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Physico-chemical characterization and thermal analysis data of alumina waste from Bayer process

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Abstract In the aluminum industries, there are several steps involved in processing since the extraction of bauxite to obtain the final product (Al). During the development of these, various steps generated wastes. One of them, from the electrostatic filter of the calcination step of the Bayer process is a very fine black powder, rich in alumina (Al_2O_3) that does not meet industry specifications, and it is discarded in the industry yard. Alumina is a noble material and has high commercial value. This black powder has great prospects for recovery, recycling, and future applications. Therefore, it is important to perform characterization of tailings and to do that we have used XRD, SEM, EDS, FTIR, Raman, and thermal analysis.

Keywords Bayer process · Black dust · Industrial waste · Thermal analysis

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Introduction

Several industrial processes produce many waste substances that are disposed to tailing dams and rivers. This causes serious pollution problems and the deterioration of the physical, chemical, and biological conditions, affecting human beings, animals, and vegetable lives [1].

In aluminum industries, the Bayer process [2–6] involves the extraction of alumina from bauxite using a hot sodium hydroxide solution under high pressure. Gibbsite is precipitated from the solution at temperatures between 65 and 70 °C and calcined to produce alumina [7].

During the Bayer process, the red mud is a waste produced in major quantity and it causes a serious pollution problem in the world. Several studies are developed related to the characterization, recycling, and solution of this waste [8–10]. Other different wastes and residues are generated in the aluminum industry. One such waste is a very fine black powder produced during the calcination step of the Bayer process, which is deposited in the electrostatic filters and is discarded to the industrial yards polluting the environment [5]. This residue is rich in alumina (Al_2O_3), a compound of high commercial value [11]. As this dust does not meet the industry specifications, it is disposed to large tailing dams and mixed with red mud, causing a major environmental problem. The black dust produced annually by an industry with an aluminum production of 122,000 tons/year may reach 2,000 tons [11].

The treatment of this residue and the recovery of pure alumina made its application in chromatography possible [11]. The literature cited several studies using pure alumina of analytical grade for adsorption of dyes [12]. In our previous study, we studied the adsorption of textile dyes using recovered alumina of the waste (black dust) [5].

This article describes the physico-chemical characterization of the black dust, produced in the calcination step of electrostatic filters in the Bayer process, for use in future research. The characterization was performed using the conventional physico-chemical and thermoanalytical techniques.

In the synthesis of polymers is very important the use of inorganic fillers due to its ability to provide mechanical properties, and various types of them are investigated by researchers in this field of study [13, 14]. Alumina is one of the finest materials used as filler in polymer synthesis. The presence of alumina in the black dust obtained in the calcination step may be used in many applications, such as flexible or rigid polyurethane foam filling, and filler for others polymeric materials. With interest in the use of tailing black dust as a filler in rigid and flexible polyurethane foams [15, 16], in future, a test was performed for the enumeration of hydroxyl groups (OH) present and available in this material. The hydroxyl number or hydroxyl index is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of 1 g of sample, and is expressed in mg KOH/g sample. This index value is a quantitative indicator of the sample composition and is important when the material is used in polyurethane foams. Some physical and mechanical parameters of flexible and rigid polyurethane foams, such as dimensional stability and compressive strength can be changed by the amount of hydroxyl groups of the reagent [17]. The hydroxyl number was determined through acetylation reaction, according to standard procedure BR ISO 14900:2001 [18]. The infrared spectroscopy was used to confirm the presence of hydroxyl groups in the waste.

Experimental

Black dust provided by Brazilian aluminum industries was characterized using thermal analysis (TG/DTG/DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), elemental analysis (C, H, N), Raman spectroscopy, and infrared spectroscopy.

