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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF MgCuZnAl LAYERED DOUBLE HYDROXIDES

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CONTENT

INTRODUCTION

Chromium compounds in oxidation state VI (chromate (CrO_4^{2-}), hydrochromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$)) ions belong to the group of the most dangerous anionic pollutants of the aquatic environment. The largest contribution to Cr(VI) emissions comes from industrial activities. Additional sources include emissions from fossil fuel combustion and effluents from leather and dye processing plants [1, 2]. International agencies and toxicological reviews classify Cr(VI) compounds as carcinogenic to humans, with inhalation exposure associated with an increased risk of respiratory tract cancers and drinking water contamination associated with numerous systemic effects. In addition, their effects on the skin, gastrointestinal tract, nervous and reproductive systems have been described [3, 4]. High toxicity, carcinogenic properties and high mobility in the aquatic environment make the removal of Cr(VI) compounds from solutions a significant challenge in environmental engineering.

In recent years, there has been considerable interest in inorganic materials with a layered structure, which, thanks to the presence of surface ion exchange centres, can effectively remove anions from the aquatic environment. Layered double hydroxides (LDHs) are materials with a structure similar to hydrotalcite, composed of positively charged brucite layers of the type $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$, between which there are charge-compensating anions (e.g. Cl^-, Br^-, NO_3^-, I^-, OH^-, SO_4^{2-}) and water molecules [5]. LDHs are characterised by high compositional flexibility, high thermal stability, high positive ζ-potential, the presence of surface –OH groups, and a unique ability to exchange anions and reconstruct their structure after calcination (the so-called memory effect) [6, 7]. Due to these properties, they can effectively adsorb anions, including chromates, from aqueous solutions.

The main aim of this work was to synthesize mixed-metal LDHs using the co-precipitation method and to investigate the effect of the hydroxide layer composition and the type of interlayer anions
on the sorption capacity of chromate (VI) anions. The following tasks were set up in order to achieve these objectives:

(1) Synthesis and characterization of LDH-CO3 and LDH-Cl forms of $Mg_2Cu_{0.5}Zn_{0.5}Al_1$.
(2) Investigation of sorption of Cr(VI) anions from solutions.
(3) Characterization of $Mg_2Cu_{0.5}Zn_{0.5}Al_1$ after sorption.

1. LITERATURE REVIEW

1.1 Layered Double Hydroxides (LDHs)

Layered double hydroxides or hydrotalcite-type compounds are anionic clays, the crystal structure of which is based on the brucite $Mg(OH)_2$ [8]. The general chemical formula of LDH is $[M^{II}_{1-x} M^{III}_x(OH)_2]^{x+}(A^{m-})_{x/m}]\cdot nH_2O$, where M^{2+} (Mg, Zn, Co, Ni, Cu, Mn, . . .) and M^{3+} (Al, Ga, Cr, Co, Fe, V, Y, Mn, . . .) are divalent and trivalent metal cations, respectively and A^{y-} is an intercalated anion that is located in interlayer spaces and in addition [9,10,11]. LDHs have high capacity of adopting organic and inorganic anions. Recently prepared LDHs have received a lot of attention because of the diverse significant areas of use such as catalysis, photochemistry, electrochemistry, magnetization, biomedical science, environmental applications and optics [8]. LDHs are highly anion exchangeable, possess high surface area and comparable anion exchange capacities with that of anion exchange resins and are thermally stable [12].

1.1.1 Crystal Structure

The general structure of the LDHs layer is founded on the one of brucite $[Mg(OH)_2]$ that belongs to the CdI_2 type that is usually linked to the presence of small polarizing cation and polarizable anions. It bears magnesium ions which are approximately octahedrally encircled by hydroxide ions. These octahedrals are made to create an infinite layer with sharing of edges and the hydroxide ions occupying perpendicular position relative to the plane of the layers as illustrated in Fig. 1 [13].

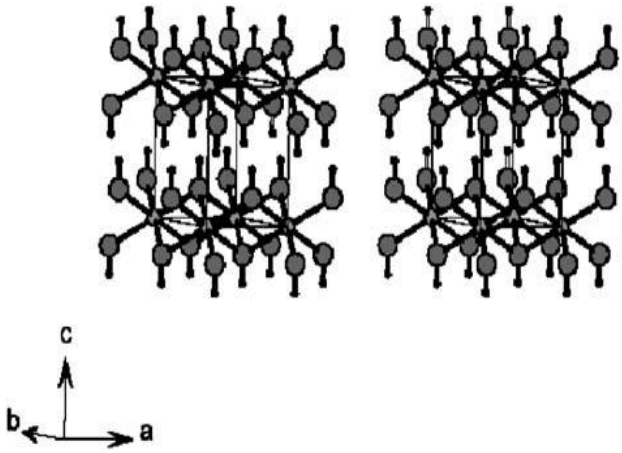

Fig.1 Stereographic projection of brucite [13]

The layers will then be placed one on top of the other to create the three dimensional structure. In a close-packing perspective, it is possible to say that the structure is made of close-packed planes of hydroxyl anions lying on a triangular lattice. The octahedral holes between successive pairs of OH planes are filled by the metal cations and therefore assume a triangular lattice which is also shared by the OH ions. As a matter of fact, both local geometry of the metal as well as close-packing of the hydroxyl anions is highly distorted with respect to the idealized arrangements [13].

The octahedra are pinched in the axis of stacking, making the local geometry at the metal to be D_{3d}, instead of O_h. This causes the O⋯O and Mg⋯Mg distances perpendicular to the plane to increase by 0.002973nm (theoretical O_h geometry) to 0.003142nm (experimental distance) and decreases the thickness of the layers to 0.2112nm 0.2427nm, with the O- M- O bondangles changing to 96.7 and 83.3 instead of 90 (theoretical O_h geometry) [13]. This deformation has been considered in a molecular orbital perspective and an almost constant deformation has been proposed to all brucite-like hydroxides in the light of the relationship between unit cell parameters and M-O distances [13].The hexagonal symmetry ($a_o = b_o = 0.3142$nm, $c_o = 0.4766$nm, $\gamma = 120^\circ$) and space group remains the same and is P3m1 even though the brucite layers are distorted. It is worth noting that the value of a_o is equal to the nearest neighbour Mg⋯Mg distances that are parallel to the plane. The O-H bonds are oriented along the threefold axes to empty tetrahedron position in other layers. The weak forces between the layers have been the subject of some dispute in the literature with various weight being placed on the role of dispersion forces and hydrogen bonding [13].

The fundamental structure of the LDH can be obtained by replacing part of the divalent cations in the brucite-type octahedral layer by trivalent cations to cause the layers to assume a positive charge. This positive charge is neutralized by the fact that the bonding between the octahedral and interlayers is a combination of both electrostatic effects and hydrogen bonding [14].

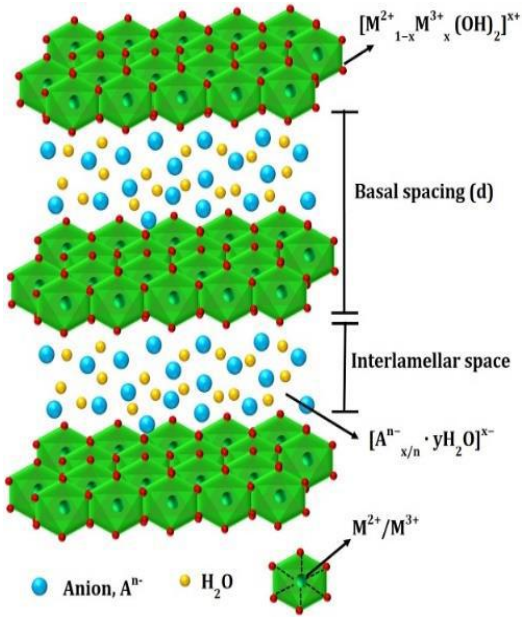

Fig. 2. Perspective view of the crystal structure LDH [16].

The lamellar crystal structure is characteristic of LDHs whose variations are wide in terms of identity and relative proportion of the di- and trivalent cations and also in the type of anions [17]. It has been said that M^{2+} and M^{3+} ions, with ionic radius not too different than the magnesium, can only be accommodated in the octahedral locations in the brucite-like layers to give rise to the LDH compounds, and that too small or too large cation does not give any results but forms other types of compounds,and additionally, the most dependable composition range roughly correlates to $0.2 \leq x \leq 0.4$ [15]. The open structure of LDHs makes them appropriate for adsorption and physico-chemical intercalation processes with a wide range of molecules, including organic and biomacromolecules. About the anions, their size and charge ratio is significant i.e. the host inorganic layer should have a hostguest relationship with the dimensions of the guest species in the interlayer [16]. Consequently, many different types of isostructural materials can be synthesized by altering the character of the metal cations, the molar ratios of M^{2+}/M^{3+} as well as the character of the interlayer anions. The brucite-like layers and the interlayer anions compositional diversity results in much diversity in physicochemical properties of the material and functional diversity that enables LDHs to be utilized in diverse applications. The interlayer galleries of LDHs have interlayer anions and water molecules as well as a complex system of hydrogen bonds between the hydroxyl groups of the layers, and among anions and water molecules. These interlayers are considerably disorganized and hydrogen bonds are at a constant flux so that the exact nature of the interlayer is highly complicated [15]. The interaction between the octahedrally arranged

layers and inter layers is a mix of both electrostatic forces and hydrogen bonding. The hydroxyl groups are highly polarized especially those that are attached to the trivalent cations and interact with the interlayer anions. All the anions must meet excess positive charges on both of the sandwiching octahedrally layered layers which are electrically compensated by two adjacent interlayers; it has been proposed that in LDHs charge compensation has numerous of the properties of resonance effects [15].

1.1.2. Metal-substituted LDHs

The exceptional compositional versatility of the layered double hydroxides enables the inclusion of different divalent and trivalent metal cations into the brucite-like layers resulting in the development of metal-substituted LDHs having customized characteristics. The ability to substitute is one of the greatest benefits of LDH materials, as it allows adjusting the physicochemical properties of the material to be utilized to match a particular case, such as adsorption, catalysis, and biomedicine. The faculties to host various metal ions in the layered structure can be attributed to the fact that ionic radii of most divalent and trivalent cations are close to each other; hence, isomorphous substitution of these ions is possible without breaking the overall layered structure [18].

The production of metal-substituted LDHs is controlled by a number of principles. To start with, the ionic radii of the replacing metal cations should be compatible with the octahedral position in the brucite-like layers. In general, it is possible to incorporate cations with ionic radii between 0.50 and 0.80 A and in case of divalent cations (M^{2+}) the most common substituents are Mg^{2+} (0.72 A), Ni^{2+} (0.69 A), Co^{2+} (0.74 A), Zn^{2+} (0.74 A), Cu^{2+} (0.73 A), and Mn^{2+} (0.83 A). In trivalent cations (M^{3+}), commonly used ions are Al^{3+} (0.53 A), Fe^{3+} (0.64 A), Cr^{3+} (0.62 A), Ga^{3+} (0.62 A) and Co^{3+} (0.54 A) [13]. The ionic radii are very close and this makes sure that the substituted cations will fit into the octahedral sites without severely distorting the layer structure.

M^{2+}/M^{3+} molar ratio that usually falls within the range of 2: 1 to 4:1, i.e. x values (the fraction of trivalent cations) of 0.2 to 0.33 is another crucial variable that controls substitution of metals and the result of this compositional range is formation of pure LDH phases without segregation of different metal hydroxide phases. A ratio of M^{2+}/M^{3+} above or below this value indicates an excessively high or excessively low layer charge, which causes repulsive interlayer electrostatic forces or inadequate anion exchange capacity, respectively [19]. The best ratio is required based on the particular mixture of metal

cations and the purpose of using the material.Several metal cations incorporated into the LDH structure have a great impact on the properties of the material; the thermal stability, surface area, surface charge, and the anion exchange capacity of the material . As an example, it has been demonstrated that replacing the Mg^{2+} by the Cu^{2+} in MgAl-LDH can alter the thermal decomposition characteristics of the material and increase its catalytic performance in oxidation reactions. Likewise, addition of Zn^{2+} into the LDH layers is capable of enhancing the photocatalytic activity of the material under consideration because of the semiconductor nature of zinc-bearing layers [20].

Various synthetic procedures have been devised to make the metal-substituted LDHs with each procedure having its own benefits in the purity of the products, their crystallinity, and their size. The most widely used technique is the co-precipitation technique because it is simple to use, reproducible, and creates homogeneous products with controlled composition [21]. The solution of mixed metal salt in this process is a mixture of desired divalent and trivalent cations in the right ratios and gradually the solution is added to alkaline solution in controlled pH conditions. This is because the precipitation is done by the concurrent hydrolysis of the metal ions to form LDH phase. It is worth noting that pH of the reaction mixture should be maintained very cautiously above precipitation pH of most soluble metal hydroxide in order to precipitate all the cations completely [22].

Post-coprecipitation aging is necessary in the formation of fully crystallized LDH materials. As the aging is generally done at high temperatures (60-80°C) over a time of several hours to several days, the original amorphous precipitates are dissolved and recrystallized to give better crystallinity and larger particle sizes and the aging environment such as temperature, time, and the inclusion of interlayer anions have a great impact on the ultimate characteristics of the metal substituted LDHs.Another method of synthesizing the metal-substituted LDHs is the urea hydrolysis technique that uses the slow hydrolysis of urea at high temperature to create the hydroxide ions in the reaction medium; they are uniformly dispersed [23]. This approach provides a better control on particle size and morphology, and commonly produces LDHs with plate-like shapes with hexagonal shapes and finely-dispersed particle sizes. The gradual dissolution of urea to produce homogenous and slow releases of hydroxide ions enables the formation of the metal hydroxides to precipitate gradually to facilitate the formation of well-ordered LDH structures of high crystallinity [24].

