IOSUD - Polytechnic University of Timisoara
Doctoral School of Engineering Studies

SYNTHESIS OF LAYERED DOUBLE HYDROXIDES FROM INDUSTRIAL WASTE WITH APPLICATIONS IN ADVANCED WATER TREATMENT PROCESSES

PhD thesis - Summary

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Contents of the PhD thesis summary

PhD thesis Content

THE EXPERIMENTAL PART

The subject of the PhD thesis is based on the urgent need for technologies development that aim to recover valuable elements from industrial waste and their capitalization under compounds with applicative potential.

Starting from this need, the objective around which the researches that are the object of the doctoral thesis were developed aimed advanced researches in the direction of iron ions recovering from sludges / wastewaters generated in the hot dip galvanizing process and their capitalization in the synthesis of layered double hydroxides, with applicability in the advanced treatment processes of some residual industrial effluents.

1. Layered double hydroxides

Definition and structure

Layered double hydroxides (LDHs), also known as hydrotalcites (HT) and anionic clays, belong to a broad group of natural or synthesized materials from suitable mixtures of metal salts which are brought into contact with an alkaline medium. The general formula of layered double hydroxides is [1-3]:

$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}\ (A^{n-}{}_{x/n}) \cdot mH_2O$$

in which:

M (II) and M (III) are the divalent and trivalent cations in the structure of the burn layer;

A^{n-}- the anions incorporated in the interlayer region together with the water molecules, which ensure the neutrality and stability of the structure;

x - molar ratio $M^{III}/(M^{III}+M^{II})$ which can vary in wide ranges: 0.17-0.33 [4]; 0.2 - 0.4 [5]; 0.2 - 0.33 [6]

Layered double hydroxides are based on the brucite structure-$Mg(OH)_2$(Figure 1) [7]. The octahedral circumference of each Mg^{2+} cation with 6 OH^- ions is observed, respectively the generation of two-dimensional layers starting from the edges of the octahedra.

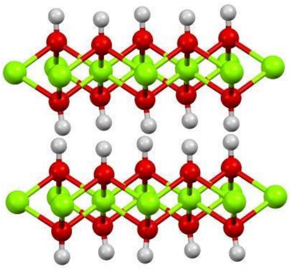

Figure 1. Crystalline structure of brucite [7]

The positive charge of the component layers of layered double hydroxides is the consequence of the partial substitution of divalent cations with trivalent cations, which have ionic rays close to those of Mg^{2+}, as is the case of Al^{3+} in hydrotalcite, respectively Fe^{3+} in pyroaurite. Between the positively charged layersare interspersed load-compensating anions (e.g. CO_3^{2-}) and hydration water molecules, which also have the role of creating hydrogen bonds between the brucite type layers.

The nature of cations

The specialty literature reports the synthesis of a very wide range of LDHs, starting from divalent and trivalent cations with ionic rays close to those of Mg^{2+}, respectively Al^{3+} and which can form similar configurations to the brucite layer. Among the divalent cations used in the syntheses can be mentioned those of Zn, Mg, Mn, Fe, Co, Ni, Cu and Ca. As trivalent cations are mentioned those of Al, Mn, Cr, Fe, Ni and La. Hydrotalcite-type structures have also been assigned to the Li - Al and Co - Ti pairs.

The nature of intercalated anions

The interlayer spaces of LDHs contain anions, water molecules, and sometimes other neutral or electrically charged organic / inorganic species. The anions can be grouped as follows:

- Halides: Cl^-, F^-, B^-, I^-;
- Oxyanions: CO_3^{2-}, NO_3^-, SO_4^{2-}, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{1-}$, $P_2O_7^{2-}$ AsO_3^-, borate and tetraborate, ClO_4^-, TcO_4^-, ReO_4^-, MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, MoO_4^{2-}, HVO_4^{2-}, VO_4^{3-}etc.
- Complex anions: CoO_4^{2-}, $NiCl_4^{2-}$, $IrCl_6^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Mo(CN)_8^{4-}$and $Mo(CN)_8^{3-}$, $Ru(CN)_6^{4-}$and $Ru(CN)_6^{3-}$, $Co(CN)_6^{3-}$;
- Organic anions: carboxylates, dicarboxylates, benzenecarboxylates, alkylsulphates, alkanesulphonates, t-butanoate anion, glycolate, etc .;
- Anionic biomolecules: amino acids, enzymes, proteins, etc .;
- Polymeric anions: poly (vinyl sulphonate), poly (styrenesulphonate) and poly (acrylate), polyaniline, ionized poly (vinyl alcohol), poly (ethylene glycol).

The distance between the layers is determined by the size, number, orientation, and strength of the bonds between the anions and the hydroxyl groups of the brucite type layers. Although the anions are extremely different in size, electrical charges, and structure, they can be easily interleaved in the interlayer space, as highlighted by the interplanar distance in the case of rhombohedral packing or gallery height [8].

