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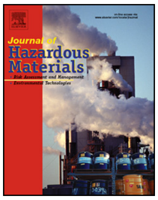

Effect of co-existing ions during the preparation of alumina by electrolysis with aluminum soluble electrodes: Structure and defluoridation activity of electro-synthesized adsorbents

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HIGHLIGHTS

- pH increases during electrocoagulation with aluminum electrodes are rationalized.
- Composition of electrogenerated aluminas is dependent upon the electrolyte used.
- All the electrogenerated aluminas contained nanoparticles of boehmite AlOOH.
- The defluoridation activity of the aluminas was dependent upon the electrolyte used.

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ABSTRACT

The electrochemical dissolution of aluminum was carried out to prepare hydrated aluminas which were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), chemical titrations and defluoridation activities. Aluminas were obtained at controlled pH depending upon the counter cations of the electrolyte. A boehmite AlOOH phase was isolated mainly in ammonium solution, while aluminas synthesized in the other media contained a mixture of phases, usually both boehmite and bayerite γ-Al(OH)$_3$. All the boehmite phases contained nano-crystallites of less than 3 nm. Batch defluoridation experiments revealed a second influence of the original electrolyte. Aluminas were very effective in defluoridation with abatement rates of 99.5%, 98.5% and 97.3% from neutral fluoride solution at 10 mg L^{-1} when they were prepared in solution of $(NH_4)_2SO_4$, $(NH_4)HCO_2$ and NH_4Cl, respectively. The maximum fluoride capacities were 46.94; 10.25 and 12.18 mg g^{-1} for aluminas prepared in solution of $(NH_4)_2SO_4$; $(NH_4)HCO_2$ and NH_4Cl, respectively. The amount of dissolved Al was found to be less than 0.19 mg L^{-1} at neutral pH. These results show that a defluoridation with electro-synthesized aluminas would be more efficient and safe than a direct electrocoagulation.

1. Introduction

Aluminum oxide and its hydrates are materials of great technological importance due to their excellent physical and chemical properties. These compounds, also denoted aluminas or hydrated aluminas, are largely used as adsorbents, catalysts, intermediates materials and especially basic material in ceramic and microelectronic industries. Thus, many methods exist for the preparation of aluminas including sol–gel [1], hydrothermal [2–4], precipitation from aluminum solutions [5,6] and thermal decomposition in supercritical water [7]. In these methods, various aluminum compounds, especially alkoxides, are used as starting chemicals. These methods have received considerable attention as they offer the advantage of low-temperature processing and the possibility of producing crystalline and pure aluminas [8]. However, their drawbacks are the cost of the starting chemicals and the large amount of reactants required for an industrial application of aluminas synthesis.

Du et al. [6] synthesize various aluminum hydroxides by chemical precipitation from aluminum salt and ammonia. The composition, microstructure and morphology of the precipitates are dependent on the pH of the solution. However, our focus was to look at developing an electrochemical preparation that would not use large amounts of ions as it is the case when alumina is precipitated from an aluminum salt solution. Indeed, instead of using aluminum salt as initial chemical, we were interested by the possible use of

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electro-synthesized aluminum ions arising from a sacrificing aluminum anode. With Al^{3+} and OH^- arising from the anode and cathode (Eqs. (1) and (2)), respectively, it is possible to consider the synthesis of aluminas in media containing a low ionic content, according to Eq. (3). The formation of hydrated alumina following the overall reaction of Eq. (4) does not involve any ionic species, except the electrolytic ions.

$$Al \rightarrow Al^{3+} + 3e^- \quad (1)$$

$$3H_2O + 3e^- \rightarrow 3OH^- + 3/2H_2 \quad (2)$$

$$2Al^{3+} + 6OH^- \rightarrow Al_2O_3{\cdot}xH_2O + (3-x)H_2O\,(x = 0,\ 1,\ 2\text{or}\ 3) \quad (3)$$

$$2Al + 6H_2O \rightarrow Al_2O_3{\cdot}xH_2O + (3-x)H_2O + 3H_2 \quad (4)$$

These reactions are often involved in the formation of coagulants as aluminum hydroxides in the electrocoagulation process applied to the elimination of pollutants from water [9,10]. The performance of electrocoagulation in which there is an electro-dissolution of anode is strongly affected by the presence of anions in the solution and the electrolyte nature [11–15]. Except for synthetic waters, co-existing ions are always present beside targeted adsorbates. The effect of major co-existing ions is a crucial step in adsorption studies [16–18]. When the formation of the adsorbent occurs concomitantly with the adsorption, as it is the case for electrocoagulation [11], co-existing ions may be involved with a double effect. Du et al. [6] and Mishra et al. [19] show that co-existing anions, that have an influence on the pH, play also an important role on the synthesis of hydrous aluminum oxides by using sol–gel or precipitation methods. That are why we thought that the microstructures of the electro-synthesized aluminas depend on the various electrolytes used to promote electro-dissolution of aluminum anode.

