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Influence of mixture uniformity on the synthesis of double hydroxides using baffles: evaluation of crystallinity and removal potential of malachite green and congo red dyes

GABRIEL, Rafaela[a], LINS, Pollyanna Vanessa dos Santos[a], MEILI, Lucas[a*]

[a] *Laboratório de Processos, Centro de Tacnologia, Universidade Federal de Alagoas, Maceió – AL,57072-970, Brasil.*

Abstract

Layered double hydroxides (LDHs) are usually produced by coprecipitation at variable pH. However, this synthesis method requires experimental equipment that rigorously controls the process variables. It is essential to systematically study the process parameters and reactor sizing to understand the mass and energy transfer phenomena, which are fundamental to ensure the homogeneity of the reaction medium and the quality of the clays formed. In this context, this work provides a description of the influence of the use of baffles in the synthesis process of LDHs by the coprecipitation method at variable pH, in a batch reactor. The results were evaluated by the variation in crystallinity of the materials produced and by the result of the application of LHDs as adsorbent agents for the treatment of water contaminated by malachite green and congo red dyes. The results demonstrated that the crystallinity and particles size (92.33–107.03) were favored by the use of baffles in the reaction medium. However, the presence of baffles did not significantly alter the adsorption (q_e) and removal (%) results, demonstrating that crystallinity did not influence the adsorption of dyes.

Keywords: adsorption; anionic clays, dyes.

1. Introduction

Layered Double Hydroxides (LDHs) are a group of minerals composed of two-dimensional layers of anionic character, commonly used in adsorption processes. Among their production routes, the variable pH coprecipitation method stands out, which requires the use of stirred tank reactors or tanks, also called STR (Stirred Tank Reactors) where it is possible to control several process variables, such as stirring speed, temperature, presence/absence of baffles and others. [1,2]

The appropriate choice of synthesis methods and, consequently, of their synthesis parameters is important for the stabilization of the laminar structure of LDHs and for the definition of their morphological and structural characteristics, such as crystallinity, porosity, surface area and others.[3]

Among the process variables, the presence or absence of baffles is a relevant factor for the agitation and mixing process, which can directly influence the homogeneity of the medium and contact between the reagents. [1,4]

This work proposes the study of process variables in a batch reactor for the synthesis of LDHs by coprecipitation. The study was carried out by varying the presence/absence of baffles in the reaction medium, with fixed rotation speed (200 rpm) and aging time (18 hours). Two materials were produced and applied to the adsorption process of two synthetic solutions produced with malachite green and congo red.

2. Methodology

The 2:1 LDHs (MgAl) used in this study were synthesized by the coprecipitation method at variable pH. [5-7] The method consisted of mixing two solutions; a solution A, containing 1.42 M $Mg(NO_3)_2.6H_2O$ and 0.71 M $Al(NO_3)_3.9H_2O$ in 434 ml of deionized water and a solution B composed of 2.2 m NaOH and 1.2 m Na_2CO_3 in 700 ml of deionized water. The solutions were stirred at 200 rpm for 18 hours, varying the presence/absence of baffles in the reaction medium. Then, the LDH gels were subjected to the following steps: a) washing, carried out in a centrifuge with 5 reproduction cycles at 2500 rpm; b) drying, carried out in an oven at 105 °C for 4 h, and c) sieving. Two LDHs with distinct characteristics were obtained, which were applied to two dye solutions, malachite green and congo red, totaling 4 experiments.

The adsorbents produced under were characterized by X-ray Diffraction (XRD) techniques. The XRD technique was used to identify the basal spacing (d_{hkl}), the lattice parameters a and c and the crystallite size (D), according to equations 1-4, respectively.

$$n\lambda = 2d_{hkl}\sin\theta \tag{1}$$

$$D = \frac{k\lambda}{\beta\cos(\theta_B)} \tag{2}$$

$$a = 2d_{110} \tag{3}$$

$$c = \frac{3}{2}(d_{003} + 2d_{006}) \tag{4}$$

Where, n is the reflection order of the peak, λ is the X-ray wavelength used in the analysis, θ and θ_B are the Bragg angle, k represents the shape factor, β is the width at half height of the diffraction peak (FWHM), and d_{003}, d_{006}, and d_{110} are the basal spacings for the (003), (006), and (110) peaks calculated by Equation 1.

For the adsorption studies, 0.04 g of LDH was placed in contact with 20 mL of each solution (20 ppm). The system was stirred at 150 rpm for 24 hours. Subsequently, the samples were centrifuged and subjected to absorbance reading, performed at maximum wavelength, 501 nm, and used later to determine the concentration of adsorbates. The adsorbed amount was determined by Equation 5 and the removal efficiency (%), by Equation 6:

$$q_e = \frac{(C_0 - C_e).V}{W} \tag{5}$$

$$\% = \frac{(C_0 - C_t)}{C_o}x100 \tag{6}$$

Where, C_0, C_t and C_e, are the initial values, at time t and at equilibrium of the adsorbate concentration ($mg.L^{-1}$), respectively. And V is the volume of the solution (L), W is the mass of adsorbent (g) and qe is the quantity adsorbed at equilibrium time. ($mg.g^{-1}$).[8]

3. Results

To evaluate the structural characteristics of the LDHs, the synthesized materials were characterized by XRD (Figure 1). According to the figure, there is the formation of symmetrical reflections for the planes (003), (006), (110) and (113), and asymmetrical reflections for the basal planes (012), (015) and (018). The presence of these planes indicates the formation of layered double hydroxides in all process conditions used. It is also observed that the peak profiles present differences between them, with changes in height and width, which are indicative of the variation in the crystalline structure between the materials.

