ARGILAS MODIFICADAS PARA ADSORÇÃO DO CORANTE RODAMINA B

Modified Clays For Rhodamine B Dye Adsorption

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RESUMO: Uma argila bentonita natural (Bofe) proveniente de um depósito localizado em Boa Vista (PB-Brasil) foi submetida a dois processos de intercalação diferentes, tais como organofuncionalização, usando cátions de hexadeciltrimetilamônio em diferentes concentrações e pilarização, usando o íon de keggin de alumínio. As amostras foram caracterizadas por difração de raios X e aplicadas a testes de adsorção do corante orgânico Rodamina B. Os testes foram realizados empregando 0,5 g da argila modificada em 100 mL de uma solução de 50 ppm de Rodanima B. Alíquotas de 1 mL foram retiradas nos tempos de 0 a 8 h, 24 h e 72h e analisadas por espectroscopia de UV-Vis. A amostra que apresentou o melhor resultado foi a Org 5/2, que alcançou, aproximadamente, 97% de remoção.

Palavras-chave: Argila Montmorillonita. Argilas Pilarizadas. Argilas Organofílicas. Rhodamina B.

ABSTRACT: A natural bentonite clay (Bofe) from a deposit located in Boa Vista (PB/Brazil) was subjected to two intercalation procedures such as organophilization using hexadeciltrimethylammnonium cations with different concentrations and pillaring using aluminum Keggin ion. The samples were characterized by X-ray powder diffraction. Subsequently, the samples from these procedures were applied in the organic dye Rhodamine B adsorption test. The tests were carried out using 0.5 g of modified clay in 100 mL of a 50 ppm solution of Rhodamine B. Aliquots of 1 mL were withdrawn at times of 0 to 8 h, 24, and 72 h, which were analyzed by UV-vis spectroscopy. The adsorption capacity of clay can be increased with treatments such as pillarization and organophilization. The d001 and swelling effect are essential properties to give accessibility to Rhodamine adsorption. The sample showing the best result was the Org 5/2, which achieved a percentage removal of approximately 97 %.

Keywords: Montmorillonite clay. Pillared Clays. Organoclays. Rhodamine B.

Introduction

Dyes and pigments are very important in the industry, especially textile, to obtain products with different colors. However, a high volume of water is used for most industrial processes, generating hazardous waste. When in contact with rivers and other fluvial waters, this waste may cause severe disorder in the biological cycle of the living creatures of those places.

Due to their high toxicity and carcinogenic nature, dye water pollution causes several environmental problems. Thus, the color removal from effluents is of great importance and can considerably influence the aquatic environment with changes in biological cycles. Organic dye residues are those that stand out for their toxicity. (CLAUSEN, 2007; KAUSAR et al., 2018).

Since ancient times, clays have been widely used by humanity; they are commonly defined as natural, earthy, fine-grained materials that exhibit plasticity when moistened with water (SOLTANI et al., 2019).

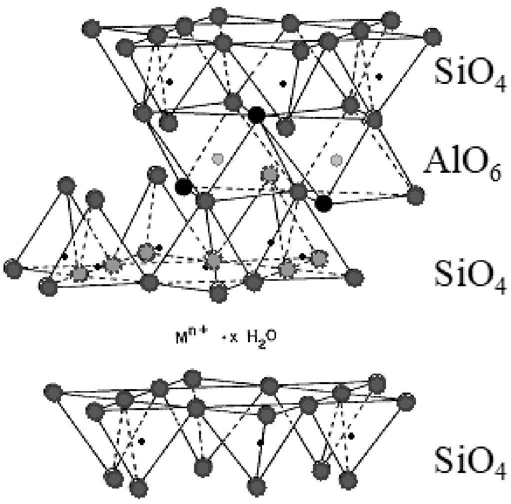
These natural materials have many applications in several processes due to their adsorption capacity and low cost. A clay mineral usually used is Montmorillonite. This material has a lamellar structure composed by the connection of three sheets. One central sheet is formed by aluminum in octahedral conformation, and the other two by silicon in a tetrahedral conformation. These layers are stocked and have a negative charge; due to this, they have interlayer cations compensating the charge. (Figure 1) These materials have high superficial area, cation exchange capacity, and swelling properties, making them interesting for adsorption. Several treatments can be done to increase these properties, such as organophilization and pillarization.