Synthesis methods

Layered double hydroxides can be synthesized by a variety of methods, of which choice generally depends by the nature of the metal cations that will form the brucite layer, by the intercalated anions and by the desired physicochemical properties for the synthesized material, such as: purity, crystallinity, porosity, morphological, electronic, and optical characteristics.

Synthesis methods can be grouped into two main classes: direct methods and indirect methods.

<u>*Direct synthesis methods*</u>

Co-precipitation in aqueous solutions

Direct co-precipitation in aqueous solutions is the most widely used method for the synthesis of layered double hydroxides for all possible applications of these multifunctional materials. In principle, the method is based on the hydrolysis of two metal cations (eg Mg^{2+} and Al^{3+}) under the action of a strong base, in the presence of a precursor containing the interlayer anion (eg CO_3^{2-}) [9].

Obtaining of a layered double hydroxide requires the choice of a correct ratio between cations and anions, which must be found in the final product:

$0.2 \leq M(III) / [M(II) + M(III)] \leq 0.4$

$1/n \leq A^{n-} / M(III) \leq 1$

The precipitation of two or more cations must be carried out under supersaturation conditions, which can be achieved either by physical methods (evaporation) or by chemical methods (pH variation).

The method of pH variation is commonly used for the synthesis of layered double hydroxides. The precipitation must take place at a pH greater than or equal to that at which the most soluble hydroxide precipitates.

Three precipitation methods are used in the synthesis of LDHs:

- Titration with NaOH and / or $NaHCO_3$ (method in which occurs the increase in pH, also called sequential precipitation)
- Precipitation at constant pH, at low supersaturation; The pH is controlled by addition

slowly in a single vessel two dilute solutions, the first solution contains metal cations and the second solution contains the base (KOH, NaOH, $NaHCO_3$);

- Precipitation at constant pH, at high supersaturation; solutions containing cations are added very quickly in a solution containing $NaHCO_3$ or NaOH [2].

Co-precipitation in non-aqueous solutions

Even if the most precipitation reactions occur in aqueous solutions, although have been reported studies in which the LDHs synthesis take place in organic solvent / water mixtures. Using organic solvents such as methanol, ethanol, propanol, ethylene glycol, glycerol and acetone, MgAl-LDH with crystalline structure were obtained.

Urea hydrolysis

Compared to the use of NaOH, urea, a very weak Brönsted base, hydrolyses slowly, which is why the degree of supersaturation during precipitation is low. Urea is highly soluble in water and hydrolyses to form cyanate in ionic form (NH_4^+, NCO^-):

$H_2N\text{-}CO\text{-}NH_2 \rightarrow NH_4^+ + NCO^-$ I.1.

By prolonged hydrolysis of urea, CO_2 is generated in acidic environment and CO_3^{2-} anion in basic medium, according to the reactions:

$NCO^- + 2\,H_2O \rightarrow NH_4^+ + CO_3^{2-}$ I.2.

$NCO^- + 2H^+ + 2H_2O \rightarrow NH_4^+ + H_2CO_3$ I.3.

During the hydrothermal treatment of a solution containing urea and nitrates of Mg and Al, a series of reactions may take place, the result of which is the formation of hydrotalcite-type compounds [2]:

$Mg(H_2O)_n^{2+} + H_2O \rightarrow Mg(OH)(H_2O)^+_{n-1} + H_3O^+$ I.4.

$Al(H_2O)^{3+}_n + H_2O \rightarrow Al(OH)(H_2O)^{2+}_{n-1} + H_3O^+$ I.5.

$Mg(OH)(H_2O)^+_{n-1} + Al(OH)(H_2O)^{2+}_{n-1} + HO^- + CO_3^{2-} \rightarrow MgAl(OH)_3CO_3H_2O$ I.6.

Thus, anionic clays with general formula $[M(II)_{1-x}\text{-}M(III)_x(OH)_2{}^{x+}][CO_3^{2-}{}_{x/2}]^{x-}\cdot mH_2O$, wherein M (III) = Al and M (II) = Mg, Ni, Zn were synthesized by precipitation of hydroxycarbonates from homogeneous solutions, after hydrolysis of urea, thermally induced. The composition and degree of crystallinity of the resulting products depends on the precipitation temperature, the total concentration of metal cations, the molar fraction M (III) / (M (II) + M (III).

Method which combines co-precipitation with other treatments: hydrothermal treatment, ultrasound-assisted co-precipitation

The synthesis by co-precipitation with a strong base of a double layered hydroxide containing two metal cations with very different hydrolysis pH (eg Mg, Al) can give a mixture which in addition to the pure phase which is the double layered hydroxide contains and other phases. The diminution of these effects can be achieved by applying post-synthesis treatments of the final product: thermal or hydrothermal treatment, ultrasound-assisted co-precipitation [10,11].

Synthesis method that also uses solid precursors

The method is based on a solid-liquid reaction that takes place in the suspension formed by the oxide of a bivalent metal and the aqueous solution of an excess trivalent metal chloride. The method was applied in order to synthesize Zn-Cr LDHs and consisted of making a suspension of ZnO and 1M aqueous $CrCl_3$ solution. The latter was added at regular intervals, under intense stirring, for several days at room temperature. During the slow reaction, the decrease in pH with each addition of $CrCl_3$ solution was corrected to the initial value, given the buffering capacity of ZnO. The reaction was stopped when the $CrCl_3$ solution did not react, being already in excess. The method was also used for the synthesis of layered double hydroxides Zn-Al-Cl and Cu-Cr-Cl, but did not give results for other tested compositions [5].

