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NANO ALUMINUM OXIDES AS ADSORBENTS IN WATER REMEDIATION METHODS: A REVIEW

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ABSTRACT

Nanoparticles of Al_2O_3, are proving to be versatile adsorbents in the purification of water/waste water in view of their large surface area, high surface energies and potentials and availability of surface functional groups for binding over the pollutants. The conventional physical and/or chemical methods of syntheses are tedious, costly, involve toxic chemicals and not eco-friendly. Hence, using the extracts of plants as reducing, capping or stabilizing agents, the researchers are synthesizing the nanoparticles and these bio-methods are producing nano-particles that are more bio-compatible and endowed with enhanced sorption nature than the nanoparticles conventionally synthesized. Moreover, these methods are simple and depend upon the naturally available non-toxic compounds in the rich flora available in our surroundings and thereby domesticating the complicated syntheses. In the present review, the investigations pertaining to the synthesis of Aluminum oxide nanoparticles with more emphasis on phyto-(green) methods, and their applications to the removal of toxic ions from water, are emphatically reviewed. The less/not trodden potential areas of research are identified in the context of using nanoparticles of Aluminum oxides as adsorbents for developing water remediation methods.

Keywords: nanoparticles, water treatment, phytomethods, Al_2O_3, adsorbents, pollutants

INTRODUCTION

In the recent past, increasing interest is being envisaged by the researchers in synthesizing metal or metal oxide based nanoparticles adopting green methods especially using the extracts of plants and using thus obtained nanoparticles in water purification methodologies.[1-5] These methods are simple, eco-friendly and economical.

The nanoparticles are the aggregate of few molecules/atoms having the size of 1 to 100 nm in at least one dimension and these small desecrate groups by virtue of their large surface area and energies, are endowed with dominant quantum characteristics besides the conventional properties which they inherit due to their chemical compositions.[6-8] This quantum nature has a remarkable influence on catalytic, optical, electrical, sorption and magnetic properties of the nanoparticles, resulting in their wide use in various industries viz., nano-electronics, clothing, sensors, cosmetics, tires, paints etc. Further, these particles turn to be indispensable components of biomedical research especially pertaining to diagnosis, imaging, nanomedicine, biochemical sensing and in antimicrobial studies[8].

Bio-synthesized nanoparticles by virtue of possessing large surface areas, sorption ability, complexing tendencies, surface energies and catalytic nature, are being found to be effective in the water/wastewater treatment.[2,9] Intensive research is progressing in developing new nanoparticles by eco-friendly methods and applying them to the water /wastewater treatment. The targeted materials for these nanoparticles are: inorganic materials, zeolites, dendrimers and carbon-containing substances. Various toxic metal ions, anions, organic substances, dyes, virus and bacteria are subjected to the adsorptive removal using these amazing particles.[10-12]

The present review article pertains to Aluminum oxide nanoparticles. In this report, the up-to-date review of investigations pertaining to the synthesis of stable nanoparticles of Aluminum oxides by conventional

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methods, their drawbacks, advantageous and progress made in the plant-mediated synthesis and their applications for the treatment of contaminated/waste waters, have been graphically presented. The potential areas of research and challenges involved in them are explicitly discussed.

Aluminum Oxide Nano Particles

The aluminum based nanomaterials comprise of metallic aluminum and aluminum oxide. The nanoparticles of metallic aluminum are highly reactive and are not adoptable in water remediation methods.[13,14] Hence, in this review, research works, trends and prospectives of using nano Al_2O_3/hydrolyzed Al_2O_3 as an adsorbent for controlling the polluting ions in wastewaters are presented.

Aluminum oxide related nanomaterials are intensively used in diverse fields such as, in biomedicines, drug delivery systems, optics, electronic devices, catalysts in various industrial synthesis, etc.[15-18] As Albert Cotton *et al.*(2007) rightly noted that though the aluminum oxide has simple stoichiometric formula, Al_2O_3, it has many manifestations such as various polymorphic forms and hydrated species and each has its own significance depending upon the nature and conditions of preparations.[19] α-Al_2O_3 and γ-Al_2O_3, are well-known forms. The α-Al2O$_3$ form is obtained by heating hydrous Al_2O_3 above 1000ºC and it has a crystalline structure with hexagonally packed oxide ion and octahedrally packed Aluminum ions such that each oxide is surrounded by four Aluminum ions.[19] This form cannot be hydrolyzed. γ-Al_2O_3 is obtained by heating hydrous Al_2O_3 below 450^0C and it possesses a defective structure with cation vacancies and hence, the surface has an affinity towards cations.[19,20] Another form, β- Al_2O_3 is considered to be a mixed oxide and the dopants being Na^+ and Mg^{2+}ions and this form exhibits clear ion-exchanging properties and high conductivity; resulting in its wide use as a solid electrolyte in batteries.[19]

