Synthesis of high-surface-area gamma-Al2O3 from aluminum scrap and its use for the adsorption of metals: Pb(II), Cd(II) and Zn(II)
Synthesis of high-surface-area $\gamma$-Al$_2$O$_3$ from aluminum scrap and its use for the adsorption of metals: Pb(II), Cd(II) and Zn(II)

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**Abstract**

Several types of alumina were synthesized from sodium aluminate (NaAlO$_2$) by precipitation with sulfuric acid (H$_2$SO$_4$) and subsequently calcination at 500 °C to obtain $\gamma$-Al$_2$O$_3$. The precursor alumina was derived from aluminum scrap. The various $\gamma$-Al$_2$O$_3$ synthesized were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), adsorption–desorption of N$_2$ (S$_\text{BET}$) and scanning electron microscopy (SEM). XRD revealed that distinct phases of Al$_2$O$_3$ were formed during thermal treatment. Moreover, it was observed that conditions of synthesis (pH, aging time and temperature) strongly affect the physicochemical properties of the alumina. A high-surface-area alumina (371 m$^2$ g$^{-1}$) was synthesized under mild conditions, from inexpensive raw materials. These aluminas were tested for the adsorption of Cd(II), Zn(II) and Pb(II) from aqueous solution at toxic metal concentrations, and isotherms were determined.

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1. Introduction

In recent years, the increasing extraction of metals has stimulated the economies of several South-American countries (e.g., Brazil, Peru, Chile). However, these activities release some unwanted by-products, such as Zn, Cd and Pb. These metals accumulate in the aquatic ecosystem and are hazardous at high concentrations. Thus, the removal of heavy metals from wastewater is a growing concern because the increasing discharges could lead to toxic water supplies [1].

Cadmium comes mainly from the wastewater of the metal plumbing industry, cadmium–nickel batteries and mining [2]. Foods high in proteins contain zinc naturally, but soluble salts of zinc, such as ZnSO$_4$, in large doses (about 10 g), have caused internal organ damage and even death [3]. Lead is hazardous in small amounts as it accumulates in brain, bones and kidney. Industrial processes, such as battery manufacturing, are also a major source of lead pollution [4]. According to the Agency for Toxic Substances and Disease Registry (ATSDR) of the U.S. Department of Health and Human Services, the permissible limits in drinking water are 0.04 mg L$^{-1}$ for Cd, 5 mg L$^{-1}$ for Zn and 0 mg L$^{-1}$ for Pb [5].

The use of adsorbents to treat wastewater has become an important topic of research, since adsorption processes are very simple, compared to chemical processes such as precipitation or ion-exchange. Additionally, in response to environmental quality requirements for drinking water, recent work includes the synthesis of new economical adsorbents with useful properties for contaminant removal, to replace conventional high-cost adsorbents (activated carbon, zeolites, SBA-15, etc.).

Alumina is obtained from bauxite industrially by the Bayer process, in which a mixture of bayerite and gibbsite is produced by acidic precipitation of sodium aluminate with CO$_2$, the final product containing impurities such as Fe$_2$O$_3$ [6]. The bayerite is calcined at >500 °C and transformed into gamma alumina, which is widely used as a catalytic support, because of its large surface area, high porosity, acidity and low toxicity.

Many methods for the synthesis of alumina are reported in the literature [7–10], involving expensive raw materials and harsh synthetic conditions that include high temperatures and pressures. Here we report a method that involves mild conditions to synthesize gamma alumina ($\gamma$-Al$_2$O$_3$) and compare the morphology and crystal structure with those of commercial alumina.

A great amount of aluminum scrap is produced worldwide, of which a major part is recovered by recycling [6], but an alternative way of using the aluminum scrap is to transform it directly into alumina, which finds several uses (in catalysts, in soft abrasives, in coatings and in adsorbents). The aim of this study was to synthesize alumina by acidic precipitation (with H$_2$SO$_4$) of sodium aluminate.
Sulfuric acid is an inexpensive raw material (on the industrial scale) and the sodium aluminate was produced from aluminum scrap; furthermore, the synthesis was carried out under mild conditions. While alumina is normally used as a catalytic support, in this report we show that it could be used as an economical and effective adsorbent, as well. The adsorption of Pb(II), Cd(II) and Zn(II) from aqueous solution was studied.

2. Experimental

2.1. Preparation of gamma alumina

Scrap metal aluminum from beverage cans (99.9% pure) reacted, at room temperature, with a stoichiometric amount of 2 N aqueous NaOH in a batch reactor to produce a solution of sodium aluminate (NaAlO₂). This solution was passed through filter paper and the clear filtrate was neutralized with 2 N H₂SO₄ to pH 6.7 or 8, resulting in the precipitation of a white gel, Al(OH)₃·XH₂O. Some aliquots of the synthesized gel were left to stand for 48 h (aging time) in the mother liquor at room temperature (approximately 25 °C), while others were left for a period of 4 h at 80 °C. The resulting gel samples were named as Gel 6-25, Gel 7-25, Gel 6-80, Gel 7-80 and Gel 8-80, according to the pH at which each gel was precipitated and the aging temperature; for example, Gel 6-25 was obtained at pH 6 and aged at 25 °C, while Gel 7-80 was obtained at pH 7 and aged at 80 °C.

Following the aging step, the gels were washed until no more sulfate ions were detected in the washings. Finally, they were dried at 80 °C for 6 h, then ground and passed through a 60 mesh sieve (Styler). The samples were then calcined for 3 h in a muffle furnace, in air, at a heating rate of 2 °C min⁻¹. Analogously to the gel samples, calcined samples were named: Ox-Al 6-25, Ox-Al 7-25, Ox-Al 6-80, Ox-Al 7-80 and Ox-Al 8-80.