Sol-gel synthesis

Sol-gel chemistry is based on a slow transition of a matter that is dissolved in a heterogeneous system. In the first phase, this is a colloidal state called the soil, which later passes into a solid phase, called the gel. Gel is a material assimilated to a wet solid, in which a solid nanostructured network is dispersed in a liquid medium.

Sol-gel synthesis is based on hydrolysis and polymerization of some metal alkoxide solutions. Thelayered double hydroxides synthesized in this way present a good homogeneity, a relatively good control of stoichiometry, have a high specific surface area and porosity, as well as high purity.The most common metal alkoxides used in these syntheses are alkoxylans - tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS).

Electrochemical deposition

In 1994, Kamath et al. Made the first electrodeposition of LDH films: Ni-Al, Ni-Mn, Ni-Cr and Ni-Fe [12] on the working electrode, in a conventional three-electrode assembly placed in a working electrode bath containing a mixture of metal nitrates. This is a one-step technique that has recently been extended to other metal couples [15-18]. The method exploits the electrically induced reduction by nitrate ions to produce hydroxide ions on the surface of the working electrode, with a consequent increase in the local pH value which, in turn, results in the precipitation of LDH films.

Indirect synthesis methods

Anionic exchange

The method is based on the fact that the lamellar structure of layered double hydroxides is liable to diffusion and anionic exchange processes. These properties have been exploited for the synthesis of new LDHs, using anionic exchange reactions such as:

$$[M^{2+}/M^{3+}\text{-}A]+B \rightarrow [M^{2+}/M^{3+}\text{-}B]+A \qquad \text{I.9.}$$

The equilibrium constant of the reaction depends on the electrostatic interactions and the free energy, in the sense that the anions with higher charge density are favoured. The method is suitable for the synthesis of hydrotalcite-type compounds containing anions other than the carbonate anion, given that in direct synthesis it is difficult to avoid CO_2 contamination from the aqueous solution [5].

Delamination

The layered double hydroxides can be delaminated, meaning they undergo a complete separation of all the brucite type layers, to produce a very stable colloidal solution of the mono-dispersed slides. If the colloidal dispersion is slowly dried, well-structured LDHs could be recovered, possibly intercalating various anionic species. Delamination could be performed by a number of methods, especially if organically modified LDHs are used [17,18]. For example, intercalated organic anions such as methoxide, acetate and lactate promote delamination in water [19]. Alternatively, nitrate-based LDHs [20] or intercalated amino acids [21] can be delaminated as an amide. By drying, well-structured LDHs as well as LDH-polymer nanocomposites were obtained that can intercalate a certain number of organic compounds [19].

Properties of layered double hydroxides

The main properties of layered double hydroxides derive from their chemical composition and morphological and structural characteristics.

As a consequence of the structure and morphology of layered double hydroxides, by calcination at certain temperature values mixed oxides are obtained which have thermal stability, basic properties and memory effect.

Both synthesized layered double hydroxides and especially calcined compounds have catalytic and anionic exchange properties (see Applications of layered double hydroxides).

Applications of layered double hydroxides

➢ *Advanced wastewater treatment processes:*

- ✓ Adsorption
- ✓ Ionic exchange
- ✓ Heterogeneous photocatalytic processes

➢ *Catalytic applications in organic chemistry:*

a. *Processes using untreated LDHs*

✓ Oxidation processes (hydroxylation; alkyl oxidation to carbonyl, alcohol group oxidation to carbonyl; Baeyer-Villiger oxidation of cyclic ketones to esters and corresponding lactones in the presence of molecular O_2; epoxidation);

✓ Base catalyzed reactions using the acid-base property of layered double hydroxides (oxidation of isopropanol; aldol addition reactions, etc.)

b. *Processes using pillar LDH:*double-layered hydroxides having free interstitial space, as a result of the intercalation of large, acid-rich polyvalent anions, which they induce to double-layered hydroxides. They are used in:

✓ Acid-catalyzed reactions (esterification in acid catalysis of acetic acid and n-butanol; adsorption of basic species such as ammonia and pyridine)

✓ Oxidation processes: conversion of thiols to disulfides; phenolic oxidation, epoxidation reactions.

✓ Alkylation reactions: e.g. alkylation of isobutane with butene.

✓ Photocatalytic processes.

c. *Layered double hydroxides - catalytic supports*

- ✓ Hydrogenation and hydrodesulfurization processes
- ✓ Polymerization of ethene
- ✓ Synthesis gas synthesis

Other areas of use include:corrosion inhibitors, electrodes, sensors, optical materials, clinical applications.

The literature review also focused on the application of LDHs in advanced wastewater treatment processes.