TG/DTG and DTA measurements were carried out using a Netzsch STA409EP instrument, temperature range from 30 to 750 °C using 10 °C min^{-1} heating rate in air atmosphere (flow rate: 100 mL min^{-1}). The sample was loaded into an alumina crucible and the mass was kept constant around 12.0 mg. The X-ray powder pattern was recorded using Siemens D5000 diffractometer with Cu-K_α radiation, 40 kV, 30 mA, scanning rate of 0.05°min^{-1}. SEM studies were carried out on a JEOL JSM 840-A instrument. The sample was uniformly spread on a carbon tape and coated with gold. EDS analysis was performed on a JEOL-8900 electron probe microanalyzer. The carbon content in the black dust was quantified by elemental analysis on Perkin-Elmer 2400-CHN. The Raman scattering experiments were performed on micro-Raman Renishaw Invia with an exciting laser line of 785 nm. The experiments were performed in geometry backscattering using a microscope with objective lens of 50× with numeric hole of 0.75, scanning scattering area of ca. 1 mm^2. The infrared spectroscopy was carried out using a Perkin-Elmer Spectrum GX FT-IR System, with KBr pellets.

The quantitative method used for counting of OH groups was the acetylation of a known mass sample with acetic anhydride in excess, in the presence of pyridine as solvent and imidazole as catalyst. After 1 h of reaction, the not consumed anhydride in the reaction was hydrolyzed and the acetic acid formed was titrated with NaOH. A blank test gave a total value of acetic acid (without sample), which by difference, revealed the acetic acid formed and the hydroxyl number of the known mass sample. The chemical acetylation equation in the sample and in the blank is shown below:

In the sample:

$$\mathrm{R-(OH)}_x + n(\mathrm{CH_3CO})_2\mathrm{O} \rightarrow \mathrm{R-(OCOCH_3)}_x + (2n - x)\mathrm{CH_3COOH}.$$

In the blank:

$$n(\mathrm{CH_3CO})_2\mathrm{O} \rightarrow 2n\mathrm{CH_3COOH}.$$

Results and discussion

The XRD powder pattern of the black dust (Fig. 1) showed alumina (Al_2O_3) and aluminum hydroxide $Al(OH)_3$ as principal components. The black dust average particle size was obtained by X-ray diffraction and the parameters obtained were used to calculate the particle size according to Scherrer's equation (1) [19],

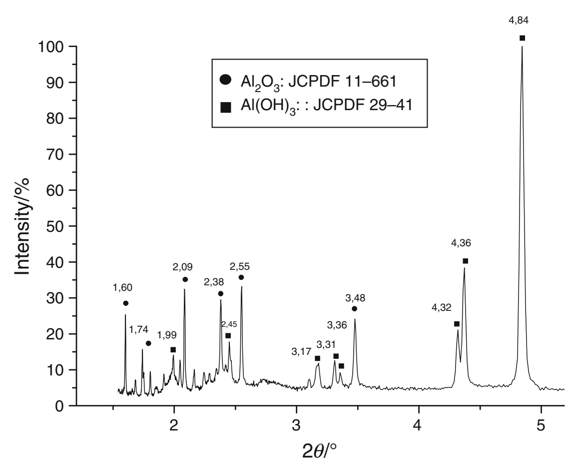


Fig. 1 X-ray diffractogram of black dust

$$\tau = (k \cdot \lambda)/(\beta \cdot \cos\theta), \quad (1)$$

where τ is the particle size, λ is the X-ray wavelength, β is the half-height width (in rad), k is a constant (0.94 for spheric crystallites), and θ is the X-ray diffraction angle.

Scherrer's equation determines the average particle size using parameter β, which is the half-height width of the highest intensity peak in the X-ray diffractogram. The average particle size calculated for black dust was 60 nm. This experiment showed that black dust contains aluminum hydroxide ($Al(OH)_3$) in its composition, as observed in Fig. 1.

Figure 2 shows the thermogravimetric curve (TG) and derivative thermogravimetric curve (DTG) for black dust. The first mass loss, with DTG peak at about 100 °C, and the second mass loss, with DTG peak at 250 °C, correspond to water loss by aluminum hydroxide, which is present in the black dust, as shown in the X-ray diffractogram (Fig. 1). The third event was assigned to the weight loss due to the decomposition of organic material (charcoal). The final residue obtained at 800 °C corresponds to pure alumina (Al_2O_3). Elemental analysis showed that this dust contains 2.8% of C and 1.2% of H.