2.2. Characterization

To study the functional groups and bonds characteristic of the alumina gels, Fourier-transform infrared spectroscopy (FTIR) was carried out on specimens made by pelleting the aged gel with KBr. FTIR spectra were collected in a Perkin Elmer 1600 T spectrophotometer, in the range 4000–400 cm⁻¹.

The crystalline phases present in the aluminum hydroxides and calcined oxides were identified by X-ray diffraction (XRD) with a Shimadzu XRD 6000 diffractometer, using Cu-Kα radiation (λ = 1.5404) generated at 40 kV and 30 mA, in which the Bragg angle (2θ) was scanned between 4° and 70°.

The porous structure of the aluminas was characterized by adsorption–desorption of N₂ (BET method) at the temperature of liquid nitrogen (77 K), with a Micromeritics instrument (ASAP 2000). The gas used for analysis was 99.9% pure. The dry materials were previously degassed at 200 °C, in order to remove water and any impurities physisorbed on the solid surface.

Thermogravimetric analyses (TGA) were performed in a Mettler Toledo Analyzer (SF1100). The samples were analyzed under an inert atmosphere of nitrogen flowing at 2 °C min⁻¹, as the temperature rose to 870 °C. TGA profiles were obtained by plotting the relative weight (%) of the sample against temperature. Scanning electron microscopy (SEM) was carried out in a LEO 440 microscope with an Oxford detector, operating with a 20 kV electron beam.

2.3. Adsorption essay

Stock solutions of 1000 mg L⁻¹ Cd(II), Zn(II) and lead Pb(II) in distilled water were prepared from the salt precursors Cd(NO₃)₂·4H₂O, Zn(NO₃)₂·4H₂O and Pb(NO₃)₂·4H₂O (Merck), respectively. By diluting these stock solutions, the working solutions for adsorption tests were prepared.

The adsorption isotherms were performed under favorable conditions for the adsorption of zinc, cadmium and lead, respectively, as previously determined: contact time (adsorbent/adsorbate) of 7 h, magnetic stirring at 400 rpm, adsorbent load in solution (w/v')= 8 g L⁻¹, initial pH of zinc and cadmium solutions = 5, pH of lead solution = 3 and all solutions at room temperature (approximately 25 °C). The concentration of metal ion varied from 10 to 200 mg L⁻¹. The initial pH of the metal solutions was adjusted by adding 0.1 M HNO₃ or 0.1 M NaOH.

After reaching equilibrium, the mixture (adsorbate/adsorbent) was filtered through a cellulose membrane (Millipore, 0.45 μm). The contents of Cd(II), Zn(II) and Pb(II) in the filtrates were analyzed in an Atomic Absorption Spectrophotometer (Perkin Elmer 3100) provided with hollow cathode lamps for zinc (λ = 213.9 nm), cadmium (λ = 228.8 nm) and lead (λ = 217.0 nm).

In the field of adsorption of contaminants, the parameter qₑ (mg of adsorbate/g of adsorbent), which measures the adsorptive capacity of the adsorbent, and the adsorption isotherms are both widely used to characterize the adsorption process. The adsorption capacity of alumina was calculated as follows: qₑ = V(Cₑ − Cₑ)/m, where Cᵢ is the initial concentration of the metal in solution (in mg L⁻¹), and Cₑ its concentration at equilibrium, V is the volume of solution in liters, m is the weight of the adsorbent (alumina) in grams and qₑ is the adsorption capacity (mg g⁻¹) at equilibrium. In liquid–solid systems, the isotherm models most used are:

- **Freundlich isotherm** based on the assumption that the adsorbing surface is energetically heterogeneous, consisting of adsorption sites of differing energies. The linearized form of the Freundlich equation is as follows:

  \[ \log qₑ = \log K_f + \frac{1}{n} \log Cₑ \]  

  (1)

  where qₑ is the amount of adsorbate retained per gram of adsorbent (mg g⁻¹), Cₑ is the concentration of adsorbate (mg L⁻¹) at equilibrium, and Kᵢ and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

- **Langmuir isotherm** based on the assumption that all adsorption active sites are equivalent and that the ability of a molecule to interact with a site on the surface of the adsorbent is independent of whether neighboring sites are occupied or not. In addition, adsorption is restricted to a monolayer and there are no lateral interactions between adsorbed molecules. The linearized form of this isotherm is represented by the following equation:

  \[ Cₑ = \frac{Cₑ_m a}{qₑ_m + b Cₑ} \]  

  (2)

  where Cₑ and qₑ are as defined previously (mg g⁻¹ adsorbent), qₑ_max (mg g⁻¹) and b (L mg⁻¹) are Langmuir constants related to the maximum adsorption capacity and adsorption energy, respectively.

3. Results and discussion

The sol–gel process involved in the synthesis of aluminas is based on polymerization reactions among the aluminum hydroxide molecules formed on acidification of aluminate, which include hydrolyses and condensation reactions involving oxolation and oleation pathways, as will be described later, to form polymer chains of aluminum hydroxide. These polymer chains are later transformed at very high temperature into aluminum oxides of various structures. These processes have been studied and detailed information is available in the literature [8,11]. Thus, we firstly characterized the polymer gel produced by the reaction of sodium aluminate with sulfuric acid.
Fig. 1 shows FTIR spectra of gels of aluminum hydroxide, obtained by aging at 25 °C and 80 °C. In those samples Gel 6-25 and Gel 7-25, the peaks located at approximately 3469 and 3562 cm\(^{-1}\) are assigned to the stretching vibration of –OH in hydration water. The spectra also show a signal of the Al–OH group at 3655 cm\(^{-1}\) (stretching vibration). The peak located at 1635 cm\(^{-1}\) is assigned to –OH bending mode in hydration water [12].