In this context, a number of research have been focused on enhancing and exploiting the anionic exchange properties of layered double hydroxides for the advanced treatment of effluents containing inorganic anions/organic pollutants with high toxicity or negative impact on aquatic ecosystems [22,23] .

2. Aspects related to hot dip galvanizing

Overview

Hot dip galvanizing is a process discovered in the 18th century by the French chemist PJ Malloiun, but almost a century later, in 1937, Sorel filed the first patent in France under the name of "galvanizing" for the coating process made by immersing steel. or cast iron in molten zinc [24-26].

The inappropriate name for "thermal galvanizing" has remained in current technology. Hot dip galvanizing is a relatively simple process that involves cleaning the steel / iron and immersing it in a molten zinc bath at a temperature of about 450 ºC to obtain a coating with a layer of zinc.

When the cleaned steel is immersed in molten zinc, a series of zinc-iron alloys are formed by metallurgical reactions, ensuring a robust layer that is an integral part of the steel, protecting the steel from harsh environments, whether they are external or internal. Since this reaction is a diffusion process, the coating is formed perpendicular to the entire surface creating a uniform thickness on all sides. The layer resulting from thermal galvanizing offers a remarkable resistance to abrasion. If there is minor damage or discontinuity in the zinc sealing layer, the protection of the steel is maintained by the cathodic action of the coated zinc layer.

Hot dip galvanizing process

The main stages that a hot dip galvanizing process includes are: surface preparation, galvanizing itself, post-treatment (optional) and technical control (figure 2).

The most important stage in the hot dip galvanizing process is the preparation of the surfaces. This step aims to obtain a clean surface by removing all oxides, paint marks, rust and other contaminant residues, so that the molten zinc forms a solid and complete metallurgical bond with the article to be galvanized. Thorough surface preparation is essential, because zinc will not react with steel if the surface is not clean.

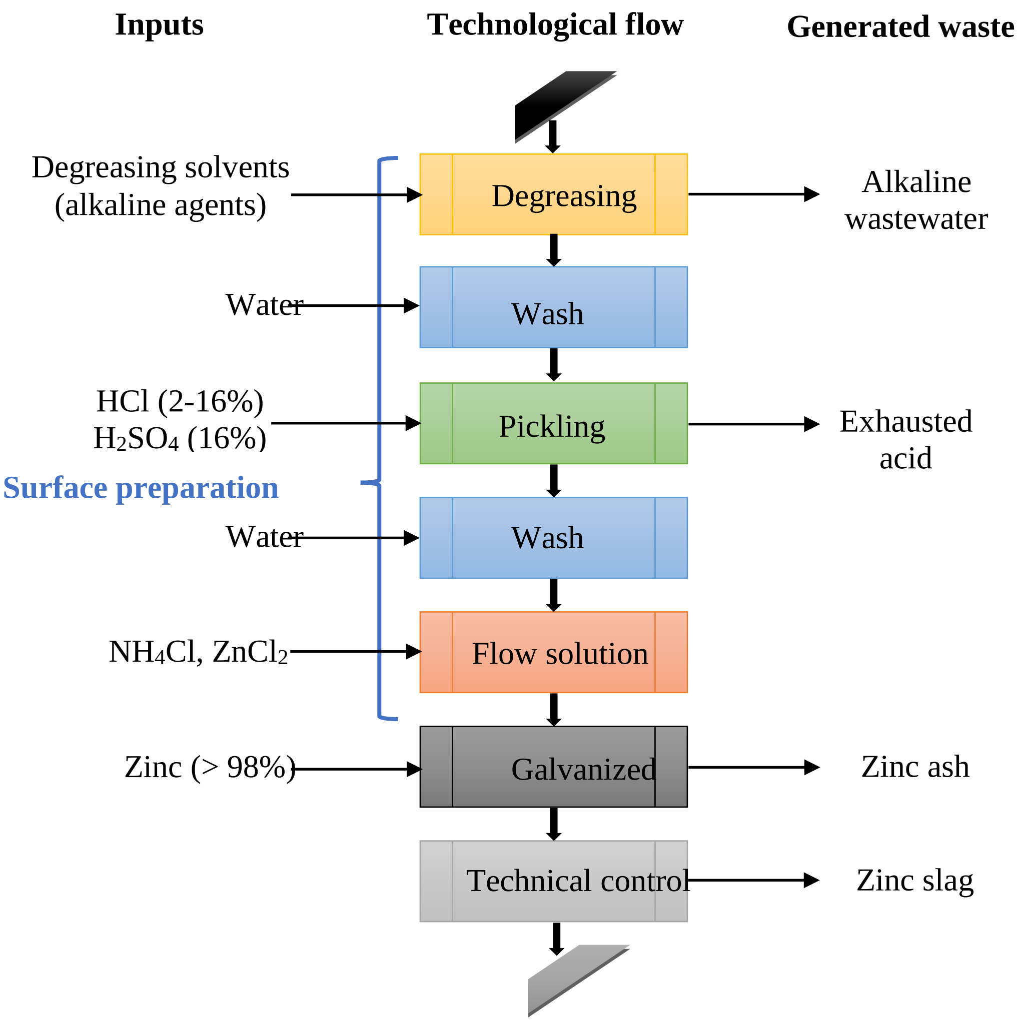

Figure 2. The stages of the hot dip galvanizing process and the waste generation points

3. Experimental results

The main objective of the PhD thesis aimed advanced research in the direction of iron ions recovery from sludge / wastewaters generated in the hot dip galvanizing process and their capitalization in the synthesis of layered double hydroxides Mg_xFe-LDH, with applicability in adsorption and heterogeneous photocatalysis.

