HIDRÓXIDOS DUPLOS LAMINARES PARA REMOÇÃO DE POLUENTES AQUOSOS

María Magdalena Costanzo

Instituto de Investigaciones en Tecnología Química (CONICET-UNSL). Campus Universitario. Ruta Prov. Nº 55 (Ex 148) Extremo Norte - CP: 5730 - Villa Mercedes - San Luis - Argentina.

Rocio Belén Garate

Facultad de Ingeniería y Ciencias Agropecuarias (FICA-UNSL). Campus Universitario. Ruta Prov. Nº 55 (Ex 148) Extremo Norte - CP: 5730 - Villa Mercedes - San Luis - Argentina.

Nora Alejandra Comelli

Instituto de Investigaciones en Tecnología Química (CONICET-UNSL). Campus Universitario. Ruta Prov. Nº 55 (Ex 148) Extremo Norte - CP: 5730 - Villa Mercedes - San Luis - Argentina.

Nora Andrea Merino

Instituto de Investigaciones en Tecnología Química (CONICET-UNSL). Campus Universitario. Ruta Prov. Nº 55 (Ex 148) Extremo Norte - CP: 5730 - Villa Mercedes - San Luis - Argentina.

RESUMO: As hidrotalcitas são argilas aniônicas, que possuem grandes superfícies específicas, caráter básico, alta dispersão de metais e alta estabilidade térmica. Se elas tivessem um elemento de transição em sua estrutura, poderão ter propriedades redox. Hidrotalcitas bimetálicas foram sintetizados nas seguintes combinações: MgAl e MgFe, para determinar o efeito da natureza catiônica na estrutura e funcionalidade da argila como adsorvente de poluentes de efluentes aquosos. As propriedades texturais foram determinadas por isotermas de adsorção de nitrogênio. A estrutura cristalina foi estudada por DRX e a presença de ânions no espaço interlaminar foi determinada por IRFT. Nos resultados obtidos, pode-se observar que a natureza dos cátions constituintes determina a pureza da fase obtida e a estabilidade da estrutura laminar. Além disso, foi observado que o cátion trivalente tem forte impacto na remoção de íons dicromato, sendo o Fe o mais efetivo.

PALAVRAS-CHAVE: óxidos derivados de hidrotalcitas; espécies de cromo; remoção em meio aquoso.

ABSTRACT: Hydrotalcites are anionic clays, which present large specific surfaces, basic character, high metallic dispersion and high thermal stability. If they have a transitional element in their structure they may have redox properties. Bimetallic HTs were synthesized in the following combinations: MgAl and MgFe, to determine the effect of cationic nature on the structure and functionality of the clay as adsorbent of contaminated aqueous effluents. The textural properties were determined by isotherms of nitrogen adsorption. The crystal structure was studied by XRD and the presence of anions in the interlayer space was determined by IRFT. From the obtained results it can be

observed that the nature of the constituent cations determines the purity of the obtained phase and the stability of the laminar structure. In addition, it was observed that the trivalent cation has a strong impact on the dichromate ions removal, with Fe being the most effective.

KEYWORDS: instructions; chromium species; removal in aqueous medium.

1 | INTRODUCTION

Currently, one of the biggest problems affecting water quality is the presence of heavy metals, such as hexavalent chromium, which represents a threat to human life and the environment due to its high toxicity (VILLANUEVA ET AL., 2017).

Chromium in aquatic environments is mainly generated from various industrial processes such as electroplating, metal finishing, leather tanning, wood preservation and dye and paint manufacturing (JIN ET AL., 2017). In these media, chromium exists mainly in its trivalent form, Cr (III), and hexavalent form, Cr (VI), the latter being 500 times more toxic than its trivalent counterpart (KAN ET AL., 2017). Exposure to Cr (VI) causes several health problems that include skin irritation, dermatitis, epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage (KAN ET AL., 2017). The hexavalent chromium can take the form of chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) and hydrogen chromate ($HCrO_4^-$) depending on the pH of the solution and the total concentration of Cr (VI), being the predominant species in solutions to pH> 5 that of $Cr_2O_7^{2-}$ (KAN ET AL., 2017).

The Argentinean National Law of Hazardous Waste No. 24051 establishes limit levels for total Chromium in water of 2 µg L^{-1} for the protection of aquatic life and 50 µg L^{-1} for human consumption (KOROL ET AL., 2018).

