



Removal of Anionic Dye by Batch Adsorption Using Layered Double Hydroxide Adsorbents Supported on Alginate and functionalized with Activated Carbon from Pine Nut Shell

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Abstract

Adsorption is one of the most effective techniques in treating pollutants, and this process is usually used to remove dyes. In this work, the objective was the synthesis and evaluation of blends of LDH with alginate functionalized with activated carbon from pine nut shell and the application in the removal of an anionic dye—reactive blue BF 5G. Adsorption tests were performed to define the best blend synthesis methodology. As a result, the LDH blends showed higher adsorption capacity. On the other hand, using activated carbon reduced the adsorption capacity of the blends, which had better results only in their LDH and alginate composition. Adsorption tests were performed for different dye pHs, obtaining an optimal pH of 4.5. It was concluded that alginate increased the mechanical strength of LDH with a high removal capacity of the reactive blue dye BF 5G, which allows its use in fixed-bed processes.

Keywords: Adsorption; Dye; LDH; Alginate; Activate carbon;

1. Introduction

Anionic dyes are emerging pollutants widely used in textile industries and commonly found in low concentrations in the tailings of these industries. A widely used method of treating these wastes is adsorption, which involves chemical and physical interactions between a solid (adsorbent) and a fluid (adsorbate). Layered double hydroxide (LDHs) are inorganic lamellae that, when applied as an adsorbent, have a high adsorptive capacity, in addition to being substances capable of synthesis that is easy to replicate on a large scale [1]. Despite its high adsorptive capacity, LDH has a low mechanical strength, which makes its application in fixed-bed processes difficult. In this context, it is proposed to support this adsorbent in sodium alginate (SA), which consists of a natural polysaccharide derived from brown algae [2]. Thus, this work aimed to synthesize and evaluate the adsorptive properties of activated carbon blends obtained from pine nut shells, functionalized with HDL and alginate.

2. Methods

2.1 Adsorbate

The Blue Reactive BF 5G textile dye was supplied by Lavanderia Nova Maringá (Maringá - PR). For concentration quantification, absorbance readings were performed in a Genesys 10 UV Scanning Spectrophotometer, Thermo Scientific, at a wavelength of 620 nm.

2.2 LDH synthesis and alginate blends

For the synthesis of LDHs, three different methodologies were selected. Methodologies A and B were modified from [3]. For methodology A, 0.03 mol of $MgCl_2$ and 0.01 mol of $AlCl_3$ were dissolved in 100 mL of distilled water, with a slow drip of another 1 mol L^{-1} NaOH solution, with magnetic stirring and at room temperature until obtaining a pH of 10. After the dripping process, the solution was aged at 80 °C, and stirring continued for another 24 h. The final solution was filtered, washed, and the product dried in an oven at 80 °C for 24 h.

For methodology B, the same process was carried out, differing only in the aging temperature,

which in this case was used at room temperature for 3 days.

Methodology C was modified from [4]. 0.0325 mol of $MgCl_2$ and 0.0125 mol of $AgCl_3$ dissolved in 20 mL of distilled water were used. 3M NaOH was slowly dripped into the cation solution with magnetic stirring and at room temperature until reaching pH 10. After dripping, the solution was aged at room temperature, under continuous stirring, for 2 hours. After that, the product was vacuum filtered, washed with distilled water, and oven dried at 80 °C for 24 h.

For the production of the blend, 2% (m/v) of sodium alginate was dissolved in 15 mL of distilled water, and then a mass of dry solid LDH was added. The proportion of LDH varied from 1, 5, and 10% (m/v). The sodium alginate and LDH solution were dripped with a peristaltic pump into 300 mL of 3% (m/v) $CaCl_2$ solution for crosslinking or ionic gelling. Then, the solution was stirred for 24 hours and washed with distilled water.

Finally, the drying step was also evaluated: in the lyophilization drying, the particles were previously frozen at -80 °C for 1 h in an ultra-freezer, and then the material was placed in the lyophilizer at -101 °C and 39 μ mHg until complete sublimation of the water (24 h) [2,5]; drying at room temperature was performed by placing the blend granules on filter paper and left at room temperature for 72 h [2,6]; drying in an oven was carried out at 60 °C for 24 h [7,8].

An experimental design of split plots was used to optimize the synthesis of the LDH and alginate blend, evaluating the LDH synthesis methodology, the percentage of LDH in the blend (1, 5, and 10%), and the drying temperature (-80°C, 25°C, and 60°C). These treatments were randomized for each LDH synthesis methodology (A, B, and C) performed in triplicate. Thus, the planning was carried out with 9 plots and 81 subplots.

To evaluate the best blend of LDH and alginate, the response variable of the experimental design was the percentage of dye removal BF 5G. For this, adsorption tests were carried out in triplicate of 0.02 g of blend in 50 mL of dye solution BF 5G 50 $mg L^{-1}$ for 168 hours at 25 °C at 80 rpm without changing the pH.