The TG/DTG curves show that the water loss in the residue black dust is around 10 wt% and this corresponds to a fraction of about 30 wt% of $Al(OH)_3$ in the waste. Therefore, according to the TG and DTG analysis, the approximate composition of the black dust was estimated:

- ~68 wt% of alumina (Al_2O_3)
- ~30 wt% of aluminum hydroxide ($Al(OH)_3$)
- ~2 wt% of charcoal.

Black dust was investigated by DTA analysis (Fig. 3). It presented one endothermic event at about 100 °C and one peak at about 300 °C, relative to the weight loss associated with water loss from aluminum hydroxide [15]. The curve presents two other peaks, at about 550 and 650 °C, relative to the oxidation (burning) of charcoal [5].

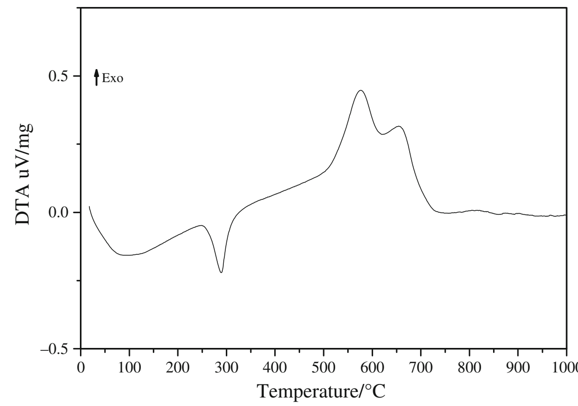


Fig. 3 DTA curve of black dust

SEM images showed that the electrostatic filter black dust has a fine granulometry and is composed of aluminum oxide (Al_2O_3) and a small percentage of coal, which is generated in the Bayer process calcination step. Figure 4 presents the scanning electron microscopy (SEM) image of black dust under magnification of 500×.

The main chemical constituents of black dust were qualitatively characterized by EDS microanalysis. It informs about the relation between the X-ray characteristic radiation wavelength and the element that originated it, making the elemental analysis of material microregions possible. The photon energy emitted in this process is quantified [20]. The presence of aluminum and oxygen was observed (Fig. 5). Although, black dust contains charcoal in its composition, the signal relative to this compound may be dubious in this technique because of the carbon tape used in the analysis to spread the sample.

The mapping of a determined sample region by EDS gives us an idea of the carbon, oxygen, and aluminum distribution in that area (Fig. 6a). We can observe that the aluminum (Fig. 6b) and oxygen (Fig. 6d) distribution in the same region is very similar and this fact suggest the

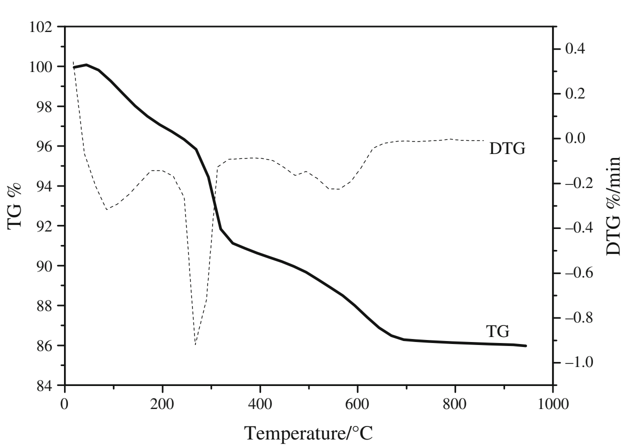


Fig. 2 TG and DTG curves of black dust

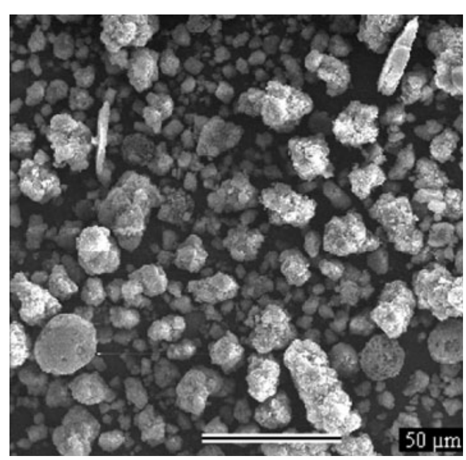


Fig. 4 SEM of black dust (×500)

