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Activated Alumina Granules with nanoscale porosity for water defluoridation

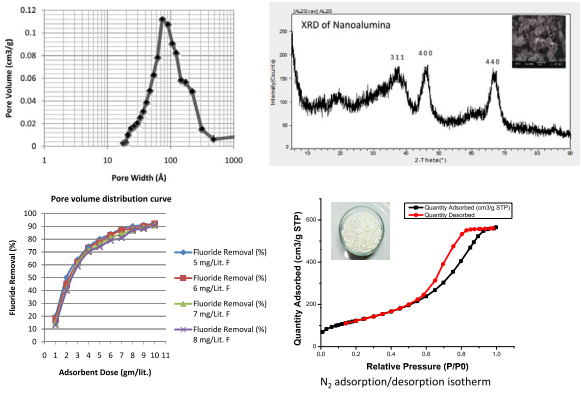
R.M. Belekar [a], S.J. Dhoble [b,*]

[a] Department of Physics, Government Vidarbha Institute of Science and Humanities, Amravati-444 604, India
[b] Department of Physics, R. T. M. Nagpur University, Nagpur-440 033, India

HIGHLIGHTS

- Activated alumina granules are efficient adsorbent material for defluoridation.
- Activated alumina granules possess large surface area compared to other adsorbent.
- AA shows better regeneration and reusability even after ten cycles of usage.
- Prepared granules have potential of field application at large scale with low cost.

GRAPHICAL ABSTRACT



N_2 adsorption/desorption isotherm

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ABSTRACT

Highly porous alumina granules have been processed by virtue of modified sol–gel method. Activated alumina (AA) granules were obtained through hydrolysis of aluminum nitrate controlled by ammonia in aqueous media and granules were formed in ammonia–paraffin oil bath. The prepared granules were found to be consisting of high porosity amorphous γ - alumina particles which were characterized by XRD, SEM, TEM, FT-IR and Brunauer–Emmett–Teller (BET) techniques. The material prepared via this method were found to be composed of nano-particles with an average grain size of 30 nm and a large BET surface area 447 m^2/g which is very high compared with commercial alumina available in the market. The fluoride removal capacity of prepared granules with variation of fluoride dose has also been studied by employing AA in domestic candle type filters. It also shows better regeneration and reusability after ten cycles of usage. Fluoride removal from aqueous solution in continuous mode depends on adsorbent doses and initial concentration of fluoride.

1. Introduction

Aluminum oxide (Al_2O_3) is one of the most promising and esteemed ceramic material which has unearthing applications in various fields like electronics, optics, metallurgy, catalysis, nanotechnology, etc [1]. Due to its conceited mechanical, thermal and chemical properties, Al_2O_3 has become an imperative material in current area of research and development. Because of its wide band gap, alumina is suitable in microelectronics as alternative material for gate oxides [2], whereas in an electro-optics as low loss dielectric waveguides [3] and in nanotechnology as a host material within the context of nano-crystals [4]. In fact, the idea of larger band gap materials as host matrices for nano-crystals has become

* Corresponding author.
E-mail addresses: rajubelekar@gmail.com (R.M. Belekar), sjdhoble@gmail.com (S.J. Dhoble).

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vibrant topic in silicon based research and technology [5]. Among other materials, aluminum oxide is heading as one of the most suitable materials to be replaced with SiO_2, the most promising oxide material in silicon based technology [6]. Moreover, in optical applications, the impurities and defects in aluminum oxide are keenly observed and accepted in order to control their emission properties in the matrix. Hence, revealing knowledge about physical and chemical properties of aluminum oxide is crucial for better understanding of this material and for expanding probable range of potential applications.

Currently, many countries (both developing and poor) are plagued with drinking water toxicity issues which are ultimately affecting food chain by creating hazardous health crises at the level of mass poisoning. Because of disposal of sewage and industrial waste waters, groundwater is found contaminated with perilous and unhealthy chemical effluents. In the water contaminations, the most impregnable toxins are Chromium, Arsenic, Cadmium, Lead and Fluoride [7–13]. From these, Fluoride is amongst the anionic contaminant which is supposed to have serious impact on bones and teeth when found in excess concentration. Since provision of safe drinking water is assumed pivotal in all embracing development of any nation, de-fluoridation is one of the most serious matters of concern for developing countries like India. Presently, number of treatments have been studied and implemented for the removal of contaminations from ground water. For the removal of such contaminations, highly porous activated alumina, polymeric resins, activated carbon, chitosan beads, and few other low cost adsorbents were successfully used [14–24]. Activated alumina (AA) has been extensively used as an adsorbent for ground water treatment in rural and urban applications because of its unique physical, chemical and textural properties that proves it better than any other transitional inorganic oxides [11].

