

**Chemically Modified Materials with Ionic Liquids Applied in Wastewater Treatment**

**PhD thesis - Summary**

for obtaining the scientific title of PhD at

Polytechnic University of Timisoara

In the field of Chemical Engineering

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month 09 year 2023

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The main goal of the PhD thesis is to carry out advanced research on the development of materials with high adsorbent potential, with efficient applicability in the treatment of waters containing both organic and inorganic compounds, with minimum costs and no waste generation, within the concept of sustainable development.

## I. Layered double hydroxides

### I.1. Structure and properties

Layered double hydroxides (LDH<sub>S</sub>) are two-dimensional, solid inorganic substances distributed in distinct layers and are also known as anionic clays. They are found both in natural form but can also be synthesised. Synthetically formed LDH<sub>S</sub> are highly hydrophilic in nature, with an amorphous hexagonal or semi-crystalline structure. The LDH structure is based on Mg(OH)<sub>2</sub> brucite layers, composed of octahedral Mg(OH)<sub>6</sub> units with common edges in which the metal cations are placed in the centre of the octahedron; each cation is thus surrounded by six OH<sup>-</sup> ions that are directed towards the corners and form infinite layers [1, 2].

The general formula of LDH is:  $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}_{x/n} \cdot m(H_2O)]$ , where M<sup>2+</sup> is a divalent cation such as Mg<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Ca<sup>2+</sup>, etc.; M<sup>3+</sup> is a trivalent cation, e.g. Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, etc.; A<sup>n-</sup> is the anion between the n valence layers. Charge-balancing anions, A<sup>n-</sup> can vary in size and nature, can be inorganic or organic, and can readily settle in that interlamellar space because of its tendency to contract or expand, offering a wide range of possibilities. Anions intercalated between LDH layers can be:

- ✓ Inorganic anions: F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, NiCl<sub>4</sub><sup>2-</sup>, CoCl<sub>4</sub><sup>-</sup>, Fe(CN)<sub>6</sub><sup>3-</sup> etc;
- ✓ Organic anions: carboxylates, phosphonates, alkyl sulphates, benzoates, etc;
- ✓ Anionic complexes: ferric and ferricyanide, (PdCl<sub>4</sub>)<sup>2-</sup> etc;
- ✓ Biomolecules: DNA, amino acids, vitamins, peptides, nucleosides, etc.

### I.2. Obtaining methods

Many methods have been developed for the synthesis of LDH<sub>S</sub>. The type of method used depends on the characteristics and required applications of the resulting material. The most commonly used methods/techniques are co-precipitation, hydrothermal synthesis, urea hydrolysis, sol-gel method, ion exchange and rehydration/reconstruction. There are also other often used methods such as autooxidation method, template synthesis method and surface synthesis method. Numerous studies related to the synthesis of LDH-based materials have addressed simple and inexpensive synthesis methods both in the laboratory and on an industrial scale [3].

The co-precipitation method is one of the simplest and most used methods for obtaining LDH<sub>S</sub> on the one hand because LDH<sub>S</sub> can be obtained with a wide variety of divalent and trivalent cations and different anions, and on the other hand because it can be applied for large-scale fabrication of compounds [4]. The co-precipitation method is based on the three processes of nucleation (growth), growth and coagulation or the flocculation process (Ostwald maturation process) [5].

In the case of urea hydrolysis, urea is used as a precipitating agent in LDH<sub>S</sub> synthesis at specific temperatures. The degree of crystallinity of LDH<sub>S</sub> depends on the synthesis temperature and the rate of decomposition [6].

In the case of LDH<sub>S</sub> obtained by the hydrothermal method the synthesis is usually carried out in autoclaves, sealed with Teflon coating, exploiting the autogenous pressure generated by heating at temperatures between 60 and 300°C and starting from the solution of metal precursors (M<sup>2+</sup> and M<sup>3+</sup>), the solution containing An-, and the alkaline solution that will form the LDH<sub>S</sub>. The mixture is kept under hydrothermal conditions for a period that can vary from hours to several days, then the precipitate formed is separated by centrifugation and washed. The process of "aging", maturation of the precipitate is carried out at lower temperatures ~60°C [7].

The sol-gel method is known for obtaining nanoparticles with high specific surface area, high purity, and homogeneity in a short time and at low cost. This method allows controlling the structural properties of the final products by changing the chemical nature of the reactants and the curing time by removing or adding reactants [8].

The ion exchange process is used when the preferred anions in the intermediate layer cannot be found using the urea hydrolysis, hydrothermal or co-precipitation methods of synthesis. The anion initially present in the LDH (usually an inorganic one) is replaced by ion exchange with another anion, inorganic or organic, to obtain the desired intercalated compound [9].

