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# Nano hybrid Layered Double Hydroxides Used to Remove Several Dyes from Water

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**Abstract:** For the preparation and characterization of several layer double hydroxides (LDH) with inorganic interlayer anions (carbonate and nitrate) and nano hybrids, two organo-LDHs were studied in detail. The dodecylbenzene sulfonate (DBS) was used as an organic interlayer anion to modify the hydrophilic nature of the interlayer. The aim of the modification of the layered double hydroxides (LDH) was to change the hydrophilic character of the interlayer to hydrophobic with the purpose of improving its ability to adsorb several (anionic and cationic) dyes from water. These compounds have been used as adsorbents of amaranth (Am), diamine green B (DGB) and brilliant green (BG) dyes. Adsorption tests were conducted using variable pH values, contact times and initial dye concentrations (adsorption isotherms) to identify the optimum conditions for the intended purpose. Adsorbents and adsorption products were characterized by several physicochemical techniques. The results of the adsorption tests showed that the organo-LDH nano hybrids could be efficient adsorbents in the removal of studied dyes from water. Thus, it can be concluded that nano hybrids studied in this work might act as suitable supports in the design of adsorbents for the removal of a wide spectrum of dyes with the aim of reducing the adverse effects on water resources.

**Keywords:** layered double hydroxide; hydrotalcite; nano hybrid; dyes; adsorption; amaranth; diamine green B; brilliant green

## 1. Introduction

Organic pollutants are often detected in natural waters, and this has raised concerns regarding the protection of health and the environment [1,2]. Dyes are a complex class of organic compounds with a wide range of applications in the textile and food industries, with a large amount of dyes being wasted, reaching natural water resources. Due to their chemical structure, dyes are resistant to light, many chemicals, oxidants and heat, and they are not biodegradable, and, therefore, once released into the aquatic environment, are difficult to eliminate. If not treated appropriately, dyes may cause serious environmental problems [3] and it is very important to identify appropriate treatments for dye wastewaters [4]. Different physicochemical techniques including membrane filtration, coagulation, electrochemical methods, oxidation, adsorption and biological technology have been developed for the remediation of dye wastewaters [5–7], adsorption being one of the most suitable methods due to its efficacy and low cost [8]. There are numerous studies using different low-cost adsorbents such as sludge, rice husks, bentonite, fly ash, chitosan and some agricultural by-products to remove dye from wastewater [8–13]. Each of these adsorbents may perform well for the adsorption of a single kind of dye, but the adsorption capacity is quite variable. Therefore, the reported adsorption capacities should

be analyzed with caution since these values are dependent on the characteristics of the material and the experimental conditions [14]. Dye wastewater released from factories often contains several kinds of these contaminants (anionic, cationic, non-polar, etc.) [15] and, therefore, it is important to find a broad-spectrum adsorbent for this aim.

Layered double hydroxides (LDH), also known as hydrotalcite-like compounds, have been reported as efficient adsorbents for anionic contaminants from water [16–20]. These compounds consist of brucite-like layers which contain the hydroxides of divalent ( $M^{II}$ ) and trivalent ( $M^{III}$ ) metal ions and have an overall positive charge balanced by hydrated anions between layers and present a general formula  $[M^{II}_{(1-x)}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ , where  $A^{n-}$  is the intercalated anion. LDH has a hydrophilic nature due to the strong hydration interlayer inorganic anions, but their surface properties could be changed to hydrophobic by intercalating of large organic anions into the interlayer space.

These organo-LDH with a suitable intercalated anion can provide interlayer spaces between 2 and 4 nanometers and might be considered as nanohybrids with hydrophobic characteristics in the interlayer and external surface [21–24]. In this way, the adsorption ability of these compounds for organic pollutants could be significantly improved [25–29].

In comparison with some other adsorbents of water contaminants such as clay minerals and activated carbon, LDH has some advantages: apart from being less expensive than activated carbon, they are more suitable for capturing anionic contaminants than clay minerals such as brucite which do not have any layer charge, and smectite which has negatively charged layers and thus adsorbs cationic pollutants by ion exchange. Furthermore, the LDH interlayer could be modified from hydrophilic to hydrophobic which could favour the adsorption of low polar contaminants even cationic contaminant. Thus, we chose LDH with different interlayer anions in order to study their different adsorption behaviour for anionic azo dyes Am and DGB, and cationic dye BG. These dyes have been selected for this adsorption study because they have a widespread use and thus present potential water contaminants [30].

There are different methods in the literature [18,31] that allow the synthesis of LDH materials with tailor-made physical and chemical properties appropriate in many applications. Coprecipitation, the urea method, induced hydrolysis, rehydration and reconstruction, the sol-gel technique, hydrothermal, microwave, and ultrasound treatments and anion-exchange reactions [31]. To obtain LDH with high chemical homogeneity, coprecipitation at constant pH is recommended [32] and this is the method used in this work which has also been chosen by its ease and speed in the preparation, and the previous experience in the preparation of hydrotalcite-type compounds with inorganic and organic anions in the interlayer space [16,17,26,29].

In this work, four different LDHs were prepared: two with inorganic anions, carbonate and nitrate (named  $MgAlCO_3$  and  $MgAlNO_3$ , respectively) and the other two nanohybrids intercalated with dodecylbenzene sulfonate (DBS) with a different ratio  $Mg/Al = 3$  and  $2$  (named  $Mg_2AlDBS$  and  $Mg_3AlDBS$ , respectively) with the aim to assess the removal of dyes of different natures: amaranth (Am), diamine green B (DGB) and brilliant green (BG) from water. The dyes are used not only for the coloration of textiles, plastics, paints, inks, and lacquers, but also for high-tech applications such as optical data storage, reprographics, display devices, dye-sensitized solar cells, light-emitting diodes, laser welding processes, etc. [30].

## 2. Results and Discussion

### 2.1. Characterization of the Adsorbents

The results of the elemental analysis of the adsorbents prepared are shown in Table 1 together with other characteristics. The amount of organic anion was determined from the ratio S/Al for the samples  $Mg_2AlDBS$  and  $Mg_3AlDBS$ . The content of S indicates that the layer charge in  $Mg_xAlDBS$  ( $x = 2$  and  $3$ ) is balanced only by the organic anion. The amount of S was more than that required in order to compensate the layer charge, suggesting that the excess of DBS remained as Na salt, according

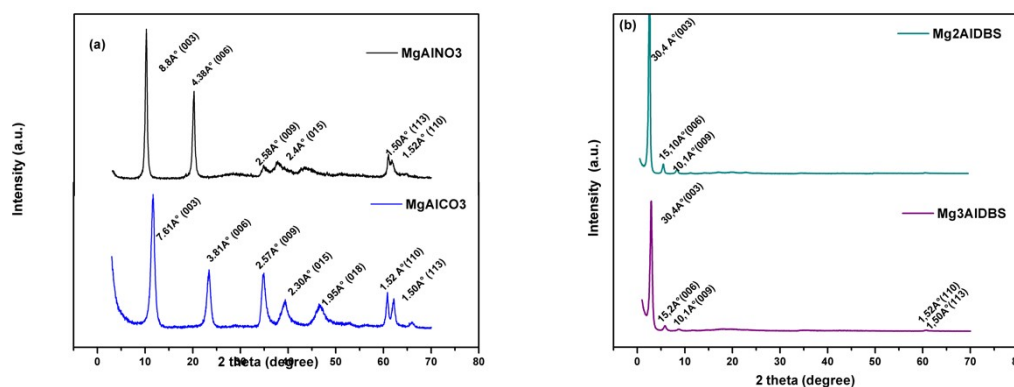
to the Na analysis (Table 1). The ratio Mg/Al = 2 and 3 was used in order to increase the charge density of the layers and consequently the content of interlayer anions as shown in Table 1.