Organophilic clays are materials synthesized by exchanging the cations in the lamellar space for organic compounds such as surfactants (HE et al., 2019). This indicates that the structure and properties of organophilic clays are affected by the type of surfactant, and the mineral used.

Pillarization is another chemical modification process in clays that may influence their adsorption capacity. Pillared clays are materials with open and rigid structures obtained by intercalating large metallic species in interlamellar space (MNASRI-GHNIMI; FRINI-SRASRA, 2019). The resulting material, after calcination, contains oxides that act as pillars, keeping the clay layers separate and exposing the internal clay surfaces (PERGHER; SPRUNG, 2005).

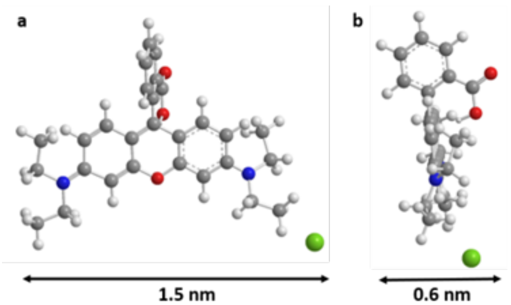
Based on this versatility of clays and the growing need for environmental treatments, the present work studies the behavior of natural clay, which has been submitted to organophilization and pillaring processes, as well as the natural sample itself for the Rhodamine B dye (Figure 2) adsorption process.

Figure 1. Montmorillonite Structure. 2:1 layer formed by two tetrahedral sheets (composed by the union of SiO_4) with one central octahedral sheet (organized by the union of AlO_6). Between these layers there are M^{n+} compensating hydrated cations



Fonte: Adapted from Pergher (2005)

Figure 2. Molecular dimensions of Rhodamine B by the longitudinal (a) and lateral (b) view



Esferas cor branca = cidrogênio; cinza = Carbono; azul = nitrogênio; vermelho = oxigênio; verde = cloro

Materials and Methods

The natural clay (Nat) used was bentonite from Boa Vista-PB- Brazil (named Bofe).

This clay was organophilized (Org) with different clay/surfactant mass ratios: 5/0.5, 5/1, 5/2, 5/4, and named according to their mass ratio. The clay was organophilized using a modified method based on the literature (KOZAK; DOMKA, 2004; LOPES, et al., 2011). In this procedure, hexadecyltrimethylammonium bromide ($C_{16}TABr$) was dissolved in 25 mL of distilled water and transferred into a beaker containing a clay suspension (5 g of clay and 50 mL of distilled water). It was magnetically stirred for 20 h at room temperature. The samples were filtered, washed, and dried at room temperature for 30 h.

The pillaring of the Nat sample was made according to the literature (BERTELLA and PERGHER, 2015). The pillaring agent solution is prepared using 0.2 mol/L $AlCl_3.6H_2O$ and 0.2mol/L NaOH solutions. The NaOH solution is dropped slowly on the $AlCl_3.6H_2O$ solution maintaining a molar ratio of OH/Al of 2. This solution was held at 60 ° C under magnetic stirring for 24 h. In another beaker, 3 g of Nat sample was mixed with 300 mL of water for 2 h. After that, the pillaring agent solution was transferred into the clay suspension and stirred for 2 h. After, the sample was filtered, dried, and calcined at 450 °C for 3 h. This sample was named PILC.

Rhodamine B adsorption tests were performed using 0.5 g of the previously prepared adsorbents and 100 mL of a 50 ppm solution of the organic compound. In contact with the adsorbent, the solution was constantly stirred on an orbital table (Solab SL-180D) at 200 rpm. To determine the amount of adsorbed dye, 1 mL aliquots were taken at intervals of 0 to 8 h, followed by measurements at 24 and 72 h. Altogether about 10 mL of the total volume was removed for analysis. Aliquots represent 10% of the total volume. Aliquots were filtered using a 0.41 μm filter (Millipore). After initial analysis of the results, the experiment was repeated, aliquots were taken every 10 minutes within 1 hour. Aliquots were analyzed on a UV-vis spectrophotometer (Hach DR5000), where the amount of dye adsorbed at the wavelength of 555 nm was observed.

