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Citrus pectin as a template for synthesis of colorful aluminates

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ABSTRACT

Synthetic inorganic pigments based on citrus pectin and metal (aluminum, iron, cobalt, and nickel) nitrates were prepared by a novel, fast, economical synthesis method that did not generate wastes. It involved gelling at 80 °C (4 h) and calcination at 600 °C (3 h). Samples' thermal (TG/DTA) and morphological (SEM) behaviors, size distribution (DLS), surface areas and porosities (BET), molecular spectroscopic (Raman spectroscopy) and electronic (UV–Vis spectroscopy) behaviors, and colors (CIELab) were investigated. Characteristic data indicated pigments had morphologies typical of porous materials with 1.40–1.64 μm particle size, which is ideal for pigment applications. Thermal curves showed an organic fraction after calcination at 600 °C, which gave a softness to the pigments. Cytotoxicity tests revealed that toxicity was within tolerable limits, and dispersion tests in commercial colorless paint showed increasing coating capacity with decreasing paint volume while maintaining color, as verified by colorimetric measurements.

1. Introduction

Aluminates are an important class of materials in the area of inorganic pigments [1], because of their thermal stability, hardness, and ductility [2]. These compounds contain an oxyanion group (AlO^{2-}). When combined in the form of mixed oxides, these compounds also have a spinel structure with the general formula $A^{2+}B_2^{3+}O_4^{-2}$ and contain an aluminum ion, Al^{3+} [3]. Among the colorful, synthetic aluminates currently used, cobalt ($CoAl_2O_4$) [1,4] is a primary example, and iron aluminate ($FeAl_2O_4$) is a prominent natural aluminate.

In recent years, synthetic inorganic pigments have attracted attention of the paint, plastics, and ceramics industries among others, and they have also become the focus of research to create materials with enhanced properties, e.g., purity, uniformity, thermal stability, color, and shade, than those of conventional materials [1].

Aluminates were initially prepared by traditional synthesis methods such as i) solid state reactions [5] ii) combustion [6], and iii) co-precipitation [7]. Each method has advantages and disadvantages due to differences in the chemical principles involved, but the drawbacks of these methods are their high energy costs and low reproducibility as reported in the work of Belina & Sulcová [8] and Marinho et al. [9].

For these reasons, the adaptation and modification of methodologies have been used to search for improved synthesis conditions that are also environmentally friendly like those demonstrated by Gomes et al. [10], using the Pechini method, and by Jafari & Hassanzadeh-Tabriz [11], using a polyacrylamide gel to obtain a cobalt aluminate pigment. A sol–gel method has also been used for the preparation of inorganic pigments that were high quality and non-toxic [12]. Currently, methods using organic polymers and biopolymers have become important in the field of inorganic materials, especially for the preparation of new oxides using precursors that are more processibile and flexible, allowing new properties to be obtained [13,14].

An example of a precursor with these desirable properties is citrus pectin, a heterogeneous polysaccharide derived from plants [15]. It is composed of α-D-galacturonic acid units that are joined by glycosidic bonds (α-1,4) with varied degrees of methyl-carboxyl esterified groups. It has an appropriate viscosity, is able to form gels, is non-toxic, and possesses stabilizing power [16–18]. These properties primarily benefit the food production [19] and pharmaceutical [20] industries. From an economic perspective, citrus

Abbreviations: $Al_{(pec)}$, aluminum matrix; BET, Brunauer–Emmett–Teller; BJH, Barrett-Joyner-Halenda; (Co–$Al_{(pec)}$), cobalt aluminate; DLS, dynamic light scattering; (Fe–$Al_{(pec)}$), iron aluminate; (Ni–$Al_{(pec)}$), nickel aluminate; pec, citrus pectin; SEM, scanning electron microscopy; STA, simultaneous thermogravimetric analysis; TG/DTA, thermal gravimetric/differential thermal analysis; UV–Vis, ultraviolet–visible.

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pectin is abundant. It can be obtained from natural sources or from industrial waste (lemon or orange peels etc.), and its reuse may add value to new materials [19,21].

This study describes the preparation of oxide/aluminates by the combination of metal (aluminum, iron, cobalt, and nickel) nitrates with a polysaccharide, citrus pectin, in a rapid synthesis performed in the two steps of gelling and calcining. Four pigments were generated and were distinguishable by color. They included white ($Al_{(pec)}$), orange ($Fe–Al_{(pec)}$), purple ($Co–Al_{(pec)}$), and green ($Ni–Al_{(pec)}$) pigments. They materials could potentially be used as synthetic inorganic pigments. The pigments' thermal behavior was characterized using thermogravimetric/differential thermal analysis (TG/DTA); their textural properties were studied using scanning electron microscopy (SEM), dynamic light scattering (DLS), and the Brunauer–Emmett–Teller (BET) method; and their spectroscopic properties were analyzed using ultraviolet–visible (UV–Vis) spectroscopy and Raman spectroscopy. Colorimetric measurements and toxicity tests indicated that potential applications for the pigments include their use as coloring agents in paint.

2. Materials and methods

In the synthesis of the oxide/aluminates pigments, Citrus pectin (pec) and various metal nitrates ($Al(NO_3)_3{\cdot}9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, and $Ni(NO_3)_2{\cdot}6H_2O$) were purchased from Vetec (grade P.A., Brazil) and used without any pretreatment. All the processes for preparing pigments were carried out with ultrapure deionized water obtained from a reverse osmosis system (Quimis, Q842 model).

