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Application of LDH/Alginate Composite Adsorption on Reactive Blue Dye BF 5G using Phenomenological Modeling

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Abstract

The layered double hydroxides (LDH) exhibit promising applications due to their adsorption capabilities in textile dye and their potential for composite formation with various materials. This study presents significant findings with its meticulous focus on applying composites with LDH/alginate to remove the Reactive Blue BF 5G textile dye. The surface characteristics and composition of the composite were obtained, with a low specific area, pore volume, and low average particle diameter. Batch adsorption tests were conducted over 53 days at 25, 40, and 55°C, gathering kinetic and equilibrium data. Freundlich and BET equations fit the data well, revealing a maximum adsorption capacity of 248.05 ± 24.45 mg g^{-1} at 40°C. The monolayer-multilayer adsorption (MMA) model adequately adjusted in the equilibrium and kinetics. The rate-limiting step was the Monolayer and Multilayer Adsorption since the MMA model provided the best fit, indicating the possibility of adsorption of multilayers for higher dye concentrations.

Keywords: Textile dye; Layered double hydroxides; Adsorption; Reactive Blue BF 5G; Modeling.

1. Introduction

The textile industry is of extreme socioeconomic importance worldwide, but it is also, one of the largest causes of wastewater pollution. The complex composition of dyes makes these compounds highly soluble and poorly degradable. The presence of these compounds in water bodies increases the chemical and biochemical demand for oxygen, impairing photosynthesis and plant growth. At the same time, when they enter the food chain, they have a bioaccumulative effect, causing organ and nervous system dysfunction in humans, as well as tumors [1].

Among several forms of wastewater purification to remove dyes, Layered Double Hydroxides (LDH) stand out, as they are materials with highly adjustable two-dimensional structures, and an excellent adsorptive capacity, low cost, and easy to synthesize from commonly available organic precursors. The characteristics of this material can be further improved with the use of a support, such as sodium alginate, a biopolymer extracted from brown algae that, in the presence of divalent cations, forms a water-insoluble and thermoreversible gel; alginate has been widely used due to its availability, biodegradability, and varied application [2].

The literature presents a research gap in adsorbent optimization and applications of phenomenological models using mass balances in both the liquid and solid phases, thus representing the adsorption process more realistically.

The aim of this work is LDH/Alginate composite application in removal, by adsorption of reactive dye BF 5G, with subsequent evaluation of phenomenological modeling.

2. Materials and Methods

The LDH/Alginate composite was previously prepared and synthesized by methodology I, LDH/sodium alginate composite with 10% (m/v) and freeze-drying were used [3].

Composite Characterization

For the synthesized composite, the size distribution was estimated by analyzing particle images using ImageJ software on a population of at least 50 spheres.

The neutral charge pH of the composite surface was obtained by the Point of Zero Charge (PZC), in which adsorbent and distilled water solutions with initial pH variations between 2 and 12 were left under stirring for 24 h and, after the contact time, the final pH of the solution was measured.

To evaluate the specific area, total volume, and pore diameter of the composite, N_2 Adsorption and Desorption isotherms were obtained at -196 °C on the Accelerated Surface Area and Porosimetry System Plus model 2020TM Micromeritics.

High angle X-ray diffraction (XRD) analyses were carried out using a Shimadzu diffractometer, with copper tube and nickel filter, CuKα radiation, scanning speed of 1° 2θ min-1 of 5 to 80° 2θ, 40 kV and 30 mA. XRD peaks were analyzed and compared with the X'Pert HighScore program database.

Adsorption

All adsorption experiments were carried out in a unilateral shaking incubator (Dubnoff EthicTechnology bath). The amount of dye removed by each sample was calculated by the component mass balance of the dye in the liquid phase of the stirred tank, as presented in Eq. (1).

$$q=\frac{v(C_0-C_f)}{m} \quad (1)$$

Where C_0 and C_f are the initial and final concentrations of the dye solution, respectively (mg L^{-1}); q corresponds to the dye adsorption capacity per mass of adsorbent (mg g^{-1}); V is the volume of solution (L); m is the mass of adsorbent used in adsorption (g).

For the adsorption kinetics, the adsorption of Blue BF 5G dye was carried out in triplicate at pH 5.5 with 0.025 g of the adsorbent composite in 50 mL of solution, stirring at 100 rpm. The percentage of removal was evaluated every 24 hours until reaching the balance. Adsorption kinetic data was obtained at initial concentrations of 25, 50, and 75 mg L-1 at 25, 40, and 55 °C temperatures.

