



Production of alpha-alumina nanoparticles using aquatic humic substances



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ABSTRACT

The aim of this work was to employ the complexation capacity of natural organic matter (NOM) to synthesize α -alumina nanopowder, using a procedure that was efficient, eco-friendly and economically viable. Several synthesis parameters were tested, such as pH and concentration of the starting sol, stirring time and calcination temperature. The best conditions determined to produce α -alumina through this method are pH 4.0, stirring time of 120 min at room temperature, drying at 100 °C and final calcination at 1000 °C for 4 h. This temperature was 200 °C lower than that usually reported for the synthesis of α -alumina. Spherical particles with average sizes of 52 ± 1 nm were produced by this method. The stoichiometry Al_2O_3 and the low level of impurities in the samples were confirmed by several methods. The water used in the synthesis was recycled and analysed according to its physico-chemical and bacteriological features. From the results, it could be concluded that the recycled water met the standards required by current legislation for potable water, highlighting the technological and environmental advantages offered by the proposed method of synthesis.

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1. Introduction

Alumina (Al_2O_3) is one of the most important oxides used in the ceramic, electronic, and petroleum industries [1–3]. It can present different crystalline phases which all revert to the most stable hexagonal alpha phase at elevated temperatures [4]. Al_2O_3 nanopowders can be used for the fabrication of ceramics with improved hardness and wear resistance, as well as for application in membranes, catalytic materials, thermal insulators, biocompatible materials and pigments [5–9].

There are several methodologies available for the synthesis of alumina nanopowders, which may be grouped into physical, gaseous and wet phase chemical processes [10–12]. In some of these routes, the reagents used can be expensive and sufficiently toxic to affect the environment in large-scale production. Additionally, to be suited for application as biomaterials, the particles must be free of harmful molecules adsorbed on their surface.

Green techniques for the production of nanoparticles have gained prominence in recent years due to the desire to develop a more environmentally aware approach to the synthesis of nanomaterials [13,14]. The purpose is to eliminate or reduce the excessive use of toxic reagents, as well as minimize the amount and toxicity of the waste generated [15–17]. Several studies concerning nanoparticle synthesis have proposed the replacement of traditional reagents by natural products

such as black tea leaves [18], *Aloe vera* [19,20] and coconut water [21,22].

This paper proposes a modified sol–gel route to produce nanoparticles, in which natural organic matter (NOM) is used for gel formation. As in the conventional sol–gel process, in which the formation of an organometallic complex is followed by organic polymerization, it is possible to employ the complexation capability of NOM to anchor the metal ions. NOM is a complex mixture of organic compounds derived from the synthesis reactions of microorganisms during the decomposition of animals and plants [23]. Most of these compounds (~80%) have not yet been identified, while the remaining 20% consists of organic compounds with known chemical structures, including carbohydrates, amino acids, and hydrocarbon [24].

The advantages of using NOM are its wide availability, low concentrations of mineral impurities and close similarity between the various NOM found in different global regions, which can be beneficial for the reproducibility of the synthesis procedure. Most of the NOM present in rivers and lakes are aquatic humic substances. These substances have a high content of oxygen-containing functional groups, including carboxyl, phenolic, hydroxyl, and carbonyl groups [25], and are widely recognized as important natural complexation agents [23–27]. Additionally, the use of NOM in the synthesis of nanomaterials could overcome a major problem in wastewater treatment, which is the formation of disinfection by-products that are potentially carcinogenic and/or teratogenic [28,29].

The main goal of the present work was to synthesize α -alumina nanoparticles using aquatic humic substances instead of the metal

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alkoxides used in the traditional sol–gel route. To minimize the environmental impact of this method, it includes the recycling of the water used in the synthesis. The physico-chemical and bacteriological properties of this recycled water are also presented and discussed.

2. Experimental

The NOM-rich water used in the synthesis was collected from a waterfall in Sergipe State, Brazil. A preliminary investigation of its features included tests of pH and electrical conductivity, determination of the amount of dissolved organic carbon (DOC) and concentration of 32 elements (from Li to Bi) of environmental interest. A pH meter (Ion PHB 500) was used to determine the pH and the electrical conductivity of the water at room temperature. DOC was determined by catalytic combustion in oxygen atmosphere, using a Shimadzu TOC 5000 analyser. The concentration of the elements from Li to Bi was determined using atomic emission spectroscopy in argon plasma (Varian ICP OES, Mulgrave, Australia). For these measurements, the ICP OES system was previously calibrated using a standard solution of HNO₃, diluted to reach pH 2.0.

The synthesis of alumina employed the precursor Al₂Cl₃·6H₂O (Vetec, 98%) which was mixed in NOM-rich water to form a colloidal suspension (sol). To adjust pH, ammonium hydroxide, NH₄OH (Vetec, P.A.), was added drop by drop into the sol, while it was stirred, and the pH values of the sol were monitored using a pH meter. This sol was continuously stirred to form a gel, which was dried at 100 °C/24 h in a distillation system that will be discussed later in this section. The dried material (xerogel) was porous and dark. It was homogenised in an agate mortar and then calcined in an open atmosphere electric furnace with a heating rate of 10 °C min⁻¹, to reach the crystalline phase. Systematic tests were conducted in order to determine the best experimental conditions to obtain α-alumina. The parameters tested were the initial concentration of the precursor sol (the concentrations 0.05, 0.1, 0.2 and 0.6 g mL⁻¹ were tested), stirring time (5, 30, or 120 min), calcination temperature (600, 800, 900 or 1000 °C), gelation temperature (unheated or heated at 60 °C) and pH of the initial sol (from 3.0 to 9.0).