Table 1 presents the relationship between the crystal planes, the lattice parameters (a and c) and the basal spacing (d_{003}), which indicate the formation of a 3-R type crystal arrangement (rhombohetric symmetry) with values close to those reported in other studies. [9]

The estimation of the particles size (D) demonstrated that the LHD produced in the presence of baffles presented a larger crystal size (107.03 nm) and corresponded to the LHD that presented better crystallinity, while the LDHs produced without baffles presented a smaller crystallite size (92.33 nm).

It is possible to see that the variation in these characteristics is associated with the homogeneity effects associated with the use of baffles. According to Figure 2, the mixtures stirred in the presence of baffles promoted better homogeneity of the medium, which may have contributed to the increase in the crystallinity of the material produced.

Fig 1. X-ray diffractogram of LDHs.

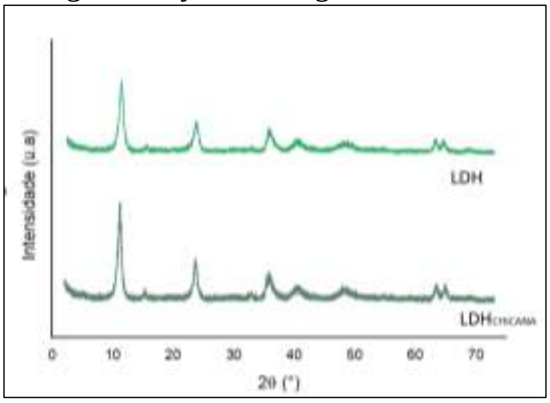
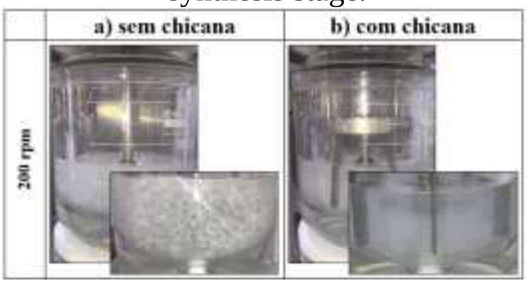


Table 1. X-ray Diffraction Parameters.

	Basal spacing (Å)	Cell Parameter (Å)		Particles size (nm)
	d_{003}	a	c	D
LDH	7.65	3.04	22.79	92.33
$LDH_{CHICANA}$	7.68	3.05	22.96	107.03

Fig 2. Influence of the chicane during the LDH synthesis stage.



Figures 3 and 4 show, respectively, the adsorbed quantity (q_e) and the removal percentage (%) of the dyes as a function of the LDHs produced with and without baffles. The analysis of the presence/absence of baffles indicates that there was a slight increase in q_e and in the removal percentage in the adsorption process of the two dyes used.

For the malachite green dye, the increase was 0.05 $mg.g^{-1}$ for q_e and 1.93 % for the removal percentage. For the Congo red dye, the increase was 0.01 $mg.g^{-1}$ for q_e and 0.48 % for the removal percentage. However, despite the difference in these analyzed parameters, the difference is not greater than 5%.

In this case, considering the q_e and the percentage of removal, the addition of baffles to the reaction medium would not be indicated, since their use would imply higher costs and complexity of the reactor, such as the need for baffle sizing studies, increased frequency of reactor cleaning due to gel fouling, etc. However, in processes that aim to produce adsorbents with better crystallinity, the use of baffles is promising and increases the crystallinity of the material produced under the conditions of this study by about 14%.

Fig 3. Equilibrium concentration (q_e) of dyes as a function of HDLs.

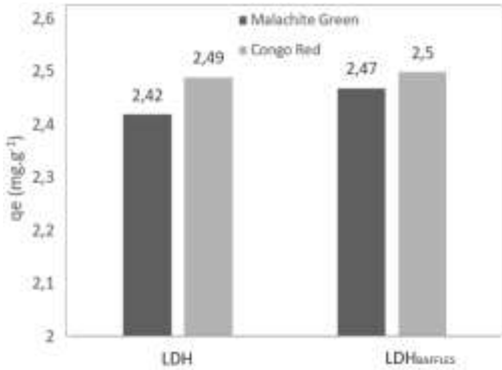
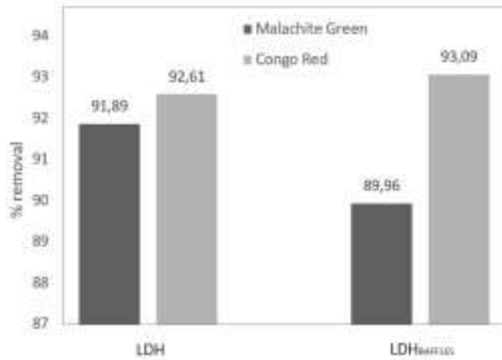


Fig 4. Removal efficiency (%) of dyes as a function of LDHs



4. Conclusion

In this study, the effect of presence/absence of baffles in the reaction medium for the synthesis of LDHs was evaluated. The presence of baffles proved to be promising for determining the crystallinity of the materials and caused an increase in the particle size, from 92.33 to 107.03 nm, in the materials analyzed. However, the presence of baffles did not demonstrate a significant effect on the amount of adsorbed (q_e) and removal efficiency (%). This behavior suggests that the increase in crystallinity did not influence the adsorption process of the solutions produced with malachite green and congo red dyes.

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