MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Influence of pH on the synthesis of layered double hydroxides for adsorption of ectoparasiticide

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Abstract

In this work, layered double hydroxides, ZnAl, were synthesized in a molar ratio of 3:1, by the coprecipitation method at increasing pH, with synthesis 1 and synthesis 2 being completed at pH equal to 8 and 12, respectively. According to the characterizations performed, the LDH was synthesized satisfactorily. The XRD showed reflections that corroborate these materials, presenting an interesting difference in the crystallite size between the materials produced. Through SEM, it was possible to observe that the adsorbents have platelet, hexagonal and layered morphologies. The adsorbents produced were used to adsorb malachite green from aqueous solutions, with adjusted pH values. Confirming that since VM is cationic, the adsorptive process is favored in conditions in which the adsorbent is negatively charged, that is, at pH above the pH_{PCZ}, as occurs in both materials. Furthermore, it was possible to observe that in S2 the material presented better crystallinity, a more ordered structure, a more uniform distribution of charges on the surface, in addition to offering a greater number of active sites, when compared to S1, important characteristics for a good adsorbent, a fact confirmed in the affinity tests, where for the VM solutions at pH 3 the removal percentage increases from 5.43% in S1 to 59.19% in S2 and for the VM solutions at pH 9 it increases from 12.96% in S1 to 70.68% in S2, evidencing the influence of the final pH 12 on the synthesis of LDHs.

Keywords: Malachite green, adsorption, LDH, synthesis;

1. Introduction

Emerging pollutants (EPs) are toxic, often unregulated chemicals that can have impacts on human and environmental health [1]. For example, malachite green (MG) is a dye that has several applications, such as therapeutic agent, antiseptic, fungicide and ectoparasiticide in fish farming. However, it is reported in the literature as highly toxic to mammals, thus inducing the formation of tumors, in addition to inhibiting thiol-containing enzymes. [2].

Due to the inefficiency of conventional water and effluent treatments against these EPs, it is necessary to search for methodologies to remove this compound. In this sense, adsorption has shown promise in the removal of several substances in aqueous media, as it is efficient and selective, in addition to the possibility of using adsorbent materials with low production and operating costs [3].

In this scenario, layered double hydroxides (LDHs) have received attention, because in addition to their high adsorption efficiency, they are easy to synthesize [4]. LDHs are anionic lamellar materials derived from brucite, containing divalent and trivalent metal cations octahedrally coordinated by hydroxyl ions, capable of accommodating anionic species between the lamellae. Due to the possibilities of combinations between the species that constitute it, as well as the synthesis method, LDHs present several properties, such as high ion exchange capacity, high porosity and surface area and good thermal stability. In addition, LDHs that have Al in their composition can be synthesized by using products previously wasted by some industries, with ZnAl and CuAl being little explored [5].

The present work aimed to synthesize and evaluate the influence of the pH of synthesis of LDHs composed of ZnAl cations, as adsorbents in the process of removal of VM from aqueous solutions. For this, the produced materials were characterized by the methods of X-ray diffraction (XRD), scanning electron microscopy (SEM), as well as, had the determination of the potential of zero charge (pHpzc). The adsorption study was carried out through the affinity test.

2. Experimental

The adsorbate used in this work was malachite green (VM), with molecular formula $C_{23}H_{25}ClN_2$. A 10 mg.L^{-1} solution was used for the affinity test with pH change (3 and 9). Absorbance readings were performed at the maximum wavelength, 617 nm, and later used to determine the adsorbate concentrations. The amount of MG adsorbed was determined by Equation 1 and the percentage of removal by Equation 2.

$$q_t = \frac{(C_o - C_f)*V}{m} \quad (1)$$

$$\% = \frac{C_o - C_f}{C_o} * 100 \quad (2)$$

Where, C_0 and C_f, are the initial and final concentration of the adsorbate (mg.L^{-1}), respectively, V, volume of the solution (L), m, the mass of adsorbent (g) and qt is the quantity adsorbed in time t (mg.g^{-1}) [6].

The adsorbents were synthesized by the coprecipitation method at increasing pH [7]. nitially, two solutions were prepared, the first being an aqueous solution containing 0.1 M sodium carbonate and the second containing zinc nitrate, aluminum nitrate, in a molar ratio of 3:1 and 200 mL of deionized water. This solution was kept under constant stirring for 20 minutes. After this, solution two was slowly added to solution one, where they remained under stirring for 10 minutes. With the aid of a burette, a 2 M NaOH solution was slowly added until pH 8 (S1). The procedure described was repeated, but the basic solution was added until the synthesis reached pH 12 (S2), generating a new adsorbent. With the pH values adjusted as desired, the syntheses were transferred to a bath with a temperature of 20 ºC, where they remained for 24 hours. [8]. Finally, the syntheses were washed and then placed to dry in an oven for 24 hours at 80 ºC. After drying, the materials were macerated until their average diameter was less than 35 mesh.

The affinity test was performed by weighing 0.04 grams of each adsorbent material produced, placing them in contact with 20 ml of the pollutant, and then placed in an incubator at 30 ºC, 150 rotations per minute for a period of 24 hours.