The materials were characterized by X-ray diffraction (XRD) on a Bruker D2 Phaser apparatus using Cu Kα radiation (λ = 1.54Å) with a Ni filter, a step size of 0.02 °, 10 mA current, 30 kV voltage, using a Lynxeye detector.

Results and Discussion

Figure 3 shows the diffractograms of the natural (Nat) and pillared clay (PILC) samples. It is observed that characteristic peaks of smectite clays (at 2θ = 6, 20, and 22 °) are maintained after the pillaring procedure, which confirms that the treatment retains the structural integrity of the layer. In addition, the peak at 2θ = 26.5 ° reveals the quartz phase as natural clay impurity. After the pillaring process, the (001) plane shifted to lower angles, which indicates the pillaring was successful. Thus, the intercalated Al_{13} Keggin ion turns into rigid aluminum oxide pillars during the calcination, keeping the lamellae separate from each other. The height of interlamellar galleries was estimated at 0.84 nm (subtracting the basal spacing of 1.82 nm from the average thickness of the type 2:1 clay lamella; 0.98 nm).

Figure 3. XRD of Nat and PILC samples

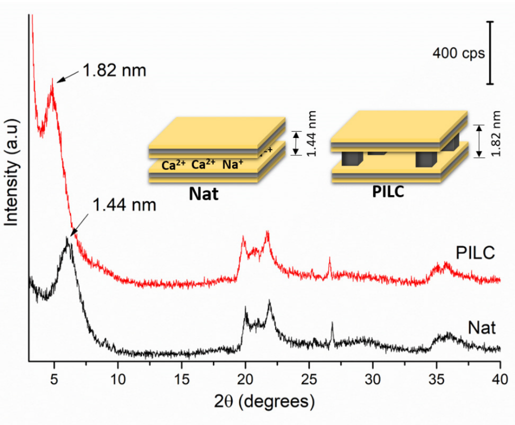
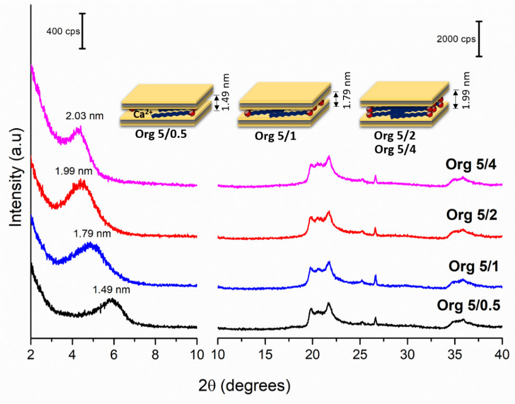


Figure 4 shows the XRD of the organoclays with different surfactant contents. The peaks of smectite-type clay also remained after the organophilization process, confirming the structural integrity of the lamellae. In addition, there is a gradual shift of the (001) diffraction plane to lower angles with the increase of the surfactant content.

Figure 4. XRD of the organoclays Org 5/0.5, Org 5/1, Org 5/2, and Org 5/4



It is observed in Figure 4 (2θ = 10 - 40 °) that the characteristic reflections of smectite-type clay also remain after the organophilization process, confirming the structural integrity of the layers. Figure 4, on the left, shows low angle diffraction analyses (2θ = 1-10 °) to see the (001) peak.

For the Org 5/0.5 sample, the basal spacing values (1.49 nm) are similar to the Nat (1.44 nm) shown in Figure 2. However, this reflection was broader than the Nat sample. It may indicate an inhomogeneous stacking of clay lamellae and a partial exchange of the alkaline cations for the surfactant molecules in lateral monolayer accommodation.

It is observed that increasing the amount of surfactant to the clay suspension in the organophilization step causes displacement of the (001) reflection to shift to lower angles.

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This shift is most evident in the sample with the highest amount of surfactant added (Org 5/4), which had a basal spacing of 2.034 nm. Whereas the surfactant employed CTMABr has a theoretical molecular size of ~ 2.0 nm and a head group size of ~ 0.67 nm, and knowing the thickness of a clay lamella (0, 98 nm), it is attributed that for samples Org 5/1 adopted a lateral monolayer accommodation and Org 5/2 and Org5/4 a lateral bilayer accommodation (see insert in Figure 4).