Thermal analysis of the xerogel was performed using a simultaneous DTA/TG (SDT 2960—TA Instruments) at a heating rate of 10 °C/min, in a flow of synthetic air (O₂/N₂—1/4), from the room temperature up to 1200 °C. The crystalline phase of the calcined powders was inspected by X-ray diffraction (XRD — Rigaku RINT 2000/PC), in continuous scanning mode using Cu Kα radiation, over a 2θ range of 10–80°. The XRD patterns were compared with the data from the Inorganic Crystal Structure Database (ICSD). The morphology of the samples was analysed by scanning electron microscopy with field emission gun (FEG-SEM, JEOL model JSM-7500F), and an energy dispersive spectroscopy (EDS) accessory was used to determine the concentration of elements with atomic mass greater than or equal to 4. Infrared spectra were acquired via a Perkin Elmer instrument (in transmission mode), in the range of 400–4000 cm⁻¹, with a resolution of 4 cm⁻¹. Nitrogen adsorption and desorption isotherms were performed at 77 K by using a NOVA 1200e analytical system made by Quantachrome Corporation (USA) to determine the surface area of calcined powders. The specific surface area was determined using the Brunauer–Emmett–Teller (BET) technique [30], for P/P₀ ranging from 0.05 to 0.30.

The water used in the synthesis was recycled during the drying of the samples, using a distillation system. This procedure consisted in keeping the precursor gel in a sealed flask while it was heated up to 100 °C to form xerogel. This drying step lasted 24 h and the vapour collected was condensed and analysed. The properties analysed were the turbidity, colour, and concentration of nitrates, chlorides and metallic ions (Ba, Cd, Cr, Ni, Fe, Al, Cu, Mn, Na, Pb, Zn). A bacteriological analysis of the recycled water (for total coliforms and *Escherichia coli*) was also performed. All the analyses were performed in triplicate, following the recommendations of the American Public Health Association [31].

3. Results and discussion

3.1. Characterization of the NOM-rich water

The values determined for pH, DOC concentration and conductivity of the NOM-rich water were pH = 3.9, DOC = 23.6 mg·L⁻¹ and $s = 89.0 \mu\text{S}\cdot\text{cm}^{-1}$, respectively. These results indicate that the NOM present in this aquatic environment is composed of macromolecules with high molecular weight and acidic functional groups (carboxyl and phenolic hydroxyl). The electrical conductivity is significantly higher than that of distilled water (7.9 $\mu\text{S}\cdot\text{cm}^{-1}$), confirming the electrolytic nature of the water found in the collection region. However, this value is lower than that measured for coconut water (7140.0 $\mu\text{S}\cdot\text{cm}^{-1}$), which is usually employed in proteic sol–gel synthesis [22], suggesting that NOM-rich water contains lower concentrations of mineral salts than coconut water. The presence of impurity salts, although common in synthesis processes using natural products, can result in extrinsic defects that affect the optical properties of the samples, so it is desirable to keep the concentrations of these salts at low levels. Table 1 lists the concentrations of 32 elements in the precursor water used in this work. These values are substantially lower than those reported in the literature [32,33], indicating that the collection area has not been significantly affected by human activity. The use of this water as a NOM-rich precursor for the synthesis of alumina was therefore suitable to yield the final product with low concentration of extrinsic defects.

3.2. Synthesis and characterization of alumina

The thermal behaviour of the xerogel produced using NOM was investigated in order to identify the best calcination temperature for the crystallisation of alumina. Fig. 1a presents the TGA/DTA curve for xerogel produced at pH 3.0. Two distinct stages of mass loss can be observed, extending up to 800 °C. The first stage occurred between 200 °C and just below 400 °C, with a mass loss of approximately 20%, and was probably due to degradation or combustion of organic material from the NOM-containing water. This hypothesis is supported by the exothermic peaks observed in the DTA curve. In the second stage, there was a small weight loss between 400 °C and 800 °C. This behaviour is in agreement with previously reported results [34,35].

The thermal analysis profile of the xerogel prepared at pH 4.0 (Fig. 1b) is similar to that observed for the sample produced at pH 3.0, probably because the dissolution of aluminium hydroxide leads to the formation of the same complex ion [Al(H₂O)₆]³⁺ in both samples [36]. The main differences between Fig. 1a and b are the position of the

Table 1

Concentrations of impurities present in NOM-rich water collected at Liana waterfall in Serra de Itabaiana National Park (Sergipe State, Brazil).

Element	Concentration (mg L ⁻¹)	Element	Concentration (mg L ⁻¹)
Ag	39.9	Sb	0.83
As	0.0018	Sc	0.22
B	12.1	Se	0.40
Be	0.040	Si	1448.1
Bi	0.12	Sn	0.06
Co	0.17	Ti	1.44
Cd	0.11	V	12.97
Hg	0.67	W	0.12
K	468.4	Zn	***
Li	0.46	Zr	0.56
Mo	0.09	Ca	704.1
Na	4909.03	Mg	1034.2
Al	115.4	Fe	94.8
Ba	9.3	Mn	1.5
Cr	0.5	Ni	0.7
Pb	1.9	Sr	8.4
Cu	23.1		

*** The concentration is zero or below the detection limit using this method.

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