Another method to obtain LDH<sub>S</sub> with the desired interlayer anion is based on the "memory effect" of these compounds. This method consists of two main steps: (1) obtaining small metal oxides by calcining LDH<sub>S</sub> in the temperature range 450-600°C; (2) reconstructing LDH<sub>S</sub> by dispersing the obtained metal oxides in a solution containing the desired anion. By rehydration due to the "memory effect" the LDH<sub>S</sub> reconstruction takes place, and the anions are incorporated into the interlayer regions of the LDH<sub>S</sub> [10].

Obtaining LDH<sub>S</sub> by solid-state reactions can be considered a valuable alternative to solution and suspension-based techniques. In this method, the raw materials (metal ion precursors and alkali salt, which contains the desired anion to be intercalated) are ground either with a pistil mill by means of mills (ball mills and planar mills). Due to the mechanical forces exerted, the LDH<sub>S</sub> formation reaction can take place [11].

### **I.3. Characterisation methods**

Flexibility and LDH<sub>S</sub> reactivity are key features of these compounds, as they offer countless application possibilities, pose a serious challenge when examining their detailed structure, as they can lead to significant defects from a crystallographic perspective. For this reason, a variety of state-of-the-art characterization techniques and methodologies have been used to fully understand the structural and related properties of LDH<sub>S</sub> as alternatives or complements to X-ray diffraction. In addition to X-ray diffraction (XRD) commonly used are: Fourier transform infrared spectroscopy, scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy, N<sub>2</sub> adsorption-desorption study (surface and porosity analysis) and thermal investigation methods such as differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Other physicochemical methods include elemental analysis, CHN analysis, and photon correlation spectroscopy [12].

#### **I.4. LDH<sub>s</sub> uses**

The compositional versatility in layers and in anions between layers leads to a functional diversity that allows LDH<sub>s</sub> to be used for a variety of scientific applications such as: materials used in environmental protection (adsorbents, ion exchangers), antacid materials, stabilisers for polymers, pharmaceuticals and agricultural products, electrophotocatalytic materials, catalysts/catalyst precursors, etc. Among these, LDH<sub>s</sub> environmental remediation applications (adsorbents and catalysts/photocatalysts in water treatment and purification) are the most intensive and the most developed [13-15].

## **II. IONIC LIQUIDS**

### **II.1. Overview**

Currently, ionic liquids are defined as chemical compounds consisting of a cation and an anion, characterized by a melting temperature below 100 °C and exhibiting ionic-covalent crystal structures [16]. The molecular structure of ionic liquids consists of different cations and anions. Anions are substantially smaller in volume than cations and have an inorganic structure, while the cation is usually represented by a large organic complex (with a positive charge). Ionic liquids are liquids at temperatures below 100°C because of the weak bond between the two constituents, given the size difference between them [17]. Each of these ions can covalently incorporate a functional group (designed to endow them with particular properties, either physical, chemical or in terms of reactivity) as part of the ionic structure, unique in the molecule [18].

The modular nature of IL means that structural changes can be made to either the anion, the cationic core, or the anion or cation substituents. Therefore, a great diversity in IL structure is possible and by modifying the cationic or anionic component of an IL, the physical and chemical properties of the IL can be easily tuned. Properly designed synthesis using different types of uniquely selected ions results in an ionic liquid with optimal properties for strictly defined needs.

### **II.2. Properties of ionic liquids**

The density of ionic liquids at room temperature is generally higher than the density of water. One of the most significant physical properties is viscosity. The viscosity of ionic liquids varies widely from 10 to 500 mPa/s. Ionic liquids are usually viscous compared to molecular solvents, which limits their applicability in industrial processes due to high handling and pumping costs [19].

The development of hydrophilic or hydrophobic ionic liquids depends on the correct choice of cations and anions. In an ionic liquid, increased hydrophobicity is caused by the growth of alkyl chains in the cations.

Ionic liquids are considered effective solvents for a wide range of inorganic, organic and polymeric compounds. By modifying the cationic and anionic structures, it is possible to precisely control how ionic liquids are soluble in organic and water-based solvents. Two things can be used to explain how the cationic structure affects miscibility: (a) the polarity

similarity between the ionic liquid and the other liquid; and (b) the free space between the molecules carried by the long side chains.

Ionic liquids are of interest as intermediates in organic reactions and other chemical processes because of their low melting point. While ionic liquids often have melting points below 100 °C and many are only liquids at room temperature, salts in molten form usually have very high freezing points. This low melting point characteristic can be explained by the replacement of simple inorganic cations by non-symmetric organic cations [20]. Also, the inorganic anion is responsible for the low melting point of an ionic liquid, and in some cases even has the most significant contribution to the lowering of the melting point.

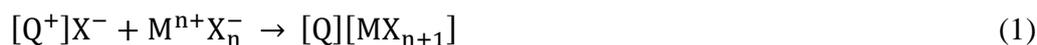
Ionic liquids belong to the 'green compounds' category because they have negligible vapour pressure. Ionic liquids are gaining popularity as new replacements for volatile organic compounds (VOCs), which have traditionally been used as industrial solvents, partly because of this favourable property.