2.1. Synthesis of aluminum matrix and aluminates

The aluminum matrix, $Al_{(pec)}$, was synthesized from pec (1.0 g) and aluminum nitrate nonahydrate (14.0 g) in 100 mL of ultrapure water. The colorful aluminates ($Fe–Al_{(pec)}$, $Co–Al_{(pec)}$, and $Ni–Al_{(pec)}$) were prepared by adding a second transition metal ion to the aluminum solution containing pec such that 1.0 g of pec, 14.0 g of aluminum nitrate nonahydrate, and 1.45 g of iron nitrate or 0.99 g of cobalt nitrate or 0.99 g of nickel nitrate were dissolved in 100 mL of ultrapure water. The solutions were heated (80 °C) for 4 h under constant agitation until complete gelation. The proportion of transition metal added to the aluminum/pec solution was 20% (weight) of the solution's aluminum content.

The gels were calcined in a muffle furnace (up to 600 °C), and the solids were macerated with an agate mortar and pestle. The finely divided powders were used for further characterization and application. The procedure for preparing the aluminum matrix and aluminates is shown in Fig. 1A. Fig. 1B shows the structural formula of the pec used, which has a high methoxylation content (about 75%) similar to that used previously [22]. Although the organic precursor does not have a definite molecular formula, it is possible to estimate its composition by considering its methoxylation content. Thus, the decomposition pattern of the pec can be proposed (Eq. (1)) for one unit of the polysaccharide. The proposed decomposition can be estimated to discuss the thermal curves of the $Al_{(pec)}$ matrix and the colorful aluminates prepared.

$$C_{27}H_{38}O_{25} + 24\,O_2 \rightarrow 27CO_2 + 19H_2O \quad (1)$$

2.2. Characterization techniques

The thermal behavior of $Al_{(pec)}$ matrix and colorful aluminates in the powder form was determined using TG/DTA (TG/DTA-6300, Seiko, Japan) at a heating rate of 15 °C/min from 30 °C to 1200 °C in a platinum pan (sample holder) with a dynamic atmosphere of compressed air at a flow rate of 300 mL/min. Morphological characterization was performed using an SEM (High Hitachi TM-3000, Japan) operated at 5 kV and low vacuum. Particle size was obtained through DLS at 25 °C with a Malvern Zetasizer Nano ZS90 (Malvern, United Kingdom) with a detection range of 0.3 nm–6.0 μm using ultrapure water as a dispersant. Measurements were performed in triplicate and the dispersion was prepared directly, i.e., by diluting 0.01 g of sample in 10 mL of water.

Nitrogen adsorption isotherms were obtained using a gas sorption analyzer (NOVA-2000, Quantachrome, United State of America). Samples were then pre-treated by heating at 180 °C under vacuum for 2 h. The samples' specific surface areas were

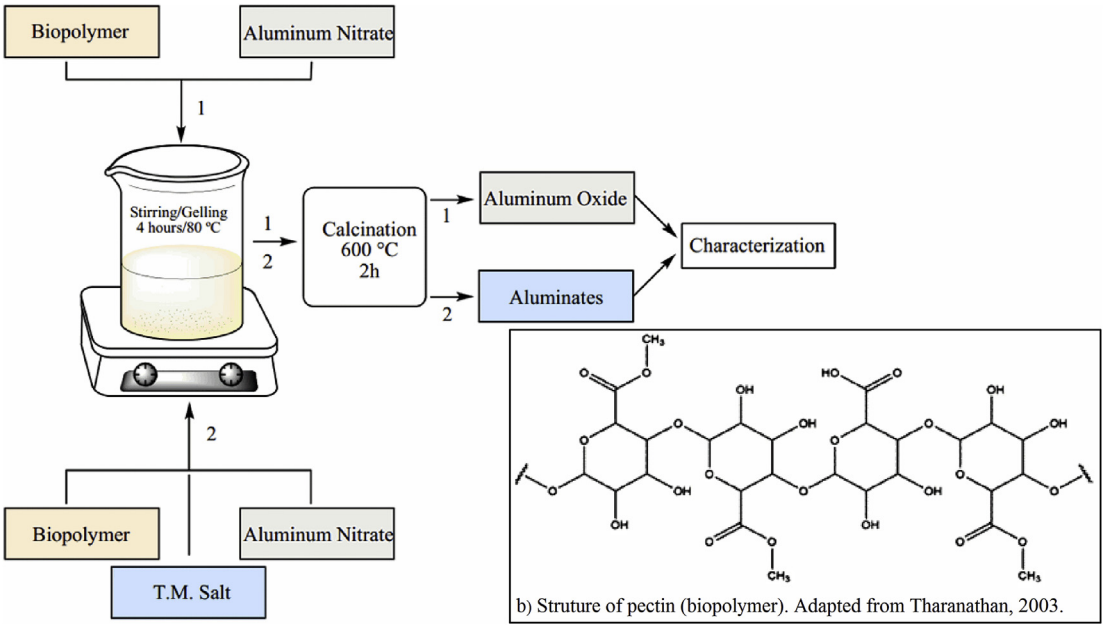

Fig. 1. a) Procedure used for the preparation and characterization of pigments. b) Structure of citrus pectin.