In these two samples, peaks at 1714, 1364 and 1224 cm\(^{-1}\) (this last peak is more noticeable in Gel 7-25) could be attributed to stretching and bending vibrations of intra-molecular interactions, such as OH···O hydrogen bonds, in the polymeric species, still present in the gel even after the aging process. According to the literature [6,8,12], among the many polymeric species, the commonest are: \([\text{Al}_2\text{O}_4\text{(OH)}_{28}]^{3+}\) and \([\text{AlO}_3\text{Al}_{12}\text{(OH)}_{24}(\text{H}_2\text{O})_{12}]^{7+}\).

These species are formed initially by oxolation and oleation processes, followed by polymerization of aluminum hydroxide molecules, and, finally by nucleation and growth processes, resulting in the formation of particles of hydrated alumina [8,11]. The terms oxolation and oleation refer to the formation of Al–O–Al bonds and Al–OH groups, respectively, during the polymerization of aluminum hydroxide molecules. The peaks observed at 1024 and 970 cm\(^{-1}\) are assigned to the bending vibrations of Al–OH and of Al–O–Al, respectively [13,14].

A well-defined peak can also be observed at 528 cm\(^{-1}\), corresponding to the octahedral coordination, \(\text{AlO}_6\). The peak located at 761 cm\(^{-1}\) is assigned to the tetrahedral coordination \(\text{AlO}_4\) [15]. The anion [\(\text{Al(OH)}_4\)]\(^{-}\) is found at high pH and absorbs at 615 cm\(^{-1}\) [14]. This anion is likely to be present in the aluminum hydroxide gel, as it was precipitated from a strongly basic solution of sodium aluminate, but this peak probably overlaps with those of \(\text{AlO}_4\) in Fig. 1.

In the Gel 7–25 spectrum, it is observed that the peak located at 1635 cm\(^{-1}\), assigned to the H–O–H bending vibration in water hydration, is less intense than that in the Gel 6–25 spectrum. This may indicate that the sample of Gel 6–25 retained more water within its structure, which could be favored by the acidic pH of precipitation. It should be noted that the absorptions at 1714, 1364 and 1224 cm\(^{-1}\), which denote the presence of polymeric species of aluminum ions, are less intense in the spectra of Gel 6–25 and Gel 6–80 than in that of Gel 7–25, Gel 7–80 and Gel 8–80 (Fig. 1). This finding may indicate that precipitation at basic pH promotes formation of polymeric species of aluminum ions that did not form large \(\text{Al(OH)}_3\) structures.

Similarly, the FTIR spectra of Gel 6–80, Gel 7–80 and Gel 8–80 show absorption peaks for the stretching vibration of –OH (of hydration water), located around 3417 cm\(^{-1}\), and the stretching vibration of Al–OH, observed around 3621 cm\(^{-1}\).

As for the samples synthesized by aging at 25 °C, the spectra for Gel-Al 7–80 and Gel 8–80 show peaks at 1706, 1364 and 1224 cm\(^{-1}\), ascribed to polymeric species of aluminum. These peaks were weaker for samples precipitated at acidic pH. This finding indicates that at pH 6 the formation of large aggregates of \(\text{Al(OH)}_3\) is favored, while at relatively basic pH (7–8) these aggregates are less favored. As a result, at pH 7–8, polymeric species of aluminum (probably \(\text{Al}_2\text{O}_4\text{(OH)}_{28}^{3+}\) and \([\text{AlO}_3\text{Al}_{12}\text{(OH)}_{24}(\text{H}_2\text{O})_{12}]^{7+}\)) are present on the surface of the gel, even after aging, formed by intra-molecular hydrogen bonds.

For the sample precipitated at pH 6 (Gel 6–80), the absorption peak for the –OH bending mode in water of hydration, at 1635 cm\(^{-1}\), is of a lower intensity than the corresponding peak for samples precipitated at pH 7–8 (Gel 7–80 and Gel 8–80), contrary to the findings in gels aged at 25 °C. This suggests the presence of more structural water in Gel 8–80 and Gel 7–80; probably both the aging temperature and pH of precipitation take part in controlling the retention of water in the structure of \(\text{Al(OH)}_3\cdot\text{H}_2\text{O}\) formed.

The crystalline nature of the synthesized gels was analyzed by X-Ray diffraction (XRD), the resulting patterns being shown in Figs. 2 and 3. The patterns show peaks related to the
crystal phases of bayerite (JCPDS 20-0011), boehmite (JCPDS 33-0018) and also gibbsite (JCPDS 07-0324).

It can be seen from these results that precipitation at acidic or neutral pH (pH 6–7) did not modify the crystal structure significantly, since the XRD patterns of the four samples: Gel 6-25, Gel 7-25, Gel-Al 6-80 and Gel-Al 7-80 are similar and contain a principal phase of boehmite and a minor phase of bayerite. On the other hand, precipitation at basic pH 8, led to the formation of mainly gibbsite phase, and bayerite in lower proportion.

The aging temperature also affected the crystal structure of the gels formed, as can be observed in the same figure, where the peaks related to the bayerite and the boehmite phases of samples aged at 80 °C are finer than the corresponding peaks of samples aged at 25 °C, showing that at 80 °C larger crystallites are formed. Additionally, the principal peak located at ca. 18° in the patterns of Gel 6-80 and Gel 7-80 was shifted to lower Bragg angles than similar peaks for gels aged at 25 °C. Three reasons have been proposed for this shift [16–18]: (i) specific stacking faults (involving a rotation of the layers in their planes and a displacement normal to the layers), (ii) limited layer stacking number and (iii) excess of water in the interlayer; this last hypothesis will be discussed in detail in the TGA section.

Fig. 3 shows the XRD patterns of samples precipitated at pH 7 and aged at room temperature for 2 h (Gel 7-25 2 h) and 48 h (Gel 7-25) and one sample aged for 4 h at 80°C (Gel 7-80). These results indicate that the gel aged for only 2 h is amorphous, meaning that 2 h of aging at 25 °C is not sufficient to form crystals of boehmite and bayerite. These crystals are only formed over long aging times (48 h) at room temperature, or short aging times at 80°C.

