PREPARATION OF ALUMINIUM OXIDE NANOPARTICLES USING GREEN SYNTHESIS

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Abstract

Nanoparticles are widely used in industry as well as biomedicine. An interesting group are aluminium oxide nanaoparticles (alumina nanoparticles) belonging to the family of metal oxide nanoparticles, which can be prepared by various methods (the sol-gel, precipitation, micro-emulsion and hydrothermal methods). In this work, alumina nanoparticles were prepared by biological synthesis using plant extract from fresh neem (*Azadirachta indica*) leaves. The particles were confirmed by the SEM analysis. The distribution diagram showed a size from 60 to 1,500, with a maximum around 200–400 nm. Alumina nanoparticles possess many potential applications in biomedicine such as drug delivery, therapy of cancer and other diseases, and immunotherapy.

Keywords: Aluminium nanoparticles, green synthesis; biotechnology; nanomedicine

1. INTRODUCTION

The sol-gel technique is one of the optimistic and explored methods due to its ability to produce ultrafine sized particles with controlled size, high surface area, purity, and crystallinity. **Figure 1** shows a schematic representation of the synthesis of alumina nanoparticles by using an ethanol solution of iron nitrate as precursor through the simple sol-gel method [1].

Rogojan et al. prepared aluminium oxide nanopowders using 2 different precursors, organic and inorganic precursors to be used as a biomaterial in medical applications. The organic precursor used was aluminium chloride ($AlCl_3$) and the inorganic precursor was aluminium triisopropylate $Al[OCH(CH_3)_2]_3$. [2]. The precursors were chemically treated by using the sol-gel protocol, and the resulting gel was calcined for 2 hours at two different temperatures, 1,000˚C and 1,200˚C. The X-ray diffraction analysis revealed that thermal treatment at 1,000 ˚C leads to the formation of $\alpha + \gamma$ - Al_2O_3 mixture having relatively low degrees of crystallinity. An increase in the heat treatment temperature to 1200˚C led to the formation of α-Al_2O_3 with higher crystallinity. The SEM and TEM analysis confirmed the production of alumina powder in nanometer-scale by the sol-gel method. Application of heat treatment at temperatures higher than 1,000 ˚C had led to the formation of crystalline α alumina as a single phase.

Li et al. synthesized nano-sized α-Al_2O_3 powder using citrate precursor that was derived from aluminium nitrate and citric acid precursor solution. The ratio of citric acid (CA) to metal nitrate (N) had a greater influence on the size of the nanoparticle prepared by the sol-gel method. Initially, the ratio was maintained as 1:1 and the precursors were heated to 400 ˚C. The precursors decomposed and resulted in the formation of amorphous nano-Al_2O_3, which further transformed into to γ-Al_2O_3 (size = 15 nm). Further heating to 800˚C resulted in the transformation of γ -Al_2O_3 to α-Al_2O_3 with a crystalline size of 75 nm. The calcination process was completed at 1,000 ˚C with the formation of 200 nm-sized alumina nanoparticles. The increasing molar ratio of CA/N favored the rapid phase transition of γ-Al_2O_3 to α-Al_2O_3, whereas 1:1 CA/N molar ratio yielded a monodispersed ultrafine α-Al_2O_3 [3].