2.3 Activate carbon synthesis

With the best conditions of the experimental planning carried out, the blends were functionalized with activated carbon.

Carbonization of pine nut shell (CCP): The dried and patterned pine nut shell was inserted into

a stainless steel reactor and placed in a 3kW power split furnace under nitrogen flow (150 mL/min). The sample was heated at a heating rate of 10 °C/min and a ramp at 450 °C for 2 h.

Chemical activation of the material (CCP-KOH): Impregnation was performed at a ratio of 1:4. Briefly, 50 g of CCP and 200 mL of 1 g/mL KOH solution were added to a beaker under heating for 6 h. Subsequently, the paste was transferred to an oven at 105 °C until the material was completely dry. After the slurry had dried, the dry mixture was heated at a heating rate of 10 °C/min and ramped to a plateau at 900°C for 1 h. The product was washed until a constant pH was obtained. The material suspension was filtered, and the retained solid dried in an oven at 105 °C for 24 h.

Functionalization of activated carbon with LDH (HT-LDH-CCP-KOH): The hydrothermal treatment was adapted from [9], where a certain amount of dry LDH and activated carbon was dispersed in 30 mL of water and transferred to a stainless steel autoclave heated at 200 °C for 24 h.

2.4 Synthesis of the alginate@LDH blends

2% (w/v) of sodium alginate was dissolved in distilled water, and then a mass of dry solid CCP-KOH-LDH or HT-LDH-CCP-KOH was added. The sodium alginate and charcoal solution were dripped with a peristaltic pump into a 3% (m/v) $CaCl_2$ solution for crosslinking or ionic gelation. Then, the solution was stirred for 24 hours and washed with distilled water.

Batch adsorption tests were performed in triplicate for all compounds synthesized using the reactive dye BF 5G. A 50 $mg L^{-1}$ dye solution was used.

2.5 pH evaluation

To evaluate the pH effect in the Blue BF 5G dye percentage of removal, adsorptions were carried out in triplicates with the two best blends in the condition of 0.03 g for 50 mL of solution, at a concentration of 50 $mg L^{-1}$, agitation of 80 rpm and 25°C. Thus, after dissolving the dye in distilled water, the initial pH of the samples was adjusted.

3. Results and discussion

3.1 LDH and alginate blends

The variables analyzed in the experimental design were proposed in the possibility of increasing dye removal. Adjustments were made to the statistical model for variance analysis to analyze the results, considering subplots within plots, so the large portion is the LDH synthesis

methodology. Residual adjustments were performed in logarithmic transformation (Neperian basis) on the observed values for model diagnosis and to improve the homogeneity of the residues. The response surfaces are shown in Fig. 1.

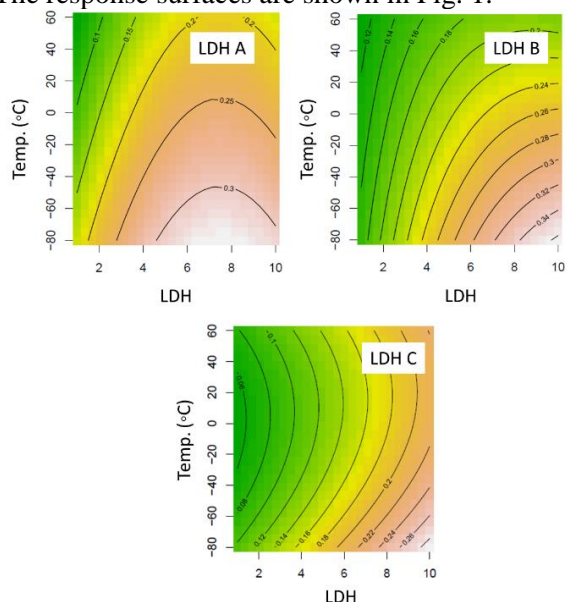


Fig. 1. Surface response for the reactive blue adsorption in the blend of LDH and alginate.

The LDH synthesis methodology factor had no significant effect on the adsorption percentage since the p-value was 0.611.

The amount of LDH and drying methods significantly affected the percentage of dye removal since the p-value was 0.000. In addition, the interaction between these two factors was also significant since the p-value was 0.0128.

In this way, observing Fig. 1 and the two significant factors: % of LDH and drying methods, greater removal was obtained with 10% of LDH added to the alginate and drying by lyophilization. As for the synthesis methodology, there was no significant difference.

3.2 LDH and alginate blends with activate carbon

Then, CCP-KOH-LDH and HT-CCP-LDH-KOH were synthesized with LDH from methodology A, 10% LDH, and dried by lyophilization. Finally, the synthesis of the blend of these materials with alginate was carried out.

LDH is the main responsible for the removal of the dye. However, it is the one with the smallest size (particle size), a factor that makes it impossible to apply adsorption in a continuous process. Thus, pine nut husk charcoal and sodium alginate are incorporated into this initial adsorbent.