The degree of crystallinity apparent in the diffraction patterns of Gel 7-25 and Gel 7-80 (Fig. 3) indicates that there is an inverse relationship between aging temperature and aging time. As reported in other studies [15,19], high temperature accelerates the formation of large crystals; thus at high temperature fewer grains are formed, allowing an orderly growth (nucleation process). According to Rinaldi [20], during aging, particles of aluminum hydroxide are solubilized and growth take place through condensation reactions; this growing process can be accelerated at high temperatures, leading to the formation of particles of large size.

According to the XRD results (Fig. 3), crystal growth is slower at room temperature, at which many grains are formed, hindering fast growth and requiring 48 h to reach the crystalline structures of bayerite and boehmite, whereas at 80 °C only 4 h are necessary for this crystalline arrangement to be established. As mentioned previously, gels treated for 4 h at 80 °C developed larger crystals than those treated at room temperature for 48 h.

Fig. 4 shows TGA curves for two precursors of alumina (Gel 7-25 and Gel 7-80) that have similar profiles. These two samples were precipitated at the same pH but aged at different temperatures.

The pattern of weight loss with rising temperature is typical for this type of material, and this profile is very similar to those found by Potdar et al. [7] and Guzmán-Castillo et al. [21] for aluminum hydroxide containing mixtures of bayerite and boehmite.

According to these results, the change of aging temperature had little effect on the capacity for water retention in the structure, since the total loss in weight did not differ significantly (25% and 27.5% for samples Gel 7-25 and Gel 7-80, respectively).

TGA profiles show four clearly-marked stages: (i) ca. room temperature – 120 °C, this weight loss is attributed to the desorption of physisorbed water from the surface of the gel and is more noticeable for Gel 7-25, possibly due to the smaller crystallites in this sample (the sizes calculated from the XRD pattern of Fig. 2, by the Scherrer equation [22], were 16 nm and 13 nm for Gel 7-80 and Gel 7-25, respectively), which could favor a higher surface area; (ii) ca. 120 °C–280 °C: due to desorption of chemisorbed water from the surface of the gel, these falls occurred readily when the aging temperature was 25 °C; (iii) ca. 280–500 °C (greatest fall in weight): this weight loss relates to dehydroxylation (caused by breaking of Al–OH bonds) and to a loss of structural water (dehydration) from the gel and possibly remaining sulfate decomposition; during these processes, the elimination of structural water takes place and Bronsted acid centers are lost (owing to dehydroxylation) [23]; the last stage involves a smaller loss in weight, between 400 °C and 500 °C, which may correspond to the transition of aluminum hydroxides contained in the gel (bayerite and boehmite) to $\gamma$-Al$_2$O$_3$; the XRD analysis shown later will support this hypothesis; (iv) above 500 °C: this (smallest) weight loss is due to dehydroxylation of the $\gamma$-Al$_2$O$_3$ formed and phase-transitions of other aluminas. These marked stages are similar to those found by Rinaldi and Schuchardt [24], Rinaldi and Schuchardt [25] and Du et al. [26].

The phases formed during the calcination of Gel 7-80 at temperatures of 200, 300, 400 and 500 °C are shown in Fig. 5. In this figure, in the XRD pattern of the sample calcined at 200 °C, the most intense peaks correspond to the bayerite phase, but peaks of relatively low intensity indicating boehmite are also seen. An unexpected increase in the intensity of both bayerite and boehmite peaks was probably favored by the loss of chemisorbed water at this temperature, as seen in the TGA profile.

At 300 °C, the peaks for bayerite disappeared and the majority phase was highly crystalline boehmite, while small peaks attributed to gamma alumina were formed. These
transformations are related to dehydroxylation (caused by breaking of Al–OH bonds) and to the loss of structural water (dehydration), as seen in the TGA curves.

At 400 °C, the boehmite formed at 300 °C lost some crystallinity and the gamma alumina peaks became more noticeable. Finally, at 500 °C, a single phase of gamma alumina (γ-Al₂O₃) was formed, confirming the above hypothesis concerning the TGA profiles. The process described above can be summarized in the following reactions [27]:

\[
2\text{Al}(\text{OH})_3(s) \overset{300-500}{\longrightarrow} 2\text{AlO} \cdot \text{OH}(s) \text{ (boehmite)} + 2\text{H}_2\text{O(g)} \quad (3)
\]

\[
2\text{AlO} \cdot \text{OH}(s) \text{ (boehmite)} \overset{500}{\longrightarrow} \gamma-\text{Al}_2\text{O}_3(s) + \text{H}_2\text{O(g)} \quad (4)
\]

\[
2\text{Al}(\text{OH})_3(s) \rightarrow \gamma-\text{Al}_2\text{O}_3(s) + 3\text{H}_2\text{O(g)} , \quad \Delta G^r = -1564.2 \text{kJ/mol} \quad (5)
\]

According to the data reported by Guzman-Castillo et al. [21] and Rinaldi and Schuchardt [25], the transition from boehmite to γ-Al₂O₃ takes place in the range of temperature 380–580 °C; their results are in agreement with those reported in the TGA section (of the present report), since the thermal treatment of the gels at 500 °C led to the formation of γ-Al₂O₃.

According to the TGA profiles of the samples Gel 7-25 and Gel 7-80 (Fig. 4), it appears that the increase in aging temperature (from room temperature to 80 °C) raised the transformation temperatures discussed above; it is probable that the higher crystallinity of the gels formed at 80 °C increased their thermal stability.

According to Okada et al. [17], the removal of excess water occurs from 200 to 450 °C, leading to the main loss in weight (as seen in the present work); these authors also suggest that this excess water in the aluminum hydroxide structures is located mainly in the interlayer, where it is possible to find water in various structural states such as Al–OH₂, Al–OH · · · H₂O, etc. Similar observations were reported by Lee et al. [16].