Sol-gel technique has also been effectively used in the synthesis of metal substituted LDHs which have the benefit of providing product homogeneity in addition to providing control over the number of metal cations to be incorporated into the product and under this method, the metal alkoxides or other such molecular precursors are subjected to hydrolysis and condensation reactions, which create a gel which is further aged and dried to produce LDH material. Sol-gel technique allows the production of LDHs with large surface areas as well as the uniform distribution of the metal cations in the layers [25].

The replacement of the various metal cations in the LDH structure gives it special properties that can be used in a number of applications. The use of transition metals including Cu, Zn, and Fe in the context of environmental remediation has been demonstrated to increase the adsorption capacity of the LDHs with the anionic pollutants. The inclusion of these transition metals provides more active sites to bind anion and can also be involved in redox reaction and be able to convert toxic species to less toxic ones.

In the case of chromium(VI), which is the subject matter of the present thesis, addition of copper and zinc to MgAl-LDH has been found to enhance its adsorption ability [26]. The LDHs with copper have greater affinity to chromate anions when they contain copper because they form a complex with the Cr(VI) species and copper centers on the surface. Also, the copper can be used to reduce highly toxic Cr(VI) to less toxic Cr(III) under specified scenarios and this offers another mechanism of chromium immobilization [27]. LDHs that are substituted with zinc have also been of interest in the application of chromium removal.. Introduction of zinc in the LDH structure alters the charge distribution of the layers and may enhance the material anion exchange capacity and in addition, zinc-based LDHs have a tendency to be more thermally stable and aqueous resistant, which is why they may be used in applications associated with adsorption in the long run [28].

A very interesting type of composition to be used in the adsorption of chromium(VI) is the quaternary Mg-Cu-Zn-Al LDH system which is investigated in this study. Magnesium, copper, and zinc form divalent cations, and aluminum forms the trivalent cation, which provides the possibilities of providing a higher adsorption performance on the basis of various mechanisms and the major divalent cation, Magnesium, gives the LDH layers its structure and the anionic exchange capacity of the material. Introduction of copper also incorporates redox active centers which can contribute to the reduction of Cr(VI) to Cr(III), and introduction of zinc also changes the distribution of surface charges and can increase the affinity of the material towards oxy-anions [29]. The synergistic effect of these various

metal cations forms a material with distinct characteristics that is not possible to obtain with binary and ternary systems.The process of Mg-Cu-Zn-Al LDH synthesis is delicate in terms of keeping reaction conditions under control to have all the four metal cations equally incorporated into the layered structure. The hydrolysis characteristics of $Mg^{2+,}$ Cu^{2+}, Zn^{2+} and Al^{3+} require the pH, temperature and aging conditions to be optimised to achieve phase-pure products of the required composition [5].

To sum up, metal-substituted LDHs are a flexible category of materials with adjustable properties that can be tailored to particular applications. The ability of adding more than one type of metal cation into the LDH structure provides the possibility of synergistic improvement of adsorption activities, and hence these materials are especially appealing to the elimination of toxic anionic contaminants of water like chromium(VI). Building on the core ideas presented in this literature review, the synthesis, characterisation, and use of Mg-Cu-Zn-Al LDHs for chromium(VI) removal are described in the following parts of this thesis.

1.1.2 ANIONIC POLLUTANTS OF THE AQUATIC ENVIRONMENT

Anionic pollutants that contaminate the water have become a very important concern of environmental issues in the world and these are negatively charged species of pollutants that are found in water that can result in different anthropogenic activities and natural processes that pose serious threats to aquatic life and human health. The anionic contaminants have also not been given a lot of attention compared to the decades of studies conducted on cationic pollutants, though they are very mobile in waters and they are barely removable through traditional water treatment systems [30].

Anionic pollutants include a wide variety of chemical species, some of which are oxyanions of metals and metalloids (as chromate, arsenate, selenate, and molybdate), inorganic anions (as nitrate, phosphate, fluoride, and chloride) and organic anions (as carboxylates, sulfonates, and many pesticide residues) and these pollutants are characterized by a common feature that in environmental pH conditions, they are negatively charged, which dictates their transport, bioavailability and toxicity within aquatic systems . They are highly liable to water and have a high rate of migration within the soil and groundwater due to their anionic nature that causes massive contamination of drinking water sources [31].

Anionic pollutants of the aquatic environment have many and diverse sources. One significant source is industrial discharges, where mining, metal plating, leather tanning, textile dyeing and chemical

manufacturing contribute significantly to the release of anionic contaminants into water bodies [32]. Agricultural activities play a vital role in the form of the run off of fertilizers (which contain nitrate and phosphate) and pesticides, whereas urban run off also imports a range of different anions to the soil through road salts, atmospheric deposition and wastewater effluents. Anionic species may also be deposited in water systems by natural processes, such as mineral weathering and volcanism, although anthropogenic sources usually predominate in polluted regions [33].

Of special concern is the environmental persistence of anionic pollutants. Some of the inorganic anions are not degradable unlike organic contaminants which can be subjected to biodegradation thus remaining in the environment forever. The pH, redox, and competing ions have a strong effect on their mobility in soil and water. In an average environmental condition, the anion species are often poorly adsorbed by negatively charged soil particles and are therefore easily washed off to the groundwater and the surface water bodies [34]. This mobility, in conjunction with the tenacity, causes the contamination of water resources in the long term and makes remediation more difficult.

Anionic pollutants may have a wide range and even ecotoxicological impacts on aquatic organisms. Nitrate and phosphate have the potential of causing eutrophication resulting in algal proliferation, reduced oxygen levels and consequently fish and other aquatic organism die-off. Harmful anions, chromate, arsenate, and selenate, may be collected in aquatic life and result in direct toxicity by disturbing metabolic actions, oxidative stress, and cell tissue damage. Bioaccumulation of such pollution by the food chain may lead to increased exposures to the successive trophic levels such as human beings who consume polluted fish and shellfish [35].

Anionic pollutants are now facing increasingly tougher water quality requirements around the globe. Maximum concentration in the drinking water of anionic species have been stipulated by the World Health Organization (WHO), the European Union and national environmental agencies [36]. To illustrate, the WHO guideline value of chromium(VI) in drinking water is

0.05 mg/L and the European Union as a parametric value is 0.05 mg/L of total chromium [36]. On the same note, there are strictly set limits of nitrate (50 mg/L as nitrate), fluoride (1.5 mg/L), and other anionic pollutants to serve the common good [37].

The elimination of anionic pollutants in water, in comparison to the elimination of cationic species, is somewhat of a challenge. Traditional water treatment strategies, such as coagulation, flocculation, and sedimentation do not usually work well with anionic contaminants since these techniques are focused on the removal of particulate matter and cationic species [38]. Sophisticated methods of treatment, including reverse osmosis, ion exchange, and electro-dialysis, can be utilized successfully to eliminate

anions but are connected with a high energy demand, high operational complexity, and production of concentrated streams of waste that need additional storage. Such constraints have motivated the efforts to find alternative, more affordable materials and techniques in removing anionic pollutants, and layered double hydroxides have become one of the most promising adsorbents [39].

The adsorption of the anionic pollutants on the solid materials has some merits in water treatment, such as, simplicity of operation, low costs and adsorbent regeneration and recovery of the pollutants are potential and the success of adsorption depends upon the physicochemical characteristics of both the adsorbent and the adsorbate such as the surface area, surface charge, and chemical functional groups, as well as the size and density of the anionic species [40]. It is especially desired to have materials with high positive surface charge, big surface areas, and readily accessible binding sites to remove anionic pollutants [41].

Chromium(VI) compounds hold the largest place of importance among the other anionic pollutants that need to be addressed because of their extreme toxicity, the prevalence, and regulatory significance [42]. The next section will be the detailed discussion of chromium(VI) as an anionic contaminant, covering its origin, chemical characteristics, toxicity, and the difficulties in the process of its elimination in the polluted waters.

1.2.1. General health issues

One of the greatest modern-day issues of the public health is the pollution of water resources with toxic compounds and chemical contamination of drinking water may lead to a broad range of negative health outcomes that may include the development of acute toxicity as well as long-term disorders that have a long latency period [43]. The extent of health effects is determined by many factors, such as; the contaminant involved, the concentration, the length and path of exposure as well as the vulnerability of the exposed populations [44].

Waterborne chemical contaminants are more harmful to the vulnerable populations, such as children, pregnant women, the elderly, and those with underlying pre-existing health conditions. Children are especially vulnerable because of their increased water uptake per body weight, developing organ systems, and their specific routes of exposure. Exposure of unborn babies or young children to harmful chemicals may lead to developmental defects, cognitive deficiency and predisposing these children to future diseases [45]. These considerations have highlighted the need to ensure strict water quality standards and use effective treatment technologies to safeguard human health.

The health outcomes of chemical pollution of drinking water may be divided into acute and chronic. Acute effects can be experienced immediately after exposure to high levels of toxic substances and it could include gastrointestinal distress, neurological effects and in the worst case, organ failure or death [46]. The chronic effects are prolonged responses gained with exposure to lower concentrations of contaminants and could include cancer, organ damage, and birth and development reproductive and developmental problems and immunological dysfunction. Many chronic diseases have long latency such that it is not easy to determine causal relationships between individual exposures and health outcomes which complicate risk evaluation and regulatory decision making [45].

The number of diseases caused by unsafe water, sanitation and hygiene is enormous globally, as millions of deaths and disability-adjusted life-years are lost every year. Although the major part of this burden can be linked to microbial pollution, chemical pollutants also play a major role in causing morbidity and mortality of water in both developed and developing nations [46]. Historical pollution of water sources with toxic chemicals in the industrial areas has left behind the issues of legacy pollution that is still detrimental to the health of people decades after the end of contaminant discharges. The industrialization processes in the developing nations have resulted in massive pollution of the water resources by the industrial chemicals like the heavy metals and other toxic anions due to the rapid industrialization with little or no environmental controls [48].

These health concerns have given rise to more advanced solutions to water quality management [49]. The multi-barrier strategy to drinking water safety, focusing on protecting the source water, efficiently treating and distributing it, has become the standard of the safe drinking water provision . In this context, it is very important to consider the correct treatment technologies to apply to a particular contaminant, and this means that the chemistry of the contaminant, the performance of the treatment process, and the possibility of by-products need to be well understood [50].

The health problems that are related to anionic contaminants are as varied as the contaminants themselves . Among the most common anionic contaminants, nitrate is linked to methemoglobinemia (blue baby syndrome) among infants and has been reported to have unfavorable reproductive effects and some types of cancers in epidemiological literature [51]. At low doses, fluoride is considered to have beneficial effects on dental health, but at high dose, it leads to dental and skeletal fluorosis in millions of individuals globally. Arsenate, a typical type of arsenic in oxygenated water, is a known human carcinogen linked to skin, lung as well as bladder and kidney malignancies, cardiovascular illness, diabetes, and progress in development [52]. Although selenate is a vital micronutrient in low

doses, it is lethal in high doses leading to selenosis, with symptoms such as loss of hair and nails, gastrointestinal, and neurological damages.

Chromium(VI) compounds are the most toxic, carcinogenic, and common types of anionic pollutants that are found in factory discharges and in industrialized surroundings [53]. The next section gives an extensive analysis of chromium(VI) chemistry and sources, toxicity and the difficulties in eliminating chromium(VI) in water.

1.2.2. Chromium compounds in their oxidation state VI.

Chromium is a transitional metal and it can occur in a number of oxidation states, between -2 and +6 with trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) being the most stable and stable in the environment respectively [54]. These two oxidation forms have radically different chemical properties, toxicities and environmental behaviors. Under neutral to alkaline pH, Cr(III) is fairly insoluble and complexes with organic matter and is regarded as an essential micronutrient in glucose and lipid metabolism at lower concentrations [55]. Conversely, Cr(VI) compounds are very soluble and free to move in aqueous environments, and are very toxic and carcinogenic [56].

Chromium(VI) in aqueous solutions is a complex chemistry that is pH-dependent and can be present in a variety of different oxy-anionic forms depending on the solution pH and concentration of chromium: chromate (CrO_4^{2-}), hydrochromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$). In alkaline pH (greater than 6.5), chromate (CrO_4^{2-}) is the prevailing species, whereas in acidic and neutral environments (pH 1-6), hydrochromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) are predominant [57]. The balance between these species can be expressed as follows

$$HCrO_4^- = CrO_4^{2-} + H^+ \ (pKa=5.9)$$

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$$

The dichromate ion is the dominant one in higher concentrations of chromium and lower pH and chromate is the dominant species in dilute, alkaline conditions and the above relations are very fundamental in the environmental fate of chromium(VI) and the development of effective removal methods because the various Cr(VI) species do not have a similar charge, size and even affinity towards the adsorbent material [58].

Natural and anthropogenic sources of chromium(VI) into the aquatic environment are equal, but in contaminated regions, mostly anthropogenic sources are predominant and the natural ones are the weathering of minerals that have chromium, like chromite ($FeCr_2O_4$), and volcano emissions [59]. The

natural sources however contribute to environmental Cr(VI) concentrations that are usually low in comparison to the industrial releases.