3.1.Extraction of Fe^{3+} ions from the sludge generated in the neutralization stage of the wastewater resulting from the hot dip galvanizing process

Identification of the optimal conditions for the extraction of iron ions from the sludge resulting from the hot dip galvanizing process using inorganic acids as extraction agents [27]

Three inorganic acids were used in the extraction process of ferric ions from hot dip galvanizing sludge: HCl, HNO_3, H_2SO_4 and was studied the influence of the main process parameters (nature and concentration of the extraction agent, the excess of the extraction agent and process duration) upon the extraction degree.

The sludge used in the extraction process was characterized from a chemical, structural, and morphological point of view. The chemical analysis showed a high content of

Fe^{3+} ions (34.4%) and Ca^{2+} ions (8.95%), respectively. Other metal ions identified in low concentrations were: Zn^{2+}, Pb^{2+}, Cu^{2+} şi Mn^{2+}.

The X-ray diffraction analysis of sludge highlighted two crystalline phases: iron oxyhydroxide-FeO (OH) and calcium carbonate - $CaCO_3$, though its structure is predominantly amorphous. The presence of calcium carbonate can be explained by the fact that the neutralizing agent used to treat the residual solutions generated in the galvanizing process was lime milk. The FTIR spectrum confirmed the presence of iron oxy-hydroxide as the major component of the sludge.

The result of the thermal analysis indicated endothermic processes, accompanied by corresponding mass losses moisture loss, dehydroxylation of iron oxyhydroxide and, respectively, decarbonation of calcium carbonate, aspects that confirmed the conclusions of the analysis by X-ray diffraction and FTIR spectroscopy.

Regarding the morphological analysis of the sludge, it highlighted agglomerates of different sizes of sludge particles. The EDX spectrum confirmed that it mainly contains iron and calcium ions, the values obtained being very close to those resulting from chemical analysis.

The study on the Fe^{3+} extraction process showed that, regardless of the nature of the acid used, the extraction efficiency increased with increasing the concentration of the acid solution from 10 to 20%. Also, the degree of extraction increased with the increase of the extraction time from 15 to 60 min, after which there were no significant increases. The highest degree of extraction was obtained when using the 20% H_2SO_4 solution, justifying its use as an extraction agent in the following experiments. The study of the influence of the excess of acid solution indicated that an excess of 20% in relation to the stoichiometric requirement ensures the obtaining of a degree of extraction of Fe^{3+} ions of over 99%. These results made it possible to identify the optimal conditions which ensure that a maximum degree of extraction is reached: 20% H_2SO_4 solution, an excess of 20% of the acid solution in ratio with the stoichiometric need and 60 minutes of process duration.

Characterization of the solution resulted from the application of optimal extraction conditions, in order to further capitalization of iron ions

The composition of the solutions resulted from the extraction presents particular importance from the perspective of the subsequent recovery of Fe^{3+} ions. In this context, it is necessary that the accompanying heavy metal ions to be found in the lowest possible concentrations. The chemical analysis indicated that the resulting solution under optimal extraction conditions had a content of 82 g / L Fe^{3+}, 2.54 g / L Zn^{2+}, the rest of the heavy metals being below 0.6 g / L. The high concentration of Fe^{3+} ions recommend the use of this solution as a precursor solution of Fe^{3+} ions in the process of layered double hydroxides obtaining.

3.2.Synthesis and characterization of layered double hydroxides Mg_xFe-LDH type

Synthesis of layered double hydroxides Mg_xFe-LDH type using as a precursor of Fe^{3+} the solution resulting in the extraction process from hot dip galvanizing sludge (MgxFe_n), respectively analytical purity reagent $Fe(NO_3)_3{\cdot}9H_2O$ (Mg_xFe_r)

Layered double hydroxides of Mg_xFe type were synthesized and characterized, with predetermined molar ratios Mg: Fe of 2; 3 and 4, respectively. The synthesis was performed by a widely used method, co-precipitation at supersaturation. The precursor of Fe^{3+} was the pure chemical reagent $Fe(NO_3)_3{\cdot}9H_2O$, respectively the extraction solution from the hot dip galvanizing sludge, with a concentration of 82 g / L Fe^{3+}.

X-ray diffraction analysis

The RX diffraction spectra of those six synthesized layered double hydroxides revealed a single crystalline phase, corresponding to pyroaurite ($Mg_6Fe_2CO_3(OH)_{16}$·$4H_2O$).