In the case of ionic liquids, the surface tension increases as the concentration of contaminants (such as halogens) increases, and the surface tension decreases when a significant amount of water is present [21]. The surface tension of ionic liquids decreases with alkyl chain extension for short alkyl chains. On the other hand, the surface tension of longer alkyl chains did not vary with increasing number of alkyl groups. With increasing alkyl chain, Van der Waals forces compensated for Coulomb interactions and therefore no change in surface tension was observed.

### II.3. Methods of ionic liquids synthesis

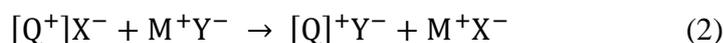
Ionic liquids are frequently produced from ammonium, phosphonium or sulphonate ions. There are two main methods of IL preparation: methathesis and acid-base neutralization [22].

The first years of study on ionic liquids were based on the simple mixing reaction between quaternary halogen salts and Lewis acids (most commonly used being AlCl<sub>3</sub>) according to reaction:



where:  $[Q^+]X^-$  - quaternary halide,  $MX_n$  - metallic halide

Obtaining ionic liquids by methathesis reactions involves the reaction between a quaternary halide and a series of Ag salts (Ag[NO<sub>3</sub>], Ag[NO<sub>2</sub>], Ag[BF<sub>4</sub>], Ag[CH<sub>3</sub>CO<sub>2</sub>]<sub>3</sub> and Ag<sub>2</sub>[SO<sub>4</sub>]), or salts of first group of metals, in methanol or aqueous methanol solution, according to reaction (2):



where:  $[Q^+]X^-$  - quaternary halide, M - metal from first group, or Ag, Y-anion, other than X

Conventional preparation of ionic liquids using excess solvents leaves much to be desired, which is why improvements have been sought. Nowadays, the quaternisation reaction is applied by unconventional methods, such as microwave and ultrasound techniques, with improved results.

## II.4. Ionic liquids classification

Ionic liquids are classified using a variety of flexible criteria from the literature, including physical state or physicochemical properties, and chemical structures of cationic and anionic constituents. Imidazolium, sulphonium, phosphonium, pyridinium, ammonium and morpholinium are some of the most popular cationic elements. Chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), iodide ( $\text{I}^-$ ), tetrafluoroborate ( $\text{BF}_4^-$ ), hexafluorophosphate ( $\text{PF}_6^-$ ), nitrate ( $\text{NO}_3^-$ ), bis(trifluoromethylsulphonyl)imide ( $\text{NTf}_2^-$ ), dicyanamide (DCA,  $\text{N}(\text{CN})_2^-$ ), salicylate (Sal), trifluoromethylsulphate ( $\text{TfO}^-$ ), saccharinate (Sacc), are all examples of anionic compounds.

Due to the large number of constituents and possible combinations, up to 1018 ionic liquids can theoretically be designed. By incorporating the relevant ions into structurally specific compounds, appropriate functionality can be achieved. Designing ionic liquids for specific uses opens virtually countless structural options, as demonstrated by the combinations of cations and anions. ILs have been classified into several types as their chemical variety has increased, such as room-temperature ILs (RTILs) [23], task-specific ILs (TSILs) [24], poly-ionic liquids (PILs) [125], and membrane-supported ILs (SILMs) [26], which include IL composites supported on metal-organic frameworks (MOFs) [27].

## II.5. Ionic liquids applications

Due to a considerable number of ion combinations and the possibility to design application-specific fluids, ILs have been recognized as "design solvents" to overcome the limitation of common volatile organic solvents [28]. Due to their excellent thermal, chemical and electrochemical stability, non-flammability and negligible volatility, ILs have been used in a number of applications: electrochemistry, as a solvent, liquid-liquid extractions, in analytical chemistry, etc [28-30].

## III. EXPERIMENTAL RESULTS

The doctoral thesis provides particularly valuable scientific contributions in a specific field of research, in accordance with the requirements of the national and international scientific community. The aim of the PhD thesis is to conduct advanced research on the development of innovative materials with adsorptive and photocatalytic potential.

The main objective of the PhD thesis was to develop high-performance materials based on  $\text{Mg}_3\text{Al}$  double layered hydroxide functionalized with methyl trialkyl ammonium chloride with applications in adsorption and heterogeneous photocatalysis processes.

Research have been developed along the following directions:

- A. Synthesis and characterization of crude and methyl trialkyl ammonium chloride functionalized  $\text{Mg}_3\text{Al}$  double layered hydroxide, respectively;
- B. Use of the synthesized and characterized materials in the treatment of waters containing organic pollutants (DCF), respectively inorganic pollutants (Pd(II)) by adsorption processes;
- C. Recovery of exhausted adsorbates from the Pd(II) adsorption process and their valorization as photocatalytic materials in the DCF degradation process from aqueous solutions.

