Synthesis and Characterization of Hydrocalumite-type Material Employing Bauxite-washing Residues from Amazon Region (Brazil)

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Abstract

This work deals with the synthesis of anionic clay with hydrocalumite-type material employing Amazonian bauxite tailings. The influence of temperature was investigated in the formation of this lamellar product. The product characterization was performed with X-ray diffraction, X-ray fluorescence, infrared and Raman spectroscopy, scanning electron microscopy and transmission electron microscopy with EDS. The results have revealed that bauxite wastes can convert into hydrocalumite by hydrothermal treatment at 75 °C for 2 days, with a high degree of crystallinity. The XRD pattern, IR and Raman bands of the hydrocalumite-type structure were identified. The results have shown that this type of industrial residue could be a low cost raw material for layered double hydroxide synthesis.

Keywords: synthesis, characterization, hydrocalumite, bauxite residues, Amazon Region.

1. Introduction

Hydrocalumite, $Ca_8Al_4(OH)_{24}(CO_3)Cl_2(H_2O)\cdot 1.6(H_2O)_8$, is a layered double hydroxide which occurs generally in soils and ores. The structure consists of brucite-type sheets linked MO_6 ($M = Ca^{2+}, Al^{3+}$) octahedra with anions and water molecules in the interlayer space. Other cations and anions can be used to obtain hydrocalumite-type materials with unique physical and chemical properties [1 – 3].

Since hydrocalumite possesses excellent ion exchange, surface chemistry, thermal behavior, electrochemical and photocatalytic properties, an extensive research has been carry out to investigate it as selective anionic-exchange, adsorbent, drug deliveries, support catalysts, catalysts, photocatalysts, and for cement industry [3 – 8].

Hydrocalumite-type materials are traditionally synthesized by co-precipitation and hydrothermal synthesis from pure reactants as starting materials and routes from natural sources (mineral, ores, and residues of the mining industry) as low cost starting material are limited [2 - 8]. Studies on the conversion of tailings into layered double hydroxides (and other technological materials) are very important because they can help in reducing the storage of by-products in the environment, as well as the possibility of obtaining products of technological importance [9].

In this work, a facile and low-cost synthesis of Fe-hydrocalumite-type material employing bauxite washing residues from Amazon Region is described.

2. Material and Methods

2.1. Synthetic Route

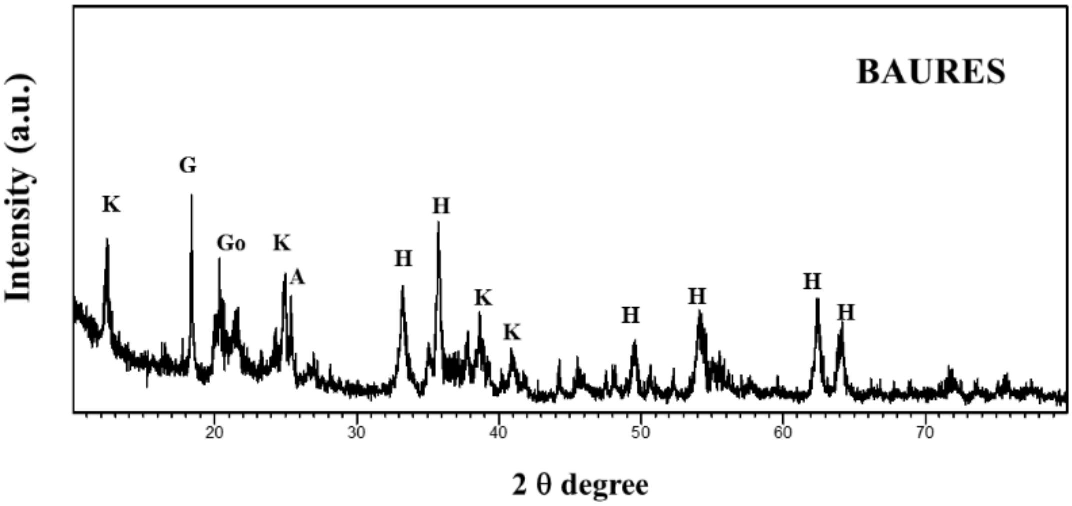
Bauxite residues from Amazon (BAURES) were employed as raw material for synthesis of hydrocalumite. About 1 g of BAURES were added to HCl solution and heated at 90 ºC to obtain a rich solution in Fe^{3+}. Later, the ideal stoichiometric ratio (Ca^{2+}/ Fe^{3+} = 2:1) for obtaining hydrocalumite was reached adding a mass of 1.5 g of $CaCl_2{\cdot}2H_2O$ (Sigma Aldrich) to the solution. Finally, NaOH solution was added dropwise slowly under stirring at 25 °C. The influence of temperature was studied at 0, 25, 50 and 75 °C.