The TGA profiles revealed that the physisorbed water and structural water of the gel were removed sooner, when the aging temperature was 25 °C (Gel 7-25), suggesting that the crystalline structure formed by Gel 7-25 facilitates the elimination of physisorbed water from the surface and the structural water from the interlayer section during thermal treatment, compared to the sample synthesized at 80 °C (Gel 7-80); hence, Gel 7-80 seems to store water molecules in the interlayer more effectively.

In the XRD patterns of gels (Fig. 2), it was found that the principal peaks related to bayerite shifted to lower Bragg angles when the aging temperature was 25 °C (in comparison to their similar ones aged at 80 °C), and additionally it was mentioned that one reason for this may be related to the excess of water in the interlayer. Since the d-spacing can be considered a measure of the distance between layers in a crystal structure, the values calculated (by the Bragg Law) for the (001) peak of the XRD patterns are 4.79 Å and 4.71 Å for Gel 7-80 and Gel 7-25, respectively. The d-spacing of 4.71 Å for Gel 7-25 is the same as that for bayerite (JCPSD 20-0011); on the other hand, the expansion of the d-spacing in Gel 7-80 (4.79 Å) may be due to the storage of more water molecules in the interlayer, as mentioned previously; probably this relatively larger d-spacing favors the conformation of the various structural states of chemisorbed water: Al–OH₂, Al–OH · · · H₂O, thus hindering its elimination from the interlayer at relatively low temperatures (see Fig. 4). These results may be related to the fact that the total loss in weight of Gel 7-80 was slightly higher than that of Gel 7-25 (25% and 27.5% for Gel 7-25 and Gel 7-80, respectively).

Fig. 6 shows the XRD patterns of the various aluminas obtained at 500 °C, compared with a commercial alumina. The equivalent crystallite sizes calculated by the Scherrer formula [22], \(D = k \lambda / b \cos \theta\), are shown in Table 1. As can be seen in this figure, and in the crystallite sizes, the calculation of the gels at 500 °C produced aluminum oxides of nano-crystalline structure, similar to that of commercial gamma alumina (surface area 220 m² g⁻¹; crystallite size = 6 nm).

The isoelectric point of bayerite Al(OH)₃ is reported to be in the pH range of 7.5–8.5 [26,28,29]; thus, at a precipitation pH of 6–7, below the isoelectric point, the positively charged bayerite particles would favor the conformation of large crystallites of bayerite, as can be seen in Fig. 3. Thus, the thermal treatment at 500 °C of Gel 6-25, Gel 6-80, Gel 7-25 and Gel 7-80, which contain a major phase of bayerite, lead to the formation \(\gamma-\text{Al}_2\text{O}_3\) (Fig. 6), as reported by Kim et al. [30], Kim et al. [31], Du et al. [26], Okada [17] and Lee et al. [16].

The precipitation at pH 8 (which is in the isoelectric point range of bayerite) seemed not to favor the ordered growth of the bayerite grains, thus leading to the formation of a gel containing a minor phase of bayerite (Fig. 2); moreover, this pH favored the rearrangement of highly crystalline gibbsite. According to Kim et al. [30], the poorly organized structure of bayerite is due to the oξolation reactions being less favored at the isoelectric point. Li et al. [32] revealed that the crystal growth of bayerite and gibbsite follows different pathways and, as can be seen in the results of the present report, the crystal growth of the bayerite and gibbsite were strongly influenced by the precipitation pH.

<table>
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<td>Results of textural analysis of aluminum oxides carried out by the method of nitrogen adsorption–desorption (Sₐ) and crystallite size (XRD).</td>
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Next, the XRD pattern of the aluminum oxide obtained by thermal treatment of Gel 8-80 at 500 °C is attributed to the formation of poorly crystalline chi-alumina, and is very similar to that found by Meephoka et al. [33], Makasuwandumrong et al. [34], Vieira-Coelho et al. [35] and Tsuchida and Ichikawa [36], with characteristic broad peaks located at 37°, 40°, 46°, 60° and 67°. As in the present report, the chi-alumina was obtained by the cited authors from pure gibbsite.

The chi-alumina structure is based on a hexagonal close packed (hcp) structure of the oxygen atoms, where the aluminum cations occupy the octahedral site within the hexagonal oxygen layers. On the other hand, the γ-alumina structure has been described as a defect spiral structure, that can be represented by a face-centered cubic (fcc) structure of oxygen atoms, with aluminum cations occupying the tetrahedrally and the octahedrally coordinated interstitial sites [33].

The results of textural analysis of the synthesized and commercial aluminum oxides are summarized in Table 1. Analyzing the surface area of the samples in relation to their pH of precipitation, it is observed that the surface area of 276 m² g⁻¹ obtained at pH 8 (Ox-Al 6-80) decreased to 197 m² g⁻¹ in the sample obtained at pH 8 (Ox-Al 8-80), both samples having been aged at the same temperature of 80 °C; a corresponding relation was found for samples obtained at 25 °C. From these results it can be concluded that acidic precipitation (pH 6 and 7) increases the surface area of the material, in agreement with previous reports [8–10].

It is known that [9] the surface area of alumina depends on the extent of aggregation and dissolution of alumina gel grains during aging, which is strongly affected by the pH of precipitation. In this connection, it is observed that at acidic pH (pH = 6), aggregation of grains of alumina gel is probably favored, leading to the formation of oxides with smaller pores and high surface area, while at higher pH (pH = 7–8) the dissolution of grains of alumina gel is favored, resulting in the formation of oxides with larger pores and lower surface area.