The conventional treatment to remove the chromate from aqueous media consists of reducing the Cr (VI) to Cr (III), which is then precipitated as chromium hydroxide or iron and chromium hydroxide at high pH, followed by the removal of the dehydrated sludge (JIN ET AL., 2017). Other treatments, including phytoextraction, reverse osmosis, electrodialysis, ion exchange, membrane filtration and adsorption have also been developed to remove metals such as chromium (JIN ET AL., 2017). Most of these methods have some disadvantages due to the complicated processes involved: high cost and high energy consumption. However, adsorption is a simple and effective method for the removal of chromium and there are several materials that can be used as an adsorbent, such as modified zeolites, clays, activated carbon, biomaterials, among others (JIN ET AL., 2017).

Within the family of clays, hydrotalcites (HTs) are anionic clays that have been widely used as adsorbents for the removal of inorganic materials from aqueous media (SÁNCHEZ-CANTÚ ET AL., 2016; TRIANTAFYLLIDIS ET AL., 2010; JABŁONSKA ET AL., 2013). The HTs are laminar solids with a structure similar to the one of the

brucite, $M(OH)_6$, where M is a bivalent cation, octahedrally coordinated with six oxydryl groups. When M^{2+} ions are replaced by M^{3+} cations, a positive charge arises that is neutralized by intercalated anions in the interlamellar regions. It is possible to produce materials of the hydrotalcite type with different divalent cations (Mg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}) and trivalent (Al^{3+}, Ni^{3+}, Co^{3+}, Fe^{3+}, Cr^{3+}), as well as different anions (CO_3^{2-}, NO_3^-, SO_4^{2-}, WO_4^{2-}, CrO_4^{2-}) (JABŁONSKA ET AL., 2013). The calcination of the HTs results in different phases of simple, bimetallic or trimetallic oxides, depending on the calcination temperature and the metals of the structure (CAVANI ET AL., 1991). The most interesting properties of these oxides are: high surface area, synergic effects between the elements and memory effect (VACCARI, 1998). These properties, added to their low cost and versatility, allow the use of oxides derived from hydrotalcites in multiple applications (JABLONSKA ET AL., 2013).

The objective of this work is to evaluate the absorption capacity of chromium (VI) species, in aqueous medium, of oxides derived from two types of hydrotalcites that differ in trivalent precursor metal, MgAl and MgFe. In addition, the influence of the "memory effect" on the removal of contaminate is studied.

2 I MATERIALS AND METHODS

2.1 Adsorbents synthesis

The Mg, Fe and Al hydrotalcites, with a molar ratio of $Me^{2+}/Me^{3+} = 3/1$, were synthesized by the coprecipitation method, adding a mixed salt solution and mixing dropwise an alkaline mixture of KOH and K_2CO_3 in water distilled, simultaneously with a vigorous mechanical stirring. The pH was maintained at 9.5-10, and the temperature at 70 °C. The metal precursors were: $Mg(NO_3)_2 \times 6H_2O$ (Mallinchrodt), $Al(NO_3)_3 \times 9H_3O$ (Merck) and $Fe(NO_3)_2 \times 9H_2O$ (Anedra). The suspension was aged at room temperature during 24 hours. The precipitate was washed to a pH of 7 and dried at 110 °C for 24 hours. An aliquot of the dried solid was calcined at 500 °C, maintained at this temperature for 1 hour. From now on the solids obtained will be called MgAl110 and MgFe110 (dried) and MgAl500 and MgFe500 (calcined).

2.2 Characterization of the solids

The textural properties were determined by nitrogen adsorption isotherms measured at -196 ºC in a Gemini V2.00 equipment (Micromeritics Instrument Corp). The crystal structure was studied by X-ray diffraction (XRD) with Cu Kα lamp, with nickel filter ($\lambda = 1.5378$ Å, 40 kV, 30 mA) in a Rigaku equipment, model D-Max III. The presence of the anions was studied by infrared spectroscopy with Fourier transform (FTIR) using a Perkin-Elmer Spectrum RX1 equipment. The solids were diluted with KBr. The metal support interaction of the synthesized solids was analyzed by means of the programmed temperature reduction technique (TPR) with a mixture of 10% H_2/N_2,

from room temperature to 600 ºC, keeping at this temperature for 1 hour, with a heating rate of 10 º/min. The samples were pretreated at 200 ºC, under a nitrogen flow.