The proposed formulae were obtained from the elemental analysis, assuming that all the positive charge is compensated by the maximum amount possible of carbonate, nitrate and dodecylbenzene sulfonate anion (DBS) for MgAlCO<sub>3</sub>, MgAlNO<sub>3</sub> and Mg<sub>x</sub>AlDBS, respectively. The amount of water was attained from thermogravimetric analysis (TGA) data and the metal content analysis. TGA curves of MgAlCO<sub>3</sub>, MgAlNO<sub>3</sub> are reported in [19] and TGA curves of Mg<sub>x</sub>AlDBS are included in Figure S1.

**Table 1.** Elemental analysis results and some structural data for the MgAlCO<sub>3</sub>, MgAlNO<sub>3</sub>, Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS samples.

Sample	%Al	%Mg	%S	%Na	Mg/Al	a (nm)	c (nm)	S <sub>BET</sub> (m <sup>2</sup> /g)	Formulae
MgAlCO <sub>3</sub>	10.49	19.16	-	-	2.03	0.304	2.28	78	[Mg <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> ](CO <sub>3</sub> ) <sub>0.165</sub> 0.64H <sub>2</sub> O
MgAlNO <sub>3</sub>	9.76	17.26	-	-	1.96	0.304	2.64	10	[Mg <sub>0.66</sub> Al <sub>0.34</sub> (OH) <sub>2</sub> ](NO <sub>3</sub> ) <sub>0.34</sub> 1.18H <sub>2</sub> O
Mg <sub>2</sub> AIDBS	3.54	6.71	6.11	1.28	2.1	0.303	9.07	7	Mg <sub>0.68</sub> Al <sub>0.32</sub> (OH) <sub>2</sub> [(DBS) <sub>0.32</sub> (DBSNa) <sub>0.13</sub> 1.02H <sub>2</sub> O
Mg <sub>3</sub> AIDBS	2.81	7.70	5.81	1.59	3.04	0.305	9.11	11	Mg <sub>0.75</sub> Al <sub>0.25</sub> (OH) <sub>2</sub> [(DBS) <sub>0.25</sub> (DBSNa) <sub>0.165</sub> 0.74H <sub>2</sub> O

The powder X-ray diffraction (PXRD) patterns of the prepared samples were analyzed with Diffract EVA 3.1 Program and reported in Figure 1, and show a typical pattern of hydrotalcite-like compounds with a series of strong basal reflections indexed, assuming a rhombohedral structure, as (003), (006), etc. These basal reflections correspond to the successive orders of the basal (interlayer) spacing  $c'$ . The interlayer spacing  $c'$  is estimated by the formula  $(d_{003} + 2d_{006} + \dots + nd_{00(3n)})/n$ . The cell parameter  $c$  is a multiple of the interlayer spacing  $c'$ , depending on the layer stacking sequence,  $c = 3c'$  for rhombohedral structure (3R). The higher-order reflections ( $n = 3$ ) are more pronounced in organic LDH compounds. Among the various non basal reflections ( $hkl$ , neither  $h$  nor  $k$  being zero), the (110) reflection gives a direct measure of  $a$  ( $a = 2d_{110}$ ). It should be noted, however, that the adjacent (113) peak often overlaps the (110) one [31].

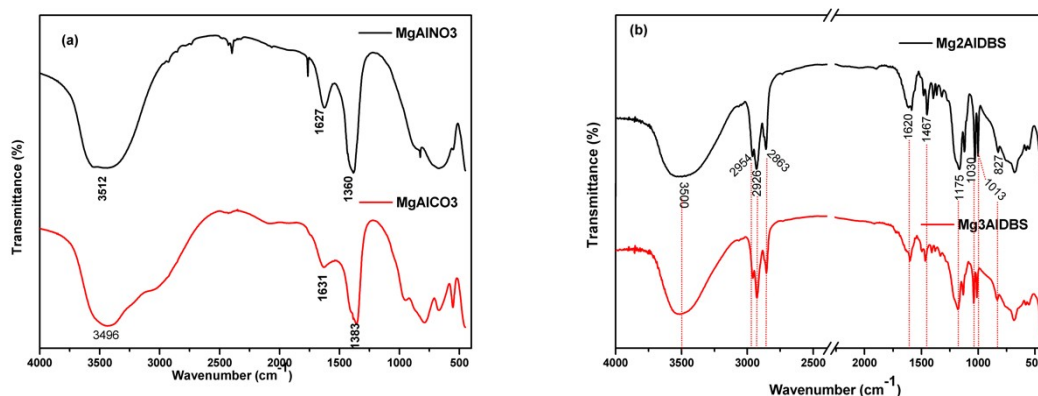


**Figure 1.** PXRD pattern of the synthesized adsorbents: (a) MgAlCO<sub>3</sub> and MgAlNO<sub>3</sub> LDH samples, (b) Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS nanohybrids samples.

The corresponding values of the  $a$  and  $c$  parameters for the adsorbents are also included in Table 1. As expected, the positions of the basal reflections of all the prepared organo-LDH hybrids are shifted to smaller  $2\theta$  reflection angles regarding inorganic hydrotalcite, which reveals expansion in the interlayer distances. Moreover, several harmonics are also observed indicating a well-ordered structure. The range of interlayer distances from a hydrotalcite with DBS in its interlayer can vary between 2.6 and 3.0 nm, depending on the orientation of dodecylbenzenesulfonate anions and on the drying method [21]. When the alkyl chains are oriented in the perpendicular position with benzene rings tilted toward the layer, and water molecules remain adsorbed between the methyl end group and the hydroxyl layer, the spacing is about 3.0 nm [32–34].

