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Synthesis, characterization, and application of Mg/Al layered double hydroxide produced from aluminum frame waste

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Abstract

This work aimed to study the feasibility of synthesizing Mg/Al Layered Double Hydroxide (LDH-Mg/Al) from aluminum waste and evaluate its efficiency in removing Congo Red (CR) dye. The LDH synthesis was performed using the coprecipitation method. The materials were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The XRD and FTIR results showed reflections and bands characteristic of hydrotalcite-type structures, evidencing the formation of LDH. The kinetic and equilibrium data presented best fit the pseudo-first-order and Sips models. A maximum adsorption capacity of 62.03 mg g^{-1}at 60ºC was observed. These results suggest a sustainable and innovative alternative for the reuse of aluminum waste.

Keywords: Layered material; Coprecipitation; Congo red dye.

1. Introduction

Industrial growth has led to significant scientific and technological advancements. However, it has also introduced challenges like waste generation and the depletion of natural resources [1]. The aluminum production industry plays a crucial role, given that aluminum is lightweight, conductive, malleable, and resistant to corrosion. This versatile material finds applications in various fields, including aerospace, civil construction, and maritime industries, among others [2]. Aluminum production generates waste that can accumulate in the environment, posing risks to flora, fauna, and ultimately human health. One such byproduct is aluminum hydroxide, which, despite its environmental impact, has high potential value and can be repurposed to produce other materials that help mitigate environmental damage. An appealing solution is the production of layered double hydroxides (LDHs), which are versatile and capable of ion exchange and regeneration. LDHs are considered environmentally friendly because their synthesis utilizes waste materials.

Given this context, the present study aims to synthesize and characterize Mg/Al layered double hydroxides (LDHs) derived from aluminum smelting residue and to evaluate their effectiveness in remediating Congo red dye. The synthesis process, conducted via coprecipitation, was assessed, followed by comprehensive characterization and analysis of the adsorptive capabilities of the resulting material.

2. Materials and Methods

2.1 Aluminum waste

The aluminum residue was purchased from an aluminum frame factory in Maceió/Al. The basic leaching process, followed by acid precipitation, obtained aluminum hydroxide [3,4].

2.1 Coprecipitation Synthesis of LDH

In the synthesis of LDH, 100 mL of an aqueous solution containing 0.075 mol of $Mg(NO_3)_2$ and 0.025 mol $Al(OH)_3$ was added to 100 mL of another solution containing 0.2 mol of NaOH and 0.05 mol of Na_2CO_3. The system was placed under constant stirring at room temperature. The final material was

filtered, washed with solution, and dried in an oven (75 °C) [5].

The surface functional groups of the CDW were analyzed using a Fourier Transform Infrared (FT-IR) spectrophotometer, specifically the IR PRESTIGE 21 model by Shimadzu. Spectra were acquired within the 4000-400 cm^{-1} range. The mineralogical composition of the LDH was analyzed by XRD using Shimadzu XRD-6000 equipment. The XRD patterns were obtained using a voltage of 40kV, CuKα radiation, and a current of 30 mA. The diffraction patterns were made from 5 to 80°, with a step of 0.02° and an angular speed of 2 degrees min^{-1}.

2.2 Kinetic and Isotherm of Adsorption

The experiments used a mixture of 0.1 g of LDH with 20 mL of a VC solution (50 mg L^{-1} and pH 7). The solutions were kept at room temperature with a stirring speed of 150 rpm. Aliquots were collected between 5 and 180 minutes and analyzed using a UV-Vis spectrophotometer. Adsorption isotherms were performed at 5 to 500 mg L^{-1} concentrations, using temperatures of 30 to 60 °C. The data obtained were fitted using the models presented in Table 1.

Table 1. Equations of kinetic models, isotherm, and thermodynamic parameters.