Based on the specific objectives of each research direction, the experimental work plan was detailed and included the synthesis and structural and morphological characterization of  $\text{Mg}_3\text{Al}$  layered double hydroxide and methyl trialkyl ammonium chloride functionalized layered double hydroxide, respectively. It was also aimed to correlate the

characteristics of the synthesized and characterized compounds with their efficiencies in adsorption and photocatalytic degradation processes.

### III.1. Synthesis and characterization of raw Mg<sub>3</sub>Al layered double hydroxide and functionalized with methyl trialkyl ammonium chloride

Mg<sub>3</sub>Al-type layered double hydroxide was synthesized by the co-precipitation method at low supersaturation. Its functionalization with methyl trialkyl ammonium chloride was carried out by two methods, co-synthesis (Mg<sub>3</sub>Al-IL-COS) and ultrasonication (Mg<sub>3</sub>Al-IL-US).

#### a) X-ray diffraction analysis

The X-ray diffraction spectra of the three synthesized compounds showed typical diffraction patterns for layered double hydroxides with a hydrotalcite-like structure with 3R rhombohedral stacking of the main layers. The RDX spectra of Mg<sub>3</sub>Al and Mg<sub>3</sub>Al-IL-US compounds showed sharp and intense peaks typical of well-crystallized materials, suggesting that the functionalization of layered double hydroxide with methyl trialkyl ammonium chloride by the ultrasonic method did not generate disorder in the Mg<sub>3</sub>Al structure. The values of the lattice parameter *c* were 23.58 Å for Mg<sub>3</sub>Al and 23.52 Å for Mg<sub>3</sub>Al IL-US, respectively, specific for CO<sub>3</sub><sup>2-</sup> intercalation in the interlayer spaces of the LDH<sub>5</sub>. In the XRD spectrum of the Mg<sub>3</sub>Al-IL-COS compound, a shift of the maxima due to reflections of the (003) and (006) planes at smaller 2θ angles was observed, respectively a flattening of these peaks, lower intensity peaks, suggesting a lower crystallinity compound. The lattice parameter *c* increased from 23.58 Å to 24.39 Å, suggesting that interlayer intercalation of trimethyl alkyl ammonium chloride occurs in the co-synthesis functionalization process. A slight decrease in crystallite size from 4.86 nm to 3.38 nm was also observed. [31-33].

#### b) FTIR spectrometry analysis

FTIR spectra of the synthesized compounds revealed the presence of carbonate anions and water in the interlayer space as well as the type of bonds formed. The FTIR spectrum of methyl trialkyl ammonium chloride showed two absorption bands located at 2920 cm<sup>-1</sup> and 2852 cm<sup>-1</sup>, attributed to -CH<sub>2</sub> and -CH<sub>3</sub> groups, respectively. The absorption bands observed at 1462 cm<sup>-1</sup> and 1377 cm<sup>-1</sup> are characteristic of the ammonium group [34].

The FTIR spectrum of the Mg<sub>3</sub>Al compound contains absorption bands specific to layered double hydroxides intercalated with the carbonate anion. In the FTIR spectrum of Mg<sub>3</sub>Al-IL-US all bands characteristic of Mg<sub>3</sub>Al were present; In addition, absorption bands attributed to the -CH<sub>2</sub> and -CH<sub>3</sub> groups in IL (2926 cm<sup>-1</sup> and 2856 cm<sup>-1</sup>) overlapping with the band attributed to CO<sub>3</sub><sup>2-</sup> - H<sub>2</sub>O (bridging mode of carbonate and water in the interlayer region) as well as the shift of the band attributed to the bending mode of water molecules from 1641 cm<sup>-1</sup> (observed in the spectrum of the Mg<sub>3</sub>Al sample) to 1628 cm<sup>-1</sup> were observed [35].

Due to the different mode of synthesis, the FTIR spectrum of the Mg<sub>3</sub>Al-IL-COS compound showed several changes because of the intercalation of ionic liquid into the interlayer space. The band at about 3500 cm<sup>-1</sup> was wider, probably due to the interaction between the IL and the hydroxide layer, causing the length of the Mg-OH and Al-OH bonds to change. The doublet attributed to the -CH<sub>2</sub> and -CH<sub>3</sub> groups in IL appeared at 2932 cm<sup>-1</sup> and 2864 cm<sup>-1</sup>. Because of this doublet, the band assigned to the carbonate-water bond mode was not visible. In addition, the band attributed to the bending mode of the water molecules was shifted to 1628 cm<sup>-1</sup>, with a new shoulder appearing in the spectrum at 1759 cm<sup>-1</sup>. The presence of this new shoulder can be attributed to the presence of small amounts of water molecules coordinated to a cation [35].