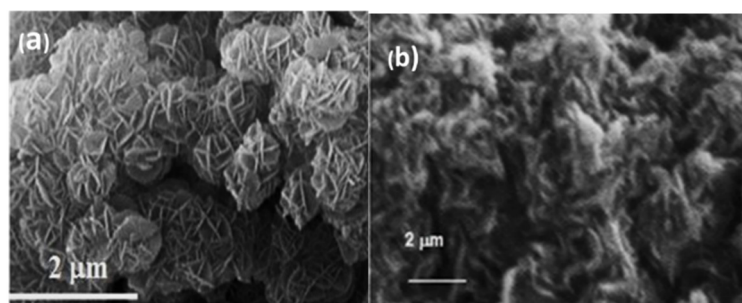
The Fourier Transform Infrared spectra (FT-IR) of the samples are included in Figure 2 and were characteristic of LDH compounds [18]. The most representative features are: a broad band

around  $3500\text{ cm}^{-1}$  corresponding to the hydroxyl groups vibrations, a band at  $1632\text{ cm}^{-1}$  due to the bending mode of water molecules and a band at  $1380\text{ cm}^{-1}$  due to the vibration of carbonate and/or nitrate anions. In the FT-IR spectra of the nanohybrids (Figure 2b) are also present dodecylbenzene sulfonate features: bands at  $2800\text{--}3000\text{ cm}^{-1}$  and  $1467\text{ cm}^{-1}$  due to C–H stretching and deformation vibration modes, respectively, and several bands in the region  $1270\text{--}800\text{ cm}^{-1}$  due to the sulfonate group vibrations.



**Figure 2.** FT-IR spectra of the synthesized adsorbents: (a) MgAlCO<sub>3</sub> and MgAlNO<sub>3</sub> LDH samples; (b) Mg<sub>2</sub>AlDBS and Mg<sub>3</sub>AlDBS nanohybrids' samples.

The SEM images, included in Figure 3, showed that the MgAlCO<sub>3</sub> sample has a sand-rose morphology (Figure 3a), whereas the particles of Mg<sub>2</sub>AlDBS (Figure 3b) are aggregated probably via hydrophobic interactions, and less defined particle surfaces are observed. This suggests that an excess of DBS could coat the outer surfaces [35,36].



**Figure 3.** SEM photographs of the adsorbents: (a) MgAlCO<sub>3</sub> and (b) Mg<sub>2</sub>AlDBS.

The curves obtained from N<sub>2</sub> adsorption and desorption analysis are shown in Figure S2 and correspond to type IV according to the IUPAC classification and are therefore characteristic of these mesoporous materials [37]. A notable characteristic of the type IV isotherm is the presence of the hysteresis loop which is associated with the condensation of N<sub>2</sub> in the pores. The values of BET surface are included in Table 1 and are quite low, as is characteristic of LDH compounds [38].

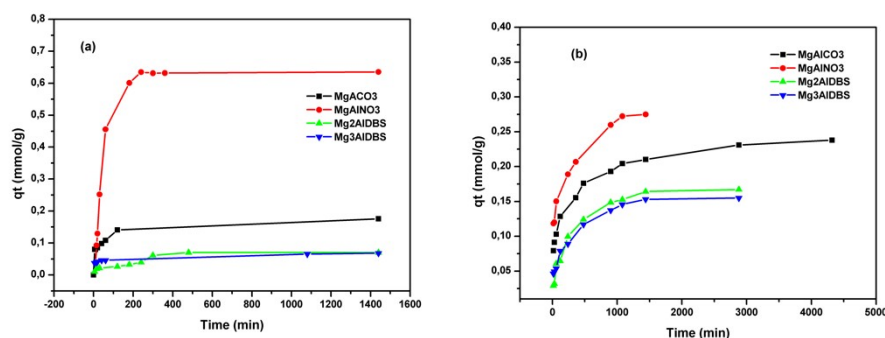
The zeta potential values of the MgAlCO<sub>3</sub>, MgAlNO<sub>3</sub> and Mg<sub>x</sub>AlDBS samples were measured in a KCl solution (0.01 M) at pH between 2 and 12, and the data are included in Figure S3. The results suggested a positive charge density on the inorganic LDH surfaces. When the anionic surfactant was intercalated into the layers, a charge inversion from positive to negative was observed on the nanohybrid samples. The surfactant DBS anions were located in the interlayer space according to the PXRD pattern of Figure 1b, and once the positive structural charge was balanced, more DBS anions were disposed in a bilayer structure, and a portion of the polar groups was adsorbed on the external surface facing the aqueous solution giving a negative charge to the particles, based on the model proposed by Rojas et al. [39].

## 2.2. Study of the Am, DGB and BG Removal by MgAlCO<sub>3</sub>, MgAlNO<sub>3</sub> and Mg<sub>x</sub>AlDBS

### 2.2.1. Adsorption of the Anionic Dyes (Am and DGB)

Am and DGB adsorption tests were carried out with the inorganic LDH (MgAlCO<sub>3</sub> and MgAlNO<sub>3</sub>) and the nanohybrids Mg<sub>2</sub>AlDBS and Mg<sub>3</sub>AlDBS for comparison purposes. The influence of pH on the adsorption process could have a relevant role and therefore this one was examined at an initial pH value between 4 and 10 for Am and DGB on MgAlNO<sub>3</sub>, MgAlCO<sub>3</sub>, Mg<sub>2</sub>AlDBS and Mg<sub>3</sub>AlDBS adsorbents. The final pH was measured after each adsorption experiment, and the maximum value obtained was between 7 and 9.5, which was consistent with the buffering properties of hydrotalcites. The pH influence results included in Table S1 indicated that the maximum adsorption of Am for MgAlCO<sub>3</sub> was at pH = 4, probably due to the elimination of the carbonate anion as CO<sub>2</sub> together with some dissolution of the LDH and possibly subsequent recrystallization with Am in the interlayer [40]. However, the adsorption was not significantly affected by the initial pH = 4 and 7 for MgAlNO<sub>3</sub> and Mg<sub>x</sub>AlDBS (x = 2 and 3). This led us to adopt an initial pH ~ 6 corresponding to the pH of the Am solutions for all adsorption tests. The DGB adsorption was almost the same at pH 4 and 8, slightly higher at pH 8 for LDH containing inorganic anions, so the pH ~ 8 corresponding to the dye solutions, was used for all the adsorption tests. In general, with the increase of the solution pH, the percentage of the removal of Am and DGB decreases for MgAlCO<sub>3</sub> and MgAlNO<sub>3</sub> adsorbents due to a decrease in the positive charge on the external surface by deprotonation and competition between the anions (anion dyes and OH<sup>-</sup>) for the positive charges of the LDH layer. For nanohybrid samples (Mg<sub>x</sub>AlDBS, x = 2 and 3), the percentage of removal is lower than for the inorganic adsorbents and a decrease in adsorption was observed with the increase of pH solution, due to the repulsion of the negative charges.

The kinetic results of Am and DGB adsorption on the prepared adsorbents are included in Figure 4. The equilibrium for amaranth adsorption on inorganic LDH was reached at 180 min for MgAlCO<sub>3</sub> and 360 min for MgAlNO<sub>3</sub>.



**Figure 4.** Evolution of dye adsorption on inorganic and nanohybrid LDH for: (a) amaranth and (b) DGB.  $q_t$  (mmol/g) is the adsorption capacities of the absorbate at time  $t$  (min).