The hydroxides AlO(OH) and $Al(OH)_3$, are amphoteric and they exhibit both physical adsorption and ion-exchange depending upon the pH of the contacting solutions.[18,20,21] Further, the spinning of $AlCl_4$ into fibers and then dehydrating it, result in oxide filaments that are stable up to 1400^0C.[19]

Aluminum oxides when doped with other metallic ions, different colored gems are produced: ruby with Cr^{3+} and blue sapphire with Fe^{2+}/Fe^{3+} and Ti^{4+}. Al_2O_3 on heating with alkali oxides at 1000ºC, results in polymeric aluminum silicates such as $Na_{14}[Al_4O_{13}]$ and $Na_{17}Al_5O_{16}$ with the anions possessing tetrahedral AlO_4 with sharing edges.[19] These compounds are known for their good ionic exchange abilities. Further, aluminum phosphate synthesized hydrothermally in presence of amines possesses cage-like structures similar to that of zeolites. Contrary to zeolites, these structures are electro-neutral and have no ion-exchange nature and hence they are used as molecular sieves with sizes as small as 12-13A^0.[19,22]

Further, zeolites are aluminum silicates of the formula $M^{n+}_{x/n}(AlO_2)_x(SiO_2)_4].nH_2O$ and have cage-like structures with cavities occupied by large ions and water molecules which can be exchanged/adsorbed reversibly to the surface of zeolites and hence, zeolites acquire affinity towards cations.[19, 22-24]

Thus different forms of oxyhydroxides, exhibit various physicochemical affinities viz., physical adsorption, ion exchange, molecular exclusions, complexing tendency etc., depending upon the structure and nature of the functional groups prevailing on the surface of the alumina. The present discussion is confined to the adoptability of various forms of Aluminum oxide/oxyhydroxides as adsorbents in the water purification methods

Nano Al_2O_3, As Adsorbents in Water Purification

Synthesis: Conventional Methods

Investigations are aimed to synthesize the Aluminum oxide-based nanomaterials with enhanced surface area, pore size, dimensionality, and conducive morphology so that the surface of the alumina nanoparticles are endowed with the desired sorption ability and thereby, they can prove to be successful adsorbents for the purification of contaminated waters.

Alumina nanoparticles are conventionally prepared by mechanical synthesis, a sol-gel method, using reactions in the vapor phase, precipitation/coprecipitation and combustion. Mechanical milling,[25] combustion flame pyrolysis,[26] magnetron sputtering[27], hydrothermal synthesis using anionic surfactants as template[28] and pulsed laser ablation[29] are reported in literature and are well adopted. Pulse lasers of short duration are also employed in the synthesis of nanoparticles of Al_2O_3.[30-32]

In the relatively simple, Sol-gel methods, precursors such as aluminum triisopropylate[33], aluminum nitrate[34,35] and aluminum secondary butoxide[36] are used. Parida *et al.*(2009), synthesized γ-alumina using aluminum nitrate as precursor and found that the precipitation by NH_4HCO_3 resulted in spherical particles of4.7–5.7 nm size with 190 m^2/g surface area and nearly 0.467 cm^3/g pore volume.[37] Yoo *et al.*(2009) synthesized a precursor, $AlO_xCl_y(OH)_z$ by hydrolyzing vapors of $AlCl_3$ at 200^0C and the obtained particles are found to have size from 30 to 200 nm.[38] Then the particles are converted to α-alumina by calcinating at 1200ºC for six hours**.** Mirjalili *et al.*(2010) synthesized α-alumina particles of size 20-30 nm with aluminum isopropoxide and 0.5 M aluminum nitrate as precursors and 1/3-benzenedisoulfonic acid disodium salt (SDBS) and sodium bis-2-ethylhexyl sulfosuccinate as capping and stabilizing agents.[39] Using aluminum isoporoxide, $Al(OH)_3$ and AlO(OH)) as precursors, Sung Lee *et al.*(2012) studied the synthesis of α-Al_2O_3 at various solution pHs.[40] It is found that with isoporoxide as precursor, α-Al_2O_3 can be prepared by calcinating (1200ºC) the precipitates obtained at all pH values and further, noted that ethylenediamine, a complexing agent, facilitates the formation of α-Al_2O_3 even at the lower temp.(1000ºC). In the case of other precursors, α-Al_2O_3 nanoparticles are not obtained with the hydroxy-precipitates obtained at high pH values even at very high thermal activation temperatures. Kamil *et al.*(2016) synthesized nano Al_2O_3 particles using an ethanolic solution of $AlCl_4$ as a precursor and 28% dil. ammonia as the precipitating agent and the gel resulted was digested for 30 hours, filtered, dried and annealed at 1000ºC.[41]

These methods based on physical and /or chemical processes, have one or other disadvantage and moreover, they are tedious, costly, involve toxic chemicals and hazardous to the environment.[42] Hence, researchers are investigating green methods of synthesis to meet the industrial demand of the Al_2O_3 nanoparticles.

