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Hybrid Pigments from Bixin Dye and Inorganic Matrices †

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Abstract: Annatto dye is a natural organic dye belonging to carotenoids, whose main components are bixin and norbixin. Due to its low stability, it is convenient to protect the dye molecules with other materials. The use of clay minerals is an alternative, which are phyllosilicates with attractive physico-chemical properties, such as high specific surface area, cation exchange capacity, mechanical/chemical stability and non-toxicity. The main purpose of this work was to develop hybrid materials, using annatto dye and clay mineral modified with different inorganic cations, and then, to evaluate the stability of the new pigments. The process of preparing the modified clay minerals involved mixing a synthetic montmorillonite in solutions containing the precursor salts of the metal cations. Subsequently, the dye was dissolved in a solution containing water and alcohol, followed by filtration and mixed with the modified clay, giving rise to the hybrid pigments. Through the characterizations, it was noted that a variety of colors were obtained, and the sample containing aluminum was the one that most adsorbed the dye and showed a significant increase in stability at high temperatures. This hybrid material was better to dye than its pure form. Therefore, the bixin/montmorillonite pigments are promising for replacing artificial colors in practical applications such as in the cosmetics, food or pharmaceutical industries.

Keywords: annatto dye; modified montmorillonite; inorganic cations; hybrid pigments

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1. Introduction

Pigment is the term used to designate a solid, organic or inorganic particle, with specific colors (white and black, for example) or fluorescent, which is insoluble in the substrate in which it will be incorporated and also does not promote any reaction with it [1,2].

Annatto dye is a natural organic pigment belonging to carotenoids, being widely used as a food dye due to its low toxicity. This dye consists of two main components, which are bixin and norbixin [3]. In addition, it is less stable and easily discolored, so that light is the most destructive agent [4].

In this sense, the protection of the dye molecule by other materials, clays for example, is one of the approaches that has been gaining prominence in recent years. Clays are natural materials, basically composed of organic matter, magnesium and aluminum lamellar silicates, quartz, feldspars and metal oxides. They also have clay minerals in their composition and among them, montmorillonite, which belongs to the smectite group, stands out.

Thus, the main purpose of this project was to develop hybrid materials, using annatto dye and clay modified with inorganic cations, aiming at the incorporation of bixin in the synthetic clay montmorillonite, and later to evaluate the stability of the new hybrid pigments.

2. Methodology

2.1. Materials

The annatto dye (bixin) was obtained commercially at an open market in the city of Teresina-PI. Synthetic sodium montmorillonite clay, calcium nitrate tetrahydrate (Ca $(NO_3)_2 \cdot 4H_2O$), purity 99%, MM = 236.15 g mol^{-1}, aluminum acetate $(CH_3COO)_2Al(OH)$, purity 99%, MM = 162.08 g mol^{-1}, magnesium acetate tetrahydrate ($(CH_3COO)_2Mg \cdot 4H_2O$), purity 99%, MM = 214.45 g mol^{-1}, iron (III) nitrate nonahydrate ($FeN_3O_9 \cdot 9H_2O$), purity 99%, MM = 404.00 g mol^{-1}, copper nitrate trihydrate (Cu $(NO_3)_2 \cdot 3H_2O$), purity 99%, Sigma Aldrich, MM = 241.60 g mol^{-1}, and ethyl alcohol (ethanol) PA were obtained from Sigma-Aldrich and used without previous purification.

2.2. Methods

Sample preparation was carried out following the method proposed by Fournier et al. [5]. The process involved the preparation of metal cation solutions. Subsequently, sodium montmorillonite clay was placed in the prepared solution, leaving it under stirring for a period of 24 h. Then, the material was centrifuged and washed, and placed again in another solution containing the same precursor salt, and the same conditions were maintained and the same procedures were repeated. Finally, there was drying in the oven at 50 °C for 24 h.

The adsorption of the dye in the modified clay minerals was carried out as follows: first, 0.225 g of the dye was dissolved in a solution of water and ethanol (1: 4 *v*/*v*), then filtered and mixed with 0.3 g of the modified clay mineral. The mixture was subjected to stirring for 4 h, then it was centrifuged, washed and dried in an oven at 50 °C for 24 h.

Subsequently, the samples were subjected to some characterizations: UV/visible spectrophotometry, spectroscopy in the Infrared Region with Fourier Transform and Colorimetric test.

3. Results and Discussion

3.1. UV/Visible Spectrophotometry

The UV/visible spectrophotometry (Figure 1) for Na-Mt-Bx, Mg-Mt-Bx and Ca-Mt-Bx samples showed similar spectra, while another set of samples, Cu-Mt-Bx, Fe-Mt-Bx and Al-Mt-Bx, presented a behavior different from those and spectra similar to each other. In general, it is noticeable that none of the samples presented a spectrum similar to that of bixin, suggesting that there was a greater variation in colors in relation to all cations used. Thus, it is evident that the amount of adsorbed dye and the nature of the metallic cations in the space between layers modified the pigment structure, influencing the different colors of the hybrids [6].