Model	Mathematical Expression	Eq.
Adsorption capacity	$q_e = \frac{(C_o - C_e).V}{m}$	1
Kinetic model		
Pseudo first order	$q_t = q_e\,(1 - e^{k_1.t})$	2
Pseudo second order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	3
Elovich	$q_t = \frac{1}{\beta_E}\ln(\alpha_E \beta_E + t)$	4
Isotherm model		
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$	5
Freundlich	$q_e = K_F C_e^{1/n}$	6
Sips	$q_e = \frac{q_{max} K_S C_e^{n_s}}{1 + K_S C_e^{n_s}}$	7

where C_o and C_e are the initial and equilibrium concentrations (mg L^{-1}), respectively; V is the volume of the solution (L); m is the mass of the adsorbent (g); q_e and q_t are the amount of dye adsorbed by CDW adsorbent (mg g^{-1}) at equilibrium and time t (min), respectively; k_1 and k_2 are the pseudo-first-order (min^{-1}) and pseudo-second-order (g mg^{-1} min^{-1}) adsorption constant, respectively; α_E (mg g^{-1} min^{-1}) and β_E are Elovich constants; C_e is the concentration of dye at equilibrium (mg L^{-1}); q_{max} is the maximum adsorption capacity of the adsorbent (mg.g^{-1}); K_L, K_F and K_S are Langmuir (L mg^{-1}), Freundlich (mg g^{-1} (mg $L^{-1})^n$), and Sips (L g^{-1}) constants of their respective models of isotherms; n is the dimensionless constant that represents the adsorption intensity; n_s is the exponent of the Sips isotherm model;

3. Results and discussions

3.1 LDH Characterization

Through the FTIR spectrum (Fig. 1), it is possible to observe characteristics of materials with hydrotalcite-type structures, with a broad absorption band around 3681 cm^{-1} and 3515 cm^{-1}, referring to hydroxyls and hydration water [6]. The band around 1630 cm^{-1} is characteristic of the vibration of intercalated water molecules; the material presented a similar band around 1843 cm-1. Bands around 1440 cm^{-1} are attributed to the vibrations of carbonate groups (CO_3^{-2}), seen at 1453 cm^{-1} in the present work [7, 8]. Regions around 400 to 800 cm^{-1} are linked to the stretching vibrations of the Mg-O and Al-O bands, observed at 922, 793, and 498 cm^{-1} [9].

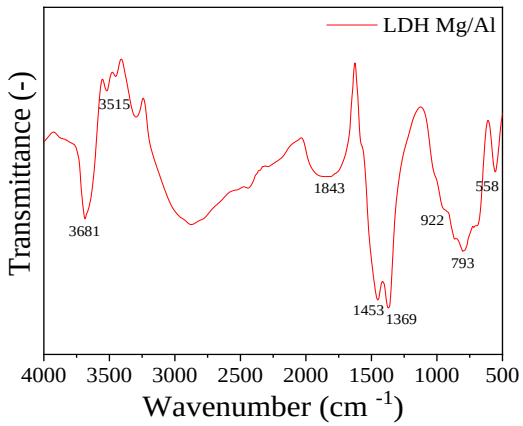

Fig 1. Infrared vibrational spectrum of Mg/Al LDH.

X-ray diffraction analyses in Fig. 2 showed peaks in (003) and (006) at approximate angles of 2θ = 11 and 23, while the (110) plane was around 2θ = 60, these peaks being characteristic of lamellar materials [10,11]. Using the Bragg equation, the

interlamellar distance of the material obtained using the (003) peak was 7.53 Å. This result is similar to that found in the literature, where d_{003} is between 7.43 Å and 7.60 Å [12].

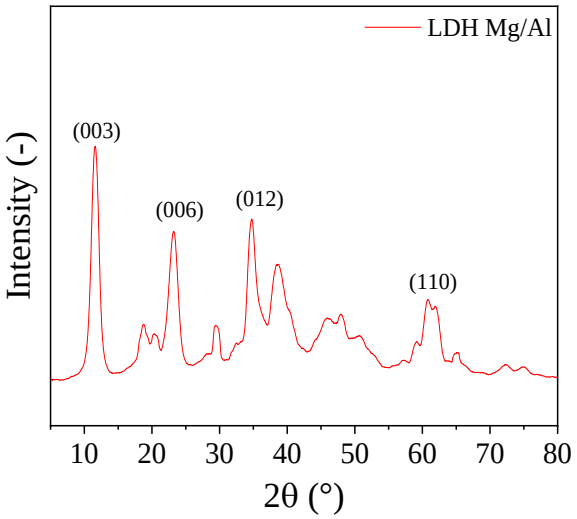

Fig 2. LDH Mg/Al diffractogram

3.2 Adsorption

The kinetics of CR were fast from the beginning, with an average removal rate of 0.804 mg min^{-1} in the first 5 minutes of adsorption. Subsequently, there was a drastic reduction in the rate to 0.0059 mg min^{-1} until reaching equilibrium after 30 minutes of reaction (Fig. 3). The maximum amount adsorbed was 4.355 mg/g.