Applications

1. Removal of Metal Ion

Investigations are being made to explore the sorption capacities of the nanoparticles of aluminum oxide (in different forms) towards various metal ions in polluted waters. Shu-Huei H, and Jao-Jia H 2007, synthesized Carbon nanotubes (CNTs) on micro-sized Al_2O_3 by dissociating methane at 700ºC using Fe-Ni nanoparticles as catalysts and thus grown CNTs on Al_2O_3 were used as an adsorbent to study the removal of Pb^{2+}, Cu^{2+}, and Cd^{2+} and found that the adsorption followed the order: $Cd^{2+} < Cu^{2+} < Pb^{2-}$ with the measured uptakes of 8.89 mg/g , 26.59mg/g and 67.11 mg/g of CNT respectively.[43] Afkhami *et al.*(2010) studied the simultaneous removal of various heavy metal ions from waters using nano alumina modified with *2,4-dinitrophenylhydrazine* and found that the said adsorbent possess high adsorption capacity for the mixtures of Cd(II), Cr(III) and Pb(II).[44]

Gupta *et al.*(2011) synthesized carbon nanotubes coated with alumina and their sorption nature towards Pb(II) was probed with respect to various parameters adopting batch as well as continuous flow methods.[45] The adsorbent is effective and further, the increase in thickness of filter-bed or decrease in flow rate or both have considerably enhanced the extraction of Pb(II) from waters. Baybas¸ D and Ulusoy U 2011, studied the adsorption of Th^{4+} on Aluminosilicate-polyacrylamide composites and found to be effective and further, the columns are regenerated with dil. HNO_3.[46] Mahapatra *et al.*(2013) prepared iron oxide–alumina mixed nanocomposite fiber using electrospinning method and its sorption nature was studied towards Cu^{2+} , Pb^{2+}, Ni^{2+} and Hg^{2+} and the % removal was found to be in order: $Hg^{2+} > Ni^{2+} > Pb^{2+} > Cu^{2+}$ with adsorption capacities 63.69 mg/g, 32.36 mg/g, 23.75 mg/g and 4.98 mg/g respectively.[47]

Shokati Poursani *et al.*(2015) prepared nano-γAl_2O_3 by precipitating hydrated Aluminum hydroxide by mixing 1,2-epoxybutane with an alcoholic solution of $AlCl_3.6H_2O$ and then diluting with water and subsequently, heating the precipitate to high elevated temperatures and then grinded[20]. The prepared nano-γ-Al_2O_3 was investigated for its sorption nature towards the cations: Cr^{3+}, Cd^{2+}, Ni^{2+} and Pb^{2+} and found that the sorption followed the order: Cr^{3+} > Cd^{2+}>, Ni^{2+}> Pb^{2+} with the sorption capacities respectively 13.3 mg/g, 6 mg/g, 1.1 mg/g and 0.33 mg/g (at temp 25°C).

Nanoparticles of alumina prepared by combustion synthesis method were investigated for their sorption nature towards Zn^{2+} and dye, Color Black G, by changing various extraction conditions.[48] The optimization of conditions for the maximum removal of $Zn^{2+}$and the dye was done using Microsoft solver[48]. Hafez Golestanifar et al, 2015 using nanoparticles of γ-Al_2O_3 of size 20 nm prepared from precipitation method, investigated the removal of Chromium (VI) from waters.[49]

2. Defluoridation and Nitrate Removal

Sushree Swarupa Tripathy *et al.*(2006) successfully removed fluoride to an extent of 99.0% from waters using activated Al_2O_3 loaded with alum at pH:6.5, agitation time: 3 h and sorbent conc. 8 g/l.[50] By using nano-AlOOH as adsorbent, Wang *et al.*(2009)investigated the removal of fluoride from waters using batch methods and found that at pH: 7, the adsorption capacity was 3.259 mg F^- g^{-1}.[51] Fentahun Adeno *et al.*(2014) studied the adsorption nature of nano-sized particles of Aluminum oxide-hydroxide towards the fluoride ions in waters by changing various physicochemical parameters and found the sorption ability as 62.5 mg of F^- g^{-1}.[21] The adsorbent was prepared by precipitating AlO(OH) with the addition of NH_4HCO_3 solution to the $Al(NO_3)_3$ solution and then filtering, washing (with acetone), drying at room temperature and grinding.