Okada et al. [17] and Paniás and Krestou [18] correlated the pH of precipitation of the gel to the crystallite size of the alumina formed. According to those authors, the crystallite sizes of the oxides increase with increasing pH, in both series of aluminas, aged at 25 °C and 80 °C (see Table 1). However, the crystallites obtained at pH 8 were the smallest among all the samples, owing to the amorphous structure of the chi-alumina formed (see XRD patterns in Fig. 6), as discussed before. The increase in crystallite size caused at pH 7 suggests the enhancement of grain growth by dissolution–reprecipitation, during the aging treatment, favored at this precipitation pH, where the dissolution of boehmite and bayerite contained in the gel is favored, leading to aluminas of larger crystallites after thermal treatment at 500 °C.

According to Table 1, the decrease in surface area at pH 7 corresponds to the increasing crystallite size of the aluminas, relative to those aluminas synthesized at pH 6. However, the decrease in surface area at pH 8 cannot be understood in this way, since this sample has the lowest crystallite size. The surface area increased with decreasing crystallite size and reached a maximum when the crystallite size was 4.8 nm (371 m² g⁻¹ for Ox-Al 6-25).

Regarding the influence of aging temperature, it is observed that samples aged at 80 °C had the largest pores diameter. This trend can be explained by the fact that during aging at high temperature, fewer grains of aluminum hydroxide are formed, allowing a more orderly growth of particles during this process, and leading to the formation of oxides with larger pores and lower surface areas. Thus, it can be inferred that the dissolution of the gel of aluminum hydroxide formed is favored at 80 °C. A contrary effect take place at room temperature (25 °C), where many grains are formed, which hinder the orderly growth of particles, leading to the formation of oxides with small pores and thus a larger surface area (Table 1).

According to values in Table 1, with increasing surface area, the average pore diameter (Davg, nm) decreases in both series of aluminas (those aged at 25 °C and 80 °C) in the following order: from Ox-Al 7-80 (crystallite size = 6.1, Davg = 5.70 nm, surface area = 273 m² g⁻¹) to Ox-Al 6-80 (crystallite size = 5.9, Davg = 4.97 nm, surface area = 276 m² g⁻¹); and from Ox-Al 7-25 (crystallite size = 6.1 nm, Davg = 4.33, surface area = 280 m² g⁻¹) to Ox-Al 6-25 (crystallite size = 4.8, Davg = 2.96, surface area = 371 m² g⁻¹). On the other hand, Ox-Al 8-80 has the smallest crystallite size (3.7 nm), which is smaller than its own average pore diameter (Davg = 6.31 nm), and thus a decrease in the surface area of this sample (the lowest value recorded 197 m² g⁻¹) must come from the decrease in the number of pores, caused by the very small alumina crystals that probably block some surface pores.

Potdar et al. [7] obtained γ-Al₂O₃ from boehmite (synthesized from Al(NO₃)₃ and Na₂CO₃, at a slightly basic pH, and aged at 70 °C for 3 h; the maximum surface area of that alumina was 258 m² g⁻¹. Kim et al. [19] also produced γ-Al₂O₃ from boehmite (synthesized from aluminum isopropoxide, acetic acid and isopropanol at a slightly acidic pH, and aged at 80 °C for 20 h); the maximum surface area attained was 307 m² g⁻¹. Meephoka et al. [33] synthesized γ-Al₂O₃ from of a mixed solution of toluene and 1-butanol in aluminum isopropoxide (aged in an autoclave system at 300 °C in the presence of N₂, and calcined at 600 °C), the maximum surface area was 226 m² g⁻¹.

Similarly, Guzman-Castillo et al. [21] prepared boehmite from solutions of Al₂(SO₄)₃·18H₂O, AlCl₃ and NH₄OH at pH 7–9 (aged at 50, 140 and 180 °C for 18 h); the maximum surface area of these aluminas was 248 m² g⁻¹. In these examples, the aging temperature and pH of precipitation are close to the conditions used in the present study, but it is worth noting that in the latter the raw materials used were aluminum scrap (to obtain NaAlO₂) and H₂SO₄ (which is cheap on the industrial scale); these materials are thus cheaper than those used in the above studies.

One of the goals of the present report is to achieve the high surface area of these aluminas, especially those synthesized at room temperature, whose peak value was 371 m² g⁻¹ for sample Ox-Al 6-25. In other words, an alumina with high surface area was synthesized under mild conditions and relatively inexpensive reagents.

SEM images of the aluminas are shown in Fig. 7a–f. According to these images, an aging temperature of 80 °C generated symmetrical solid structures; in fact, Ox-Al 6-80, Ox-Al 7-80 and Ox-Al 8-80 seem to consist of regular hexagonal prism forms.

These particles become larger as the pH increases from 6 to 8, confirming that the basic pH allowed the formation of aluminas with larger nanostructures. Regarding the aging temperature, aluminas aged at 80 °C reached larger particle sizes than those aged at room temperature. These trends are in agreement with the trend seen in the crystallite sizes calculated from the XRD patterns (see Table 1).

Aluminas treated at room temperature showed the same trend as those treated at 80 °C; alumina precipitated at pH 6 did not show a regular form (see Ox-Al 6-25 in Fig. 7), while alumina precipitated at pH 7 showed particles of solid pyramid form, which were very little compared to the particles obtained at 80 °C. Commercial alumina does not show a regular morphology and is very similar to sample Ox-Al 6-25.

From the results obtained and discussed above, it can be concluded that in general precipitation at acidic pH leads to formation of smaller particles, while larger particles are formed at basic pH, and aging at higher temperature leads to an acceleration of the formation of larger structures. These hypotheses are consistent with the crystallite sizes found by XRD analysis (see Table 1) and with the previous discussion.
Adsorption isotherms of Cd, Zn and Pb on alumina are shown in Fig. 8a–c. It can be seen that overall the isotherms are of Type I, characteristic of microporous materials, with formation of a monolayer of adsorbate (respectively the ions Cd$^{2+}$, Zn$^{2+}$ and Pb$^{2+}$) on the surface of alumina, where each active center acts individually.