The anthropogenic sources of chromium(VI) are very multiple and varied. Industrial processes that include chromium processing and use also contribute the largest. Metallurgical industry employs the use of chromium to produce stainless steel and other alloys and chromium is emitted in mining, smelting and manufacturing process [60]. The electroplating and metal finishing sectors contribute to one of the important aspects, where chromic acid baths are used to deposit chromium on the metal surfaces, and rinse waters and spent plating solutions are highly concentrated with Cr(VI). Historically, chromium salts were used in the leather tanning industry, where chromium-contaminated effluents coming out of tanneries were extensively contaminating the environment [61]. In the dyeing processes in the textile industry, chromium compounds are used as mordants, and they add to Cr(VI) in the dye house wastewaters. Others are wood preservation, where chromated copper arsenate (CCA) has been extensively utilized, in pigment production, and refractory materials production [62].

Another route of entry of chromium in aquatic systems is through atmospheric deposition. The burning of fossil fuels and the burning of coal, in particular, emits chromium to the atmosphere, which is then deposited on the land and water surfaces [63]. Atmospheric emissions of chromium are also produced by waste incineration and cement production [33]. Once deposited, chromium may be carried to a surface water by means of runoff or enter the groundwater and continues its contamination cycle [64].

The acuteness of chromium(VI) materials to humans and other creatures has been widely reported. The toxicity of Cr(VI) is the most toxic of the two due to variations in cellular uptake and the mechanism of action of the different metal. The chromate oxyanion (CrO_4^{2-}) structurally related to sulfate (SO_4^{2-}), phosphate (HPO_4^{2-}), it can find its way to the cells via nonspecific anion channels [65]. The Cr(VI) is reduced by reactive intermediates by rapidly reducing the Cr(VI) to the final form of Cr(III) once inside the cell, involving Cr(V) and Cr(IV). In this process of reduction, there is the generation of reactive oxygen species (ROS), leading to oxidative stress, DNA damage and lipid peroxidation [66]. The resulting Cr(III) is capable of stable complexation with the cellular macromolecules such as DNA and proteins which leads to genotoxicity and mutagenesis.

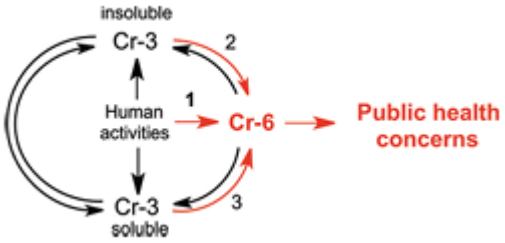

Fig 3. Origin and interconversion of different forms of Cr in water. Route 1 is the most important overall source of Cr(VI), whereas route 2 describes the most important natural process of Cr(VI) formation.[53]

Carcinogenicity of chromium(VI) compounds has been solidly supported by epidemiological studies of occupationally exposed workers as well as experimental animal studies [67]. International Agency of Research on Cancer (IARC) has categorized chromium(VI) compounds in Group 1 carcinogens, i.e., carcinogenic to human beings and exposure to Cr(VI) through inhalation in work places, which include chromate manufacturing, chrome plating and stainless steel welding, is linked to a higher risk of lung cancer. Epidemiological research articles have indicated that there are considerable higher rates of mortality related to lung cancer in workers with Cr(VI) exposure and the risk is increased with total exposure [68].

Other deleterious health effects linked to exposure to chromium(VI) in addition to lung cancer have been noted [69]. Contact dermatitis, skin ulcers (chrome ulcers), allergic reactions in sensitized people may be the result of dermal exposure and exposure to Cr(VI) in large amounts in drinking water may lead to gastrointestinal distress, manifesting as abdominal pain, nausea, vomiting and diarrhea [70]. Chronic oral exposure has been shown to affect the liver, kidney, and the hematopoietic system as well as possible reproductive and developmental toxicity [71].

Reproductive and developmental consequences of chromium(VI) have gained more and more attention over the last few years . There have been animal studies that have found negative effects on male reproductive parameters such as low sperm count, motility, and histopathological alterations in the testicular tissue. Some of the reproductive effects of female sex are alterations in the estrous cyclicity, decreased fertility, and poor pregnancy outcomes. In developmental toxicity research, Cr(VI) has been found to cause fetal growth retardation, skeletal defects, and behavioral alterations in children when a pregnant mother is exposed to the chemical. Human epidemiology research on the effects of Cr(VI) on human populations in the form of contaminated drinking water has cited the relationship of higher incidences of spontaneous abortion, congenital malformation, and low birth weight, but the evidence has been inadequately studied and needs to be further expounded [72].

A new concern is the neurotoxicity of chromium(VI). A study in animals has shown that exposure to Cr(VI) can penetrate through the blood-brain barrier and build up in the brain tissue, inducing oxidative stress, neuroinflammation, and changes in neurotransmitter levels . Learning and memory have been impaired in behavioral studies after exposure to Cr(VI). The neurodevelopmental impacts of early-life exposure to Cr(VI) are especially worrisome since the growing nervous system is vulnerable to toxic insults at this stage [73].

Chromium(VI) has been reported to be immunotoxic and Chromium compounds have the ability to regulate immune functions and both immunosuppressive and immunostimulatory effects have been reported to depend on the conditions of exposure [74]. The occupational health problem of chromium exposure in workers is well-known workers developing hypersensitivity reactions to chromium in the form of allergic contact dermatitis. Recent research has further proposed that the exposure to Cr(VI) can as well impact the systemic immune functions that can predispose one to infections and alteration of the immune-based disease pathophysiology [75].

Due to its high toxicity, carcinogenicity and prevalence in the environment, elimination of chromium(VI) in polluted water has been a priority to environmental protection and human health [76]. Chromium in drinking water has serious regulations set by regulatory agencies across the world. The maximum contaminant level (MCL) of total chromium established by the United States Environmental Protection Agency (USEPA) is 0.1 mg/L, but some individual states (such as California) have established a more restrictive limit of chromium(VI) (0.01 mg/L). European Union has established a parametric level of 0.05mg/L of total chromium in drinking water. The total chromium value recommended in the World Health Organization is 0.05 mg/L, which was noted to be protective with Cr(VI) under the assumption that all the chromium present is in the hexavalent form [77].

Some available technologies in the removal of chromium(VI) in water include reduction-precipitation, ion exchange, membrane filtration, electrochemical treatment and adsorption. Reduction-precipitation is the chemical reduction of Cr(VI) to Cr(III) by reducing agents, e.g. ferrous sulfate, sodium bisulfite, or sulfur dioxide then the reduction of the Cr(III) hydroxide at alkaline pH . The technique is commonly applied in the treatment of industrial wastewater but it produces large amounts of sludge that need to be disposed of [78]. Anion exchange resins Ion exchange can effectively do a good job of removing Cr(VI) oxyanions, with high removal efficiencies, but the resins are costly, and must be regenerated, resulting in concentrated brines that must be further handled . It can also be excellently removed by membrane processes, such as reverse osmosis and nanofiltration, which are energy-intensive processes vulnerable to fouling. Electrochemical techniques, including

electrocoagulation and electroreduction have the benefit of paying little attention to the quantity of chemicals added, but need electrical power and can be also very costly in terms of capital investment [79].

One of such technologies is adsorption which has proved to be one of the most promising methods of removing chromium(VI) especially in decentralized water treatment and also in polishing treated effluents to fit the high discharge requirements [80]. Adsorption has the following benefits namely; simplicity of operation, low cost, design flexibility and possibility of adsorbent regeneration and chromium recovery. The success of adsorption mechanisms is highly influenced by the characteristics of adsorbent material that encompasses the surface area, surface charge, chemistry of functional groups, and selectivity towards Cr(VI) species.

The layered double hydroxides have received special interest as adsorbent of chromium(VI) owing to their special properties combination [81]. They have a high positive surface charge that gives them strong electrostatic attraction to anionic species of Cr(VI) and large surface areas and interlayers spaces allow many binding sites. Exchange of interlayer anions permits LDHs to absorb chromate by ion exchanges and their memory effect on rehydration and calcification gives further avenues to chromium immobilization [5]. The next section is an in-depth review of the adsorption capacity of LDHs to chromium(VI) and other anions.

1.3. ADSORPTION PERFORMANCE OF LDHs

Among the most promising adsorbent material to remove anionic pollutants in aqueous solutions is the Layered Double Hydroxides. Their physicochemical properties, such as high anion exchange capacity, high surface area, positively charged layers, and the capacity to reorganize their structure, in particular to take in hazardous anions, chromate, arsenate, and phosphate, make them especially useful. The process of adsorption by LDHs is affected by a great number of factors, which are the composition of the metal hydroxide layers, the character of interlayer anions, the method of the synthesis and the conditions used in adsorption experiments [12].

The way of adsorbing anion on the LDHs is a set of complementary processes and the first one is anion exchange, the initial interlayer anions that were initially in the LDH structure are substituted with the target anions in solution [82]. This is made possible by labile interlayer anions and the electrostatic affinity between the positively charged layers and the anionic species. Normal anion exchange capacity of LDHs is 2-4 mEq/g, depending on the density of the layer charge and the molar

ratio of M^{2+}/M^{3+} [83]. An increase in the trivalent metal content enhances the layer charge and hence the anion exchange capacity but this must be offset against the requirement of structural stability.

A second mechanism of adsorption is the surface complexation, an inner-sphere or outer-sphere complexation between the anionic species and the hydroxyl groups on the surface of the LDH particles [84]. Surveillance of surface -OH groups, especially of trivalent metal cations, offers a high number of binding sites of the anion attachment due to the ligand exchange mechanisms. This is adsorption via surface that is especially significant in the case of oxyanions like chromate and arsenate that may develop stable complexes with metal centers in the LDH surface [85].

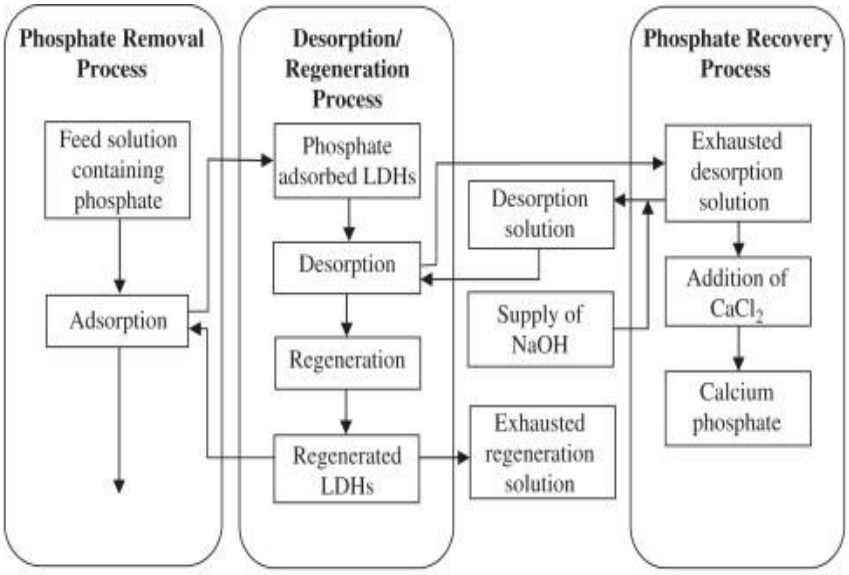

Fig. 4. Schematic diagram of the system for PO_4^{3-} removal/recover ,regeneration of LDHs, and regeneration of desorption solution [39].

The third is a unique mechanism of the calcined LDHs; it is the so-called memory effect [5]. At moderate temperatures (usually 400-500°C), (LDHs) dehydroxylate and lose their interlayer anions to yield mixed metal oxides and When reacted with aqueous solutions of anions, these mixed oxides can regenerate the initial layered structure, with anions of the solution incorporated in the interlayer galleries and this leads to increased adsorption capacities in many instances relative to the pristine LDHs, since the reconstruction process may be able to receive a larger amount of anions and may also uncover new adsorption sites [86].

The pH of the solution is also known to depend on the adsorption performance of LDHs. LDH particle surface charge is influenced by pH, which influences the activity of their electrostatic interactions with anionic adsorbates. In low PH, the LDH surface is protonated which increases its

positive charge and intensifies the electrostatic attraction of anion. Unwarranted low pH may, however, result in partial dissolution of the LDH structure especially on materials that contain highly soluble divalent cations. Competition with hydroxide ions may inhibit uptake of the anions at high pH values, and LDH surface could become deprotonated reducing the positive charge [87]. Optimal pH adsorption of anion is mostly in the slightly acidic to neutral range where the electrostatic attraction is the most efficient without compromising the structural integrity.

The first level of concentration of the target anion and the contact time of the solution and adsorbent are the most important parameters which influence the adsorption performance. It offers much information on the capacity of adsorption and affinity by adsorption isotherms, which are the distribution of adsorbate between the solid and liquid phases at equilibrium. The data of adsorption of LDH is often modeled using the Langmuir isotherm model which assumes that monolayer adsorption occurs on homogeneous binding sites. The Langmuir model of adsorption capacity maximization permits comparing the various LDH materials and optimization of their composition to a particular application. Freundlich isotherm model used to describe adsorption on heterogeneous surfaces is also widely used [88].

Kinetics of adsorption explain the speed of adsorption of the ions in the solution and give evidence regarding the adsorption process. The two most commonly used pseudo-first-order and pseudo-second-order kinetic models have been used to analyze LDH adsorption data [89]. Pseudo-second-order model: This model is commonly the most effective fit to LDH adsorption systems, and is based on the assumption that the rate-limiting step is chemisorption, meaning that the adsorption process is controlled by chemical interactions between anions and surface sites. The intra-particle diffusion models can determine whether diffusion in the films is in control of the overall adsorption rate [90].