On the other hand, aluminas are good adsorbents often used to remove excess fluoride ions from water [20–22]. In our former works [23,24], we synthesize low cost fluoride adsorbents as charcoals which contain inorganic oxides. So, in this work we were interested by a study of the fluoride removal with electro-synthesized aluminas. Fluoride excess in drinking water is a global environmental problem with incidence on people health. Fluoride in drinking water is extremely toxic when it is above the maximum acceptable concentration ($1.5\,mg\,L^{-1}$) according to the World Health Organization (WHO) [25]. It leads to gastrointestinal disorders [26], dental and skeletal fluorosis [27,28] and is involved in the decrease of growth and intelligence [29,30]. Electrocoagulation has been applied to the defluoridation of drinking water [31–33]. Since drinking waters present low ionic contents, it is obvious that they are not adapted to an electrolytic process. Moreover, drinking waters contain ions which may interfere at two levels. The first is their influence in the electrolytic process of alumina formation. The second level is their interference as coexisting ions during the fluoride removal: even at this level, the anions play an important role because they influence the pH of the adsorption medium, modifying the electrostatic forces or acidic-basic interactions between adsorbent and pollutant, thus changing the ability of the adsorbent to fix adsorbates [9,11]. We were interested by the idea that a two-step process may be more efficient and rational than a hyphened electrocoagulation–defluoridation process. In this paper, we present the electrolytic preparation of alumina by dissolution of aluminum anode in various electrolytes. This electrochemical synthesis method has some undeniable advantages: it is held at low temperature, it is possible to control the kinetic synthesis through current intensity, and it does not require chemical addition, except the electrolyte. The characterizations and applications of synthesized aluminas in defluoridation of water are presented and discussed.

2. Experimental

2.1. Electrochemical synthesis

All solutions used for electrolysis were prepared from analytical grade chemicals reagents with de-ionized water. The various electrolytes were aluminum, ammonium and sodium salts, each consisting of chloride, nitrate and sulfate anions. $(NH_4)HCO_2$, $NaCH_3COO$, $Na_2C_2O_4$, $NaClO_4$ and $(NH_4)_2S_2O_8$ solutions were also used.

The electrochemical set up was constituted with two parallel aluminum plates with a rectangular shape (23.5 mm × 70.0 mm × 2.0 mm). The electrodes were washed prior to electrolysis experiments with 2 M NaOH during 10 min, then rinsed with de-ionized water and dried in an oven at 105 °C for 1 h. The electrodes were immersed in a cell containing 200 mL of an electrolyte of 0.05 or 0.1 mol L^{-1}. The gap between anode and cathode was of 1 cm. The current was controlled at 1 A during 3 h. It was furnished by a direct current power supply (DC Microlab 600 V–2 A). The solution was magnetically stirred. The measurements of pH, turbidity and conductivity were made using an electronic pH-meter (Metrohm), a turbidimeter (Hach) and a conductivity meter (Radiometer Metrolab CDM 210), respectively. At the end of the electrolysis, alumina particles were collected by filtration and then rinsed tree times for 1 h with de-ionized water under agitation and dried in an oven at 105 °C for 24 h.

2.2. Characterization techniques and methods

Observations with a Scanning Electron Microscope (SEM) and element analysis by energy dispersive spectroscopy (EDS) were performed using Jeol JSM 6400 equipment operating at an accelerating voltage of 20 kV.

For microstructural analysis, powder X-ray diffraction (XRD) data of grounded crystals of alumina were collected at room temperature with a Siemens D500 diffractometer operating with the parafocusing Bragg-Brentano geometry, using monochromatic Cu Kα (1.54060 Å) radiation selected with an incident beam curved-crystal germanium monochromator. The data were recorded over the angular range 6–129° (2θ) with a counting time of 55 s step-1 and a step length of 0.02° (2θ). For phase identification, powder XRD patterns were also collected with a INEL XRG 3500 diffractometer using CuKα (1.54060 Å) radiation. The data were recorded at 30 kV and 30 mA with an angle between $2\theta = 5–120°$ and step length of 0.02° (2θ). Instrumental line profiles were obtained with the NIST standard reference material SRM660a LaB6. The microstructure analysis was carried out from line-broadening analysis based on the whole pattern fitting technique by means of the program FULLPROF [34] in the WinPLOTR interface [35]. The integral breadths of the individual Bragg reflections are derived from a pseudo-Voigt approximation to separate apparent volume-weighted size (calculated from the Scherrer equation [36]) and reticular distortions (calculated from the Stokes & Wilson equation [37]). Taking into account the lameral structure of boehmite with layers perpendicular to b axis, crystallite sizes have been calculated from anisotropic model of platelet-shape crystallites with orientation of anisotropy along [0k0] vector.

The pH of point of zero charge (pH_{PZC}) was determined by the following method. 100 mg of the solids were contacted with 50 mL of 0.05 M $NaNO_3$ deoxygenated aqueous solution with a pH range of 3–11. Blanks with no solid were also run in the same initial pH values. After shaking for 24 h at 250 rpm at room temperature, the final pH was measured: The pH_{PZC} was determined as the pH of $NaNO_3$ solution that remained unchanged after contact with the samples.