2.3 $Cr_2O_7^{2-}$ adsorption

The capacity for removal of $Cr_2O_7^{2-}$ ions was evaluated by preparing suspensions with 70 mg of each oxide sample (MgAl500 and MgFe500), in 20 mL of a potassium dichromate solution (Mallinckrodt) with a concentration of 800 ppm. The suspensions were maintained at different contact times, 24, 48 and 72 hours, under magnetic stirring, at room temperature. Once the adsorption time was reached, the adsorbent was separated by centrifugation, for 20 min at 3000 rpm. The supernatant was diluted 1/100 with tridestilated water and the dichromate ion concentration was obtained using a UV-visible spectrophotometer (Shimadzu) at 257.5 nm.

3 I RESULTS Y DISCUSSION

The hydrotalcites were synthesized by the coprecipitation method, using an acid solution of the precursors, the nitrates of the constituent metals of their structure, and a solution with KOH and K_2CO_3, used as a precipitating agent. The dry and calcined solids were physicochemically characterized to study the influence of the cations to obtain the laminar structure of the clays and the oxides coming from them after the calcination stage.

Table 1 shows the specific surface areas and pore sizes of the synthesized solids, both dried and calcined, obtained from physisorption tests with nitrogen. It is possible to observe a different behaviour of the solids according to the trivalent cations present in the structure. It is observed that for solids with aluminum the surface area increases with calcination, whereas if the trivalent cation is iron, the temperature appreciably decreases this property. The behaviour with aluminium has been reported in the literature (COCHECI ET AL., 2010), attributing it to the fact that the calcination leads to a destruction of the laminar structure, which originates the formation of phases of low crystallinity (oxides of the constituent metals). All solids synthesized, dried and calcined, have a pore size distribution in the mesoporous region (pore size between 20 and 500 Å), according to the IUPAC classification (HUI ET AL., 2005).

Solids	Specific surface area, S_{BET} (m² g⁻¹)	Pore volume, V_p (cm³ g⁻¹)	Pore diameter, d_p (Å)
MgAl110	103	0.632	176.2
MgAl500	128	0.796	192.3
MgFe110	63	0.376	181.9
MgFe500	39	0.262	173.1

Table1. Textural properties of the dried and calcined solids.

After calcinations, in the hydrotalcites with aluminum the pore volume increases, while with iron it decreases. The pore diameter presents the same tendency as the volume, being higher for solids with magnesium, except for MgFe calcined at 500 °C. The hydrotalcite has a mesoporous structure due to the size and shape of the particles and their interconnection pattern. It can be inferred from the results obtained that the morphology of these solids is modified by the nature of the trivalent cation, since under the same conditions of synthesis the chemical behaviour of the metals is remarkably different.

The diffraction lines of all the solids studied are presented in Figure 1. The diffractograms of the solids dried at 110 °C and containing Al have the laminar structure of the corresponding hydrotalcite, although they present impurities of simple and mixed spinel-type oxides. The calcination stage leads to the formation of the simple oxides of the metals present or the mixed phases, depending on the nature of the metals. In addition, the elimination of the hydroxyl groups and intercalated anions occurs. (HUI ET AL., 2005).

The diffraction lines of MgAl110 show a shift towards lower diffraction angles when compared to those that would correspond to a hydrotalcite structure at $2\theta = 11.66°$; $23.44°$; $34.91°$ (PDF 01-089-0460). Also, it is possible to observe peaks attributable to spinel phases, $2\theta = 38.82°$; $65.76°$ (PDF 00-002-1086) and $2\theta = 54.31°$ (PDF 01-087-0343). This calcined solid only has the MgO phase (PDF 01-089-7746). The alumina phase (Al_2O_3), which may be present, cannot be identified because it is amorphous. The Al^{3+} cations could be forming this phase or crystalline phases of low concentration, highly dispersed.
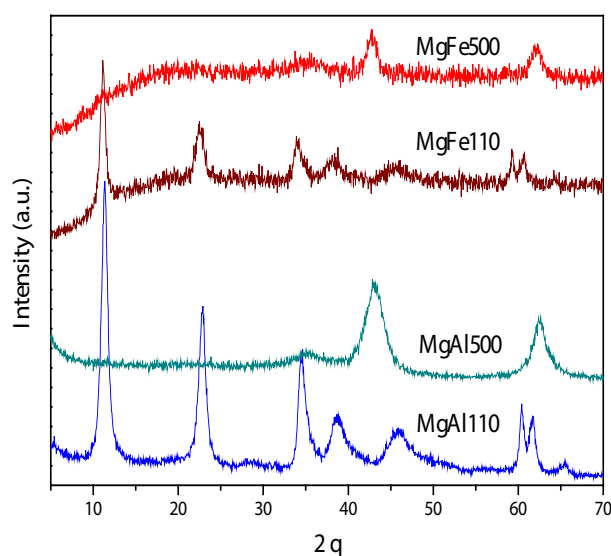

Figure 1. Diffractograms of the dried and calcined solids.