Competing anions should be considered when the target pollutants are adsorbed which is relevant in practice. Natural waters and wastewaters usually have diverse anions that may outcompete the target pollutant with adsorption sites on LDHs. Typical counter ions are chloride, sulfate, nitrate, carbonate and phosphate. The specificity of LDHs to various anions is governed by a general order of anions charge density and size $CO_3^{2-} > SO_4^{2-} > HPO_4^{2-} > OH^- > F^- > Cl^- > NO_3^-$ [91]. The affinity of LDHs to carbonate is especially high and since carbonate is abundant in natural waters, it has the ability to strong compete with target anions like chromate. This competition has to be taken into consideration during the realization of the LDH performance in the real conditions.

The reusability and regeneration of LDH adsorbents are also important aspects to apply them practically and economic feasibility. Rather spent LDHs can be regenerated in a number of ways, such as by exposure to strong salt solutions that push off anion adsorbates, by calcinations then rehydration, or alkaline solution treatment . The regeneration efficiency is related to the intensity of anion binding and the stability of the LDH structure in the process of regeneration. A series of adsorption-regeneration cycles are usually researched to determine the service life and structural integrity of LDH materials in the long term [92].

1.3.1. Adsorption of chromium(VI) by LDHs

The utilization of the layered double hydroxides in the disposal of chromium(VI) in aqueous solutions has received a lot of exploration during the last 20 years. The toxicity and rampant presence of Cr(VI) in industrial effluents have necessitated the exploration of effective and cost-effective removal technologies and LDHs have proved to be one of the most promising tools in the category of adsorbents. It has been shown that LDHs can obtain high Cr(VI) removal efficiencies (highly exceeding 90% under idealized conditions) and adsorption capacities as high as 20-200mg/g (depending on the LDH composition and experimental parameters) [93].

Cr(VI) adsorption by LDHs takes place by a complex of anion exchange and complexation of the surface [94]. Electrostatically the chromate oxyanion (CrO_4^{2-}) and its protonated form ($HCrO_4^{2-}$) are attracted to the positively charged layers of LDH and are capable of replacing interlayer anions. At the same time, the species of chromates are able to generate inner-sphere complexes with surface hydroxyl groups, especially with those that are attributed to aluminum and other trivalent metal centers of the LDH structure. The contribution of these mechanisms relative to each other is dependent on the LDH composition, the pH of the solution and the availability of competing anions [95].

The LDH composition has been systematic in the effects it has on the performance of adsorption of Cr(VI). The most commonly studied system is the binary MgAl-LDHs which usually have adsorption capacities of Cr(VI) in the range of 40-120 mg/g. The adsorption capacity rises with the concentration of aluminum to an optimal rate of about 3:1 (M^{2+}/M^{3+}) where further addition leads to structural instability and decreased performance. The addition of transition metals like copper, zinc, nickel and iron to the LDH Layer has been reported to increase the adsorption of Cr(VI) in several ways [27].

The latterform of copper-substituted LDHs have also been of special interest in the removal of Cr(VI). The existence of copper within the hydroxide layers includes redox-active centers which are capable of playing the role of reducing Cr(VI) into the less toxic Cr(III) [27]. Such a reduction can be done by transfer of electrons of Cu(I) species and can be produced under specific circumstances or by photocatalytic reactions consisting of copper centers . The lower Cr(III) may then be precipitated as Cr(OH)3 or may enter into stable complexes with LDH structure offering another route of chromium immobilization other than simple adsorption. Cu LDHs have been studied with improved Cr(VI) removal capacities than the corresponding MgAl-LDHs with values up to and over 150 mg/g [96].

Zinc-replaced LDHs have also shown a good performance in adsorption of Cr(VI). Zinc can be incorporated in the LDH structure to alter the distribution of the layer charges and may be used to enhance the affinity of the material to oxyanions [97]. LDHs that contain zinc tend to be more crystalline and stable to temperatures, which could aid in their adsorption efficacy. Also, photocatalytic reduction of Cr(VI) can also be achieved by use of the semiconductor properties of zinc oxide domains that could be developed during partial decomposition of Zn-containing LDHs when subjected to UV or visible light irradiation [98].

The tertiary Mg-Cu-Zn-Al LDH system considered in this thesis is an endeavor to achieve the positive attributes of several metal cations with one commodity. It is anticipated that the synergistic relationship between magnesium, copper and zinc in the LDH layers will improve the Cr(VI) adsorption due to complementary reaction. Magnesium also offers the structural framework and aids in the exchange of anions, copper adds redox potential to Cr(VI) reduction and zinc alters surface charge and can also contribute to photocatalytic action. This combination in an optimum proportion provides the possibility of excellent performance of Cr(VI) removal than simpler binary or ternary systems [40].

The interlayer anions characteristically play a key role in determining the performance of LDHs in the adsorption of Cr(VI). In most cases, LDHs with monovalent anions, including chloride or nitrate, have higher anion exchange rates and anion exchange capacities than those with carbonate, which is highly affinity of the layers and hard to remove. LDHs that are intercalated with chloride are of special use in Cr(VI) uptake as chloride ions are easily replaceable with chromate species in solution. Nevertheless, carbonate-loaded LDHs are more stable and could be used in the processes where a slow release of anions is required [99]. The study of the difference of LDH-CO3 and LDH-Cl forms of the same LDH composition, which is being conducted in this thesis, offers an interesting scope of information about the necessity of interlayer anions in adsorption of Cr(VI) [5].

Kinetics of Cr(VI) adsorption on LDHs is usually quick, where large part of the uptake took place during the initial few hours of contact [100]. The pseudo-second-order kinetic models can generally be the most appropriate to fit the experimental results, and it is necessary to state that the rate-limiting step is chemisorption. Some of the factors affecting the adsorption rate include the concentration of the starting concentration of Cr(VI), dosage of the adsorbent, temperature and mixing conditions. An increase in temperature can also reduce the kinetics of adsorption, as well as increase adsorption capacity, indicating that adsorption is endothermic in most LDH systems [101].

Langmuir isotherms commonly explain adsorption of Cr(VI) onto LDHs, which is a monolayer adsorption on the homogeneous binding sites. The Langmuir maximum adsorption capacity (q) is a convenient parameter to use in the comparison of various LDH materials. Relative (q) values of Cr(VI) adsorption on different LDHs are quite varied and range over 20 mg/g in the case of some carbonate-intercalated MgAl-LDHs to above 200 mg/g in favorable conditions . In other situations the Freundlich model also fits well, which is the surface heterogeneity, and multilayer adsorption effects at higher Cr(VI) concentrations [102].

The impact of the solution pH on adsorption of Cr(VI) by LDHs is complicated because it has effect on adsorbent surface charge and the speciation of Cr(VI). The optimum adsorption point is usually found within the pH of 5-7 in which the LDH surface is still in its positively charged state and the Cr(VI) is predominantly in the form of HCrO4- and CrO42- anions that can easily be exchanged with ions. When the pH is low, there is a probability that the LDH structure will be partially dissolved and adsorption capacity will decrease . Higher pH values lead to more competition with hydroxide ion and the surface of LDH may get less positive in charge, reducing electrostatic attraction with chromate anions [103].

Solution presence of competing anions may greatly slow down the adsorption of Cr(VI) on LDHs . Carbonate and phosphate are very strong competitors because they are highly charged and bind to the LDH binding sites . Competition between sulfate and chloride and nitrate are also good competitors . The specificity of the LDHs to various anions is in keeping with the overall hierarchy mentioned above, with chromate having intermediate affinity towards the strongly binding divalent anions and the weakly binding monovalent anions [104]. The knowledge of these competitive effects is vital in forecasting the behavior of LDH in actual wastewater treatment outlay where there is a combination of anions.

In a number of studies, regeneration and reuse of LDH adsorbents in the removal of Cr(VI) has been tested [105]. Treatment with alkaline solutions (e.g. NaOH or Na_2CO_3) to remove adsorbed chromate, followed by washing and re-equilibration in the treatment process are all previous successes .

Alternatively, adsorbed organic matter on the spent LDHs can be removed by calcination at moderate temperatures and the mixed metal oxide precursor can be regenerated which can be rehydrated to reassemble the LDH structure with new interlayer anions . The LDH composition and a regeneration technique allow determining the number of adsorption-regeneration cycles without noticeable loss of capacity [104].

The interaction mechanisms of Cr(VI) with LDHs have been clarified with the help of different characterization methods. The X-ray diffraction (XRD) of the LDHs following adsorption of Cr(VI) is usually characterized by the variation in basal spacing in relation to the insertion of chromate anions into the galleries composed of layers . The FTIR spectrum shows new absorption bands that have been attributed to chromate species in the LDH structure, which confirms their existence in the LDH structure [105]. X-ray photoelectron spectroscopy (XPS) may be used to determine the oxidation state of chromium on LDH surface differentiating between adsorbed Cr(VI) and reduced Cr(III) species. The method has proven useful especially in the illustration of the decrease of Cr(VI) to Cr(III) on the substituted transition metal-substituted LDHs [105].

2. EXPERIMENTAL

2.1. Reagents

$Mg(NO_3)_2 \cdot 6H_2O$ (CarlRoth), $Al(NO_3)_3 \cdot 9H_2O$ (CarlRoth), $Cu(NO_3)_2 \cdot 2.5H_2O$ (SigmaAldrich), $Fe(NO_3)_3 \cdot 9H_2O$ (SigmaAldrich), $Zn(NO_3)_2 \cdot 6H_2O$ (CarlRoth), Na_2CO_3 (CarlRoth), NaOH (CarlRoth), NaCl (POCh), HCl 36% (POCh), H_2SO_4 95% (POCh), K_2CrO_4 (SigmaAldrich), Na_2HPO_4 (POCh). All chemical reagents used were of analytical grade without additional purification.

2.2. Synthesis

LDH materials (Mg_2Al_1, and $Mg_2Cu_{0.5}Zn_{0.5}Al_1$) were synthesized by the co-precipitation method. The cationic solution (150 mL) composed of appropriate amounts of metal nitrates ($Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$) was prepared and added dropwise to Na_2CO_3 solution with a concentration of 1 mol/L (100 mL) under vigorous stirring. The solution was maintained at a pH about 10 using the NaOH solution. After adding the whole cationic solution, the mixture was stirred, initially while heating at 80 °C for 3 h and then at room temperature for 24 h. The solution was vacuum filtered and the precipitate was washed with distilled water until the washing will register a pH of 7.0. The precipitate was dried in an oven at 70 °C for 24 h, and then ground in a mortar.

Anion exchange was performed in 250 mL of a 2 mol/L NaCl solution with addition of hydrochloric acid (to maintain pH at 7). 1 g of LDH-CO_3 was used. The reaction was carried out at room temperature with stirring for 24 h. The final products (LDH-Cl) were obtained by vacuum filtration without any additional washing followed by drying for 8 h at 70 °C.

The schematic diagrams for sample preparation are shown in Fig. 5.

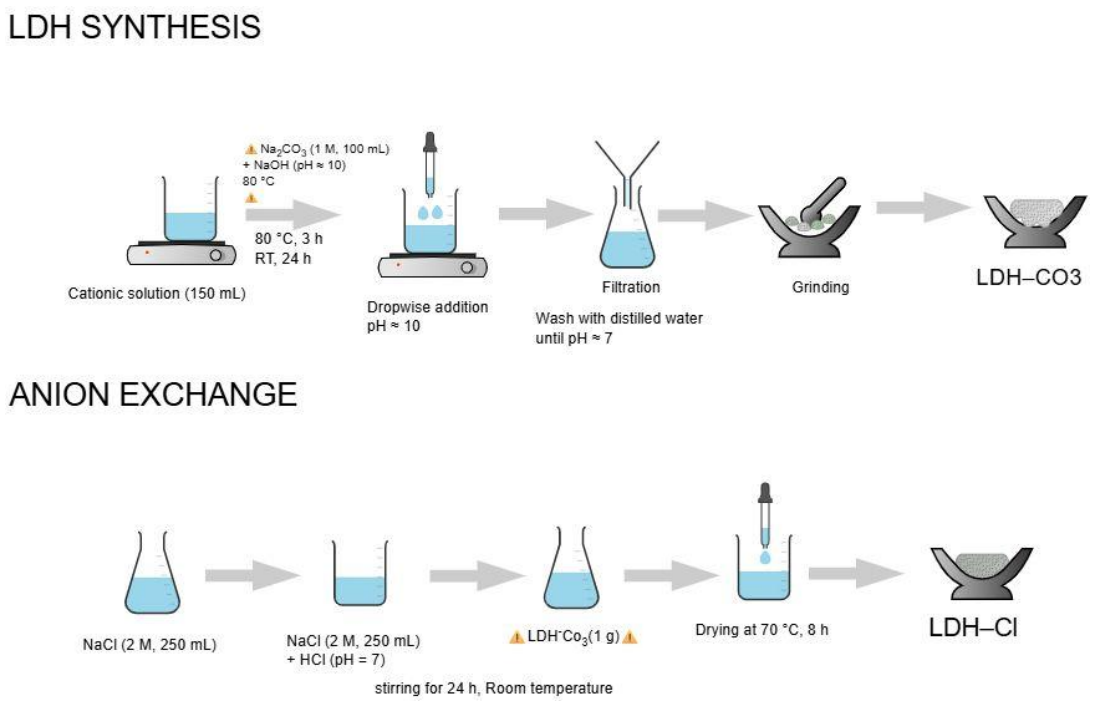

Fig. 5. Schematic diagrams for the LDHs preparation.