2.2. Characterization

The chemical composition of BAURES was obtained by X-ray fluorescence (Axios Minerals, from Panalytical) spectrometer. X-ray diffraction (XRD) was performed in a D2Phaser diffractometer (Bruker), copper tube (CuKα = 1.5406 Å) at 30 kV and 10 mA. FT-IR spectra was obtained by using a spectrometer Vertex 70 (Bruker). The Raman spectrum was performed in a Bruker FT 100/S spectrophotometer, with a laser excitation YAG:Nd operating at 1064 nm. The morphology of the synthesized material was obtained by scanning electron microscopy Vega-Tescan, current of 90 mA, voltage of 20 kV and working distance of 15 mm. HR-TEM (Tecnai G2-20 SuperTwin FEI - 200 kV) with EDS measurements were also used to obtain the morphology and microanalysis of the final synthetic product.

3. Results and Discussion

The X-ray diffraction pattern of the bauxite residues (BAURES) which was employed as the starting material is presented in Figure 1. The mineralogical composition showed that kaolinite, hematite, goethite and gibbsite were the main component. The chemical composition showed Fe_2O_3 (~ 50 w.t. %), Al_2O_3 (~ 15 w.t. %) and SiO_2 (~ 10 w.t. %) as main constituents.



Legend: K = kaolinite, G = gibbsite, Go = goethite, A = anatase, H = hematite

Figure 1: XRD pattern of BAURES.

In order to study the influence of crystallization temperature on the formation of hydrocalumite, the crystallization temperature was changed from 0 to 75 ºC for 2 days. Figure 2 shows the

XRD patterns of products under different temperatures. After treatment at 0 °C, the main component was calcite with some hydocalumite. When the temperature was increased to 5, 25 and 50 ºC, the main peak of calcite at 29.37 º (2θ) was decreased, suggesting that higher temperatures favored the formation of lamellar product. At 75 ºC, the characteristics peaks were indexed to a trigonal hydrocalumite-type material (JCPDS 045-0572). The XRD pattern with sharp and intense peaks shows that layered phase with good crystallinity were synthesized. The lattice parameters calculated for the phase were: a = 5.87 Å, c = 47.10 Å, V = 1402 Å^3, and space group R3c. Therefore, the material obtained at 75 ºC was chosen to characterize the phase of hydrocalumite by FT-IR, Raman spectroscopy, SEM and TEM analysis.