Determination by calculation of the network parameters showed very close values of the compounds synthesized only from chemical reagents with the values obtained for the compounds in the synthesis of which the extraction solution was used as iron precursor. More significant differences were observed in the size of the crystallites, smaller in the case of layered double hydroxides of Mg_xFe_n type, an aspect that was explained by the stress induced in the growth of crystals by the impurities present in the Fe^{3+} precursor solution.

X-ray diffraction spectra of compounds Mg_xFe-LDH calcined at 450 ° C showed amorphous structures of mixed oxides of Mg and Fe; a slight increase in crystallinity with increasing molar ratio Mg: Fe was observed for compounds that were synthesized only from chemical reagents. The amorphous structure of the resulting mixed oxides can be exploited in their application in adsorption processes.

The X-ray diffraction spectra of the compounds obtained by calcination at 900 ° C of the synthesized double stabilized hydroxides revealed the formation of magnesium ferrites, for which the lattice parameters and the average size of the crystallites were also calculated.

Analysis by FT-IR spectrometry

The FT-IR spectra of all synthesized compounds were similar and highlighted the absorption bands characteristic of layered double hydroxides. In the FT-IR spectra of the compounds that had as extraction precursor the extraction solution was observed a low intensity absorption band at approx. 1100 cm^{-1}, which was attributed to the asymmetric vibrations of the S-O bonds belonging to the sulphate present in the extraction solution.

The FT-IR spectra of the compounds calcined at 450°C showed a decrease in the intensity of the absorption bands due to the presence of water and carbonate. This was explained by the elimination of the physisorption water and partly of the hydroxyl groups from the brucite type layers, respectively of the carbonate anion from the interstate space.

The FT-IR spectra of the compounds obtained by calcination at 900°Care characteristic of mixed crystalline oxides, as such they showed only the vibration absorption bands of the metal-oxygen bonds.

In the series of the three Mg: Fe ratios, a shift of the maximum absorption bands characteristic of water and carbonate anion vibrations towards higher wave numbers was observed with the increase of the Mg: Fe ratio. This was explained by the increase in the vibration intensity of the O – H bonds, respectively of those in the carbonate anion, an increase because in the interstitial space there are several bonds of this type, so more water molecules and carbonate anions respectively.

BET specific surface analysis

For all the synthesized compounds it was observed that, with the increase of the molar ratio Mg: Fe, the increase of the specific surface area takes place. The compounds obtained by calcination at 450ºC have an amorphous structure that justifies the practically double values of the specific surface area. Also, compounds synthesized based on iron precursor obtained from sludge have a specific surface area slightly larger than their counterparts obtained from chemical reagents. These results are also in accordance with the data provided by X-ray diffraction analysis, indicating once again that the presence of sludge impurities in the structure Mg_xFe_n, even in very low concentrations (undetected by chemical analysis, X-ray diffraction analysis and EDX) causes a slight change in structure and a slight decrease in crystallinity.

Morphological analysis

The SEM images obtained are specific for layered double hydroxides synthesized by the low supersaturation co-precipitation method. Although apparently, they are in the form of fluffy particles, the lamellar structure can still be observed.

The SEM images of the compounds resulting from the calcination at 450 °C of the layered double hydroxides show structures with a more pronounced amorphous character, respectively particles of irregular shapes of smaller dimensions. For products obtained by calcination at 900°C, SEM images show the presence of micrometric aggregates of uniform shape and size, specific to well-crystallized particles, similar to other ferrites synthesized by different methods and reported in the literature.

The theoretical values of the Mg: Fe ratios were compared with the values obtained by chemical analysis of the synthesized layered double hydroxides and with those resulting by EDX spectroscopy, being observed a good concordance of values.

3.3. *Application of layered double hydroxides Mg_xFe in the advanced treatment of residual effluents*

Application of Mg_xFe-LDHs and calcined products at 450 ºC in adsorption processes [28]

The adsorption capacity of layered double hydroxides synthesized from both analytical purity reagents (Mg_xFe_r) and for which the Fe^{3+} precursor was the extraction solution from the thermal galvanizing sludge (Mg_xFe_n) was tested in the process of retaining the molybdate anion from aqueous solutions. In this adsorption process, the calcined products at 450 ºC were also tested.

The influence of pH

The study of the influence of pH on the adsorption capacity of the molybdate anion indicated for all compounds the value of 6 as optimal pH. This study also highlighted the fact that calcined materials have developed a higher adsorption capacity compared to those synthesized, a feature that resulted from the amorphous structure of mixed oxides resulted through calcination. Also due to slightly diminished crystallinity which characterise the layered double hydroxides Mg_xFe_n, their adsorption capacity was higher compared to the adsorption capacity developed by Mg_xFe_r compounds.

Kinetic studies

The variation in time of the adsorption capacity indicated that for all the compounds involved in the process, the optimal time to reach equilibrium was 60 min.

Among the kinetic models applied in process modelling, it has been shown that the adsorption process accurately followed the pseudo-second order kinetic model for all the compounds involved in the study, obtaining correlation coefficients higher than 0.99.