Among the aluminas synthesized at room temperature, the average pore diameter of sample Ox-Al 7-25 ($D_{\text{avg}} = 4.33$ nm) is larger than that of Ox-Al 6-25 ($D_{\text{avg}} = 2.96$ nm), which could explain the higher adsorption values of all three cations on the first of these samples. The same reasoning can be applied to the series of aluminas obtained at 80 °C, where the adsorption of each cation is higher on Ox-Al 7-80 ($D_{\text{avg}} = 5.7$ nm) and Ox-Al 8-80 ($D_{\text{avg}} = 6.3$ nm) than on Ox-Al 6-80 ($D_{\text{avg}} = 4.9$ nm).

These results suggest that the divalent cations are more readily adsorbed on surfaces with large pores. It can also be said that a precipitation pH of 7–8 and an aging temperature of 80 °C, which led to the large hexagonal prism morphology, promoted the adsorption of these metals on the alumina surface, sample Ox-Al 7-80 showing the best overall performance, closely followed by Ox-Al 8-80.

In contrast to the adsorption of cadmium and lead, the aluminas treated at 25 °C adsorbed zinc as well as those treated at 80 °C, Ox-Al 7-25 being the best adsorbent of all the aluminas. Since this alumina has a smaller pore diameter ($D_{\text{avg}} = 4.3$ nm) than those aged at 80 °C (Table 1), there is a strong possibility that zinc ions (whose ionic radius is smaller than those of cadmium and lead) are more readily adsorbed in smaller pores (aluminas aged at room temperature). The general similarity between the adsorption isotherms of cadmium and zinc on alumina (Fig. 7) relates to the fact that both metals belong to the same group in the periodic table and they have very similar chemical behavior.

From the above discussion of adsorption assays, it can be seen that among the aluminas treated at room temperature, Ox-Al 7-25 was by far the best adsorbent for Zn$^{2+}$ ions, while Ox-Al 7-80 was the best adsorbent for Cd$^{2+}$ and Pb$^{2+}$ ions. The profiles of the adsorption isotherms of cadmium, zinc and lead (Fig. 8) show that adsorption of these metals on Ox-Al 7-80 has the following order of selectivity: Pb(II) > Cd(II) > Zn(II), which follows the decreasing order of their atomic radii: Pb(1.75 Å) > Cd(1.54 Å) > Zn(1.38 Å) [37]. Although the values of the ionic radii are less well-defined, their sequence must match that of the atomic radii. It can be inferred that the size of the metallic species has an influence on the adsorption process. A larger ionic radius results in a weaker repulsion from the positively-charged alumina surface, favoring adsorption on larger pores.

A different sequence is observed for Ox-Al 7-25 (the best adsorbent of the aluminas treated at 25 °C), with the following order of selectivity: Pb(II) > Zn(II) > Cd(II), which does not follow the order of decreasing atomic radii observed for Ox-Al 7-80. By contrast, this alumina adsorbs more zinc than cadmium; this preference would have to be explained by the functional groups formed on the surface of the alumina during preparation. Since the observed order of selectivity matches the decreasing order of solubility: \( K_{\text{H}} \\text{Pb} = 7.7 < K_{\text{H}} \text{Zn} = 9.0 < K_{\text{H}} \text{Cd} = 10 \) [37], the trend found suggests that species of lower solubility are more readily adsorbed on the surface of Ox-Al 7-25; the functional groups on the surface of the alumina are probably involved in the adsorption phenomena.

The FTIR spectrum of Gel 7-25 (Fig. 1) shows absorption peaks located at 1714, 1364 and 1224 cm$^{-1}$ (assigned to intramolecular hydrogen bonds in the aluminum ion polymer species) at higher intensities than any other gel. The strong intensity of these peaks
Table 2
Langmuir and Freundlich parameters for the adsorption of cadmium on the aluminas.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Langmuir parameters (Cd)</th>
<th>Freundlich parameters (Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox-Al 6-25</td>
<td>$q_{max}$ (mg g$^{-1}$) 5.34</td>
<td>$K_L$ 1.63 4.08</td>
</tr>
<tr>
<td>Ox-Al 7-25</td>
<td>$b$ (L mg$^{-1}$) 0.16</td>
<td>$n$ 0.99 $R^2$ 0.98</td>
</tr>
<tr>
<td>Ox-Al 6-80</td>
<td>$q_{max}$ (mg g$^{-1}$) 5.16</td>
<td>$K_L$ 2.20 4.12</td>
</tr>
<tr>
<td>Ox-Al 7-80</td>
<td>$b$ (L mg$^{-1}$) 0.45</td>
<td>$n$ 0.99 $R^2$ 0.88</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$q_{max}$ (mg g$^{-1}$) 7.53</td>
<td>$K_L$ 2.85 4.13</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$b$ (L mg$^{-1}$) 1.79</td>
<td>$n$ 0.99 $R^2$ 0.95</td>
</tr>
</tbody>
</table>

Table 3
Langmuir and Freundlich parameters for the adsorption of zinc on the aluminas.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Langmuir parameters (Zn)</th>
<th>Freundlich parameters (Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox-Al 6-25</td>
<td>$q_{max}$ (mg g$^{-1}$) 5.27</td>
<td>$K_L$ 1.62 3.74</td>
</tr>
<tr>
<td>Ox-Al 7-25</td>
<td>$b$ (L mg$^{-1}$) 0.30</td>
<td>$n$ 0.99 $R^2$ 0.97</td>
</tr>
<tr>
<td>Ox-Al 6-80</td>
<td>$q_{max}$ (mg g$^{-1}$) 5.13</td>
<td>$K_L$ 1.85 4.13</td>
</tr>
<tr>
<td>Ox-Al 7-80</td>
<td>$b$ (L mg$^{-1}$) 0.49</td>
<td>$n$ 0.99 $R^2$ 0.98</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$q_{max}$ (mg g$^{-1}$) 7.16</td>
<td>$K_L$ 2.94 4.43</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$b$ (L mg$^{-1}$) 0.86</td>
<td>$n$ 0.99 $R^2$ 0.96</td>
</tr>
</tbody>
</table>