2.3. Characterization

The synthesized adsorbents were characterized by thermal analyses applying the thermogravimetric (TG) and differential scanning calorimetry (DSC) methods using the SETSYS16/18 analyzer (Setaram). The samples (about 8-10 mg) were heated in the alumina open cruicibles in the temperature range of 30-1000 °C at a heating rate of 10 °C/min in the dynamic air atmosphere (v=0.75 L/h). Fourier transform infrared spectroscopy (FTIR) of obtained materials was performed using an Alpha spectrometer (Bruker, Inc., Germany) in the wavenumber range from 4000 to 450 cm^{-1}, with a resolution of 4 cm^{-1}. Powder X-ray diffraction (XRD) patterns were registered using a Rigaku MiniFlex II diffractometer. The specific surface area was measured by the Brunauer–Emmet–Teller (BET) method under vacuum for degassed at 120 °C samples by N_2 adsorption-desorption isotherm (at 77 K) using a Tristar II instrument (Norcross, GA, USA). The pore size distribution of the material produced was obtained using the Barrett–Joyner–Halenda (BJH) method. Scanning electron microscopy (SEM) images were taken for the description of surface morphology using Hitachi TM3000. The concentration of Mg, Al, Cu, and Zn ions in the solutions was determined by ICP-OES. Quantitative elemental analysis of the solid MgCuZnAl-LDH samples was performed using a Perkin Elmer Optima 7000DV inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin-Elmer, Waltham, MA, USA). A blank sample was used - 5% HNO_3 nitric acid solution. Standard

solutions of all analyzed metals (Mg, Al, Cu, Zn, Cr) were also used (single-element ICP standard, 1000 mg/L, Roth). All analyses described above were carried out before and after the Cr(VI) ion sorption processes. Sorption of CrO_4^{2-} ions on the obtained LDH materials was carried out in a system containing 0.025 g of the sorbent sample and 25 mL of K_2CrO_4 solution with a concentration of 0.5 mmol/L. The sorption process took place at room temperature. The shaking time was 1, 2 or 24 h for preliminary (screening) tests. A mechanical shaker was used to contact the phases. After the specified time, the systems were filtered and then the concentration of Cr(VI) in the solution was determined by ICP-MS method. Calculations concerning the sorption of chromate ions were performed based on the following equations:

$$c_s = \frac{c_{in} - c_{eq}}{m} \cdot V \quad (1)$$

$$\%A = \frac{c_{in} - c_{eq}}{c_{in}} \cdot 100 \quad (2)$$

where: c_s refers to the amount of adsorbed Cr(VI) adsorbed (mol/g), c_{in} is the concentration of Cr(VI) ions in the initial solution, c_{eq} is the concentration of Cr(VI) ions in the solutions after sorption (mol/L), $\%A$ is the percentage of sorption, m is the mass of the corresponding LDH expressed in g, and V is the volume of the solution used for sorption.

3. RESULTS AND DISCUSSION

3.1. *Synthesis of LDH-CO_3 and LDH-Cl forms of $Mg_2Cu_{0.5}Zn_{0.5}Al_1$*

XRD data analysis indicates that the synthesized sorbents exhibit a characteristic pattern for LDH materials (Fig.6) [5]. Based on the shifts of the 003 basal diffraction peak position, effective ion exchange was confirmed, consisting in replacing a significant amount of carbonate ions with chloride ions in the LDH interlayer.

The FTIR spectrum of $Mg_2CuZnAl$ sample before chromate(VI) sorption is shown in Fig. 7. In the $Mg_2CuZnAl$-CO_3 spectrum the strong band at 1358 cm^{-1} is attributed to stretching vibrations of carbonate anions (CO_3^{2-}) from the interlayer. The absorption bands in the range of 500–1000 cm^{-1} are caused by vibrations of the hydrotalcite structure in the LDH network, i.e. Mg-O / Al-O / O-Al-O / O-Mg-O, Al-OH and H_2O groups.

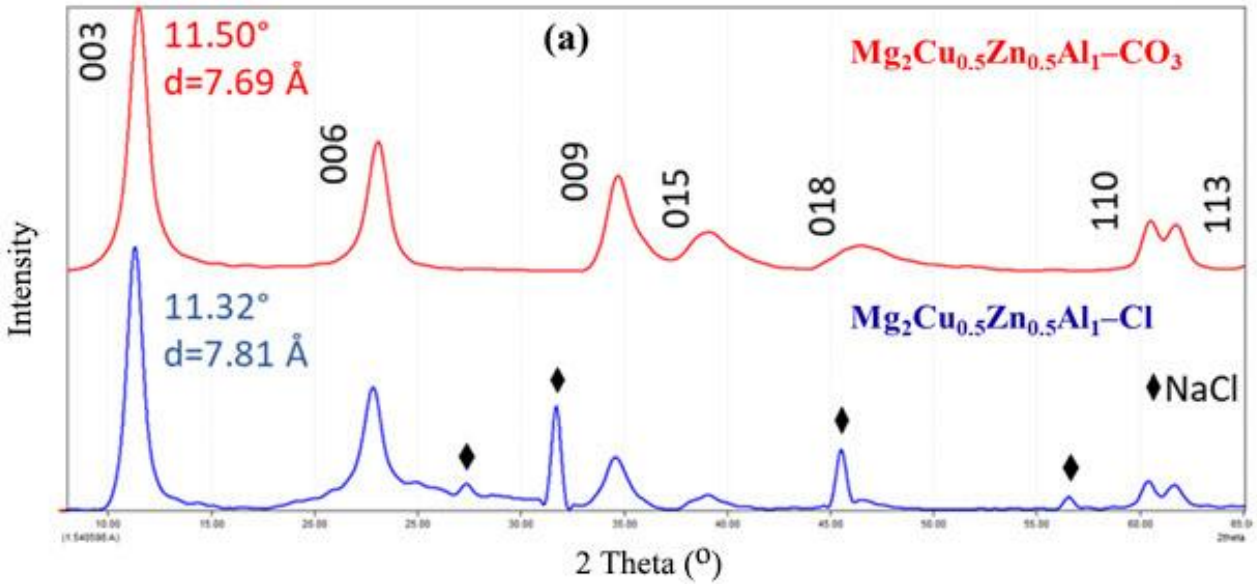

Fig. 6. Powder XRD patterns of LDH-CO_3 and LDH-Cl forms of $Mg_2Cu_{0.5}Zn_{0.5}Al_1$ before CrO_4^{2-} sorption.

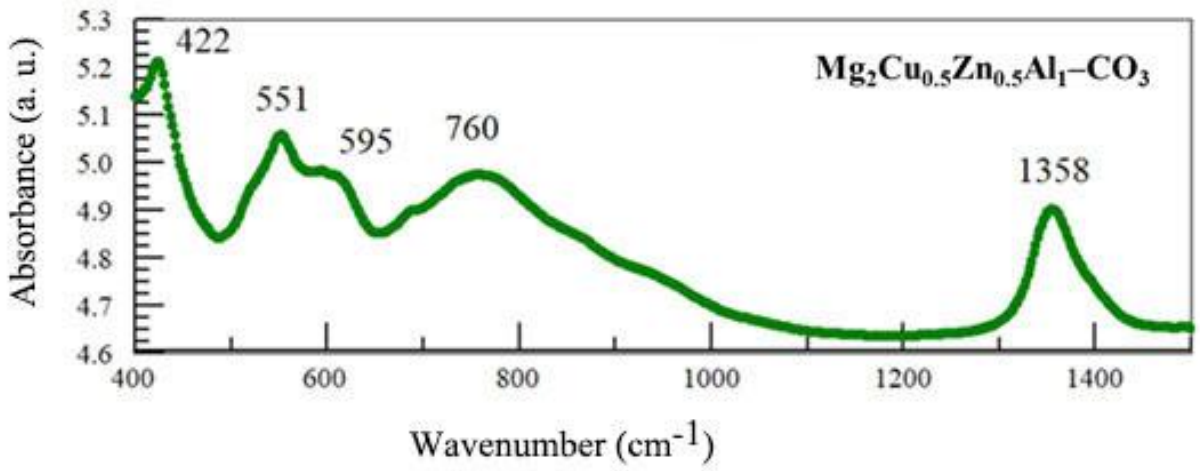

Fig. 7. FTIR spectrum of LDH-CO_3 form of $Mg_2Cu_{0.5}Zn_{0.5}Al_1$ before CrO_4^{2-} sorption.

SEM images (Fig. 8) show the morphology of the Mg2CuZnAl–Cl sample surface before Cr(VI) ion adsorption. As seen, a plate-like structure typical of hydrotalcite materials is visible, consisting of irregular, thin plates forming loose agglomerates.

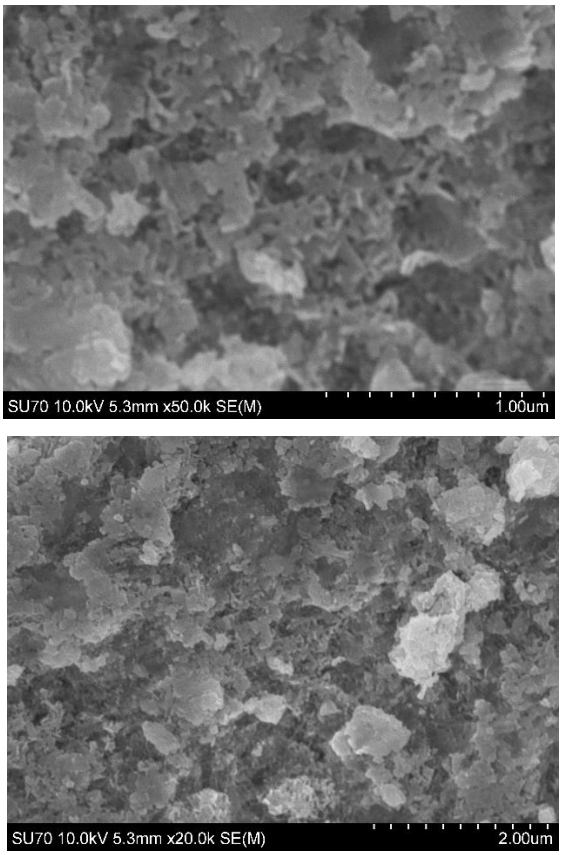

Fig. 8. SEM images of MgCuZnAl–LDH–Cl samples before adsorption obtained at different magnifications.

3.2. Sorption of Cr(VI) anions from solutions

Initially, screening tests were carried out using all six LDHs in order to select the most effective sorbent. The form of the adsorbent (LDH-CO3 or LDH-Cl), the weight of the sample (0.025, 0.05 or 0.1 g) and the phase contact time (1 or 2 or 24 h) were taken into account. The adsorption processes of chromate(VI) anions was successfully carried out on all synthesized materials. Generally, higher sorption parameters were obtained for layered double hydroxides in the chloride form, compared to the carbonate one, while the best adsorption capacity for analyzed ions was demonstrated by LDHs containing copper and zinc ions in their structure. Sorbents $Mg_2Cu_{0.5}Zn_{0.5}Al_1$ ($Mg_2CuZnAl\text{-}CO_3$ or $Mg_2CuZnAl$-Cl) were selected as the best one and used for the further sorption experiments.

Sorption studies have shown that $Mg_2CuZnAl$-Cl is a better chromium sorbent (Fig. 9), with the sorption capacity value being 1.35 mmol/g, compared to the $Mg_2CuZnAl\text{-}CO_3$ form, which is 0.65 mmol/g (see Figs. 9 and 10).

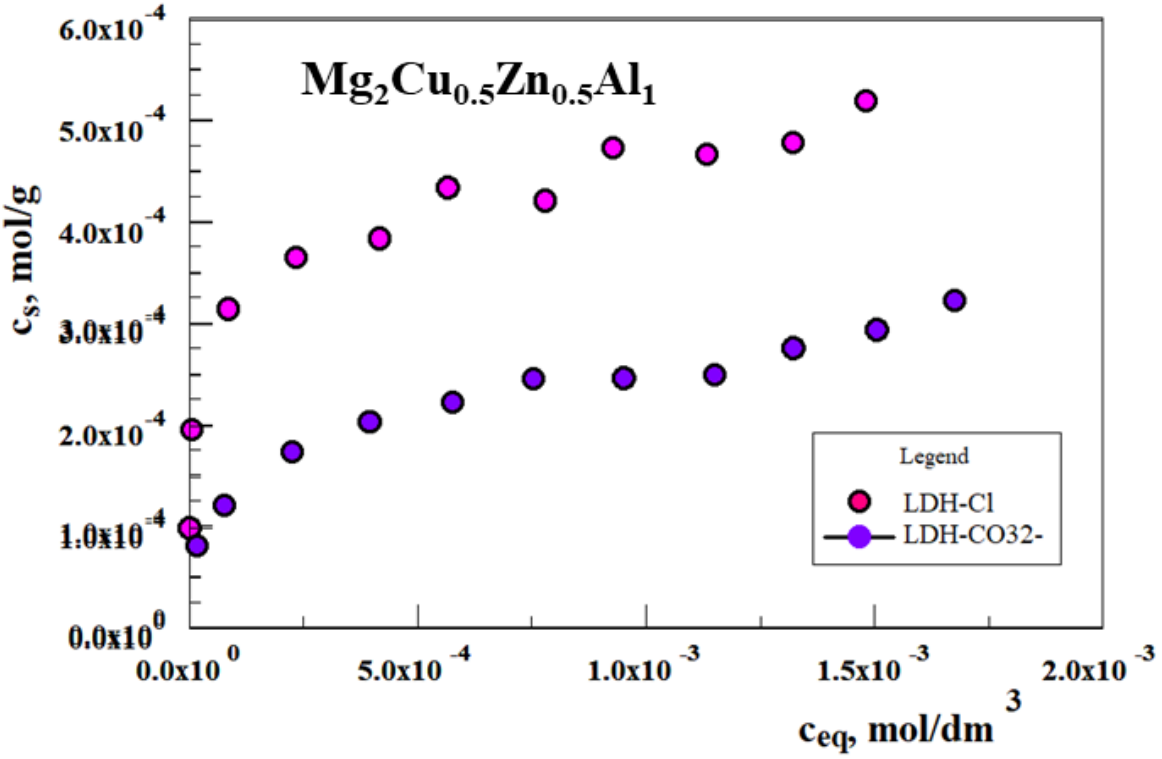

Fig. 9. Changes in the sorption quantity on $Mg_2CuZnAl$-Cl and $Mg_2CuZnAl\text{-}CO_3$ forms depending on the initial concentration of Cr(VI).