Also, the rate constants calculated for this model had the same order of magnitude, without being able to observe a significant variation depending on the Mg: Fe ratio, the nature of the iron precursor and the fact that the adsorption was performed on the resulting compounds from the synthesize or the calcined ones.

An important aspect that contributes to the validation of the pseudo-second order kinetic model is that the values of the adsorption capacity obtained experimentally were very close to the values obtained from the modelling, for all the studied materials.

Equilibrium studies

The study of the adsorption process equilibrium indicated an increase of the adsorption capacity developed by the studied materials with the increase of the equilibrium concentration until reach a constant value, which corresponded to the saturation of the adsorbent surface with molybdate anions.

Among the studied equilibrium isotherm, the Langmuir model best described the equilibrium of the adsorption process, over the entire concentrations range and for all the studied materials. The calcined materials developed higher maximum adsorption capacities than their precursors, in accordance with the results obtained from the structural and morphological analysis of the compounds.

To propose a possible mechanism of the adsorption process, X-ray diffraction analysis of the adsorbent materials was performed before and after the molybdate anion retention process. This analysis showed that after adsorption, the diffractograms of the materials involved in the process did not change, all the diffraction spectra indicating the specific structures of the layered double hydroxides of pyroaurite type. Specific diffraction maxima of pyroaurite were present, with no evidence of the presence of the molybdate anion in the interlamellar space. This indicated that the molybdate anion did not displace (replace) the carbonate anion from the interlamellar space.

A mechanism has been proposed for the retention of molybdate ions from aqueous solutions consisting in its adsorption on the surface, by electrostatic interactions between positively charged brucite type layers and molybdate.

The results obtained corroborated with the data from the literature led to the conclusion that the values of the maximum adsorption capacity reached by layered double hydroxides starting from a secondary source of Fe^{3+} were comparable or even larger than other materials.

Photocatalytic degradation studies of Congo Red dye [27]

The idea of evaluating the photocatalytic activity of the Mg_xFe-LDH layered double hydroxides was the consequence of theFe^{3+} presence in the structure of the brucite layer, which can induce photocatalytic activity.

In this sense, in our studies the photocatalytic activity of the Mg_3Fe-LDH layered double hydroxides synthesized both from chemical reagents and from the secondary source of iron in the process of degradation of Congo Red dye from aqueous solutions was investigated.

The initial UV-VIS spectrum of Congo Red dye highlighted three absorption maxima, attributed to the different bonds and groups present in the dye structure, which absorb radiation in different domains: a maximum in the visible (498 nm), characteristic of the azo bond, respectively the chromophore groups, and two maximums in UV, at 235 nm and 340 nm. UV absorption is attributed to aromatic nuclei (benzene and naphthalene).

The spectrum analysis recorded after 30 min of adsorption in the dark showed a constant decrease in the intensity of all characteristic peaks, due to the adsorption of dye molecules on the surface of catalyst particles.

The UV-VIS spectra analysis recorded after different irradiation times indicated a rapid decrease in the maximum intensity of 498 nm, suggesting that the process of discoloration of the solution, due to the breaking of the azo bond, proceeded at a relatively high speed; a gradual decrease in absorbance was also observed at 235 nm and 340 nm, respectively, associated with the opening of the aromatic nuclei; In the spectrum recorded after 180 min of irradiation, all peaks were flattened and the intensity of the remaining absorbance was attributed to the organic intermediates formed in the photocatalytic degradation process.

After 180 minutes of irradiation, the values of the discolouring efficiency achieved for both compounds were close, slightly higher value for Mg_3Fe_r (80.2%), compared to the value achieved in the presence of Mg_3Fe_n (78.5%). One argument in support of this result is precisely the higher adsorption capacity of the compound Mg_3Fe_n, which adsorbed a larger amount of dye, preventing the penetration of UV radiation at the surface of the catalyst.

The discolouring and degradation process of Congo Red dye was kinetically described by the Langmuir-Hinshelwood model. The model allowed the evaluation of the apparent velocity constants for the processes of discoloration and decyclization of aromatic nuclei (naphthalene and benzene).The order of variation of the apparent velocity constants was: k_{app}, 498 nm> k_{app}, 340 nm> k_{app}, 235 nm.

The obtained results were the basis for the proposal of a photocatalytic degradation mechanism of the Congo red dye, in which the two photocatalysts were involved.

Also, a technological flow scheme was proposed for the recovery of iron ions from the sludge resulting from the lime neutralization of the wastewater discharged from the hot dip galvanizing industry and their recovery in the synthesis of layered double hydroxides of Mg_xFe type-LDHs.

The results obtained in the adsorption process of molybdate anions on the calcined forms at 450 ºC of Mg_xFe_n layered double hydroxides entitles us to state that they can be successfully applied in anadsorption process of some metal anions, as a step of advanced treatment of some residual effluents.

On the other hand, layered double hydroxides Mg_xFe_n resulted from the synthesis have photocatalytic activity and can be applied in photocatalytic degradation processes by UV irradiation of effluents with low dye content.