*c) Structural analysis by N<sub>2</sub> adsorption-desorption*

The specific surface areas of synthesized materials decreased in order: Mg<sub>3</sub>Al > Mg<sub>3</sub>Al-IL-US > Mg<sub>3</sub>Al-IL-COS. Regardless of the synthesis method, all isotherms were type IV according to the IUPAC classification and belong to the H3-type hysteresis loop. The Mg<sub>3</sub>Al and Mg<sub>3</sub>Al-IL-US compounds exhibit mesopores with sizes between 10 and 20 nm, and the Mg<sub>3</sub>Al-IL-COS compound exhibits large mesopores and macropores, with sizes between 30 and 70 nm.

*d) Morphological characterisation*

The morphology of the Mg<sub>3</sub>Al compound was in the form of hexagons arranged regularly in overlapping layers, an appearance typical of layered double hydroxides. The morphology of the compound prepared by co-synthesis was different, in that a lattice change was observed, the brucite-like layers being disordered due to the entry of the ionic liquid into the interlayer. The sample surface had the appearance of cotton flowers. In the case of ultrasonic functionalization, only the attachment of the ionic liquid to the surface of the solid support in the form of a film was observed, leading to a homogenization of the surface. EDX spectra of the synthesized materials confirmed the functionalization of Mg<sub>3</sub>Al with methyl trilachyl ammonium chloride, being present the specific peaks of Cl and N, elements characteristic of the studied ionic liquid.

*e) Thermal analysis*

For the Mg<sub>3</sub>Al compound, the main thermal decomposition processes (dehydration, dehydroxylation and decarbonization) occurred in the temperature ranges 20 - 300, 300 - 700 and above 700 °C. The endothermic peak at 85 °C observed on the DSC diagram of the Mg<sub>3</sub>Al sample was attributed to the loss of adsorbed water; the endothermic peak at 188 °C occurred because of dehydration and partial dehydroxylation processes. The total mass loss due to decomposition of the Mg<sub>3</sub>Al sample was 45.7%.

By comparison, the DSC curve of the Mg<sub>3</sub>Al-IL-US sample showed two endothermic shoulders, at about 70 °C and 166 °C as well as an endothermic peak at 206 °C which were attributed to the loss of interlayer water molecules and partial dehydroxylation. A shift of the maximum temperature to lower values for the shoulders and to a higher value for the peak was also observed, which was attributed to the interaction of organic IL with physically adsorbed water molecules and those located in the interlayer space of LDH. The sharp exothermic peak with maximum at 251 °C and the exothermic shoulder at about 300 °C appear to be the consequence of combustion of the organic ionic liquid chain. The broad endothermic peak at about 630 °C and the small shoulder at about 900 °C are due to the formation of small metal oxides. The total mass loss for the Mg<sub>3</sub>Al-IL-US material was 49.3 %.

The behaviour of the thermoanalytical curves of the Mg<sub>3</sub>Al IL-COS sample was slightly different from the other two samples. Due to the ionic liquid being placed in the interlayer space, it probably replaced water molecules and interacted with carbonate anions placed in the interlayer space and hydroxyl anions on the brucite-type layer. Thus, in the first temperature range (20 - 200 °C), a single endothermic peak with a maximum at 129 °C was shown on the DSC curve, instead of two or three endothermic peaks as observed in the other samples. The exothermic peak due to ionic liquid combustion shifted to a slightly higher temperature than in the Mg<sub>3</sub>Al -IL-US sample (256 °C versus 251 °C), suggesting that higher energy was required to break some of the interactions between IL and LDH. The total mass loss of this material is 47.9% [36].

### III.2. Application of synthesized materials in the adsorption of diclofenac from aqueous solutions

The synthesized and characterized compounds were used as adsorbent materials in the removal of diclofenac from aqueous solutions. Their efficiency in the DCF adsorption process was studied considering a series of physicochemical and operational parameters: initial pH of the aqueous solution, stirring time of the reaction mass, temperature, and initial concentration of the DCF solution, respectively.

#### a) pH influence

The study of the influence of pH on the adsorption capacity of DCF on the synthesized materials indicated the value of 7 as the optimal pH. At pH value of 8, there was a decrease in both the degree of DCF removal from solution and the adsorption capacity of the studied materials. At higher pH values, an increase in adsorption capacity was observed, which was attributed to a aggregation process of DCF and not to the adsorption process [37].

#### b) Kinetic studies on DCF adsorption on synthesized materials

On the kinetic curves corresponding to adsorption on the studied materials at different initial concentrations of DCF, it was observed that the adsorption capacity increased with increasing contact time up to 60 minutes, after which it remained constant. With increasing initial concentration of DCF in aqueous solutions the adsorption efficiency of the studied materials increased. The adsorption capacity showed a slight, insignificant increase with increasing working temperature. Operating the adsorption process at higher temperatures is not justified.

Across the studied kinetic models, a good agreement of the pseudo-second-order kinetic model with the experimental data was found. The correlation coefficients resulting from the linear representations had values greater than 0.98 for all studied situations. Also, the experimentally obtained adsorption capacity values were very close to the modelled values. This indicates that the adsorption process corresponds to chemisorption, the rate-determining step being the sharing or exchange of electrons between the DCF and the active sites/functional groups of the adsorbent materials studied [37, 38].