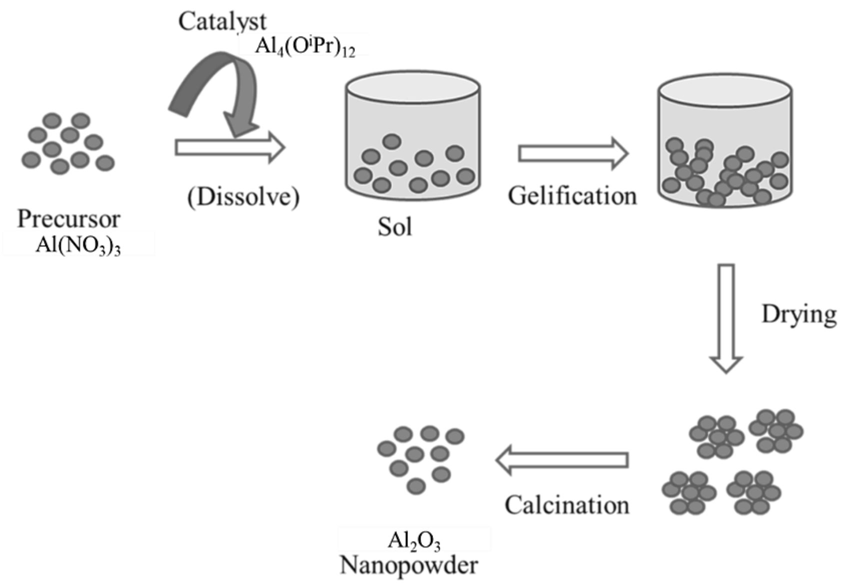

Figure 1 Scheme for the synthesis of alumina nanoparticles by the sol-gel method

Khazaei et al. synthesized porous γ-aluminium oxide nanoparticles using sodium aluminate liquor as a precursor. The effect of two surfactants namely, polyethylene glycol (PEG) and polyvinyl alcohol (PVA) were investigated for their stabilizing action on alumina nanoparticles (**Figure 1**). The calcination temperature was maintained at 80˚C. PVA as stabilizing agent offered better structural properties (average crystallite size of 2.063 nm, the average particle size of 46 nm, the specific surface area of 201.1 m^2/g and pore volume of ~ 0.246 cm^3/g) when compared with PEG (average crystallite size of 2.313 nm, the average particle size of 20 nm, the specific surface area (SSA) of 138.8 m^2/g, and pore volume of ~ 0.166 cm^3/g). PEG stabilized synthesis resulted in the formation of ultrafine nanoparticles (20 nm), whereas PVA stabilized nanoparticles are comparatively larger, thus the adhesion between the nanoparticles was less and remained in a more dispersed state [4].

Mirjalili et al. synthesized ultrafine α-alumina nanoparticles using aluminium isopropoxide, aluminium nitrate hydrate (0.5 mol/L) as precursors and sodium dodecylbenzene sulfonate (SDBS), sodium bis-2-ethylhexyl sulfosuccinate (Na-AOT) as stabilizing agents to prevent the aggregation of nanoparticles. The surfactants played a major role in controlling the size and shape of the nanoparticle and in addition the degree of aggregation has also been influenced by the two stabilizing agents. Using sodium dodecylbenzene sulfonate as a stabilizing agent resulted in the fine and well-dispersed nanoparticles (20−30 nm). The better stabilization action of SDBS can be attributed to the higher ionization of SDBS in comparison Na-AOT that resulted in negative charge adsorption in the positively charged precursor. This charge-charge interaction decreased particle aggregation [5].

The aim of this work was to use the sol-gel method for the green synthesis of alumina nanoparticles.

2. METHODS

2.1. Plant material and preparation of the extract

Generally, biosynthesis of nanoparticles occurs when plant aqueous extract undergoes bioreduction process with an aqueous solution of suitable metal salt. Fresh neem (*Azadirachta indica*) leaves were collected from the institute and washed twice with distilled water to remove all the debris present on it. About 20−30 g of leaves was crushed with mortar and pestle and the obtained extract was filtered with muslin cloth. The extract was then stored at room temperature for further experiments [6]. The leaves extract contains flavonoids and phenolic acids with various functional groups, which are capable of forming nanoparticles by acting as reducing and stabilizing agents.