To evaluate the removal of reactive blue dye BF 5G, adsorption was performed with the

experimental conditions of 0.04 g of adsorbent, 100 mL of dye solution at a concentration of 50 mg L⁻¹, the temperature of 25°C, and adsorption time of 216 hours (or 9 days). The adsorption results are shown in Fig. 2.

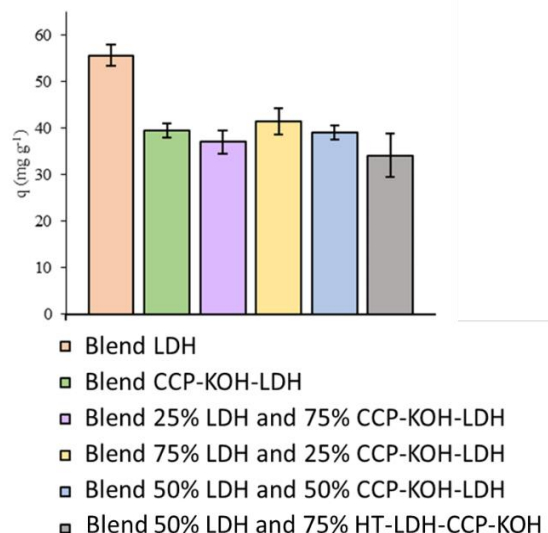


Fig. 2. Adsorption capacities of the reactive blue dye adsorption in the alginate blends.

As can be seen in the results presented in Fig. 2, the highest adsorption capacity was found in the blend of composition only with LDH (without charcoal), of 55.65 mg g⁻¹, which corresponds to the removal of 43.5% of dye. In the synthesis of this blend, 2% (m/v) of sodium alginate was dissolved in distilled water, and 10% (m/v) of solid LDH was synthesized by methodology A. This percentage of LDH was the maximum possible to be used due to handling the viscous alginate solution with dissolved solids.

Comparatively, studies that used other adsorbents for the adsorption of the Reactive Blue BF 5G dye obtained similar adsorption capacities to the blend, of 42.58 mg g⁻¹ with malt bagasse [10] and 72.21 mg g⁻¹ [11] with biomass of banana.

3.3 pH evaluation

To evaluate the influence of pH on adsorption, the determination of the zero-charge point of the adsorbent was identified at a pH of 7.9, indicating that at pHs below this value, the surface of the adsorbent is positively charged and above this value, negatively. For the reactive dye BF 5G blue, we have two pKas in the values of 4.6 and 7.0. Still, the presence of sulfonic groups in the structure indicates a pKa below zero, characterizing this dye as anionic [12].

To experimentally observe the influence of pH on the removal of dye, adsorption was carried out with the experimental conditions of 0.025 g of

adsorbent, 50 mL of dye solution at a concentration of 50 mg L⁻¹, the temperature of 25°C, and adsorption time of 216 hours (or 9 days). The adsorption results are shown in Fig. 3.

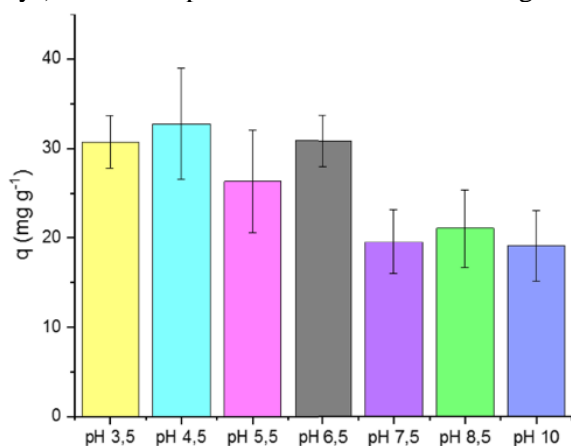


Fig. 3. Reactive blue dye BF 5G adsorption with LDH and alginate blends at different initial pHs.

We can conclude from the observation of the results in Fig. 3 that the pHs with the greatest capacity to remove the dye were 4.5 and 6.5. When dissolving the dye in distilled water, the pH of the solution is measured to be 4.5, so this pH value for adsorption was used without the addition of acid or base. As it is the pH value with the highest adsorption capacity and the least change in the system, this was the optimal pH chosen for adsorption. Furthermore, at this pH, the surface of the dye molecule has a negative charge and is attracted by the positive charge on the surface of the adsorbent (pH below the PCZ).

4. Conclusions

In this work, it was observed that the removal of dye Reactive Blue BF 5G using blends of LDH supported on sodium alginate as adsorbent proved efficient with the optimum condition at 10% LDH, methodology A of synthesis, lyophilization drying, and pH 4.5. Thus, the blends' synthesis increased the adsorbent's mechanical strength (LDH), allowing subsequent application in fixed beds.

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