The adsorption of DGB was much slower than that of Am for all adsorbents. The larger size of DGB (29.4 Å × 7 Å for DGB vs. 15 Å × 9 Å for Am, from Chem Draw 3D 5.0 software package Program cause bigger steric hindrances for its adsorption on LDH. Kinetic modelling of the adsorption process provides a prediction of adsorption rates and allows the determination of suitable rate expressions characteristic of possible reaction mechanisms. In this study, the most frequently used models, the pseudo-first-order, Equation (1) [41], the pseudo-second-order, Equation (2) [42], and the intraparticle diffusion model, Equation (3) [43] were tested:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

$$q_t = k_{ip} t^{0.5} + C \quad (3)$$



where  $q_e$  and  $q_t$  (mmol/g) are the adsorption capacities of the adsorbate at equilibrium and at time  $t$  (min), respectively;  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mmol}^{-1} \text{min}^{-1}$ ) are the rate constants of pseudo-first-order and pseudo-second-order models; and  $k_{ip}$  ( $\text{mmol g}^{-1} \text{min}^{-1/2}$ ) is the intraparticle diffusion rate constant. If the intra-particle diffusion is involved in the process, the plot of  $q_t$  vs.  $t^{1/2}$  will be linear, and, if this line passes through the origin, the rate limiting process is only due to the intra-particle diffusion. Such plots may present a multilinearity indicating that two or more steps take place. The slowest of these steps determines the overall rate of the adsorption process [44].

The kinetic parameters calculated for Am and DGB adsorption on the prepared samples are listed in Tables 2 and 3. The pseudo-second-order model is the most suitable in describing the adsorption kinetics of dyes on LDH based on the correlation coefficient ( $R^2$ ). The applicability of the pseudo-second order suggested that chemisorption might be the rate-limiting step that controls these adsorption processes. Furthermore, the theoretical  $q_e$  calculated values are closer to the experimental  $q_e$  values and explain the kinetics of most adsorption systems very well for a whole range of adsorption periods using different concentrations of dye and adsorbent dosages which present an advantage over pseudo-first order equation [45].

**Table 2.** Kinetic parameters of pseudo-first-order, pseudo-second-order and intra-particle diffusion models for amaranth adsorption by MgAlNO<sub>3</sub>, MgAlCO<sub>3</sub>, Mg<sub>2</sub>AlDBS and Mg<sub>3</sub>AlDBS.

Adsorbents	$q_e$ Exp	Pseudo-1st-Order			Pseudo-2nd-Order			Intra Particle Diffusion		
		$k_1$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$	$k_{ip}$	C	$R^2$
MgAlNO <sub>3</sub>	0.64	0.035	0.622	0.985	0.022	0.680	0.999	0.039	-0.012	0.897
MgAlCO <sub>3</sub>	0.18	0.012	0.157	0.885	0.184	0.184	0.986	0.022	0.086	0.861
Mg <sub>2</sub> AlDBS	0.07	0.009	0.064	0.733	$4 \times 10^{-6}$	0.075	0.963	0.018	0.012	0.797
Mg <sub>3</sub> AlDBS	0.07	0.004	0.028	0.991	0.004	0.068	0.999	0.0008	0.037	0.976

**Table 3.** Kinetic parameters of pseudo-first-order, pseudo-second-order and intra-particle diffusion models for DGB adsorption by MgAlNO<sub>3</sub>, MgAlCO<sub>3</sub>, Mg<sub>2</sub>AlDBS and Mg<sub>3</sub>AlDBS.

Adsorbent	$q_e$ Exp	Pseudo-1st-Order			Pseudo-2nd-Order			Intra-Particle Diffusion		
		$k_1$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$	$k_{ip}$	C	$R^2$
MgAlNO <sub>3</sub>	0.275	0.0001	1.117	0.618	0.058	0.279	0.998	0.003	0.124	0.851
MgAlCO <sub>3</sub>	0.237	0.007	0.427	0.776	0.030	0.241	0.997	0.002	0.095	0.879
Mg <sub>2</sub> AlDBS	0.167	0.004	0.138	0.977	0.175	0.037	0.997	0.003	0.035	0.871
Mg <sub>3</sub> AlDBS	0.155	0.002	0.101	0.939	0.051	0.159	0.997	0.002	0.046	0.891

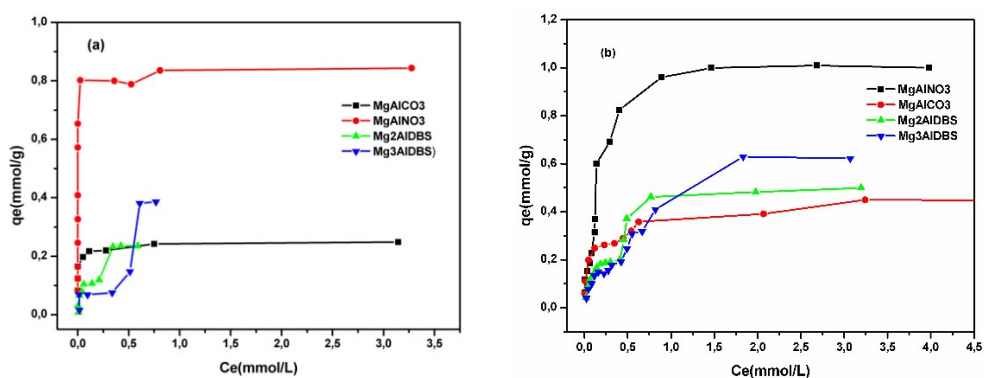
The adsorption isotherms of the two anionic dyes at room temperature and a constant initial pH of the dye solution are illustrated in Figure 5. The adsorbed amount of the dyes was higher on MgAlNO<sub>3</sub> than on MgAlCO<sub>3</sub> because of the lower affinity of the nitrate anion for the hydroxide layer favoured the anionic exchange and produced a greater number of adsorption sites. The small amount adsorbed for MgAlCO<sub>3</sub> probably occurred over the surface of the adsorbent. The adsorbed amount of both dyes was lower for hybrids than for MgAlNO<sub>3</sub>, since the external surface charge of the nanohybrid was negative (as suggested by the zeta potential values (Figure S3) and suffers electrostatic repulsion with the sulfonate groups of the dye molecules. The experimental adsorption data were fitted to the Langmuir and Freundlich models, often used to describe adsorption processes and in which lineal forms are represented in Equations (4) and (5), respectively, and the model of Sips, nonlinear form, Equation (6):

$$C_e/q_e = (1/q_m)C_e + 1/(q_m K_L) \quad (4)$$

where  $q_e$  is the amount of dye adsorbed at equilibrium ( $\text{mmol}\cdot\text{g}^{-1}$ );  $q_m$  is the maximum monolayer sorption capacity ( $\text{mmol}\cdot\text{g}^{-1}$ );  $C_e$  the equilibrium concentration of dye in solution ( $\text{mmol}\cdot\text{L}^{-1}$ ) and  $K_L$  ( $\text{L}\cdot\text{mmol}^{-1}$ ) is a constant related to the sorption energy:

$$\log q_e = \log K_f + N_f \log C_e \quad (5)$$

where  $K_f$  and  $N_f$  are the Freundlich constants that are characteristic of the adsorbent–adsorbate systems [46].