#### c) Thermodynamic studies on DCF adsorption on synthesized materials

To assess the nature of the DCF adsorption process on the synthesized materials, the thermodynamic parameters: standard enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ) and Gibbs free energy ( $\Delta G^\circ$ ) were calculated. The DCF adsorption process on the synthesized materials is endothermic. In the case of the functionalized samples ( $Mg_3Al$ -IL-COS and  $Mg_3Al$ -IL-US) the feasibility and spontaneity of the adsorption process was confirmed by the obtained negative values of  $\Delta G^\circ$ . These values are more negative with increasing temperature and increasing initial DCF concentration, suggesting that at higher DCF concentrations in solution more active groups are available in solution, which provide better contact with the adsorbent surface and lead to higher adsorption efficiency. The positive entropy value,  $\Delta S^\circ$  suggested an increase in random interactions at the solid/liquid interface during DCF adsorption on functionalized samples. In the case of unfunctionalized  $Mg_3Al$ , due to the absence of IL-conferred functional groups on the adsorbent surface, these random interactions at the solid/liquid interface decreased, which was also suggested by the negative values obtained for entropy,  $\Delta S^\circ$ .

#### d) Equilibrium studies on DCF adsorption on synthesized materials

The study of the equilibrium of the adsorption process showed that functionalization processes resulted in an increase in adsorption capacity, which doubled in the case of ultrasonication and tripled in the case of co-synthesis. This increase is evidence that functional groups in the ionic liquid contribute to the removal of DCF from aqueous solutions. Comparing the isotherm parameters used for modelling the experimental data, it can be

concluded that DCF adsorption on the studied materials is best described by the Sips model. In this case, correlation coefficients close to unity and maximum adsorption capacities calculated from the model close to those obtained experimentally were obtained. These aspects indicate that DCF adsorption on the studied materials occurs as a heterogeneous process, and not as a monolayer coating. By FTIR spectrometry before and after DCF adsorption, its retention mechanism on the synthesized materials was revealed [39, 40].

Comparison of the adsorption capacities developed by the synthesized materials with the adsorption capacity developed by other adsorbents presented in the literature resulted in similar and even higher values, especially Mg<sub>3</sub>Al functionalized with methyl trialkyl ammonium chloride by co-synthesis. This indicates that our synthesized materials can be used with high performances in the treatment process of diclofenac-containing waters [41-43].

### **III.3. Application of synthesized materials in the adsorption of palladium from aqueous solutions**

The compounds Mg<sub>3</sub>Al, Mg<sub>3</sub>Al-IL-US and Mg<sub>3</sub>Al-IL-COS were used as adsorbent materials in the recovery of Pd ions from aqueous solutions. The efficiency of the materials was determined by studying the dependence of the adsorption capacity developed by them on stirring time, temperature, and initial concentration of Pd ions in aqueous solutions [44].

#### *a) Kinetic studies on Pd(II) adsorption on synthesized materials*

From the adsorption studies performed at different time durations, it was concluded that regardless of the working temperature, the adsorbent-adsorbate equilibrium was reached within 60 minutes. The adsorption capacity showed insignificant increase with the increase of the working temperature, which does not justify the operation of the adsorption process at higher temperatures. The kinetics of Pd(II) adsorption on the synthesized materials was described by the pseudo-second-order kinetic model. The application of this model led to values of the correlation coefficients close to 1, and the adsorption capacity at equilibrium resulting from the modelling was close to the value determined experimentally. These findings suggest that the rate-determining step may be chemical adsorption or chemisorption, processes that involve valence forces through the sharing or exchange of electrons between the adsorbent and the adsorbate [44].

#### *b) Thermodynamic studies on Pd(II) adsorption on the synthesized materials*

From the values obtained for the activation energy, it was found that the adsorption of Pd on Mg<sub>3</sub>Al corresponds to a physisorption process in the pores of the adsorbent material ( $E_a=2.97\text{kJ/mol}$ ), while the adsorption on the functionalized materials is due to some chemisorption processes ( $E_a= 14.72\text{ kJ/mol}$  for Mg<sub>3</sub>Al-IL-COS, respectively  $E_a=10.68\text{ kJ/mol}$  for Mg<sub>3</sub>Al-IL-US). Positive enthalpy values indicate the endothermic nature of Pd(II) adsorption. The values obtained for the Gibbs free energy are negative and increase in magnitude with increasing temperature, suggesting that Pd(II) adsorption on the studied LDHs is a spontaneous process. A positive value was obtained for the entropy suggesting an increase in random interactions at the solid/liquid interface during the adsorption of Pd(II) ions on the studied materials [45].