The obtained results indicate that both the chemical nature and the type of interlayer anion determine the complex mechanism of Cr(VI) adsorption on the tested materials.

One of the most important factors determining the adsorption mechanism is the solution pH, as it influences both the speciation of Cr(VI) ions in the solution and the surface charge of the adsorbent.

The effect of pH on the sorption process of chromate ions (Cr(VI)) onto $Mg_2CuZnAl$ in its carbonate and chloride forms was studied over an initial pH range of 4 to 11. Significant changes in sorption efficiency were observed within the studied pH range - the highest Cr(VI) removal occurred in an acidic environment, while the process efficiency gradually decreased with increasing pH. Fig. 11 shows the dependence of the partition constant Kd of chromate ions Cr(VI) on the initial pH value of the solution. The partition constant decreases significantly with the increasing pH. This is primarily due to the increasing concentration of OH^- ions, which compete with Cr(VI) ions for sorption sites in the LDH material. Sorption occurs primarily due to the ion exchange:

$$Mg_2CuZnAl\text{-}Cl + OH^- \rightarrow Mg2CuZnAl\text{-}OH + Cl^- \quad (3)$$

$$Mg_2CuZnAl\text{-}CO_3 + 2OH^- \rightarrow Mg_2CuZnAl\text{-}(OH)_2 + CO_3^{2-} \quad (4)$$

This is the dominant mechanism in the case of chromate sorption on $Mg_2CuZnAl$ with carbonate and chloride anions in the interlayer. The LDH structure has a positive layer charge and strongly bound carbonates in the interlayer, i.e. anions with a high charge and low mobility. The carbonate anion has a low exchange capacity because it is strongly bound by hydrogen bonds to the layers, and its charge (–2) and symmetry make it thermodynamically preferred. Thus, the exchange reaction:

$$Mg_2CuZnAl\text{-}CO_3 + 2HCrO_4^- \rightarrow Mg_2CuZnAl\text{-}(HCrO_4)_2 + CO_3^{2-} \quad (5)$$

between chromate and carbonate ions can only minimally occupy exchangeable surface positions, but not deep within the interlayer. However, in the case of LDH-Cl, i.e. if some of the interlayer anions are $Cl^–$, their bond is weaker than $CO_3^{2–}$ and then Cr(VI) can partially enter through exchange:

$$Mg_2CuZnAl\text{-}Cl + HCrO_4^- \rightarrow Mg_2CuZnAl\text{-}HCrO_4 + Cl^- \quad (6)$$

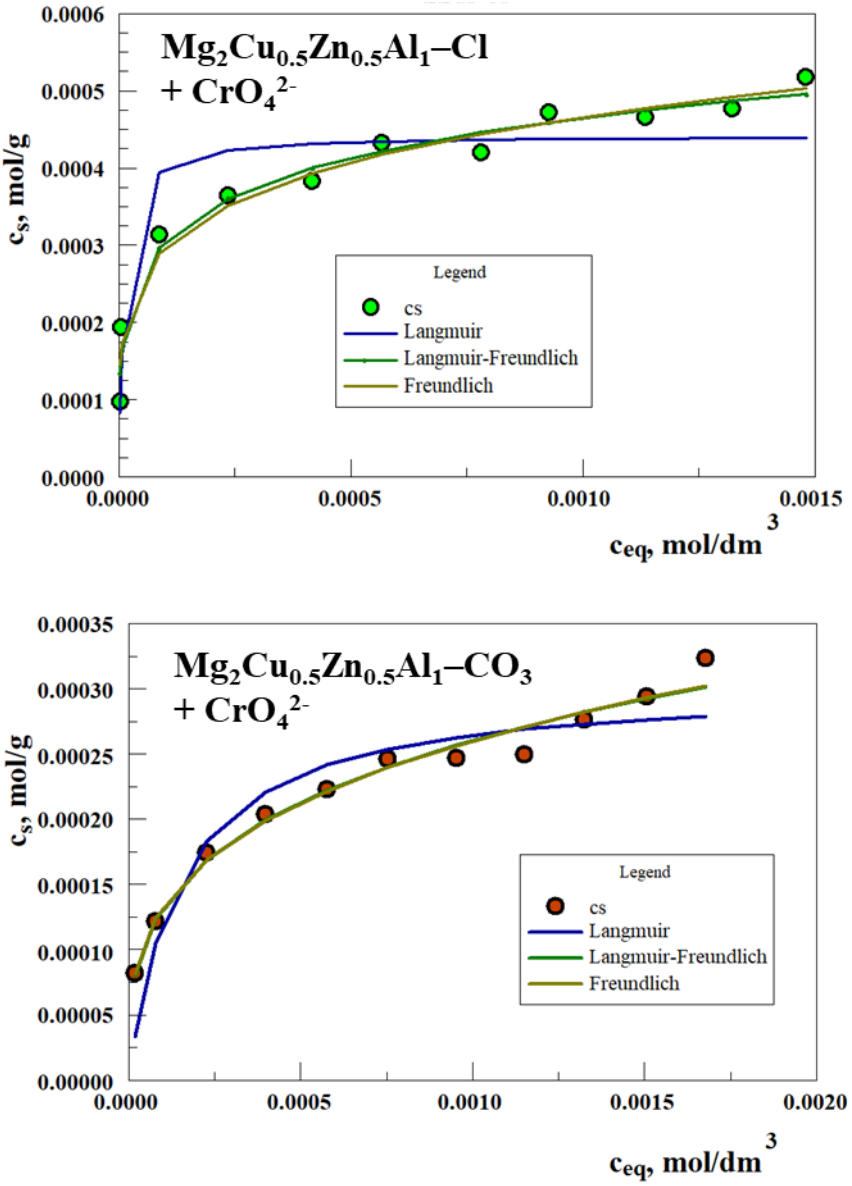

Fig. 10. Sorption isotherms for Cr(VI) ions on $Mg_2CuZnAl$-Cl (a) and $Mg_2CuZnAl$-CO_3 (b) forms of sorbent.

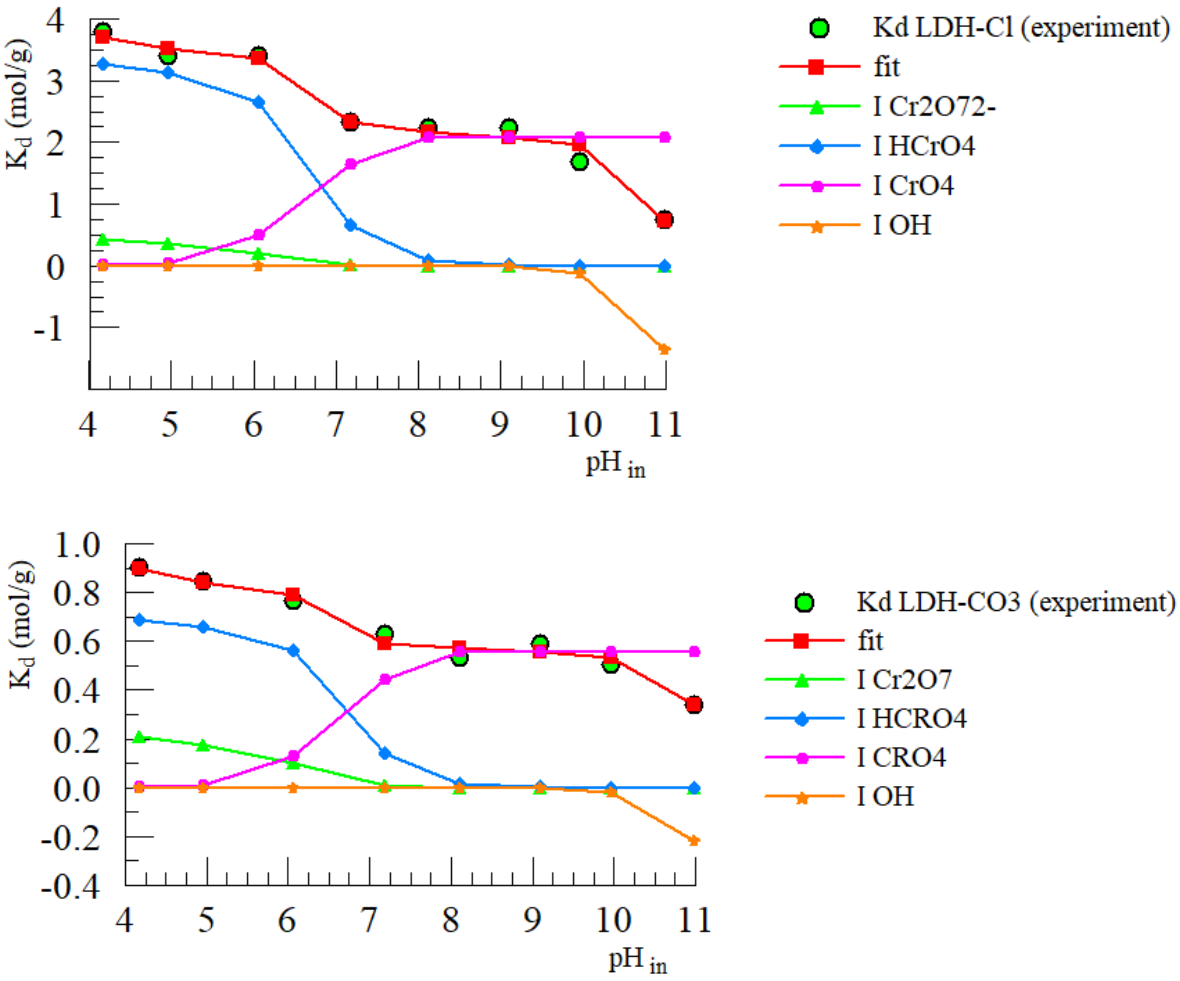

Fig. 11. Dependence of the Kd coefficient on the pH of the initial solution.

Cr(VI) anions can also coordinate with surface metals (Mg^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}) and form inner-sphere complexes as a mechanism of chemisorption without electron transfer.

In the studied system chromate ions occur in various forms (Fig. 12). The total concentration of $Cr(VI)_t$ in the initial aqueous phase is defined by the equation:

$$[Cr(VI)_t] = 2[Cr_2O_7^{2-}{}_{in}]+[HCrO_4^{-}{}_{in}]+[CrO_4^{2-}{}_{in}] \quad (7)$$

The distribution constant (Kd) for Cr(VI) can be expressed by an equation that includes the effect of OH^- ions in the initial aqueous phase:

$$Kd = a[Cr_2O_7^{2-}{}_{in}]+b[HCrO_4^{-}{}_{in}]+c[CrO_4^{-}{}_{in}]+d[OH^{-}{}_{in}], \quad (8)$$

where the a, b, c, d coefficients are the parameters of the influence of various Cr(VI) ions and OH^- ion on the partition constant Kd, equivalent to the affinity of these ions for the sorbent surface.

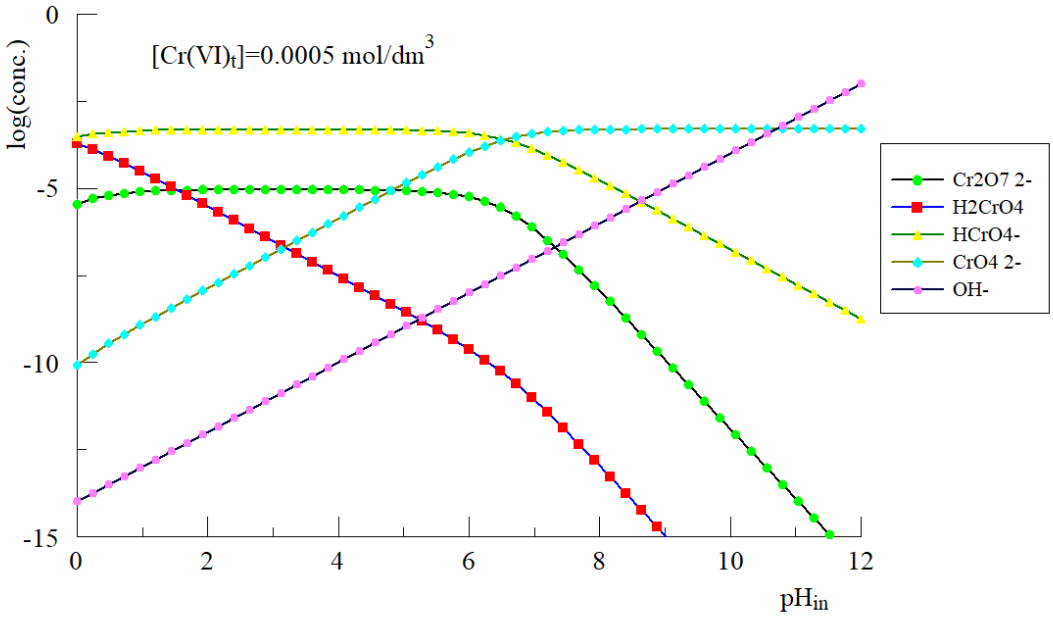

Fig. 12. Ionisation of chromium(VI) ions in aqueous solutions depending on pH.