**Figure 5.** Isotherms data of the dye adsorption (a) amaranth and (b) DGB by MgAlCO<sub>3</sub>, MgAlNO<sub>3</sub>, Mg<sub>2</sub>AlDBS and Mg<sub>3</sub>AlDBS adsorbents,  $q_e$  is the amount of dye adsorbed at equilibrium ( $\text{mmol}\cdot\text{g}^{-1}$ ).

The Sips isotherm model [47] is a combination of the Langmuir and Freundlich isotherms that is used to describe heterogeneous adsorption systems:

$$q_e = \frac{q_m K_s C_e^{1/n}}{1 + K_s C_e^{1/n}} \quad (6)$$

The Sips isotherm has the advantage of being reduced to the Freundlich isotherm at low concentrations, and at high concentrations approaches the capacity of the formation of a monolayer such as in the case of the Langmuir isotherm. When  $n$  is equal to 1, the Sips equation is reduced to the Langmuir equation and involves a homogeneous adsorption process.

The influence of the concentration (adsorption isotherms) of Am at room temperature was studied for the four adsorbents and included in Figure 5a. The isotherm shape obtained for MgAlCO<sub>3</sub> was of L-type [48] which suggests a progressive saturation of the adsorbent. This type of isotherm is indicative of molecules adsorbed flat on the surface, or sometimes of vertically oriented adsorbed ions with a particularly strong intermolecular attraction. Moreover, the shape of the isotherms was of type H for dye adsorption on MgAlNO<sub>3</sub> (Figure 5a,b). The H-curve, whose initial section of the isotherm is vertical, arises in special cases of the L-curve, in which the solute has such a high affinity that it is completely adsorbed in dilute solutions. The adsorbate is strongly attracted to the adsorbent mainly by electrostatic interaction [49].

In solid sorbent adsorption, multilayers often form and there may also be a change of orientation of the adsorbed molecules as they increase in concentration on the adsorbent surface. The adsorption isotherms of both dyes on nanohybrids were of the L-4 subtype, characteristic of the isotherms with two slopes (Figure 5a,b). This isotherm type suggests the possibility of adsorption on different types of sites, successively. In both cases, the shape of the isotherms does not change with the increase in the amount of DBS in the interlayer of the hybrids, indicating that the type of interactions between the hybrids and dyes is not affected by the DBS amount. Tables 4 and 5 include the parameters obtained from fitting the data to the different isotherm models discussed above. It was observed that the isotherms adjusted to the Sips model describe a heterogeneous adsorption, indicated by the  $R^2$  values

obtained. The application of the Freundlich model does not allow a satisfactory refinement of the results in all adsorbents.

**Table 4.** Parameters of Langmuir, Freundlich and Sips models of Am adsorption by MgAlCO<sub>3</sub>, MgAlNO<sub>3</sub>, Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS.

Adsorbents	Langmuir				Freundlich			Sips			
	qm Exp	qm	K <sub>L</sub>	R <sup>2</sup>	N <sub>f</sub>	K <sub>f</sub>	R <sup>2</sup>	qm	K <sub>S</sub>	n	R <sup>2</sup>
MgAlNO <sub>3</sub>	1.01	1.259	3.06	0.994	0.47	0.897	0.964	1.083	8.2	0.74	0.998
MgAlCO <sub>3</sub>	0.44	0.279	60.19	0.978	0.25	0.380	0.938	0.314	14.623	0.71	0.991
Mg <sub>2</sub> AIDBS	0.50	0.543	3.26	0.982	0.37	0.327	0.998	1.069	0.486	0.49	0.999
Mg <sub>3</sub> AIDBS	0.63	0.864	0.84	0.998	0.52	0.350	0.985	0.835	0.9125	1.04	0.999

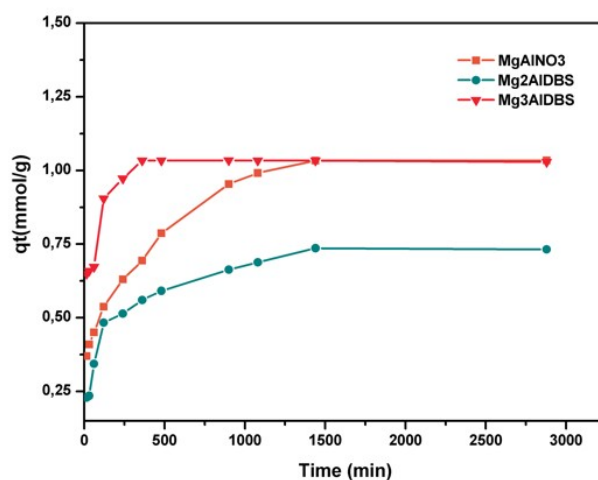
**Table 5.** Parameters of Langmuir and Freundlich and Sips models of DGB adsorption by MgAlNO<sub>3</sub>, MgAlCO<sub>3</sub>, Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS.

Adsorbents	Langmuir				Freundlich			Sips			
	qm Exp	qm	K <sub>L</sub>	R <sup>2</sup>	N <sub>f</sub>	K <sub>f</sub>	R <sup>2</sup>	qm	K <sub>S</sub>	n	R <sup>2</sup>
MgAlNO <sub>3</sub>	0.84	0.794	0.0036	0.557	0.318	0.967	0.998	0.789	2431	0.73	0.999
MgAlCO <sub>3</sub>	0.32	0.221	3083	0.495	0.088	0.251	0.996	0.451	1.218	0.15	0.999
Mg <sub>2</sub> AIDBS	0.24	0.285	10.30	0.974	0.428	0.315	0.964	0.317	5.549	0.85	0.976
Mg <sub>3</sub> AIDBS	0.39	0.788	1.368	0.968	0.695	0.492	0.966	0.923	0.998	0.07	0.968

The shape of the adsorption isotherms for the anionic dyes Am and DGB on nanohybrids Mg<sub>x</sub>AIDBS ( $x = 2$  and  $3$ ) can be related to the fact that the adsorption at low concentrations occurs through anion exchange mechanism, but, as the concentration of dye increases, the large size of the dyes anions impedes their intercalation and probably occurs on the surface through hydrophobic interactions.

### 2.2.2. Adsorption of the Cationic Dye BG

The adsorption process for BG was studied on MgAlNO<sub>3</sub> and the nanohybrid Mg<sub>x</sub>AIDBS,  $x = 2$  and  $3$ . The results of the adsorption kinetics of the BG cationic dye on the MgAlNO<sub>3</sub>, Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS samples shown in Figure 6 indicate that the adsorption equilibrium was reached faster for Mg<sub>3</sub>AIDBS (in 6 h) and slower for Mg<sub>2</sub>AIDBS (in 24 h) similar to MgAlNO<sub>3</sub>.



**Figure 6.** Evolution of BG adsorption on MgAlNO<sub>3</sub> and nanohybrids.  $q_t$  (mmol/g) is the adsorption capacities of the adsorbent at time  $t$  (min).