3. Results

The XRD patterns of the synthesized LDHs are presented in Figure 1, indicating the formation of crystalline structures and displaying the characteristic reflections of the material composed of zinc and aluminum according to Seftel et al., 2008 [9]. The sample corresponding to S2 has well-defined peaks at approximately 11.8°; 23.4°; 34.4° and 39.2° which correspond to reflections (003), (006), (012) and (015) respectively. S1, on the other hand, has a peak at 46.7° which corresponds to reflection (018). The peaks at approximately 60° and 61.7° corresponding to reflections (110) and (113) are present in S1 and S2, corroborating the data obtained by [10,11].

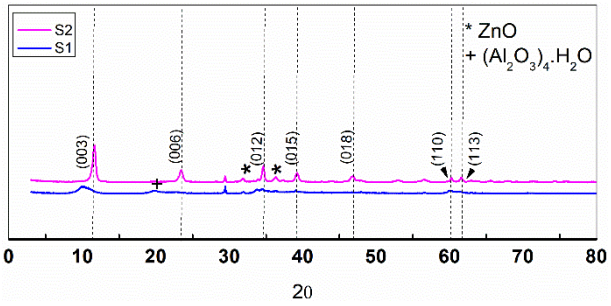

Figure 1: X-ray diffractogram of the synthesized materials.

Table 1: Values obtained by X-ray diffractometry.

HDL	Espaçamento Basal (Å)		Parâmetros de Rede (Å)		D(nm)
	d_{003}	d_{006}	a	c	
S1	8,5	3,8	3,1	24,3	49,3
S2	7,5	3,8	3,1	22,7	181

Low intensity reflections can be attributed to a secondary phase (ZnO), observed in syntheses with pH greater than 10, as can be seen in S2, when 2Θ

~ 32° and 37°, this result is similar to that presented by Abderrazek, et al., 2017. As for S1, the materials are a mixture phases of ZnAl and (Al_2O_3) 4.H_2O. [12].

The basal spacing corresponding to the d_{003} and d_{006} reflections, the lattice parameters a and c, as well as the average crystallite size of the adsorbents produced, are presented in Table 1, where it is possible to see the large difference in the values relative to the crystallite size, with S2 being almost four times larger than S1.

The morphology of the materials (Figure 2) presents characteristics attributed to LDHs, such as a dense body, apparently in layers, with a rough surface. In the morphology of S1, it is possible to observe a layered structure, apparently in a hexagonal format, with pores. In S2, in addition to having the characteristics mentioned, it presents a possibly crystalline structure such as sheets [13].

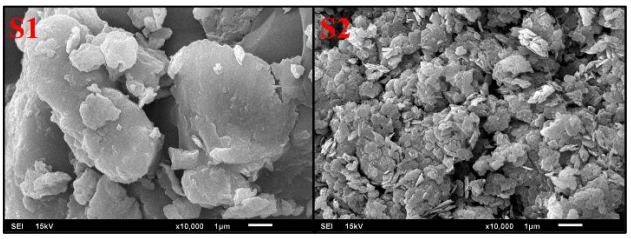

Figure 2: Scanning electron microscopy of synthesized materials.

Table 2: Quantity adsorbed and percentage of removal, using Malachite Green solutions with adjusted pH (3 and 9).

LDH	pH=3		pH =9	
	$q_{mg/g}$	% Removal	$q_{mg/g}$	% Removal
S1	0,31	5,43	0,74	12,96
S2	3,39	59,19	4,05	70,68

MG is a cationic compound, therefore, its adsorption will be favored in conditions where the surface of the HDLs is negatively charged, that is, at a pH above the PZC, as observed in both materials. In this sense, electrostatic interactions predominate in the adsorption process [14].

Table 3: Zero charge potential of materials.

LDH	pH_{PZC}
S1	6,26
S2	6,92

In S1, lower crystallinity is observed, as indicated by less sharp XRD patterns, suggesting a less ordered structure and fewer available adsorption sites. Furthermore, the amorphous or incomplete structure may not provide a favorable surface charge distribution for the cationic adsorption of malachite green. However, in S2 the opposite is observed, where better crystallinity and a more ordered structure favor the creation of a surface with a more uniform and stable charge distribution, in addition to offering more adsorption sites [15].

At pH = 3, the surface of S1 will be positively charged (pH < PZC), resulting in a lower adsorption of malachite green (5.43%) due to the less defined structure and the electrostatic repulsion between the positive charges on the surface of the adsorbent and the cationic adsorbate. In S2, even with a net positive surface charge, it presented better adsorption capacity at all pH values, which can be explained by the better crystallinity of the material, which offers more active sites and a better distribution of charges, when compared to the other material. [16].

In both materials, the basic medium favored the adsorption process, being more pronounced in S2 (70.68%) due to its more defined properties, which can be attributed to the better structural quality, crystallinity and crystallite size, observed in XRD. [17].

4. Conclusion

According to the results obtained, we can propose that the final pH of the synthesis of HDLs composed of zinc and aluminum had a significant influence on the adsorptive capacity of the materials produced, regardless of the pH of the dye solutions evaluated, as well as that the synthesis of the materials was performed satisfactorily, corroborating with results existing in the literature, in view of the result of the characterizations.

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