Nano materials are predominantly composed of surface atoms. Decrease in particle size leads to increase in the ratio of particle surface area to its overall volume. As reactions occurring at the surface of nano materials, accurate prediction of surface area is detrimental to anticipate environmental fate for hazard assessments. The Brunauer–Emmett–Teller (BET) method [25] is one of the most widely employed models for determination of surface area of powdered samples. The BET model is an extended version of the Langmuir approach to accommodate multilayer formation, in which multiple physically adsorbed probe molecules are required to cover the surface and the cross-sectional area of each probe, the total adsorbent surface area can be calculated [26]. The main problem with BET method is that, it does not allow one to distinguish the contribution of pores of various sizes, with any larger pore to accommodate the probe molecule to be measured. However, in the BJH method, it allows determining surface areas; along with the lengths and diameters of the pores known, the surface area of each pore is easily measured, with total surface area obtained by summing over the pores [27]. The main function of fine pores can be studied by careful choice of this summation range.

It is conventionally assumed that physical properties of alumina particles are liberally governed by particle morphology, size, surface and phase homogeneity which can be controlled by adopting an efficient synthesis strategy [28]. In the present investigation similar method was used to synthesize activated alumina granules with slight modifications. Produced alumina granules were characterized by XRD and the specific surface area (S_{BET}) was measured by nitrogen adsorption employing BET method. Also, the present study has been undertaken to explore in depth various aspects of fluoride removal through activated alumina by carrying out batch studies and continuous down flow column studies.

2. Materials and methods

For the preparation of alumina sol, aluminum nitrate (from Merck AR grade) and ammonia solution were taken as initial precursors. Starch solution was used as surfactant. Freshly prepared 4% starch solution was added to 0.1 M aluminum nitrate solution to form homogeneous solution. Ammonia solution was added to the solution till complete precipitation. After completion of reaction, the solution was allowed to settle for overnight and supernatant liquid was then discarded carefully by centrifuge. For granulation process, this sol was ultrasonically dispersed by homogenizer after adding 1M HNO_3 and aged at 70 °C for 1–2 h until the mixture reached the point of gel formation. This partially gelled sol was then transferred into dropper for the generation of sol droplets of about 3 mm in size. The droplets fell through a liquid bath containing paraffin oil layer (mineral oil from Merck Chemicals) and a 10% ammonia solution layer. The paraffin oil layer facilitated the droplets into spherical wet-gel granules because of surface tension. The structures of the wet-gel particles were strengthened after aging in ammonia solution for 1 h. The granules were then collected with sieve and washed several times with alcohol and distilled water. After this, granules were dried at 40 °C for 48 h and were sintered at 500 °C for 2 h.

To study the application of activated alumina for fluoride removal, down flow column study was conducted using domestic candle type filter by filling hollow column by AA and then plugging it with cotton. The test solution was prepared using ordinary tap water spiked with 5 to 8 mg of fluoride per liter. To study the effect of increase in the dose of activated alumina on removal of fluoride, experiments were conducted by adding varying doses of 2.5, 5.0, 10.0, 15.0 and 20.0 g l^{-1} to a test solution containing initial fluoride concentration. The samples were then agitated up to equilibrium time.

3. Results and discussion

The crystalline structure of alumina granules was investigated by wide angle X-ray diffraction, using a powder X-ray diffractometer with Cu- K_α source. All scans were recorded in the 2 θ region of 5°–90° at a scan rate of 0.020 per second. Fig. 1 reveals the X-ray diffraction pattern of finely grinded alumina granules sintered at 500 °C. The peaks observed were relatively broader showing average crystallinity, fine size and amorphous γ- Al_2O_3 phase. The prepared alumina granule samples display distinct diffraction peaks for γ-Al2O3 (ICDD JCPDS No. 98-000-0059; a spinel-type structure; space group Fd3m) [29–31], with all γ-Al2O3 nanoparticles showing similarity in relative peak intensities. The X-ray diffraction pattern was compared with standard data, the 100% intensity occurred at 2θ value of 66.90°, which was nearly similar to reference data [32]. The γ-alumina sample obtained through this method shows weak crystallinity and there tend to be a peak broadening effect. The average crystallite size of 30 nm obtained from Scherrer peak broadening formula, which lies within the requirement of nano dimension powder. At the certain elevated temperature of 500 °C, progressive desorption and dehydration of hydroxyl groups present on the surface lead to the formation of γ-Al_2O_3 which is based on distorted spinel structure [33]. When the obtained peaks were analyzed by curve fit, the peaks exhibit broad and diffuse profiles which indicates presence of small crystalline grains and compositional fluctuations. This is consistent with the location of the Al^{3+} ions either by the tetrahedral or octahedral sites within the spinel structure.

Fig. 2(a) explores SEM image of as-prepared grinded alumina granules synthesized through sol–gel method. SEM image manifests large number of pores which reflects nearly amorphous nature of mesoporous γ-alumina. When viewed with very high