The kinetic parameters obtained from the application of the different models are shown in Table 6. The pseudo-second-order model is the most suitable in describing the adsorption kinetics of BG in

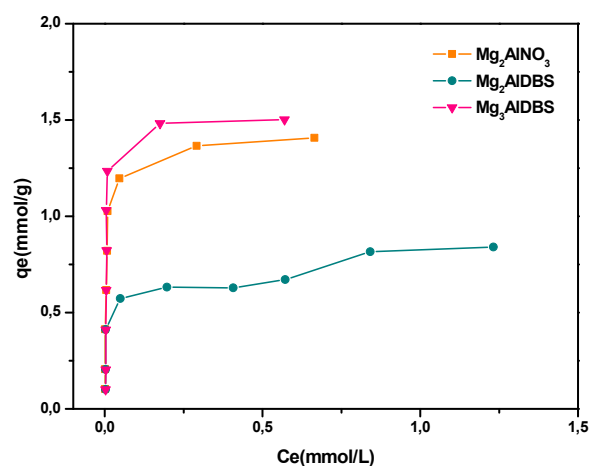


all cases, based on the correlation coefficient ( $R^2$ ) and the agreement between the experimental and calculated values of  $q_e$ .

**Table 6.** Kinetic parameters of pseudo-first-order, pseudo-second-order and intra-particle diffusion models for BG adsorption on MgAlNO<sub>3</sub>, Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS.

Adsorbants	$q_e$ Exp	Pseudo-1st-Order			Pseudo-2nd-Order			Intra Particle Diffusion		
		$k_1$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$	$k_{ip}$	C	$R^2$
MgAlNO <sub>3</sub>	1.03	0.008	0.954	0.885	0.008	1.075	0.996	0.015	0.378	0.889
Mg <sub>2</sub> AIDBS	0.74	2.401	0.998	0.982	0.015	0.752	0.998	0.017	0.292	0.807
Mg <sub>3</sub> AIDBS	1.03	0.003	0.039	0.228	0.095	1.036	0.999	0.008	0.738	0.563

The results of the adsorption isotherms of the cationic dye BG presented in Figure 7 are of H type [48], suggesting a very high affinity between the adsorbent and the adsorbate.



**Figure 7.** Adsorption isotherms of BG on MgAlNO<sub>3</sub> and the nanohybrids,  $q_e$  is the amount of dye adsorbed at equilibrium ( $\text{mmol}\cdot\text{g}^{-1}$ ).

According to the results shown in Table 7, for the three adsorbents, the Sips model fits the experimental data of adsorption equilibrium better than the other models and this is used to describe heterogeneous adsorption systems. The  $n$  value is near to 1 for MgAlNO<sub>3</sub>, therefore adsorption can be represented more appropriately by a monolayer adsorption. However, the nanohybrids Mg<sub>x</sub>AIDBS ( $x = 2$  and  $3$ ) show a value of  $n$  much lower than 1; therefore, the adsorption is not represented by a homogeneous process.

**Table 7.** Parameters of Langmuir, Freundlich and Sips isothermal models of BG adsorption by MgAlNO<sub>3</sub>, Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDB.

Adsorbents	$q_m$ Exp	Langmuir			Freundlich			Sips			
		$q_m$	$K_L$	$R^2$	$N_f$	$K_f$	$R^2$	$q_m$	$K_s$	$n$	$R^2$
MgAlNO <sub>3</sub>	1.40	1.40	190	0.968	0.17	1.62	0.817	1.373	425.2	0.87	0.971
Mg <sub>2</sub> AIDBS	0.84	154.50	0.82	0.850	0.17	0.87	0.786	1.622	1.1	0.69	0.862
Mg <sub>3</sub> AIDBS	1.50	1.53	155	0.977	0.18	1.80	0.873	1.492	38485	0.50	0.999

The high amount of BG adsorbed on inorganic LDH could be due to the hydrotalcite buffer properties, i.e., initial pH solution increases during experiments, which provokes the precipitation of this dye. Nevertheless, for Mg<sub>x</sub>AIDBS ( $x = 2$  and  $3$ ) adsorbents, DBS incorporation changes the electrical properties of the particles making the surface potential negative (according to the zeta

potential shown in Figure S3) and favours the adsorption of cationic dye. Surprisingly, a minor amount of BG was adsorbed on the Mg2AlDBS regarding the Mg3AlDBS sample, which has a higher permanent charge due to the isomorphous substitution of divalent for trivalent metal, and, consequently, a higher DBS content. It could be because the higher DBS loading on Mg2AlDBS provokes steric hindrances for BG intercalation and, in the case of Mg3AlDBS, there is probably some cationic dye co-intercalated with DBS in the interlayer space as will be suggested below by the PXRD pattern of adsorption product (Figure S6c).

### 2.2.3. Characterization of the Adsorption Products

The solids obtained after the adsorption experiments were analyzed by the PXRD technique in order to ascertain how the dye is located in the adsorbent. Figures S4 and S5 show the PXRD patterns of the products of Am and DGB adsorption, respectively, together with the patterns of the adsorbents and of the dyes. The results indicated that the positions of the diffraction lines of the MgAlCO<sub>3</sub> sample were not modified after the Am and DGB adsorption process, possibly due to the fact that the small amounts of dye were adsorbed on the external surface of the adsorbent. However, for the Am adsorption product obtained with MgAlNO<sub>3</sub>, the PXRD pattern included in Figure S4a shows a shift in the position of the reflection lines (*00l*) to the lower angle ( $2\theta$ ) with a change in the  $d_{(003)}$  value from 8.9 Å to 17.7 Å. These lines were very sharp, indicating that the adsorption product retained the crystallinity of the adsorbent according to an anionic exchange process [49]. Similar results were obtained for the DGB adsorption product. However, in this case, the DGB intercalation process is strongly dependent on the concentration of the dye. The PXRD pattern included in Figure S5a shows a shift of the position of reflection line corresponding to  $d_{(003)} = 8.9$  Å to 15.3 Å at low DGB concentration (0.06 mmol/L) according to the intercalation of the anion in the interlayer space. However, at a high DGB concentration (3.7 mmol/L), the interlayer space does not increase any further, indicating that the adsorption takes place on the external surface of the particles, which can be attributed to the large size and elongated shape of the dye anion. The adsorption of dye occurs provided the interlayer spacing of the LDH is greater than the size of the molecule; otherwise, the adsorbent can not accommodate the pollutant [1]. At low concentrations of dye, it is possible to intercalate the DGB ions in a parallel manner or with a small inclination with respects to the sheets of LDH, giving rise to an interlayer space close to that observed in Figure S5a (15.3 Å). This disposition of the ions would allow the cancellation of the layer charge by means of the electrostatic interaction with the sulfonate groups. However, as the concentration of the dye increases, the arrangement of bulky ions becomes more difficult, thus impeding their intercalation and favouring the adsorption on the external surface of the LDH particles.

The PXRD patterns of the Am adsorption products on nanohybrids adsorbents (Figure S4c,d) showed no change in the position of the planes (*00l*), so it can be deduced that the adsorption takes place on the external surface of the particles in the adsorbents studied. Similar results were obtained for the DGB adsorption products on nanohybrids (Figure S5b).