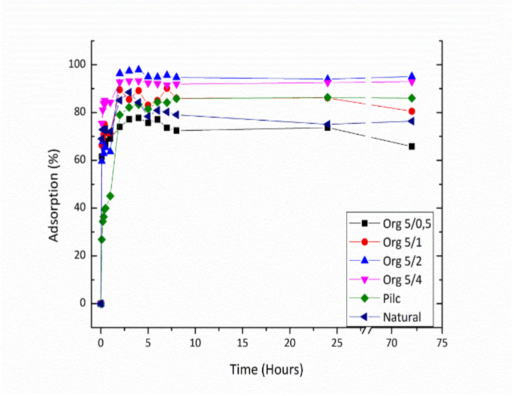
The adsorption results are shown in Figure 5. It is observed that after 2 h, the system goes into equilibrium and no more adsorption of Rhodamine B occurs. Thus, the best result was the Org 5/2 sample, that showed a reduction of 97% up to 5 h and remained after 24 and 72 h. The clay with the highest surfactant concentration, Org 5/4, showed adsorption in the 92% range after 5 h of the test and remained constant at 24 and 72 h. These samples have the highest d001 (1.99 nm and 2.03 nm), justifying the bigger adsorption capacity than other materials. The Org 5/4 sample has more organic content than the Org 5/2 sample; it may block the Rhodamine B adsorption. This indicates that an ideal quantity of surfactant permits more accessibility and adsorption capacity.

The Nat sample obtained an adsorption result of 88% in a time of 3 h, this being its maximum adsorption point. This sample has the lowest d001 (1.44 nm) but it is expansible. So, this high adsorption capacity is mainly due to the swelling capacity of the clay and its cation exchange capacity since Rhodamine B has a positive charge which can be exchanged for the natural clay cations.

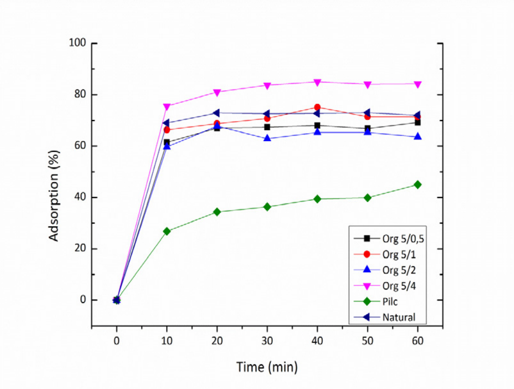
The other samples, Org 5/0.5 and Org 5/1, had a maximum adsorbed amount of 77% and 90% at 4 and 7 h, respectively. These samples have lower d001 (1.49 nm and 1.79 nm) than other organophilic samples, which justifies the lower adsorption capacity.

For initial adsorption times, it can be seen from Figure 4.b that the Org 5/4 has fast adsorption, followed by Nat and other organophilic clays. This is indicative of accessibility. High d001 and swelling d001 make them more susceptible the adsorption. PILC samples have a rigid stacked structure that limits the diffusion of Rhodamine B in initial times.

Figure 5. Rhodamine B adsorption results (a) times from 0 to 72 h and (b) times from 0 to 1 h



(a)



(b)

Conclusion

Layer disposal and cation exchange capacity play an important role in adsorption processes. All materials have the same structure layers. The Nat has high CEC and it can swell, having a good Rhodamine B adsorption. Pillared clay has a staked structure with increased porosity and area, but it limits the accessibility of Rhodamine B and its diffusion. Organiphilized clays have similar behavior to natural clay, but adsorption is increased by the influence of organophilization processes.

It is concluded that bentonite clays are attractive materials for dye adsorbents, specifically Rhodamine B. The adsorption capacity of clay can be increased with treatments such as pillarization and organophilization. The d001 and swelling effect are essential properties to give accessibility to Rhodamine adsorption.

The most efficient material was Org 5/2 organophilized clay which achieved a percentage of dye removal in the range of 97% up to 5 h.

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