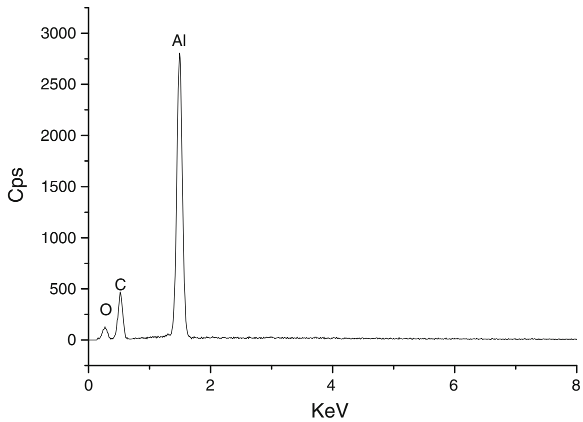


Fig. 5 EDS microanalysis of black dust

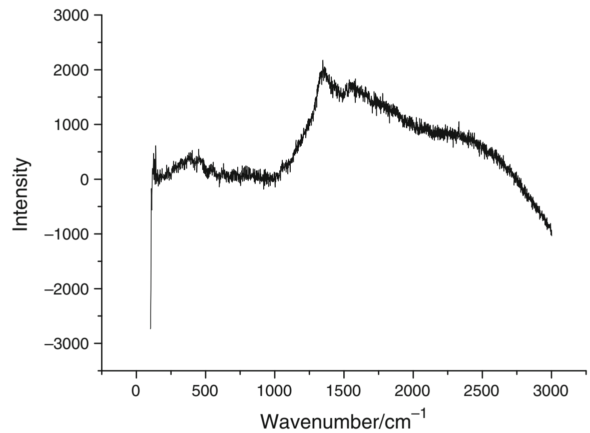


Fig. 7 Raman spectra of black dust

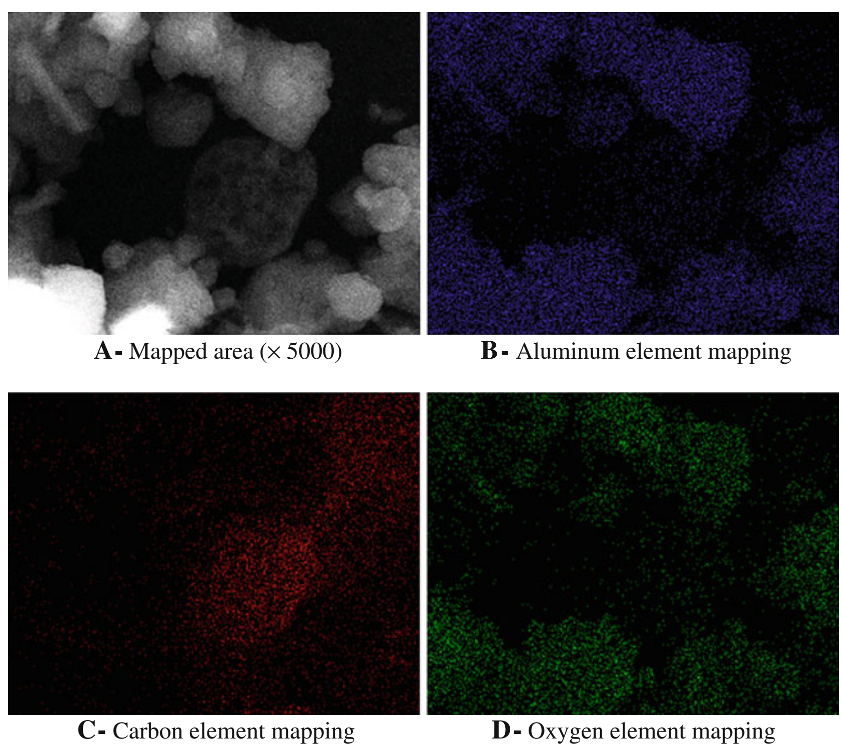
alumina (Al_2O_3) or aluminum hydroxide [$Al(OH)_3$] presence. Apparently, the carbon present in the sample (Fig. 6c) is not evenly distributed. The images show that the carbon presence is more pronounced in regions where there is less oxygen and aluminum (presumable less Al_2O_3 and $Al(OH)_3$). This is an indication that the inorganic alumina/aluminum hydroxide particles are not uniformly covered by carbon layer.