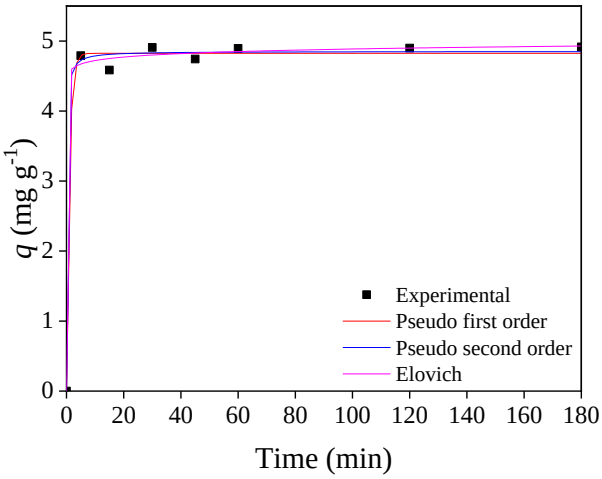

Fig 3. Kinetics of adsorption for CR on the LDH

Within the kinetic parameters in Table 2, it is possible to infer which model had the best fit to describe the adsorption process. The model determination was based on statistical metrics such as mean relative error (ARE) and Akaik criterion (AIC). The adsorption model preferably followed the pseudo-first-order model, as it obtained the lowest values for ARE (1.16) and AIC (-33.76).

Tabela 2. Kinetic model parameters for the pseudo-first order, pseudo-second order, and Elovich models

Model	**Parameter**	
Pseudo-first order	q_e (mg g^{-1})	4.82
	k_1 (min^{-1})	0.99
	R^2	0.99
	$R^2_{adjusted}$	0.98
	AIC	-33.76
	ARE	1.16
	SSE	0.05
Pseudo-second order	q_e (mg g^{-1})	4.85
	k_2 (g mg^{-1} min^{-1})	1.53
	R^2	0.99
	$R^2_{adjusted}$	0.98
	AIC	-80.47
	ARE	1.67
	SSE	0.08
Elovich	β_E (mg.g^{-1})	13.96
	α_E (mg g^{-1} min^{-1})	30.60
	R^2	0.99
	$R^2_{adjusted}$	0.98
	AIC	-33.39
	ARE	1.19
	SSE	0.05

The adsorption equilibrium experiments were performed at different temperatures (30, 45, and 60°C). The results obtained were evaluated from nonlinear fits of Langmuir, Freundlich, and Sips, as presented in Table 3. All models presented an R2. However, the low ARE and AIC values observed for Sips, 6.96 and -5.0, respectively, suggest that the experimental data fit better for this model.

Table 2. Parameters of the Langmuir, Freundlich, and Sips equilibrium models

Model	Parameter	Temperature 30 °C	45 °C	60 °C
Langmuir	K_L (L mg^{-1})	3x10^{-3}	3x10^{-3}	1x10^{-3}
	q_{max} (mg g^{-1})	39,29	41,14	62,03
	R^2	0,99	0,97	0,99
	$R^2_{adjusted}$	0,98	0,92	0,97
	AIC	-0,71	12,56	5,26
	ARE	10,37	22,10	12,77
Freundlich	K_F (mg g^{-1} (mg L^{-1})$^{-1/n}$)	0,53	0,45	0,34
	n	1,59	1.49	1.37
	R^2	0.97	0.94	0.98
	$R^2_{adjusted}$	0.98	0.92	0.97
	AIC	12.22	12.56	12.12
	ARE	35.95	22.09	30.29
Sips	K_S ((g L^{-1})$^{-1/ns}$)	1x10^{-3}	2x10^{-4}	1x10^{-3}
	q_{max} (mg g^{-1})	31.34	25.92	47.06
	n_s	1.24	1.75	1.17
	R^2	0.99	0.98	0.99
	$R^2_{adjusted}$	0.98	0.92	0.98
	AIC	-5.00	4.84	3.77
	ARE	6.96	17.76	6.24

4. Conclusions

The coprecipitation method effectively synthesized the material, as confirmed by the characterizations. This study demonstrates that the approach is a viable and environmentally friendly way to produce a material with potential applications in pollutant removal from water bodies.

Acknowledgments

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