The PXRD patterns of the BG adsorption products are shown in Figure S6. It is interesting to note that there are no changes between the adsorbent Mg2AlDBS and the adsorption product Mg2 AlDBS-BG Figure S6a,b. However, in the case of Mg3AlDBS, a decrease in the basal spacing of the adsorption product Mg3AlDBS-BG compared with the pristine adsorbent, from  $d_{003} = 30$  Å to  $d_{003} = 27.3$  Å Figure S6c, is observed. The reason for this decrease could be the change of orientation of the DBS chains as a result of some co-intercalation of BG between them [50,51].

Table 8 shows the maximum adsorption capacity of some adsorbents compared to the double layered hydroxides prepared in this study. It was observed that the LDH reach the highest adsorption values due to their structural characteristics, anion exchange capacity, the intercalation of anion and/or the ability to modify the hydrophilic nature of the interlaminar space.

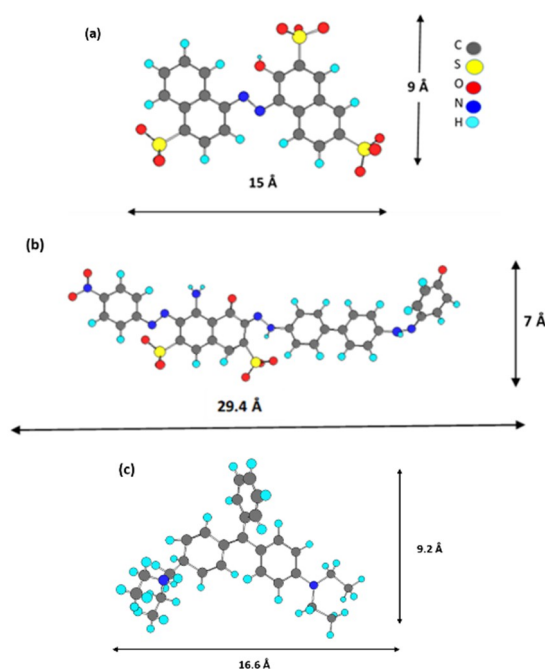
**Table 8.** Maximum adsorption capacity of several adsorbents used to remove the dyes Am, DGB and BG.

Adsorbent	Dye	qm (mmol/g)	Reference
MgAlNO <sub>3</sub>	Am	0.8	This study
MgAlCO <sub>3</sub>	Am	0.2	This study
Mg <sub>2</sub> AlDBS	Am	0.29	This study
Mg <sub>3</sub> AlDBS	Am	0.466	This study
FeO <sub>3</sub> ZnO <sub>2</sub> /Rgo	Am	0.13	[52]
Ashes	Am	0.013	[53]
Alumina/polystyrene	Am	0.033	[54]
MgAlNO <sub>3</sub>	DGB	1.089	This study
MgAlCO <sub>3</sub>	DGB	0.305	This study
Mg <sub>2</sub> AlDBS	DGB	0.557	This study
Mg <sub>3</sub> AlDBS	DGB	0.791	This study
Mahogany sawdust	DGB	0.4	[55]
Polyaniline	DGB	0.26	[56]
AC/CP	DGB	0.15	[57]
MgAlNO <sub>3</sub>	BG	1.418	This study
Mg <sub>2</sub> AlDBS	BG	0.827	This study
Mg <sub>3</sub> AlDBS	BG	1.534	This study
Ni-SBA-16	BG	0.66	[58]
Red clay	BG	0.26	[59]

### 3. Materials and Methods

The inorganic salts were supplied by Panreac (Barcelona, Spain). The organic salts used for the preparation of the organo-LDH nanohybrids containing DBS and the dyes, were supplied by Sigma-Aldrich (Barcelona, Spain). The dyes used were: Amaranth (Am) (trisodium 3-oxo-4-[(4-sulfonatophthalen-1-yl)hydrazinylidene] naphthalene-2,7-disulfonate) whose empirical formula is C<sub>20</sub>H<sub>11</sub>N<sub>2</sub>Na<sub>3</sub>O<sub>10</sub>S<sub>3</sub> and the formula mass is 604.47. This dye presents a maximum absorption at  $\lambda = 520$  nm. Diamine green B (DGB) (disodium 4-amino-5-hydroxy-3-[[4'-[(4-hydroxyphenyl)azo] [1,1'-biphenyl]-4-yl]azo]-6-(phenylazo)naphthalene-2,7-disulphonate whose empirical formula is C<sub>34</sub>H<sub>22</sub>N<sub>8</sub>Na<sub>2</sub>O<sub>10</sub>S<sub>2</sub> and the formula mass is 812.7, presents a maximum absorption at  $\lambda = 623$  nm. Brilliant green (BG) (4-(4-(diethylamino)-alpha-phenylbenzylidene)-2,5-cyclohexadien-1-ylidene) diethylammonium sulfate whose empirical formula is C<sub>27</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>S and the formula mass is 482.63, presents a maximum absorption at  $\lambda = 624$  nm.

The estimated bidimensional molecular size of the dyes was calculated from ChemDraw 3D 5.0 software package program and it has been included in Figure 8.



**Figure 8.** Chemical structure of the dyes: (a) Amaranth, (b) Diamine green B and (c) Brilliant green.

### 3.1. Synthesis of the Adsorbents

#### 3.1.1. Synthesis of MgAlCO<sub>3</sub> and MgAlNO<sub>3</sub> Samples

MgAlCO<sub>3</sub> was coprecipitated by the drop wise addition of a Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O mixed aqueous solution of 1 M concentration of metal in 100 mL, with Mg/Al ratio = 2, to a solution of 2 M Na<sub>2</sub>CO<sub>3</sub>; 2 M NaOH aqueous solution was simultaneously added to keep the pH constant at 10.0 ± 0.3. The MgAlNO<sub>3</sub> sample was also co-precipitated using the same concentration of metal aqueous solution, but this was added to 100 mL of distilled and CO<sub>2</sub>-free water by passing N<sub>2</sub> current. The reaction was carried out under N<sub>2</sub> to minimize carbonate contamination from atmospheric CO<sub>2</sub> and 2 M NaOH aqueous solution was simultaneously added to keep the pH constant at 10.0 ± 0.3. In both cases, the resulting suspensions were hydrothermally treated at 80 °C and then washed and dried at 60 °C [21].

#### 3.1.2. Synthesis of Mg<sub>x</sub>AlDBS (x = 2 and 3) Samples

The nanohybrids, LDH containing DBS anions with Mg/Al = 2 and 3 ratios, were obtained by the coprecipitation method using N<sub>2</sub> atmosphere and CO<sub>2</sub>-free water. For the Mg<sub>2</sub>AlDBS sample, a solution A containing a mixture of 0.04 mol of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.02 mol of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 100 mL of distilled and CO<sub>2</sub>-free water, was added drop wise to a solution B containing 0.12 mol of NaOH and 0.05 mol of dodecylbenzene sulfonate in 500 mL. The resulting suspension was hydrothermally treated at 80 °C and then washed and dried at 60 °C. The procedure for the synthesis of the Mg<sub>3</sub>AlDBS sample was the same, except that the solution A contained a mixture of 0.06 mol of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.02 mol of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 100 mL of distilled and CO<sub>2</sub>-free water [26].