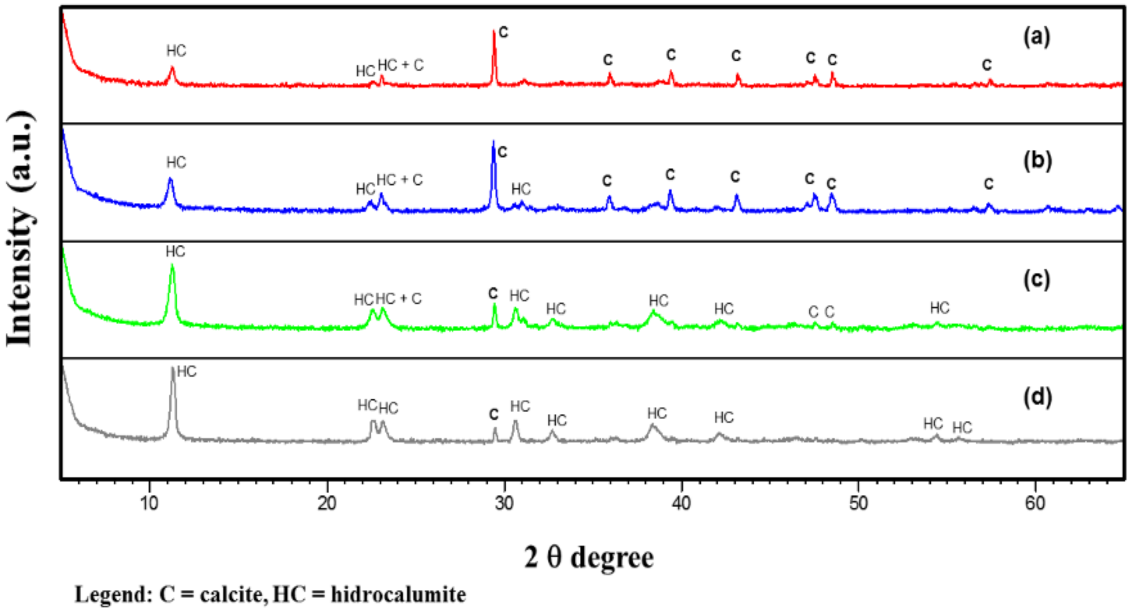


Figure 2: XRD patterns of the synthesized as-products obtained at 0 ºC (a), 25 ºC (b), 50 ºC and 75 ºC (d).

IR and Raman spectra of the hydrocalumite phase is displayed in Figure 3. Although vibrations in the region between 3700 and 3400 can be assigned to Me_3OH, some displacement here were easily identified (Figure 3a). For that reason, the bands at 3595, 3430 and 3201 cm^{-1} were related to the $Ca(Fe, Al)_2OH$ and $Ca_2(Fe, Al)OH$ vibrations. Two sharp IR bands could be observed at 1510 and 1420 cm-1, which is formed by hydroxyl bending modes. The typical band associated to OH-stretching of Ca-OH was identified at 1032 cm^{-1}. The bands at 877, 860, 790 and 740 cm^{-1} could be attributed to the (Fe, Al)-O vibrations. The Raman spectrum of hydrocalumite (Figure 3b), revealed a band around 1085 cm^{-1} that was assigned to the modes of carbonate groups in the interlayer region [7, 10].

