J., *Micropor. Mesopor. Mater.* 2007, 102 (1-3), 265-273.
- [34] Lazaridis, N. K.; Asouhidou, D. D., *Water Res.* 2003, 37 (12), 2875-2882.
- [35] Kratochvil, D.; Pimentel, P.; Volesky, B., *Environ. Sci. Technol.* 1998, 32 (18), 2693-2698.
- [36] Bai, R. S.; Abraham, T. E., *Water Res.* 2002, 36 (5), 1224-1236.
- [37] Sa, Y.; Aktay, Y., *Process Biochem.* 2000, 36 (1-2), 157-173.
- [38] Bhattacharya, K. G.; Sharma, A., *Dyes Pigm.* 2005, 65 (1), 51-59.
- [39] Unnithan, M. R.; Anirudhan, T. S., *Ind. Eng. Chem. Res.* 2001, 40 (12), 2693-2701.
- [40] Zouboulis, A. I.; Kydros, K. A.; Matis, K. A., *Sep. Sci. Technol.* 1993, 28 (15-16), 2449-2463.
- [41] Rajakovic, L. V., *Sep. Sci. Technol.* 1992, 27 (11), 1423-1433.
- [42] Edwards, M., *J. Am. Water Wor. Assoc.* 1994, 86 (9), 64-78.

- 
- [43] Zhao, Y. C.; Zouboulis, A. I.; Matis, K. A., *Hydrometallurgy* 1996, 43 (1-3), 155-167.
- [44] Zhao, Y. C.; Zouboulis, A. I.; Matis, K. A., *Hydrometallurgy* 1996, 43 (1-3), 143-154.
- [45] Matis, K. A.; Zouboulis, A. I.; Malamas, F. B.; Ramos Afonso, M. D.; Hudson, M. J., *Environ. Pollut.* 1997, 97 (3), 239-245.
- [46] Dambies, L.; Guibal, E.; Roze, A., *Colloid Surf. A* 2000, 170 (1), 19-31.
- [47] Jobbágy, M.; Regazzoni, A. E., *J. Colloid Interface Sci.* 2013, 393 (1), 314-318.
- [48] Sato, T.; Wakabayashi, T.; Shimada, M., *Ind. Eng. Chem. Prod. Res. Dev.* 1986, 25 (1), 89-92.
- [49] Miyata, S., *Clays Clay Minerals* 1980, 28, 50-56.
- [50] Al-Asheh, S.; Banat, F.; Al-Omari, R.; Duvnjak, Z., *Chemosphere* 2000, 41 (5), 659-665.
- [51] Zouboulis, A. I.; Peleka, E. N.; Zamboulis, D.; Matis, K. A., *Sep. Sci. Technol.* 2005, 40 (4), 861-876.
- [52] Matis, K. A.; Zouboulis, A. I., *Sep. Sci. Technol.* 2001, 36 (16), 3777-3800.
- [53] Wu, X.; Tan, X.; Yang, S.; Wen, T.; Guo, H.; Wang, X.; Xu, A., *Water Res.* 2013, 47 (12), 4159-4168.
- [54] Lazaridis, N. K.; Matis, K. A.; Webb, M., *Chemosphere* 2001, 42 (4), 373-378.
- [55] Raji, C.; Anirudhan, T. S., *Water Res.* 1998, 32 (12), 3772-3780.
- [56] Zouboulis, A. I.; Kydros, K. A.; Matis, K. A., *Water Res.* 1995, 29 (7), 1755-1760.
- [57] Evanko, C. R.; Dzombak, D. A., *Remediation of metals - Contaminated soils and groundwater*. TE-97-01, GWRTAC: Pittsburgh, 1997.
- [58] Lehmann, M.; Zouboulis, A. I.; Matis, K. A., *Chemosphere* 1999, 39 (6), 881-892.
- [59] Meyn, M.; Beneke, K.; Lagaly, G., *Inorg. Chem.* 1993, 32 (7), 1209-1215.
- [60] Matis, K. A., *Flotation Science and Engineering*. Dekker: New York, USA, 1995.
- [61] Zouboulis, A. I.; Matis, K. A., *Crit. Rev. Environ. Sci. Technol.* 1997, 27 (3), 195-235.
- [62] Matis, K. A.; Lazaridis, N. K., *J. Min. Metall. A* 2002, 38, 1-27.