Fig. 13 shows the concentration of magnesium, copper, zinc and aluminium in solutions with different initial pH values after contact with the corresponding LDH: Mg2CuZnAl-CO3 (A), Mg2CuZnAl-CO3+Cr(VI) (B), Mg2CuZnAl-Cl (C), Mg2CuZnAl-Cl+Cr (VI) (D). Analysis of Fig. 13 shows that in all systems, c(Mg) decreases significantly with increasing pH, which indicates a decrease in LDH dissolution and, at the same time, an increase in stability in neutral and alkaline solutions. The decrease in magnesium content in solutions ranges from $2.03 \cdot 10^{-4}$ to $2.88 \cdot 10^{-5}$ mol/L for Mg2CuZnAl-CO3, from $1.90 \cdot 10^{-4}$ to $1.79 \cdot 10^{-5}$ mol/L for Mg2CuZnAl-CO3+Cr(VI), from $2.18 \cdot 10^{-4}$ to $3.75 \cdot 10^{-5}$ mol/L for Mg2CuZnAl-Cl, and from $2.30 \cdot 10^{-4}$ to $2.99 \cdot 10^{-5}$ mol/L for Mg2CuZnAl-Cl+Cr(VI). The most stable system is therefore Mg2CuZnAl-CO3+Cr(VI). The chloride form of LDH is clearly less stable, as can be seen not only from the magnesium concentration but also from the zinc and copper content in solutions with pH 4, 5 and 6. In solutions with a pH of 4, the zinc concentration is 30 times higher and the copper concentration is 10 times higher in solutions for chloride LDH forms than for carbonate forms. The addition of chromate (VI) ions increases the stability of both LDH forms, especially in alkaline solutions, and this is more pronounced in the case of the Mg2CuZnAl-Cl+Cr(VI)

form. Significantly lower contents of magnesium, zinc and copper are present in solutions contacted with the carbonate form than with the chloride form of LDH. In the case of aluminium, its concentration c(Al) is at the level of 10-6 mol/L and varies minimally across the entire pH range, regardless of the LDH form. This is probably due to the fact that Al remains in the solid phase or reprecipitates quickly, i.e. it first dissolves and then, when the solution conditions allow, forms a solid phase again.

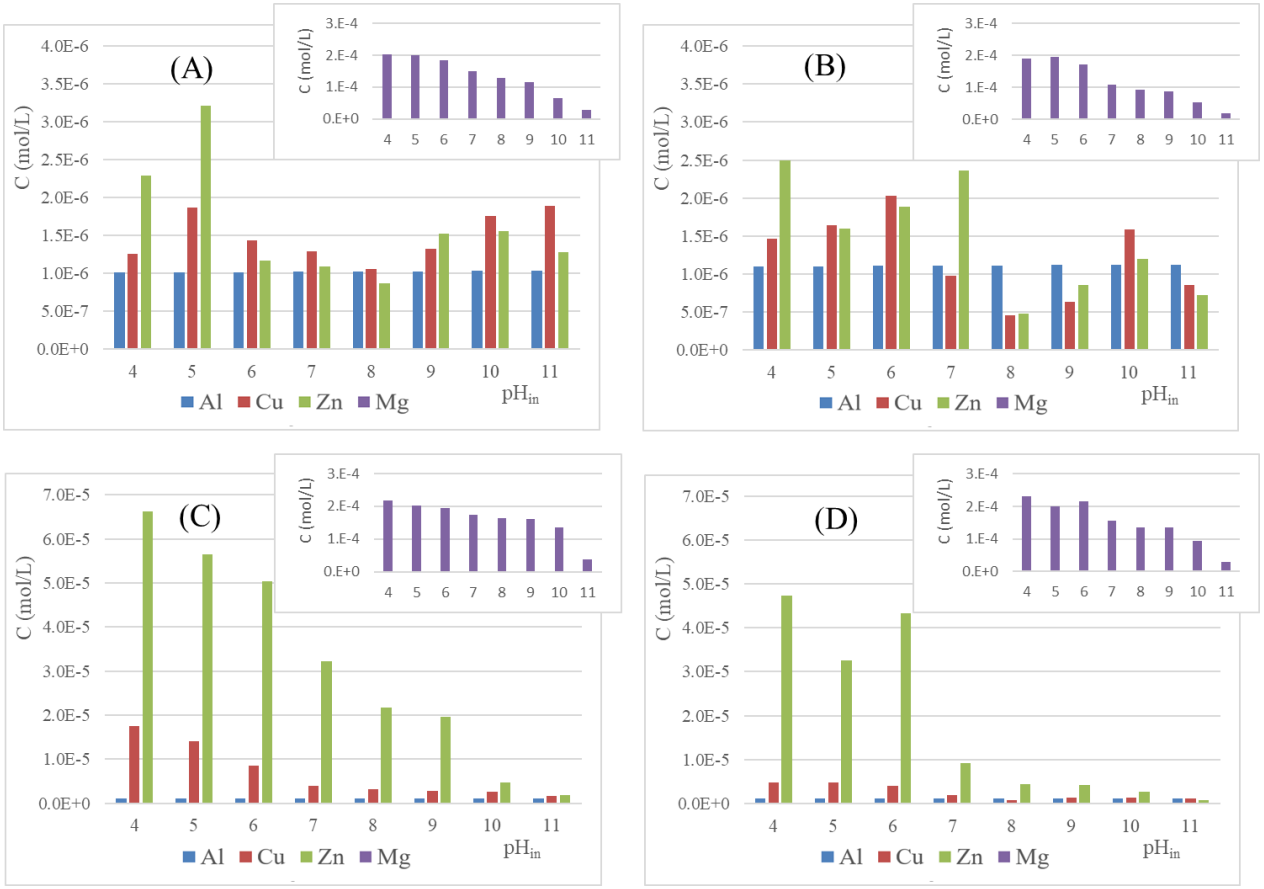

Fig. 13. Stability of the LDH structure depending on pH (A) Mg2CuZnAl-CO3, (B) Mg2CuZnAl-CO3+Cr(VI), (C) Mg2CuZnAl-Cl, (D) Mg2CuZnAl-Cl+Cr(VI).

3.2. Characterization of Mg2Cu0.5Zn0.5Al1 after sorption

Powder XRD patterns of LDH-CO_3 and LDH-Cl forms of $Mg_2Cu_{0.5}Zn_{0.5}Al_1$ after CrO_4^{2-} sorption are presented in Fig. 14.

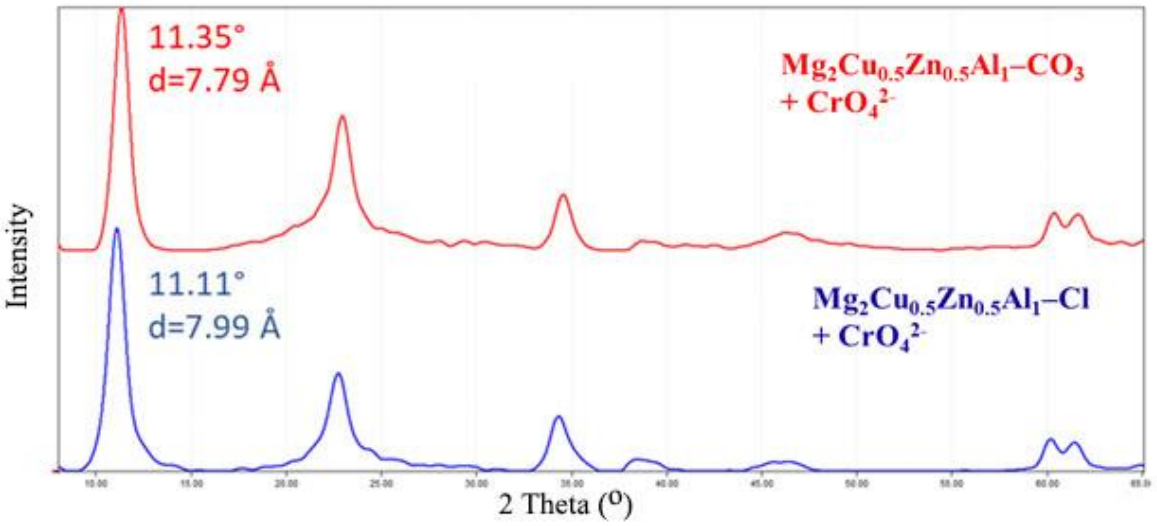

Fig. 14. XRD patterns of LDH-CO_3 and LDH-Cl forms of $Mg_2Cu_{0.5}Zn_{0.5}Al_1$ after CrO_4^{2-} sorption;

It can be concluded from XRD analysis data, that in the case of carbonate-containing LDH, mainly surface adsorption of Cr(VI) ions takes place. In the chloride form of this material, ion exchange in the interlayer space also occurs to a significant extent.

The FTIR spectra of Mg2CuZnAl samples after chromate(VI) sorption shown in Fig. 15 provide evidence for the presence of CrO_4^{2-} ions in the LDH structure.

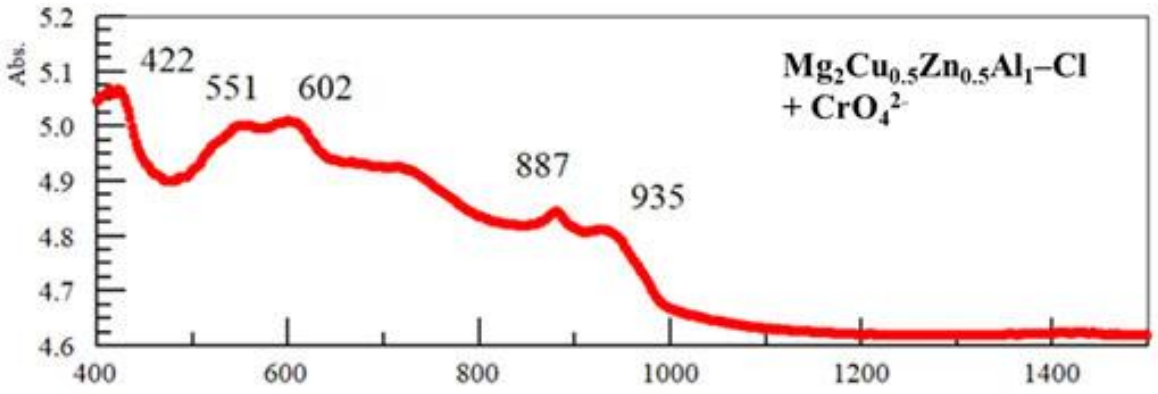

Fig. 15. FTIR spectra of LDH-Cl saturated with CrO_4^{2-}.

In the spectrum of the Mg2CuZnAl sample strongly saturated with chromate(VI) ions, two characteristic absorption bands appear at 887 and 935 cm^{-1}. These bands correspond to symmetric and asymmetric Cr–O stretching vibrations in tetrahedral chromate groups (CrO_4^{2-}). Their positions are consistent with the literature data for chromate compounds. The presence of these bands confirms the

effective binding of chromate(VI) anions by Mg2CuZnAl-CO3. In the Mg2CuZnAl-CO3 spectrum detected strong band at 1358 cm^{-1} attributed to stretching vibrations of carbonate anions (CO_3^{2-}) from the interlayer is less intense in the spectrum of the Mg2CuZnAl-CO3+Cr(VI) sample. The lowering of the peak characteristic of the carbonate ion confirms that the CO_3^{2-} ions have only been partially replaced by chromate(VI) ions, as they are strongly bound to the LDH network. The absorption bands in the range of 500–1000 cm^{-1} are caused by vibrations of the hydrotalcite structure in the LDH network, i.e. Mg-O / Al-O / O-Al-O / O-Mg-O, Al-OH and H_2O groups. These bands have a different arrangement for samples with Cr(VI), which indicates that the vibrations of the network are disturbed by the sorbed chromates.

The BET analysis revealed clear differences in the porous structure of the tested LDH materials, as well as significant changes occurring after Cr(VI) sorption (Table 1). The Mg2CuZnAl-CO3 sample has the largest specific surface area (56.65 m^2/g) and a significant pore volume (0.262 cm^3/g), which is typical for LDHs containing carbonate ions. CO_3^{2-} anions are quite large and divalent, so they stabilise the ordered interlayer structure, which promotes the development of porosity and high accessibility of the adsorption surface. Partial replacement of CO_3^{2-} with smaller, monovalent Cl^- anions leads to a significant reduction in specific surface area – the BET value for Mg2CuZnAl-Cl is only 27.24 m^2/g, which is almost half that of Mg2CuZnAl-CO3. Chloride ions do not provide the same stability of interlayer interactions, which leads to a more compact and compressed LDH structure. As a result, access to micropores becomes more difficult, and the aggregation of plates further reduces the total active surface area. After Cr(VI) ion sorption, both materials exhibit contrasting behaviour. In the case of Mg2CuZnAl-CO3, the specific surface area decreases from 56.65 to 47.85 m^2/g, indicating partial pore blockage by chromate anions. At the same time, the unchanged pore volume combined with an increase in pore diameter (from 18.65 to 21.90 nm) suggests that Cr(VI) penetrates smaller pores and induces their widening or structural reorganisation without increasing their total volume. In the case of Mg2CuZnAl-Cl, the sorption effect is reversed: the specific surface area increases from 27.24 to 30.69 m^2/g, while the pore volume increases from 0.140 to 0.172 cm^3/g. This indicates the opening of additional porous spaces. Chromate(VI) anions, partially penetrating the interlayer area of Mg2CuZnAl-Cl, loosen the layer arrangement and lead to the reorganisation of aggregates, resulting in increased internal surface availability. The increase in pore diameter (from 20.62 to 22.43 nm) further confirms that Cr(VI) promotes the development of mesoporousness.