The diffraction lines of MgFe110 correspond to the hydrotalcite phase (PDF 01-070-2150), although the presence of an hydrated iron carbonate (PDF 00-046-0098) could not be ruled out, since both crystalline phases present lines of similar diffraction

to 2θ, so it is not possible to differentiate which is the contribution of each phase to the intensity of the peak in the diffractograms obtained. The diffractogram of MgFe500 shows the MgO phase (PDF 01-089-7746) and the Fe_3O_4 phase (PDF 01-089-0951) at 2θ = 36.90°; 42.86 °; 62.23° and 2θ = 29.76°; 35.05°, respectively. The FeO phase (PDF 01-077-2355) could be present since it presents signals similar to the reduced spinel.

The phases with aluminium present a higher crystalline order, in comparison with those with Fe. This is due to a modification of the parameters of the crystalline cell and in the electrostatic interaction between the components of the sheets and the anions in the interlaminar space, since the difference of the ionic radii of the cations involved and their electronic natures (COCHECI ET AL., 2010). As a consequence, the cations could be outside the structure, forming other phases, and thus it is possible to obtain impure hydrotalcites. With Mg at the position of the divalent cation it is possible to obtain hydrotalcites with a difference in the crystallinity due to an increase in the interplanar distance when having Fe and instead of Al (ion radii: Fe^{3+}: 0.67 Å; Al^{3+}: 0.57 Å) (GRZONA ET AL., 2011). The result obtained is in agreement with the observed in the reduction profiles, where it is observed that for the solid calcined at 500 °C, the iron would be reduced to Fe^{2+} (ionic radius Fe^{2+} = 0.82 Å (CHANG, 2007).
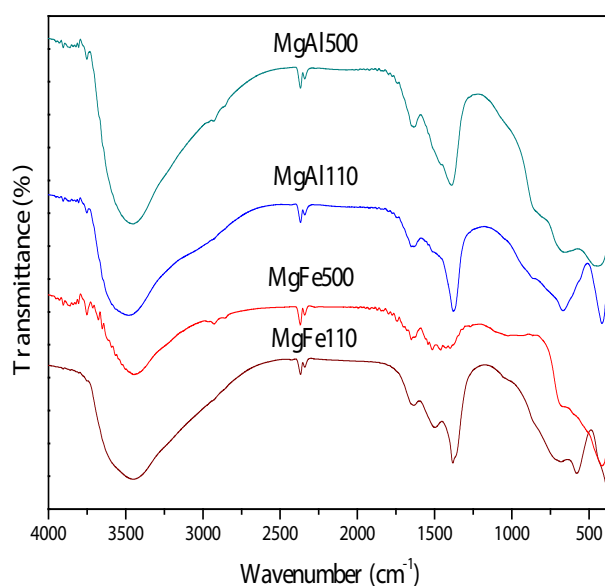

Figure 2. FTIR spectra.

The infrared spectra are shown in Figure 2. The IRFT analyses were carried out in order to obtain information of the anions present in the interlaminar space. All the spectra have similar bands, with differences in the intensity and width of the same. It can be observed in the spectra the stretching bands that are attributed to the bonds of the metal oxides, between 400 and 700 cm^{-1}, as well as broad bands at approximately 3400 cm^{-1}, which correspond to the vibrations of stretching of the hydroxyl groups,

and another band at approximately 1630-1650 cm^{-1}, which is assigned to the bending vibrations, d$_{OH}$, of the same anions. These vibrations correspond to the vibrations of the water molecules interspersed in the structure (COCHECI ET AL., 2010).