To identify the carbon form present in the black dust Raman spectroscopy was used. It observed characteristic bands of amorphous carbon around 1300 cm^{-1}, whereas the band at 1500 cm^{-1} may be attributed to some carbon in graphite form (Fig. 7). The Raman spectra were not well resolved because the carbon content in the black dust is low, as shown by elemental analysis.

The infrared spectroscopy (Fig. 8) show characteristics absorption bands of free OH groups (3624 and 3529 cm^{-1}) and bands of polymeric association OH groups between 3500 and 3200 cm^{-1}, indicating the presence of hydroxyl groups in the material. The hydroxyl bands showed in infrared spectroscopy confirm the presence of this group in the black dust, probably from water, aluminum hydroxide, and from the complex organic material present in the waste.

The quantitative result to a hydroxyl number, measured by reaction with acetic anhydride in pyridine and titration with sodium hydroxide solution was equal to 254 mg KOH g^{-1}.

Fig. 6 EDS mapping of black dust



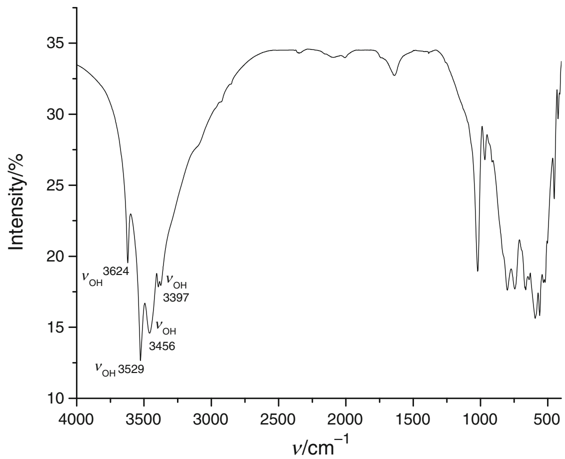


Fig. 8 Infrared spectra of black dust

In recent studies, the black dust was utilized as inorganic charge in flexible polyurethane foams and then as flame retardant of this polymer [21]. The high number of hydroxyl groups and the large amount of alumina found in the tailing indicate that this material can have good future applications as filler for flexible and rigid polyurethane foams. The presence of large number of hydroxyl groups may indicate a possibility of chemical interaction between black dust and the foam polymeric matrix. This fact can indicate that the waste can be a filler with good properties. The alumina and aluminum hydroxide present in the waste in large quantities would make of this material a good flame retardant to flexible and rigid foams and improve mechanical properties to the black dust.

Conclusions

XRD, EDS, and Raman spectroscopy showed that the main components of the black dust generated in the calcination step in electrostatic filters of the Bayer process are alumina (Al_2O_3), aluminum hydroxide ($Al(OH)_3$), and amorphous carbon (charcoal).

Thermal analysis (TG, DTG, and DTA) of black dust, in air atmosphere, showed the dehydration steps of aluminum hydroxide, the oxidation of charcoal, and that the final product over 700 °C is pure alumina (Al_2O_3).

The characterization of this dust is very important for its future application in several environmental research areas.

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