#### *c) Equilibrium studies on Pd(II) adsorption on the synthesized materials*

From the equilibrium isotherms, it can be seen that the adsorption capacity increases with the equilibrium concentration of Pd(II) ions in the aqueous solutions. The adsorption capacity developed by functionalized Mg<sub>3</sub>Al is almost twice higher (especially in the case of co-synthesis - Mg<sub>3</sub>Al IL-COS) than the adsorption capacity developed by raw Mg<sub>3</sub>Al. Among the isotherms studied, the Langmuir isotherm best describes the adsorption process of Pd(II) ions on the studied materials, obtaining almost unity correlation coefficients. Moreover, the maximum adsorption capacity obtained from the Langmuir isotherm is very close to that

obtained experimentally. Due to the fact that the Langmuir isotherm fits best with the experimental data, we can mention that Pd(II) ions are uniformly adsorbed on the surface of the studied adsorbent, due to the homogeneous distribution of active sites on the surface [46-47].

*d) The adsorption mechanism of Pd(II) ions on the synthesized materials*

By correlating the results obtained in the process of characterizing the adsorbent materials with the results obtained from the kinetic, thermodynamic and equilibrium studies, we can conclude that in the case of the raw Mg<sub>3</sub>Al sample, Pd recovery takes place through a physisorption mechanism, it being adsorbed in the pores of the material. In the case of samples functionalized with IL (methyl-tri-alkyl-ammonium chloride), Pd recovery is due to a chemisorption process, indicating that the functional group of the ionic liquid confers a beneficial influence on the adsorbent material.

We appreciate that the chemisorption process may be the consequence of ion pair interactions between Pd(II) and quaternary ammonium in the studied IL, with the formation of stable complexes.

The best adsorption capacity was developed by the co-synthesis functionalized sample, with the synergistic effect between the ionic liquid and Mg<sub>3</sub>Al-LDH contributing to the palladium ion adsorption. We believe that in this case, the ionic liquid is intercalated in the intermediate layer of Mg<sub>3</sub>Al-LDH, favoring ion pair interactions as well as electrostatic interactions with the IL; in addition, a physical sorption process may also occur on the LDH surface. In the case of the ultrasonically synthesized material, the ionic liquid is found on the Mg<sub>3</sub>Al-LDH surface and not in the interlayer space. As such, Pd(II) ions are retained by interacting with the IL, but the physisorption process is diminished because the presence of the IL on the LDH surface decreases the sites available for physisorption [48].

*e) The influence of competitive ions*

To determine the influence of foreign ions in the recovery process of Pd from aqueous solutions, the material that developed the best performance in the recovery process of Pd ions from aqueous solutions was used as adsorbent material, namely, the layered double hydroxide of type Mg<sub>3</sub>Al functionalized by co-synthesis with methyl trialkyl ammonium chloride. The increase of the ionic strength and competitive ions caused the decrease of the adsorption capacity of Pd on the studied materials [49, 50].

#### **III.4. Use of the adsorbent materials resulted from the Pd adsorption process in photocatalytic processes**

The exhausted adsorbent materials resulted from the treatment process of waters containing palladium were used as photocatalytic materials in the photodegradation process of DCF from aqueous solutions. Photocatalytic materials with a loading of 0, 10, 30, and 100 mg/g Pd were used for the photocatalytic treatment of waters with a content of 250 and 500 mg/L DCF.

*a) Efficiency of the DCF photocatalytic degradation process*

The materials resulted from the palladium recovery process from aqueous solutions can be successfully used as photocatalytic materials in the process of diclofenac degradation from water.

The efficiency of the photocatalytic materials increased with increasing of Pd content. The ionic liquid functionalized samples, especially those functionalized by co-synthesis showed higher efficiency than non-functionalized samples.

The Mg<sub>3</sub>Al-IL-COS material loaded with 30 mg/g Pd was successfully used in 4 photodegradation cycles of waters containing 250 mg/L DCF, its efficiency remaining almost constant.

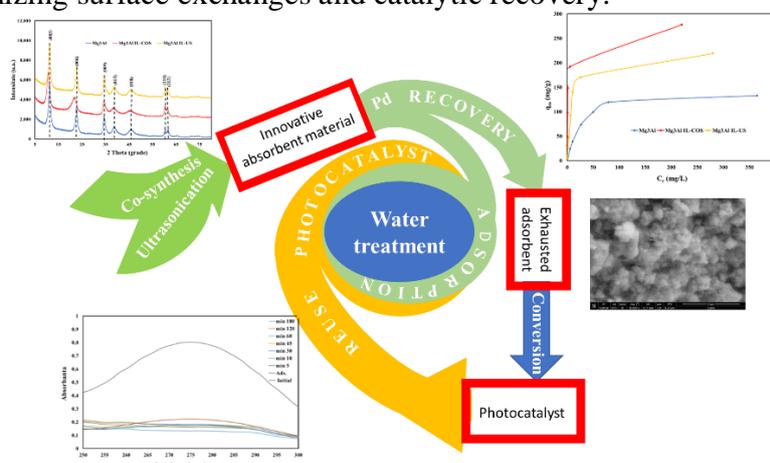
*b) Kinetic study of the photocatalytic degradation process of DCF from aqueous solutions*

The photocatalytic degradation process on the studied materials is described by the second-order kinetic model; the rate-determining step in the photocatalytic degradation process of DCF from aqueous solutions is chemical adsorption in the monolayer by photoinduced electron transfer between DCF molecules and photocatalyst particles, followed by organic compound degradation.