2.2. Biosynthesis of Al_2O_3NPs

Aluminum chloride (Merck, India) was used as the primary chemical for the synthesis of aluminum oxide nanoparticles. The prepared extract was mixed with saturated solution of aluminum chloride and kept for two hours in magnetic stirrer (REMI, Laboratory Instruments, India) for appropriate mixing of the solutions. The pH change was observed after stirring process to check the reaction occurring between the phytochemicals present in the extract and the metal ions to produce metal oxide nanoparticle. The reaction mixture was then centrifuged at 2500 rpm for 20 minutes using cooling centrifuge (REMI C-24 Plus) to settle down the unused extract and the obtained supernatant was again ultra-centrifuged at 14,000 rpm for 30 minutes. The resulted supernatant was discarded and the pellets were repeatedly washed with water and ethanol and dried in hot air oven at 60 °C to obtain Al_2O_3NPs. The alumina nanoparticles were characterized by the SEM method.

3. RESULTS AND DISCUSSION

Aluminium oxide nanoparticles (Al_2O_3NPs) are class of metal oxide nanoparticles that have various biomedical applications due to their excellent physicochemical and structural properties (chemical and mechanical resistence, very good optical characteristics, a porous vast surface area etc.) as well as their low cost of preparation [7]. The synthesis of metal oxide nanoparticles is the major technological challenge. The behavior of aluminium oxide nanoparticles for different applications is determined by the physical, chemical, optical and magnetic properties, which, in turn, are influenced by the structural characteristics of the nanoparticles. Numerous production methods are developed such as sol-gel, precipitation, micro-emulsion, and hydrothermal method. Al_2O_3NPs have various potential biomedical applications − drug delivery, biosensing, cancer therapy, anti-microbial agens, treatment other diseases such as asthma, biomolecular preservation and stabilisation, and immunotherapy [7]. Due to their biomedical applications, it is needed test their environmental biotoxicity. **Table 1** summarizes the data on the synthesis of alumina nanoparticles using various methods and techniques. Thus, it was possible to prepare nanoparticles with sizes from 4 to 100 nm.

Table 1 Brief description of the different methods applied for the synthesis of the aluminium and aluminium oxide (alumina) nanoparticles used in various research studies

Method of preparation	Precursor	Nanoparticle	Particle size (nm)	Reference
Sol-gel method	aluminium chloride and aluminium triisopropylate	α-Al_2O_3	-	[2]
	aluminium nitrate and citric acid	α-Al_2O_3	75 nm	[3]
	sodium aluminate liquor		20 nm	[4]
	aluminium isopropyloxide, aluminium nitrate hydrate	α-Al_2O_3	20−30 nm	[5]
Precipitation method	SDS, PEG 6000	$Al(OH)_3$	80−100 nm	[8]
	polysulfone and polystyrene	$Al(OH)_3$		[9]
	ammonium bicarbonate, ammonium carbonate, sodium bicarbonate and sodium carbonate	γ-alumina	4.7–5.7 nm	[10]
	-	γ-Al_2O_3	4.5 nm	[11]
	polyethylene glycol	Al_2O_3	-	[12]
	-	*γ* and *α* phases of alumina nanoparticles	20−50 nm	[13]
Micro-emulsion method	Triton X-100 and n-butyl alcohol	-	-	[14]
	silane agent	Al_2O_3	-	[15]
Hydrothermal method	polyethyleneglycol (PEG)	γ-aluminium oxide	10−15 nm	[16]
	cationic (cetyltrimethylammonium tosylate, CTAT) and anionic (sodium dodecylbenzene, sulfonate, SDBS)	δ–Al_2O_3	-	[17]

A study has also been conducted to explain the complete process for producing aluminium hydroxide with improved whiteness. In the initial step, the colorant containing aluminium hydroxide was dissolved as the solution. The solution was treated with colorant-collecting reagent and separated as a solid phase. The solid phase was removed from the solution and the aluminium hydroxide was precipitated as a pure white powder.