Table 1. Results of the BET analysis.

Sample	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)
LDH-CO_3	56.65	0.262	18.65
LDH-CO_3-Cr(VI)	47.85	0.262	21.90
LDH-Cl	27.24	0.140	20.62
LDH-Cl-Cr(VI)	30.69	0.172	22.43

3.8. Thermal analysis

The thermal behavior of the investigated samples was studied using thermogravimetry (TG), differential thermogravimetric analysis (DTG), and differential scanning calorimetry (DSC) in an air atmosphere (Fig. 16).

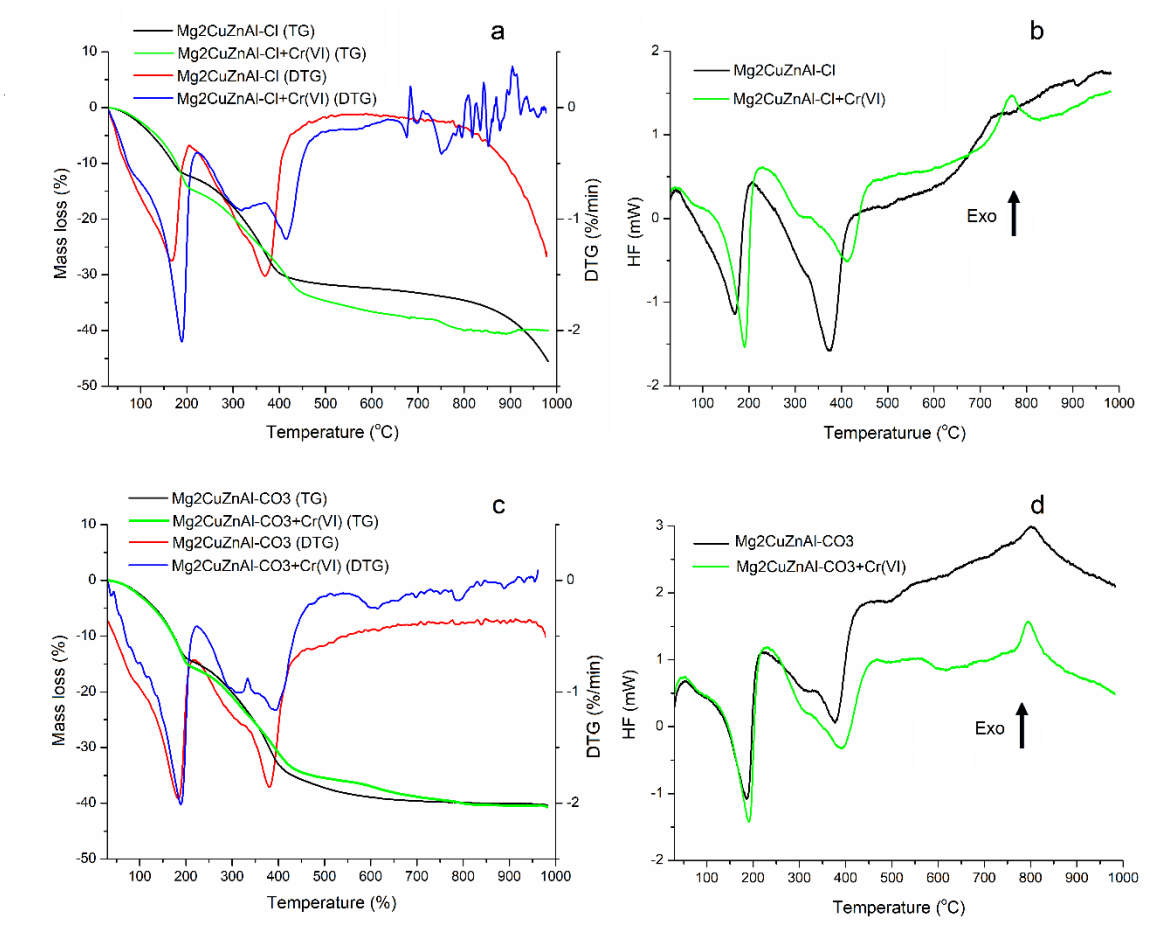

Fig. 16. TG-DTG (a and c) and DSC (b and d) curves of Mg2CuZnAl-CO3, Mg2CuZnAl-CO3+Cr(VI), Mg2CuZnAl-Cl and Mg2CuZnAl-Cl+Cr(VI) recorded in air atmosphere.

The thermal decomposition of all tested samples occurs in three main stages, within the temperature ranges of about 30–200°C, 200–450°C, and 450–1000°C. The first stage is most likely associated with the release of weakly bonded water molecules. The observed mass losses at 200°C are 13.8%, 14.7%, 12.2%, and 14.2% for Mg2CuZnAl-CO3, Mg2CuZnAl-CO3+Cr(VI), Mg2CuZnAl-Cl, and Mg2CuZnAl-Cl+Cr(VI), respectively. These values suggest different amounts of water molecules present in the tested samples. The samples after chromate(VI) ions sorption exhibit the higher water content. A very weak endothermic effect is observed on the DSC curves, as well as changes in the DTG curve shapes between 30 and approximately 90 °C for the Mg2CuZnAl-CO3, Mg2CuZnAl-CO3+Cr(VI), and Mg2CuZnAl-Cl+Cr(VI), samples. This is attributed to the removal of the weakest bonded water molecules, i.e., those located on the surfaces of the polycrystallites. The loss of water molecules located among the layers in the LDH structures is accompanied by a significant endothermic effect. Notably, for the Mg2CuZnAl-Cl sample, the top peak temperature of this endotherm is 170°C, whereas for the other samples it is around 190°C. This observation suggests that the incorporation of chloride ions between the layers, partially replacing carbonate ions, leads to a reduction in hydrogen bond formation and weaker bonding of water molecules.

After adsorption of Cr(VI) ions, the surface of Mg2CuZnAl–Cl undergoes significant morphological changes (Fig. 17). The plate-like structure becomes less pronounced and the surface takes on a flatter appearance. Numerous heterogeneous smaller lumps and agglomerates are visible, forming a more compact layer covering the surface. This may be due to the fact that Cr-O-M (M=Mg, Cu, Zn, Al) bondings are formed on the outer surface in the form of a fine sediment.

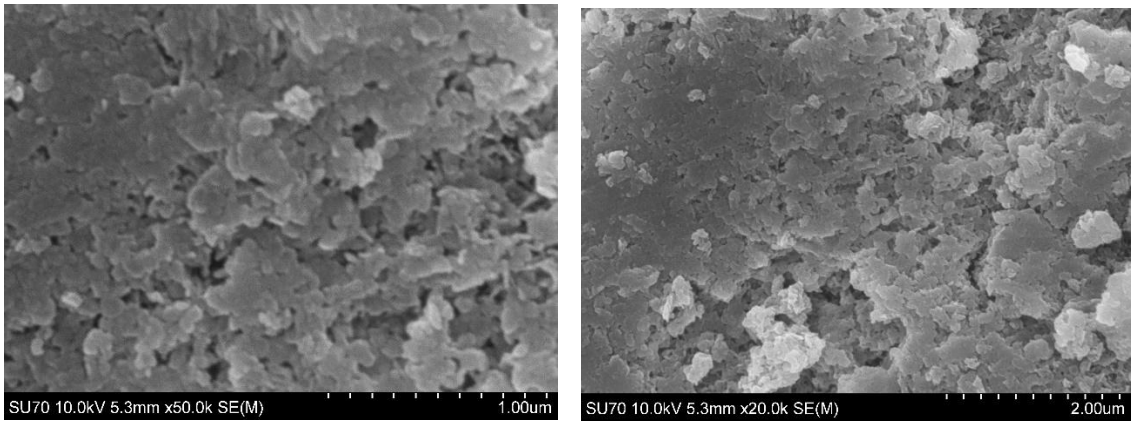

Fig. 17. SEM images of MgCuZnAl–LDH samples after Cr(VI) adsorption obtained at different magnifications.

CONCLUSIONS

1. Layered double hydroxides ($Mg_2Cu_{0.5}Zn_{0.5}Al_1$; Mg_2CuZnAl-LDH) having carbonate-intercalated (LDH-CO_3) and chloride-intercalated (LDH-Cl) forms were successfully synthesized using co-precipitation method followed by anion exchange. XRD analysis revealed the typical hydrotalcite-like structure with typical basal reflections. The shift of the (003) diffraction peak after an exchange of anions confirmed the effective replacement of carbonate ions by chloride ions in the interlayer galleries.
2. It was determined, that the chloride form of Mg_2CuZnAl-LDH had a significantly higher Cr(VI) sorption capacity (1.35 mmol/g) than the carbonate form (0.65 mmol/g). This difference is explained by the fact that the chloride ions are weakly bound to the positively charged layers, which makes them exchangeable with the chromate anions; carbonate ions, in turn, are strongly bound by the hydrogen bonds and electrostatic forces, which means that they cannot easily change their place in the interlayer region.
3. The sorption of Cr(VI) on the two forms of LDH was highly dependent on the pH of the solution and the highest maxima degree of removing Cr(VI) was observed in acidic conditions. In the chloride form, the pre-eminent process is anion exchange (Cl^- replaced by $HCrO_4^-$), whereas in the carbonate form an adsorption process takes place, which is predominantly on the external surface.
4. XRD analysis following Cr(VI) sorption showed that in the carbonate form chromate binding occurs on the surface only with little penetration between the layers whereas in the chloride form the penetration between the layers is substantial with the binding occurring on the surface only with minimal penetration between the layers. The presence of chromate ions in both materials was confirmed using FTIR spectroscopy as both materials had characteristic Cr-O stretching vibrations at 887 and 935 cm^{-1}.
5. BET analysis revealed that carbonate form has a greater specific surface area (56.65 m^2/g) than the chloride form. The surface area of the carbonate form decreased to 47.85 m^2/g after sorption of Cr(VI) and the chloride form showed a slight increase to 30.69 m^2/g indicating that additional porous spaces were opened and the layer arrangement was loosened upon intercalation of chromate.
6. Thermal analysis (TG-DTG-DSC) showed that all samples experienced three-stage thermal decomposition. The chloride form was found to have a lower value of dehydration temperature (170 ^oC) than the carbonate form (approximately 190 ^oC), which is an indication of weaker

hydrogen bonding of water molecules between the layers in the presence of chloride ions. The patterns of the thermal decomposition of Cr(VI) after sorption changed, which confirmed the introduction of chromate into the LDH structure.

7. SEM imaging revealed that the plate-like morphology of hydrotalcite materials was maintained after sorption, but the chloride form had a flatter, more compact surface with heterogeneous agglomerates, indicating that the Cr–O–M surface precipitates formed.
8. It could be concluded, that the $Mg_2Cu_{0.5}Zn_{0.5}Al_1$-LDH in the form of a chloride is a highly effective sorbent in the removal of the toxic Cr(VI) anions of aqueous solutions with a sorption capacity of 1.35 mmol/g. The fact that the chloride form outperforms the carbonate form shows that the careful selection of interlayer anions is important in the optimization of LDH materials to be used in environmental remediation applications.

SUMMARY IN LITHUANIAN (SANTRAUKA)

Šio darbo tikslas buvo susintetinti mišrių metalų sluoksniuotus dvigubus hidroksidus (LDH) ir ištirti hidroksido sluoksnio sudėties bei tarpsluoksnių anijonų įtaką chromato(VI) jonų sorbcijai. $Mg_2Cu_{0.5}Zn_{0.5}Al_1$ LDH buvo gauti bendro nusodinimo būdu, po to buvo vykdomi anijonų mainai, kad susidarytų karbonato (LDH-CO_3) ir chlorido (LDH-Cl) formos. Medžiagoms apibūdinti buvo naudojami XRD, FTIR, SEM, BET, TG-DSC ir ICP metodai. Gauti rezultatai leido padaryti išvadas, kad chlorido forma turėjo daug didesnį Cr(VI) sorbcijos pajėgumą, palyginti su karbonato forma. Po sorbcijos FTIR spektruose buvo matomos tipinės chromato juostos (887 ir 935 cm^{-1}). XRD ir BET analizės parodė, kad chlorido formoje vyksta tarpsluoksniniai anijonų mainai, o karbonato formoje vyrauja paviršiaus adsorbcija. Apibendrinant galima teigti, kad $Mg_2Cu_{0.5}Zn_{0.5}Al_1$ -LDH yra efektyvus adsorbentas, šalinantis toksiškus Cr(VI) anijonus iš vandens. Tyrimo rezultatai rodo, kad tinkamas tarpsluoksninių anijonų pasirinkimas yra raktas į veiksmingų aplinkos atkūrimo medžiagų kūrimą.

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