Three models are proposed, two of which are diffusional, in which only one stage of mass transfer was considered, this being the rate-limiting stage of the adsorption process, and a reaction model, in which mono- and multilayer adsorption is the limiting step of adsorption.

In the External Resistance to Mass Transfer (ERMT), a laminar sublayer is considered around the adsorbent particles due to viscous effects (or non-slip conditions). In this mass transfer in the liquid film, diffusion occurs in a one-dimensional manner, with the driving force given by the difference in concentration between the liquid phases in a region very close to the external surface of the adsorbent [4].

In the Internal Resistance to Mass Transfer model (IRMT), internal diffusion is the limiting step of the adsorption process, and the concentration profile is considered a function of the radial coordinate and time [5].

The kinetics are controlled by the adsorption itself in the Monolayer-multilayer adsorption (MMA), neglecting the effects of resistance to the adsorbent particle's internal or external mass transfer [6]. The BET isotherm model also presents the monolayer and multilayer constants as the equilibrium constants K_S and K_L. Thus, these constants can be inserted into the MMA model.

For equilibrium investigation, the adsorption of Blue BF 5G dye was carried out in triplicate at pH 5.5, with 0.025 g of composite in 50 mL of solution, stirring at 100 rpm and up to an adsorption time longer than the equilibrium obtained in the kinetics. The isothermal curves were performed at initial concentrations of 25, 50, 75, 100, 150, 200, 300, 400 and 500 mg L^{-1} at 25, 40 and 55 °C temperatures.

To model the adsorption equilibrium, the mechanism proposed by Langmuir (1918) was applied. In this mechanism, it is considered that there is no interaction between the adsorbed species, and the adsorbate molecules interact with a fixed and defined number of solids and a homogeneous monolayer adsorption surface of the adsorbent.

There are several hypotheses to be considered in the adsorption process, so in addition to the Langmuir Isotherm, several other equations describe the adsorption equilibrium, such as Freundlich and BET.

3. Results and Discussion

Composite Characterization

The particle size distribution showed relatively normal behavior, with an average diameter of 0.451 cm.

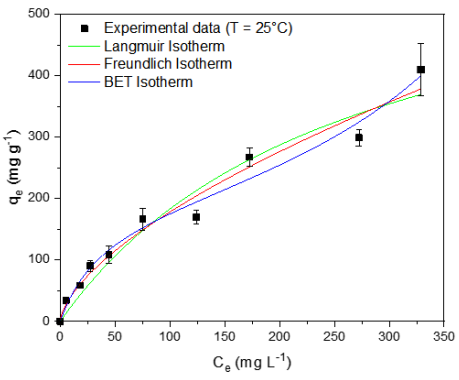
The PCZ experiments indicate a value of 7.9 and present a near-neutral surface within the pH range between 4 and 8. Therefore, the pH used, 5.5, was defined in previous experiments as being optimal for adsorption without adding acid or base to obtain this pH in solution.

The Composite presented a specific area of 6.18 $m^2\ g^{-1}$, pore volume of 0.019 $cm^3\ g^{-1}$, and average particle diameter of 0.451 cm. The dimensions of the Reactive Blue BF 5G dye molecule are 24.6 and 12.79 Å (or 2.46 and 1.28 nm); thus, the material's pore size (12.23 nm) is 4.9 times larger than the size of the adsorbate molecule, a value that represents the effective adsorption area.

The LDH diffractogram indicated typical reflection peaks of Magnesium Aluminum Hydroxide Carbonate Hydrate with ICSD number 081964, identified as a review of hydrotalcite crystal chemistry. Thus, LDH particles were effectively encapsulated in sodium alginate. Sodium alginate does not contribute peaks to the diffractogram, as it is an amorphous (non-crystalline) biopolymer composed of multivalent cations.

Adsorption

The dye adsorption isotherms under different temperatures, presented in Fig. 1, show a non-linear sigmoidal shape, which can be classified according to Giles classification as type S3. Type S3 isotherms result from two adsorption mechanisms, which are characteristic of monolayer adsorption on the surface of the adsorbent. The adsorbed dye molecules in the monolayer can rearrange to make more active sites available, indicating that the adsorbed dye has some intermolecular interaction with the dye in the solution, leading to multilayer adsorption.