The rate constant increased with increasing amount of Pd in the catalyst structure. In the case of materials functionalized with IL, the rate constants corresponding to the photocatalytic process were higher compared to those obtained when  $Mg_3Al$  photocatalyst is applied [51, 52].

In conclusion, the research related to the doctoral thesis focused on the development of new efficient materials based on  $Mg_3Al$  double-layered hydroxide functionalized with methyl trialkyl ammonium chloride with improved properties in the processes of adsorption and heterogeneous photocatalysis.

A solution was proposed for the valorisation of exhausted adsorbent materials resulted from the Pd adsorption process from aqueous solutions, in the form of photocatalysts in the DCF degradation process from water. The system designed by us combines the advantages of both homogeneous and heterogeneous catalysis, combining the catalytic properties of all the involved components: LDH, IL and Pd and minimizing all the disadvantages of their individual use in photocatalytic processes. Pd adsorbed on IL-impregnated LDH is the active component, the ionic liquid immobilized on LDH behaves as a homogeneous phase with improved mass transfer properties and higher activity, while immobilization on LDH allows easy product separation, potential recycling of photocatalyst and development for continuous processes. This concept allows minimizing the amount used of IL and Pd and mass transfer resistance, optimizing surface exchanges and catalytic recovery.



Circular use of materials based on  $Mg_3Al$  double layered hydroxide functionalized with methyl trialkyl ammonium chloride in water treatment

The proposed method is in accordance with the European "green" agreement (European Green Deal's: "Clean environment and zero pollution"), proposing a solution that is in the frame of closed-cycle technologies for the recovery and reuse of palladium.

#### IV. ORIGINAL CONTRIBUTIONS

The main original theoretical and experimental contributions are:

- ✓ A well-systematized bibliographic study was carried out regarding the definition of layered double hydroxides, respectively ionic liquids, their structure and properties, as well as the numerous application fields;
- ✓ Experiments were designed for the synthesis of a new material with adsorptive and photocatalytic properties, by functionalizing the double layered hydroxide of  $Mg_3Al$  type with methyl trilacyl ammonium chloride;
- ✓ Two techniques were developed to functionalize  $Mg_3Al$ -LDH with studied IL: co-synthesis and ultrasound;
- ✓ A wide range of specific characterization techniques from a structural and morphological point of view was used for the 3 synthesized compounds;
- ✓ The adsorptive properties of the synthesized materials in water treatment with organic compounds (diclofenac) and inorganic compounds (Pd(II) ion) were determined;
- ✓ The optimal operational parameters (initial pollutant concentration, pH, process duration and temperature) and control (residual pollutant concentration) of the adsorption process were established;
- ✓ Equilibrium, kinetic and thermodynamic studies were carried out in order to identify the models underlying the adsorption processes and the calculation of all the corresponding parameters.
- ✓ By correlating the characteristics of the synthesized materials with the performances of the adsorption processes, the adsorption mechanisms of the targeted pollutants on the studied materials were identified and discussed.
- ✓ The requirements of the European Union regarding sustainable development were taken into account; in this sense, a method was proposed for the recovery of exhausted adsorbents, resulting from the retention process of Pd(II) ions from aqueous solutions, in the form of photocatalytic materials.
- ✓ The photocatalytic efficiency of the materials in the DCF degradation process from aqueous solutions was established.
- ✓ The kinetics of the photocatalytic oxidation processes were modelled to identify the process mechanisms.
- ✓ The beneficial role and synergistic effect of all the components in the structure of the studied composites (LDH, IL, respectively Pd) was highlighted both in the water treatment processes by adsorption and by heterogeneous photocatalysis.
- ✓ A closed cycle water treatment technology was proposed by developing materials based on  $Mg_3Al$  double layered hydroxide functionalized with methyl trialkyl ammonium chloride.

During the PhD internship I was a member of the research team of **3 research projects**, and I won a scholarship "**InoHubDoc DOCTORAL STUDENT SCHOLARSHIP**" within the project POCU/993/6/13/153437.

The results obtained from the original research carried out were disseminated as follows:

- **3 articles published** in journals indexed in **Web of Science, Clarivate Analytics**, **2 framed Q1**, and **one Q2**, accumulating an impact factor from the date of publication **FIC=17.839**;
- **11 articles** presented at national or international scientific conferences;
- submission of **1 invention patent application** to OSIM: A/00056 dated 08.02.2023.

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