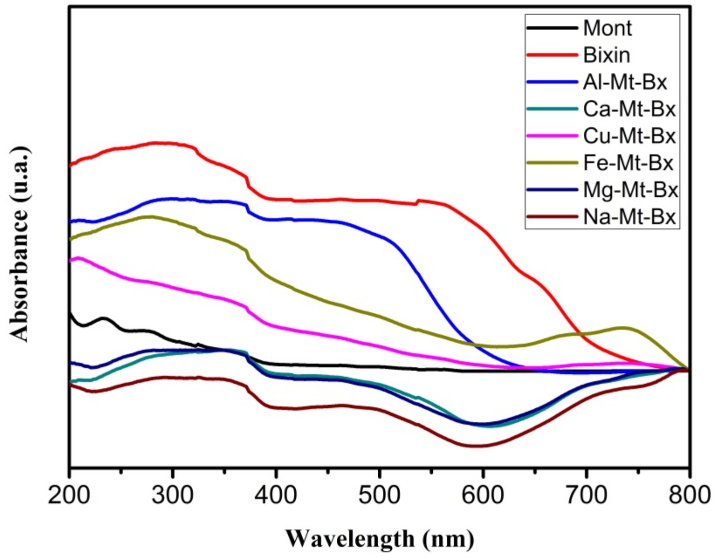

Figure 1. UV-Vis spectrum for Na-Mt-Bx, Mg-Mt-Bx, Fe-Mt-Bx, Cu-Mt-Bx, Ca-Mt-Bx, Al-Mt-Bx, montmorillonite and bixin samples.

3.2. Infrared Spectroscopy with Fourier Transform

For clay mineral, the spectra can be divided into two regions: the region with a low wave number or deformations (1700 cm^{-1} to 500 cm^{-1}); and the region of high wave numbers or stretching of those referring to the hydroxyl group Al-OH (3635 cm^{-1}) and to the hydration hydroxyl around 3390 cm^{-1} [7,8].

The vibrational spectra of the hybrid materials (Figure 2) showed similarities in their bands, with the OH bands initially being observed in the high frequency region, around 3638 cm^{-1} attributed to the stretches of the Al-OH bond, and in 3440 cm^{-1}. The bands at 3444 cm^{-1} and 1640 cm^{-1} indicate the presence of stretching and deformation, respectively, of the hydroxyl group in the water. The bands in the region around 1640 and 922 cm^{-1} were associated with angular deformations of the OH bonds of water and OH linked to the metallic cation of the octahedral sheet, in the case of aluminum [9,10].

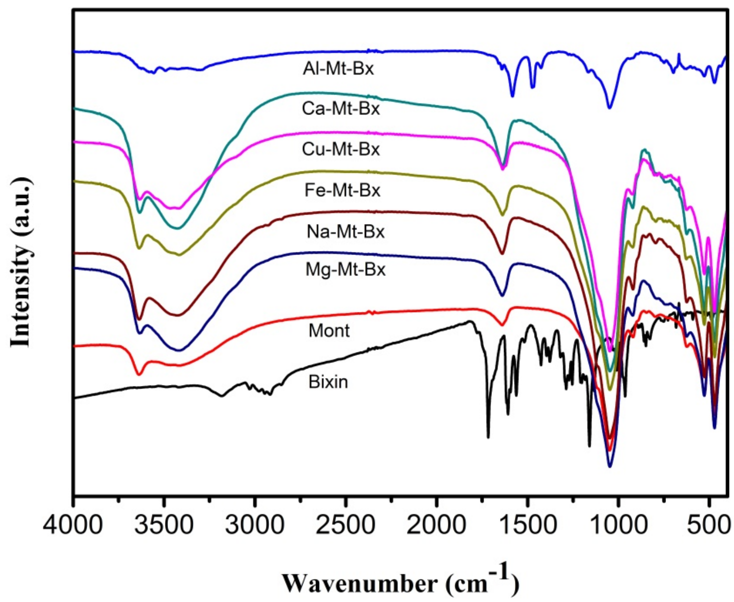

Figure 2. Infrared spectra for samples Na-Mt-Bx, Mg-Mt-Bx, Fe-Mt-Bx, Cu-Mt-Bx, Ca-Mt-Bx, Al-Mt-Bx, montmorillonite and bixin.