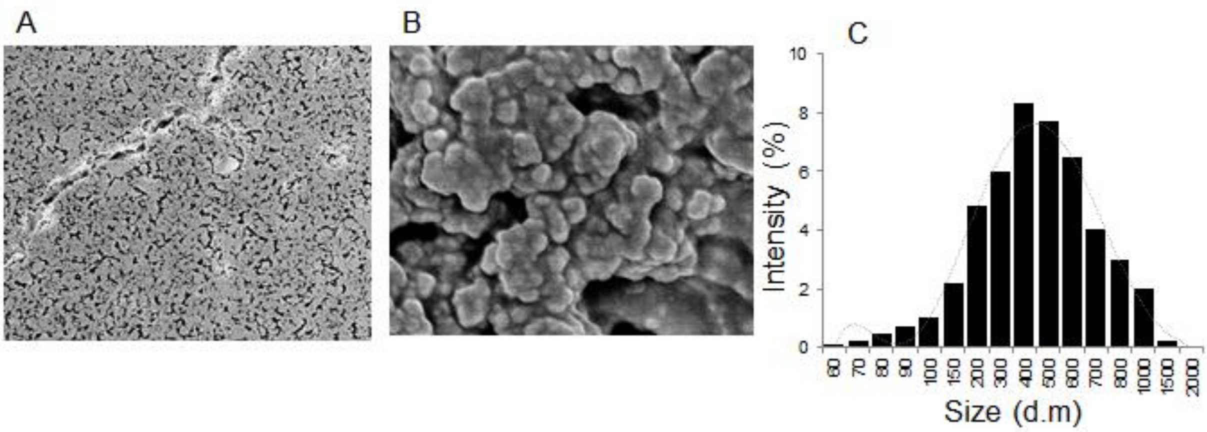

Figure 1 Characterization of alumina nanoparticles – A) SEM images 1000x; B) 30 000x; C) Size distribution

In this study, alumina nanoparticles were prepared biologically – by green synthesis from neem (*Azadirachta indica*) leaves. This plant belongs to the so-called ethnomedical herbs, which has antibacterial, antiviral and anticancer properties. Green-synthesized alumina nanoparticles were characterized by the SEM technique. The method showed the irregular arrangement, wherein the spherical shaped nanoparticles were aggregated (**Figures 1A,B**). Distribution diagram shown in **Figure 1C** displayed showed a size of nanoparticles from 60 to 1,500, with a maximum around 200–400 nm. The zeta potential of prepared alumina nanoparticles was +19.5 mV. The size of nanoparticles formed by the sol-gel method ranged from 20−200 nm. From the above results, it is also clear that maintaining the calcination temperature within 800−1,000 °C results in the formation of ultrafine, monodispersed alumina nanoparticles, which is important for its various applications.

Sutradhar et al. used microwave-assisted green chemistry and synthesized alumina nanoparticles using tea and coffee extracts with a size of 50–200 nm which were spherical in shape, and also oval shaped nanoparticles using triphala extract with an average size of 200–400 nm [18]. Hasanpoor et al. found that average size of clusters of alumina nanoparticles varied with different routes from of 60–300 nm. They used extracts from five different plants (*Syzygium aromaticum*, *Origanum vulgare*, *Origanum majorana*, *Theobroma cacao* and *Cichorium intybus*) for their synthesis [19]. Narayanan and Rakesh prepared alumina nanoparticles using lemon extract [20]. Recently, alumina nanoparticles were also synthesized using leaf extract of *Ocimum sanctum* [21]. Neem extraxt has been used in previous studies for the green synthesis of gold [22], silver [23,24], iron [25], zinc [26,27] and copper [28] nanoparticles. However, to the best of the authors' knowledge, alumina nanoparticles have not yet been synthesized using this plant.

4. CONCLUSION

Alumina nanoparticles were prepared by green synthesis from *Azadirachta indica*, containing a number of phenolic compounds (nimbin, azadirachin, nimbidin, salannin). The nanoparticles slightly aggregated with the most frequent size of 400 nm and zeta potential +19.5 mV. We expect their further potential in use in biomedical applications, especially those antibacterial and antiviral.

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