### 3.2. Adsorption Experiments

Dye adsorption isotherms on the prepared adsorbents were obtained by the batch equilibration procedure. Duplicate 25 mg adsorbent samples were equilibrated by shaking at room temperature with 25 mL of dye solutions with initial concentrations (C<sub>0</sub>) ranging between 0.083 mmol·L<sup>-1</sup> and 6.62 mmol·L<sup>-1</sup> for Am, 0.061 mmol·L<sup>-1</sup> and 3.69 mmol·L<sup>-1</sup> for DGB and 0.10 mmol·L<sup>-1</sup> and 2.02 mmol·L<sup>-1</sup> for BG mmol·L<sup>-1</sup>. After a suitable contact time of equilibration, the supernatants were

centrifuged and separated to determine the concentration of the dyes by UV-visible Spectrophotometry. The amount of dye adsorbed ( $q_e$ ) was calculated from the difference between the initial ( $C_0$ ) and equilibrium ( $C_e$ ) solution concentrations.

### 3.3. Experimental Techniques

Elemental chemical analyses were obtained using ICP-mass spectrometry after the dissolution of the solids in 0.1 M HCl (PerkinElmer Nexion X), XRD patterns of powdered samples were recorded on a Bruker D8 discover 28 instrument, the measurements were carried out at room temperature under atmospheric conditions, Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) was used, and the step size and step counting time used were  $0.02^\circ(2\theta)$  and 0.65 s, respectively. FT-IR spectra were obtained on a PerkinElmer Spectrum Two spectrophotometer by using a KBr disk method (the disk containing approximately 1 wt.% of sample in KBr). Nitrogen adsorption–desorption isotherms were recorded on a Micromeritics ASAP 2101 apparatus), using samples previously outgassed at  $100^\circ\text{C}$  under vacuum for 1 h. Specific surface areas (SSA) were calculated by applying the BET method over the relative equilibrium pressure range  $0.05 < P/P_0 < 0.30$ , in the N $_2$  adsorption isotherms. Scanning electron microscopy (SEM) micrographs were obtained using a JEOL JSM 6300 instrument; the samples were prepared by deposition of a drop of sample suspension on a Cu sample holder and covered with an Au layer by sputtering in a Baltec SCD005 apparatus). Thermogravimetric analysis (TGA) was carried out in NETZSCH Leading equipment at a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$  in nitrogen atmosphere. Zeta potential measurements were carried out on Zetasizer Nano ZSP Malvern.

## 4. Conclusions

We examined four samples as potential adsorbents of amaranth (Am), diamine green B (DGB) and brilliant green (BG) dyes from simulated wastewaters. The prepared products are two layered doubled hydroxides (LDH) with carbonate and nitrate as interlayer anion (MgAlCO $_3$  and MgAlNO $_3$ ) and two nanohybrids of LDH intercalated with dodecylbenzene sulfonate (MgxAIDBS,  $x = 2$  and  $3$ ).

The key findings of this study are:

- According to the kinetic studies, the adsorption equilibrium of the dyes was reached in 3 h with LDH containing inorganic anions and less than 24 h for the nanohybrids LDH.
- The dye adsorption process follows the pseudo-second order model in all cases, although it is slower for the cationic dye (BG) than for the anionic ones (Am and DGB), which could be due to its bulky size.
- The three dyes have a high affinity for MgAlNO $_3$ . The structural analysis (PRXD) of the adsorption products suggests that the adsorption at low concentrations occurs through anion exchange. However, at high dye concentrations, the adsorption probably occurs on the LDH surface through hydrophobic interactions. This could be because the large size of the dye anions hinders their intercalation. The adsorption isotherms of Am and DGB adsorption on the MgxAIDBS ( $x = 2$  and  $3$ ) samples occurs in two steps, which suggests the possibility of adsorption on different types of sites.
- According to the PXRD patterns of the adsorption products, the BG adsorption takes place on the external surface of the particles in the three adsorbents studied. This adsorption works best in the nanohybrid samples, probably due to the precipitation of the dye together with the co-intercalation process and/or multilayer adsorption over the DBS (interlayer anion).
- Different types of interactions, such as electrostatic interactions, ion exchange, hydrogen bonding and van der Waals forces, may be involved in the adsorption process, whose interaction dominating the process depends on the nature of the adsorbent and adsorbate.
- The optimal conditions for the adsorption of Am and DGB were for the unmodified pH of the dye solution. The maxima adsorption was achieved for the MgAlNO $_3$  sample.

As such, we found that MgAlNO $_3$  and nanohybrids MgxAIDBS may be used in the design of adsorbents for the removal of anionic and cationic dyes to reduce their adverse effect on water resources.



**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2305-7084/3/2/41/s1>, Figure S1: TG curves in N<sub>2</sub> atmosphere of the samples (a) Mg<sub>2</sub>AIDBS and (b) Mg<sub>3</sub>AIDBS Figure 2: Adsorption–desorption isotherms of N<sub>2</sub> on the LDHs samples (a) MgAlNO<sub>3</sub> and MgAlCO<sub>3</sub> and (b) Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS. Figure S3: Zeta potential values obtained in a KCl solution (0.01 M) at pH between 2 and 12 of the adsorbents: MgAlNO<sub>3</sub>, MgAlCO<sub>3</sub>, Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS. Figure S4: PXRD patterns of the Am adsorption products on the LDH samples: (a) MgAlNO<sub>3</sub>, (b) MgAlCO<sub>3</sub>, (c) Mg<sub>2</sub>AIDBS and (c) Mg<sub>3</sub>AIDBS. Figure S5: PXRD patterns of the DGB adsorption products on the LDH samples: (a) MgAlNO<sub>3</sub>, and (b) Mg<sub>3</sub>AIDBS. Figure S6: PXRD patterns of the BG adsorption products on the LDH samples: (a) MgAlNO<sub>3</sub>, (b) Mg<sub>2</sub>AIDBS and (c) Mg<sub>3</sub>AIDBS. Table S1: Values of the initial and final pH of the adsorption process and the percentage of Am and DGB dyes adsorbed by MgAlCO<sub>3</sub>, MgAlNO<sub>3</sub>, Mg<sub>2</sub>AIDBS and Mg<sub>3</sub>AIDBS. Co = 0.16 mmol·L<sup>-1</sup> except for the Am adsorption experiment by MgAlNO<sub>3</sub> Co = 1.7 mmol·L<sup>-1</sup>, solid solution ratio = 1 g/L.

**Author Contributions:** Conceptualization, I.P. and C.B.; methodology, I.P. and C.B.; investigation, K.A.; writing—original draft preparation, I.P. and C.B.; writing—review and editing, I.P. and C.B.; supervision, C.B.

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