Table 4
Langmuir and Freundlich Parameters for the adsorption of lead on the aluminas.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox-Al 6-25</td>
<td>$q_{max}$ (mg g$^{-1}$) 9.86</td>
<td>$K_L$ 2.12 2.78</td>
</tr>
<tr>
<td>Ox-Al 7-25</td>
<td>$b$ (L mg$^{-1}$) 0.44</td>
<td>$n$ 0.99 $R^2$ 0.82</td>
</tr>
<tr>
<td>Ox-Al 6-80</td>
<td>$q_{max}$ (mg g$^{-1}$) 11.06</td>
<td>$K_L$ 2.95 3.38</td>
</tr>
<tr>
<td>Ox-Al 7-80</td>
<td>$b$ (L mg$^{-1}$) 0.53</td>
<td>$n$ 0.99 $R^2$ 0.70</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$q_{max}$ (mg g$^{-1}$) 10.94</td>
<td>$K_L$ 5.85 6.43</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$b$ (L mg$^{-1}$) 1.82</td>
<td>$n$ 0.99 $R^2$ 0.88</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$q_{max}$ (mg g$^{-1}$) 13.11</td>
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<tr>
<td>Ox-Al 8-80</td>
<td>$b$ (L mg$^{-1}$) 1.82</td>
<td>$n$ 0.99 $R^2$ 0.82</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$q_{max}$ (mg g$^{-1}$) 12.64</td>
<td>$K_L$ 6.59 6.18</td>
</tr>
<tr>
<td>Ox-Al 8-80</td>
<td>$b$ (L mg$^{-1}$) 2.54</td>
<td>$n$ 0.99 $R^2$ 0.84</td>
</tr>
</tbody>
</table>

in the Gel 7-25 spectrum could be related to the strong adsorption of zinc on the alumina made from this gel; possibly, the greater formation of these polymer species may favor the adsorption of this ion on the resulting Al$_2$O$_3$ structure.

The trend found for cadmium and lead adsorption on aluminas aged at 80 °C (Fig. 8) corresponds to a falling intensity of the peaks near 1700 cm$^{-1}$, 1364 cm$^{-1}$ and 1224 cm$^{-1}$ in the gels as follows: Gel 8-80 > Gel 7-80 > Gel 6-80 (see Fig. 1); the adsorption of these metals is probably also influenced by the formation of these polymeric surface groups in the precursor gels.

Tables 2–4 show the correlation of the experimental adsorption results with the Langmuir and Freundlich models (Eqs. (1) and (2)). It is seen in these tables that the Langmuir model fits the data best, as shown by the higher correlation coefficient ($R^2$). In this model, the adsorption process takes place by the formation of a monolayer of adsorbate (cadmium, zinc or lead) on the surface of the alumina, where there is a finite number of homogeneous adsorption sites, energetically equivalent and with no interaction between them [38].

Table 5
Comparison of adsorption capacity ($q_e$) of various adsorbents for Pb(II), Cd(II) and Zn(II) removal.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbent dosage (g L$^{-1}$)</th>
<th>Cadmium</th>
<th>Zinc</th>
<th>Lead</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated alumina</td>
<td>8</td>
<td>8.24</td>
<td>7.60</td>
<td>13.11</td>
<td>This report</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>10</td>
<td>–</td>
<td>13.69</td>
<td>–</td>
<td>[39]</td>
</tr>
<tr>
<td>Activated bituminous carbons</td>
<td>4</td>
<td>–</td>
<td>7.60</td>
<td>–</td>
<td>[40]</td>
</tr>
<tr>
<td>Powder activated carbon</td>
<td>0.5</td>
<td>–</td>
<td>13.04</td>
<td>–</td>
<td>[41]</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>7.5</td>
<td>6.3</td>
<td>–</td>
<td>–</td>
<td>[42]</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>5</td>
<td>–</td>
<td>–</td>
<td>8.50</td>
<td>[42]</td>
</tr>
<tr>
<td>Composite material: polystyrene/alumina/carbon</td>
<td>10</td>
<td>–</td>
<td>–</td>
<td>10.64</td>
<td>[43]</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>20</td>
<td>0.5</td>
<td>–</td>
<td>–</td>
<td>[44]</td>
</tr>
</tbody>
</table>
4. Conclusions

It was possible by the method described to prepare various types of aluminum hydroxide (from aluminum scrap) which, when precipitated at pH 6–7 and then calcined at 500°C, led to the formation of γ-Al2O3. These aluminum hydroxides were synthesized from sodium aluminate (derived from aluminum scrap) and sulfuric acid under several sets of conditions: pH 6, 7 and 8 and aging temperatures of 25°C and 80°C. The samples prepared at lower pH had larger surface areas and smaller pores than their counterparts prepared at higher pH.

Aluminas aged at 80°C had larger pores, favoring the adsorption of voluminous ions such as lead, while the smallest ion, Zn, was better adsorbed on aluminas with smaller pores.

All adsorption isotherms of cadmium, zinc and lead were of Type I. The highest adsorption of zinc was achieved on samples OxAI 7–25 (qe = 7.44 mg g⁻¹) and OxAI 7–80 (qe = 7.0 mg g⁻¹), while for cadmium the best adsorbent was the OxAI 7–80 (qe = 8.2 mg g⁻¹).

The highest values for lead adsorption were obtained with samples OxAI 7–80 (qe = 13.1 mg g⁻¹) and OxAI 8–80 (qe = 12.6 mg g⁻¹).

The aluminas synthesized in this work exhibited high adsorptive capacities showing a promising future for the utilization of alumina in the removal of Pb(II) and Cd(II) ions present in aqueous solution.

Acknowledgments

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References