3.4.Synthesis of double layered hydroxide Mg_4Fe-LDH with the use as Fe^{3+} precursor of the acid solution resulting from the pickling step of the hot dip galvanizing process and its characterization

For the synthesis of Mg_4Fe-LDH layered double hydroxide was used as a precursor of Fe^{3+}, the residual solution with a high content of iron ions (65 g / L), generated in the pickling stage of the hot dip galvanizing process. The residual solution also contains other metal ions, but in a lower concentration, ions that did not influence the structure of the synthesized compound.

The synthesis of the layered double hydroxide Mg_4Fe-LDH was performed by the co-precipitation method at low supersaturation [29].

X-ray diffraction analysis

The X-ray diffraction spectrum of the compound Mg_4Fe showed a single crystalline phase, which corresponded to pyroaurite. In the diffractogram of the compound resulting from calcination, a phase with reduced crystallinity corresponding to MgO (periclas) was identified, with Fe^{3+} cations probably dispersed in the structure. The absence in the diffractogram of the calcined compound of crystalline phases of Fe^{3+} is the consequence of the high ratio Mg: Fe (4: 1) as well as the relatively low temperature of thermal activation. The calcined sample, which has a predominantly amorphous character, is expected to develop a higher adsorption capacity compared to the Mg_4Fe-LDH layered double hydroxide.

Morphological analysis

The SEM images of the two compounds indicate an aerated structure of fluffy-looking particles belonging to Mg_4Fe - LDH, respectively the amorphous structure of the calcined sample at 450 ºC.

From the EDX spectra can be observed the peaks of the Mg and Fe elements characteristic of the materials obtained by synthesis, respectively calcination. No characteristic peaks of other metal cations present in the precursor solution appear, which confirms that their presence does not affect the structure of the synthesized Mg_4Fe-LDH.

3.5. Application of Mg_4Fe-LDH layered double hydroxide and calcined compound in the adsorption process of the molybdate anion [29]

Equilibrium studies

The experimental isotherms have shown that, as the initial concentration of molybdate solutions increases, the occupancy rate of the active centers available for adsorption increases, and therefore the values of the adsorption capacity of the two compounds involved in the process increase. Mg_4Fe has developed a maximum experimental adsorption capacity in the process of removingMo^{6+} from aqueous solutions of 39.9 mg / g. Due to the memory effect, the calcined sample showed a significantly higher maximum experimental adsorption capacity (q_{mexp}. = 52.8 mg / g).

It was concluded that the adsorption of the molybdate anion from aqueous solutions follows the Langmuir isotherm, the adsorption taking place in a monomolecular layer on the energetically uniform surfaces of Mg_4Fe-LDH and Mg_4Fe_450 materials. This conclusion derives from the approximate unit values of the correlation coefficients obtained by applying the Langmuir isotherm and from the fact that there is no significant difference between the calculated maximum adsorption capacity and the experimentally determined one.

Kinetic study

The kinetic studies, performed at three temperature values, aimed the evaluation of the optimum time necessary to establish the equilibrium between the Mo^{6+} ions and the adsorbents studied. The adsorption of the molybdate anion took place quite quickly in the first minutes of contact between the adsorbent and the adsorbed, especially when the calcined sample was used in the process. After 60 minutes of stirring, the adsorption capacity increased slowly, so that it was considered that the equilibrium was achieved in 60 minutes for all 3 temperatures studied and for the both adsorbent materials. The increase in temperature caused a slight increase in the adsorption capacity of Mg_4Fe and Mg_4Fe_450.

Among the kinetic models studied, it was concluded that the adsorption of the molybdate anion on Mg_4Fe and Mg_4Fe_450, respectively, was best described by the pseudo-second kinetic model. In this case, for all three studied temperatures, almost unitary correlation coefficients were obtained, and the calculated adsorption capacities were similar to those determined experimentally.

The adsorption process of Mo^{6+} on the studied materials was endothermic, due to the positive values obtained for ΔH^o and spontaneously because the Gibbs free energy showed negative values that decreased with increasing temperature.

Manifestation of the memory effect

After adsorption of the molybdate anion, the two adsorbents were subjected to X-ray diffraction analysis. The synthesized material, Mg_4Fe, did not undergo any change in the crystal structure after adsorption, the parameters of the unit cell a = 3.11 Å and c = 24.0 Å being practically identical to those calculated before adsorption: a = 3.11 Å and c = 23 , 9 Å. This showed that the adsorption of the molybdate anion was performed on the surface of LDH and not by anion exchange, it is known that the carbonate anion is the most difficult to replace among the anions present in the interlamellar layers of layered double hydroxides.

On the other hand, the calcined material, Mg_4Fe_450, regained its structure of double layered hydroxide, all the characteristic peaks of pyroaurite being present in the diffractogram. Moreover, the higher value of the unit cell c parameter after adsorption (c = 24.7 Å) than that of the synthesized material Mg_4Fe (c = 23.9 Å) suggested that the adsorption of the molybdate anion on the calcined material is performed both on the surface of the double layered hydroxide, as well as in the interlamellar space, by replacing the carbonate anion.

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