The spectra of all solids show the band corresponding to the presence of free nitrate ions (1370-1384 cm^{-1}), which shows a slight shift towards higher wavenumbers with the presence of Fe. The presence of this signal is more notorious for dried solids. The n$_3$ mode of the antisymmetric stretch of the CO$_3^{2-}$ presents a band at similar wavenumbers. The spectra of the solids with Fe present the bands corresponding to the carbonate ions and the coordinated mono and bidentate nitrates (1545 cm^{-1}) (HUI ET AL., 2005). The difference between the spectra when modifying the trivalent cation could be assigned to a different interaction of the interlaminar anions, because the lamellas have different electrostatic forces.
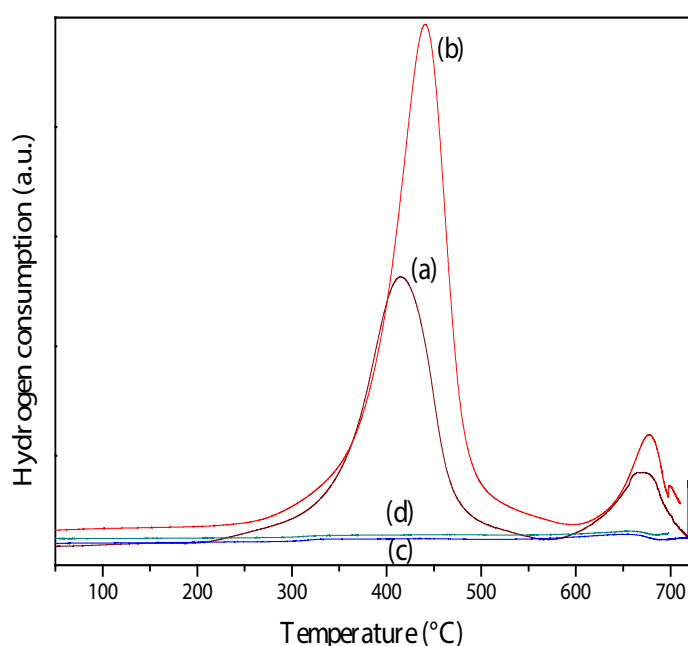

Figure 3. Hydrogen reduction curves: (a) MgFe1100; (b) MgFe500; (c) MgAl110; (d) MgAl500.

The reduction profiles (Figure 3) present differences in all the divalent combinations synthesized. The solids present a reduction signal at temperatures higher than 600ºC. According to what is reported in the literature (LIANG AT AL., 2009), the difference in the hydrogen consumption of all solids, at this temperature range, is due to the reduction of nitrates of the metals precursor, which they can be observed in the FTIR spectra. In the solids with Fe, in the range of 450-480 ºC and 540-620 ºC, the reduction of the iron phases is observed (JABŁONSKA ET AL., 2013). According to the literature, the nitrate ion is reduced to NO$_2^-$, NO and NH$_3$ (MERINO ET AL., 2016; GRZONA ET AL., 2011), while the phases with iron are reduced in the following order: Fe$_3$O$_4$ ® FeO ® Fe (JABŁONSKA ET AL., 2013; LIANG ET AL., 2009).

Solid	Dichromate initial concentration (mg L^{-1})	Contact time (h)	Retention percentage
MgFe	743.50	0	0
		24	12.39
		48	42.99
		72	5.18
MgAl	782.40	0	0
		24	1.93
		48	3.90
		72	0.08

Table 2. Quantifications of the chromium species before and after the addition of the HDL.

In order to determine the amount of dichromate ions removed from the aqueous solutions, the actual initial concentration of the starting solutions and the concentrations of ions remaining in the solutions after the adsorption tests were determined by means of UV-Vis spectroscopy at 257 nm.

The removal tests were carried out from solutions of approximately 800 ppm of potassium dichromate. Figure 4 shows the behaviour of the solids used, MgAl500 and MgFe500. It is clearly observed that when the Fe is a metal precursor it is possible to retain a higher concentration of the aqueous contaminant, reaching the maximum saturation at 48 hours, with a maximum retention of the chromium species of 43%. Moreover, it is observed a longer contact time does not cause an increase in contaminant retention, as it has already been reported in the literature (DAS ET AL., 2007).