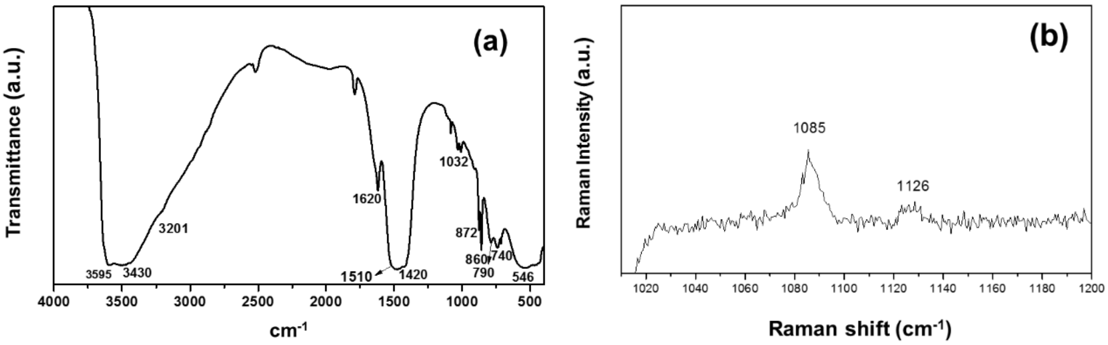
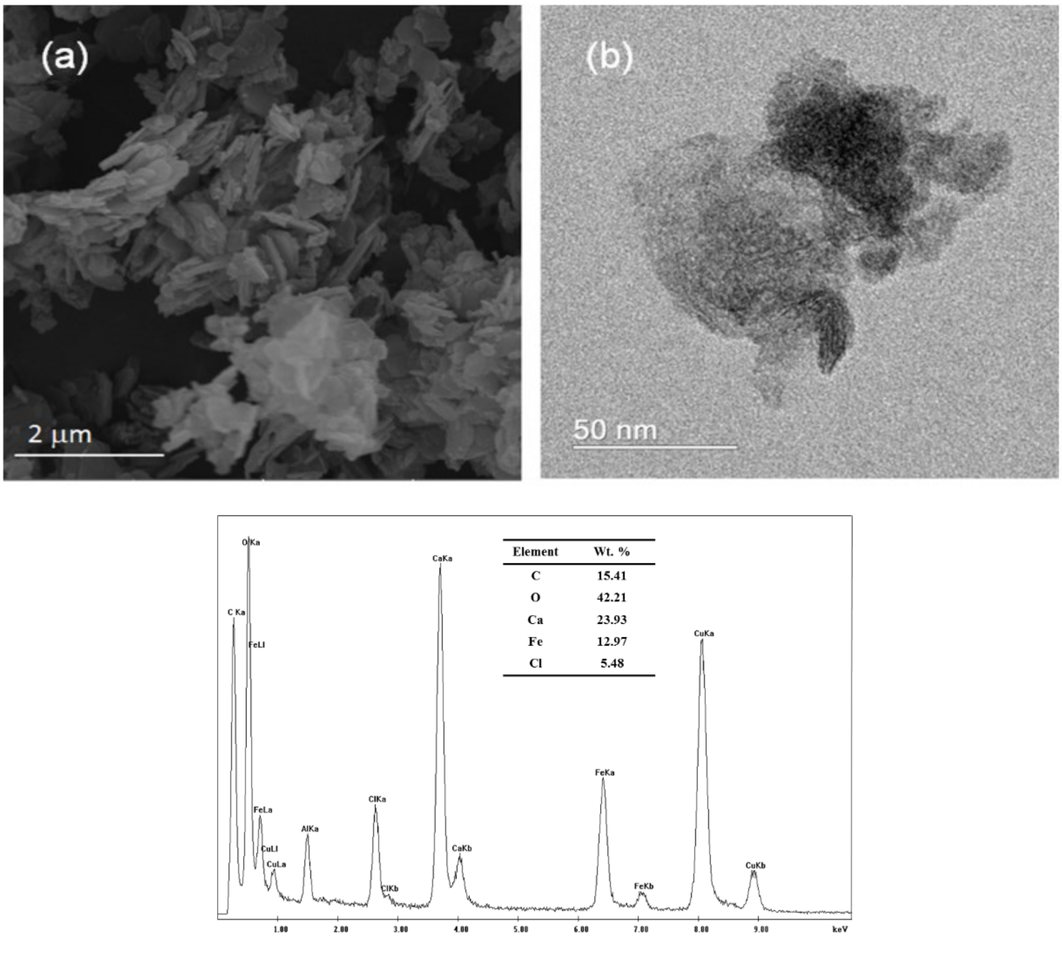


Figure 3. (a) FT-IR and (b) Raman spectra of hydrocalumite-type material.

In Figure 4, the SEM and HR-TEM investigations of the hydrocalumite synthesized at 75 °C for 2 days are presented. Plate-shaped crystals with a mean diameter of 1 μm were observed (Figure 4a) and are characteristic of lamellar materials obtained from natural and commercial reagents [4, 5, 7]. According HR-TEM analysis (Figure 4b), the product revealed a complex network layered structure, consisting by different particles with diameter around 50 nm. The EDS measurement (Figure 4c) showed Ca^{2+}/Fe^{3+} ratio of 1.84, which was in good agreement with the theoretical formula as already reported in [12].



Element	Wt. %
C	15.41
O	42.21
Ca	23.93
Fe	12.97
Cl	5.48

Figure 4. SEM (a) and HR-TEM (b) images of hydrocalumite-type material.

4. Conclusions

The bauxite washing residues composed of kaolinite, goethite, hematite, gibbsite, anatase and quartz were successfully converted into Fe-hydrocalumite-type material. The hydrothermal synthetic route described here showed that temperature influenced the synthesis of well-crystallized lamellar nanomaterial; ideal conditions were around 75 °C for 2 days.

5. Acknowledgements

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