3.3. Colorimetric Test

The colorimetric tests (Figure 3) proved that the bixin showed a dark red color, with this color prevailing over the other colors in RGB, which is based on 100% red, 0% green and 0% blue, that is, (255,0,0) [11]. Montmorillonite was white in color. In the RGB color model, it is compromised of 100% red, 100% green and 100% blue, which corresponds, in the cube, to (255,255,255). The hybrid materials Ca-Mt-Bx, Fe-Mt-Bx and Cu-Mt-Bx showed a color closer to light or dark brown. The Mg-Mt-Bx and Na-Mt-Bx samples had tones closer to gray and yellow. The hybrid pigment that showed the color that most differed from the others was the one that contained aluminum, as it had an orange tint.

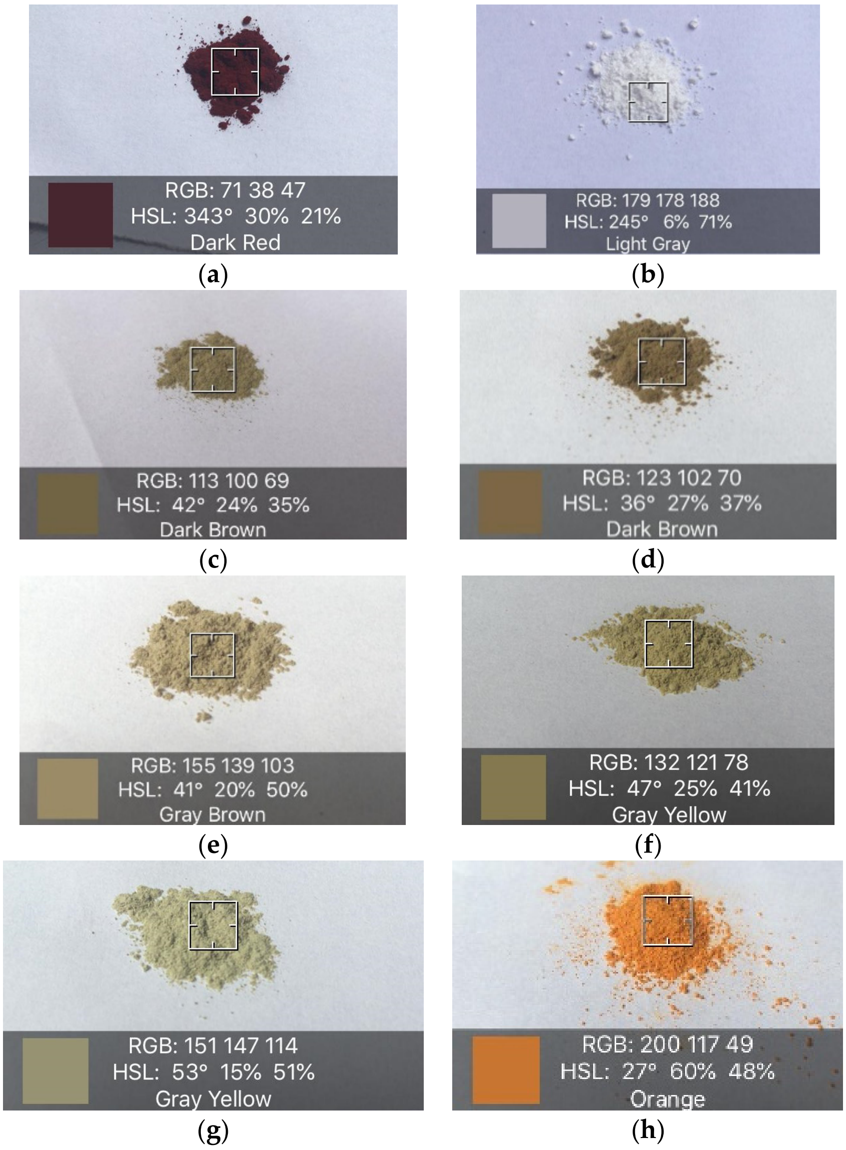

Figure 3. Color evaluation of samples (**a**) bixin; (**b**) montmorillonite; (**c**) Ca-Mt-Bx; (**d**) Fe-Mt-Bx; (**e**) Cu-Mt-Bx; (**f**) Mg-Mt-Bx; (**g**) Na-Mt-Bx and (**h**) Al-Mt-Bx.

4. Conclusions

The process of obtaining the hybrid pigments was successful. Observing the reflectance curves, the amount of dye adsorbed and the nature of the metallic cations in the space between layers modified the structure of the pigments, influencing the difference, as to the color of the hybrids.

The FTIR spectra showed that the characteristic bands of the dye were more noticeable when it was adsorbed on the mineral clay modified with aluminum, and through the colorimetric test, a variety of colors were found, according to the type of cation used.

Therefore, the hybrid pigment consisting of bixin and montmorillonite modified with Al^{3+} cations was the one that stood out the most, presenting improved properties when compared to the dye in its pure form. It is believed that, in the future, it may be used in the most diverse industrial areas, mainly in cosmetics and pharmaceuticals, where it is gaining more and more prominence.

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