Figure 5 shows that the oxides derived from the hydrotalcites, after the removal tests, present the laminar structure, due to the property of "memory effect" of these clays. From the observed results it can be inferred that the removal of the dichromate ions from the aqueous medium would allow the reconstruction of the structure and the ions would be interspersed in the laminar space. Figure 6 compares the diffractograms of the hydrotalcites synthesized with carbonate ions in the interlaminar space and the hydrotalcites obtained when the oxides obtained after the calcination were in contact in solution with the dichromate ions, for 24 hours. The solid MgAl-24 h, which presents the crystalline structure, exhibits a slight shift at lower diffraction angles (2θ = 11.24°, 22.86°, 34.85°), which would indicate the presence of the species of chromium in the interlaminar space, which would have a greater interplanar distance than when the carbonate ions are presented.
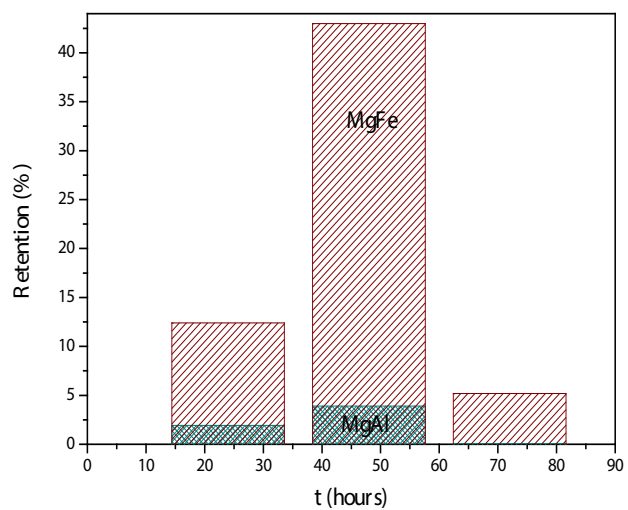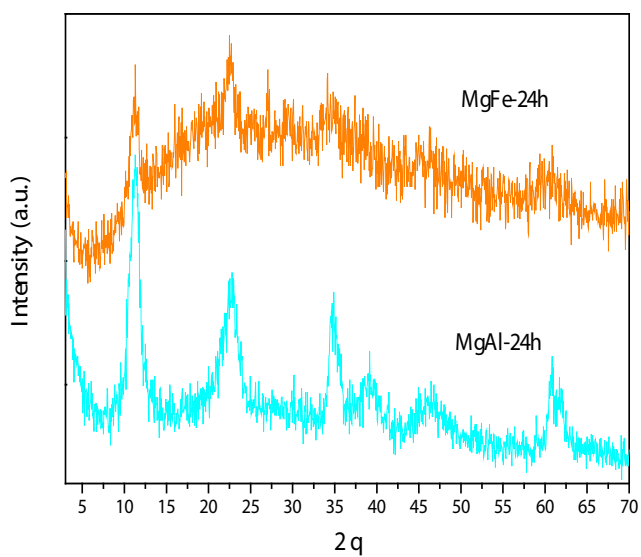
Figure 4. Percentage of the $Cr_2O_7^{2-}$ removed.

Figure 5. Diffractograms of the solids after the removal tests.

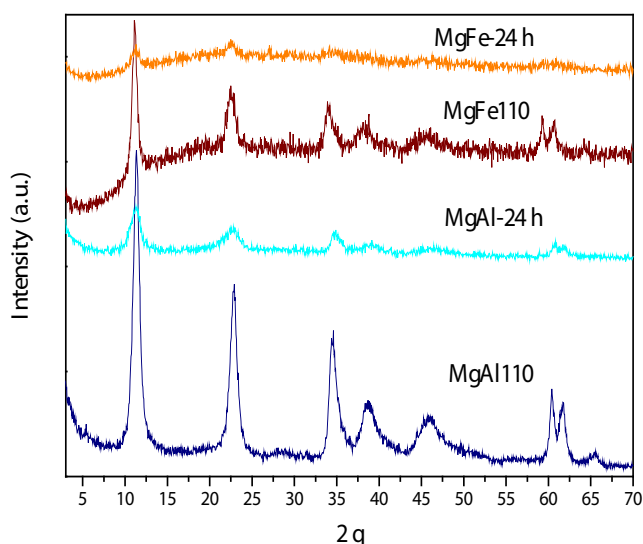Figure 6. Diffractograms of the HTs prepared with CO_3^{2-} and the HTs with $Cr_2O_7^{2-}$ after 24 h of contact.

4 I CONCLUSIONS

In this work, the synthesis of hydrotalcite-type solids is presented by the coprecipitation method. The laminar structure was obtained, with segregation of impurities, evidenced by both XRD and TPR. This can be explained considering that both cations have different electronic configurations and sizes of the ion radii, so their electrostatic interactions differ. The calcination of these solids leads to the collapse of the laminar structure, with the obtaining of simple and mixed oxides, according to the constituent cations of the structure. These oxides showed a different behaviour in the reduction tests, attributable to the different synergy of the metals with the oxydryl groups, the interlamellar anions present in the structure and to the fact that the metals are forming different phases according to the bimetallic precursor combinations.

The results of the dichromate removal tests in aqueous solution showed that the oxides derived from laminar hydroxides have a removal capacity of up to 43% in 48 hours. This capacity can be explained due to the structural, textural and thermal properties of the oxides, which could be used as potential adsorbents of chromium species in aqueous effluents

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