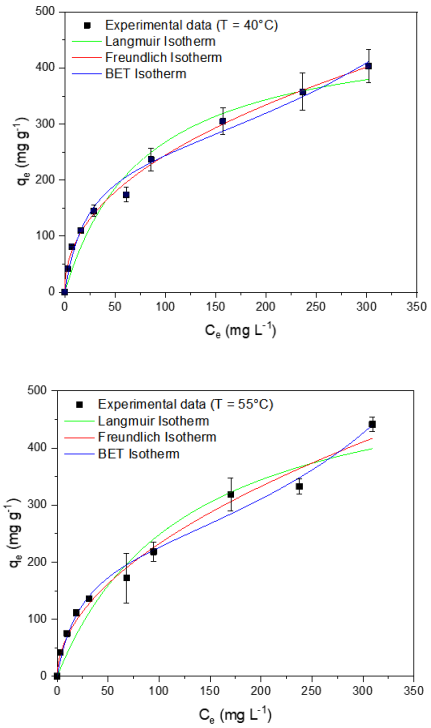


Fig. 1. Simulations of isotherms adjusted to experimental adsorption equilibrium data at 25, 40, and 55 °C.

It was possible to observe that the BET model described the adsorption isotherm well at a temperature of 25 °C, while the Freundlich model was the best fit at temperatures of 40 and 55 °C. The maximum adsorption capacity of 248.05 ± 24.45 mg g-1 at 40 °C. Both isotherm models describe multilayer adsorption, as also described by Giles for S3 type isotherms shape.

The adsorption kinetics of removal of the Reactive Blue BF 5G dye with LDH/Alginate composite was evaluated for different concentrations and temperatures (Fig. 2). Diffusional modeling was performed with Freundlich and BET adjustments; however, all concentrations and temperatures had more minor deviations when used with the BET equation.

Evaluating the fitting-quality statistical parameters for adsorption kinetics at 25 and 55 °C yielded better mathematical modeling of monolayer and multilayer adsorption, corroborating the system's characteristics for S3 type isotherms shape.

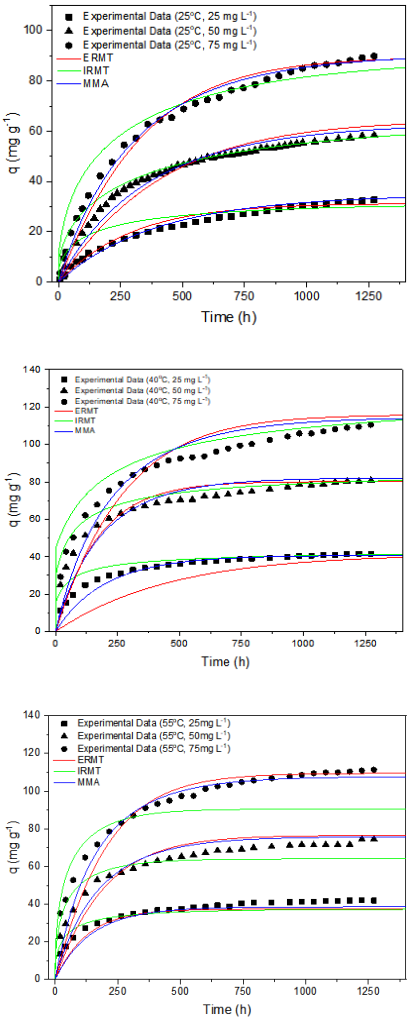


Fig. 2. Adsorption kinetics experimental data for different initial concentrations and temperatures of 25, 40, and 55 °C and kinetic models fitting.

When observing the previously presented results of characterization of the adsorbent particle, with a low specific area, low pore volume, and average particle diameter of 0.451 cm, these results agree with the fit to the MMA kinetic model and BET isotherm. Considering the low values of surface area and pore volume, as well as the large pore sizes compared to the molecular size of the BF 5G dye, the internal resistance to mass transfer is not expected to be relevant.

4. Conclusions

Applying these materials to remove the Reactive Blue BF 5G dye successfully synthesized LDH/alginate composites. The composite was characterized, obtaining the main results of low specific area and pore volume with an average particle diameter.

The BET model best described the equilibrium experimental data. The diffusional steps (External Resistance to Mass Transfer and Internal Resistance to Mass Transfer) were negligible for kinetics. Hence, the rate-limiting step was the Monolayer and Multilayer Adsorption since the MMA model provided the best fit at all temperatures and concentrations, indicating the possibility of adsorption of multilayers for higher dye concentrations.

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