Bhatnagara *et al.*(2010) studied the removal of Nitrate from waters using nanoparticles of alumina and the sorption capacity of the adsorbent was found to be 4.0 mg/g at optimum pH: 4.4 and at 25 ± 2 °C.[52] Kumar *et al.*(2011) used nano-AlOOH as adsorbent for defluoridation studies and found to be effective.[53]

3. Biological Remediation

The nano-Aluminium oxide particles were investigated for their antibacterial and antimicrobial activities besides their various other uses in various aspects of biological sciences such as biosensors, drug delivery, and bio-filtration membranes.[54-60] Amitava Mukherjee *et al.*(2011) reviewed the antimicrobial activities of alumina nanoparticles and their applications in clinical medical research.[58]

4. Degradation of Dyes

Abiyu Kerebo *et al.*(2016) used nano Aluminium hydroxide for the extraction of methyl violet from wastewaters and found to be successful.[61] Deepak Pathania *et al.*(2016) studied the degradation of the dye malachite green using nano Al_2O_3 particles synthesized by adopting electrochemical method.[62]

5. Inferences

The studies so far available in the literature are limited to some cations and anions and few dyes besides biological remediation. Efforts are to be made in controlling/removing toxic ions especially heavy metal ions, phosphate, nitrate/nitrite/ammonia and chromates by evoking the physical, ion exchange, complexation and molecular exclusion (through zeolite formations) properties of the nanoparticles of the Al_2O_3.

Literature on Green Synthesis and Water Remediation Methods

On perusal of the literature, it is evident that the reports available using green methods of synthesis based on plant extracts and their applications to water remedial purposes are few and far between.

Gholamhossein Mohammadnezhad *et al.*(2016) developed a Sol-gel method without the addition of toxic capping and stabilizing agents.[63] The method involves the hydrolysis of aluminum 2-propoxide or aluminum 2-methoxyethoxide, and subsequent separation and calcination. The prepared nanoparticles have high surface area and pores. However, the uses of thus prepared nanoparticles for the removal of various toxic organic and inorganic ions present in wastewaters are not investigated.

Ali Ashraf Derakhshan and Laleh Rajabi (2012) prepared nano Carboxylate–alumoxanes of size between 3 to 100 nm by treating boehmite $[Al(O)(OH)]_n$ with carboxylic acids and its surface was covered by the organic moiety, carboxylate groups.[64] Instead of using synthetic carboxylic acids, Ángela B. Sifontes et al, 2014 used colophony extracts from Pinus caribaea (which contain many eco-friendly organic substances having carboxylic acids) for the preparation of nanoparticles of carboxylate-alumoxane which on calcination at 650° C produced nano-γ-Al_2O_3 of size : 5 to 8 nm.[18]

Prasant Sutradhar *et al.*(2013) synthesized nanoparticles of alumina using aluminum nitrate and extracts of coffee, tea, and triphala under microwave irradiation.[65] The obtained nano particles are 'spherical' in shape with 50-200 nm size with the extracts of coffee and tea and 'oval' in shape with size: 200-400 nm with the extracts of triphala. Gholamhossein Mohammadnezhad *et al.*(2015) synthesized nanoparticles of alumina using the extracts of lemon grass and assessed its antimicrobial activity against P. aeruginosa, a multi-drug resistant strain.[63]

CONCLUSION

The review of the literature reveals that the investigations pertain to the synthesis of nanoparticles of Al_2O_3 adopting green methods based on plant extracts and their subsequent utility as potential adsorbents in controlling the polluting ions in wastewaters, are less trodden and the investigations are at 'nascent' stage. The identified areas of research are:

1. New green methods of syntheses of nanoparticles of Aluminum oxide/hydroxides based on the extracts of plants that serve as capping and stabilizing agents for the nanodispersions of the particles are to be investigated. For this, the flora available is to be probed for the identification of suitable extracts.
2. The nanoparticles obtained from the green synthesis are to be investigated for their adsorption nature towards polluting ions.
3. Aluminas prepared differ in their properties depending upon the method of preparation: γ-Al_2O_3 has defects in crystals; β- Al_2O_3 has ion-exchange properties. The hydroxides of Alumina viz., AlO(OH) (boehmite) and $Al(OH)_3$ possess remarkable adsorptive forces (physical, ion-exchange, and ion-association) which are widely explored in chromatographic separations. All these manifestations of oxide/hydroxides of alumina in their nano size that possesses these important binding tendencies are to be explored for developing simple, economical and eco-friendly water remediation methods.
4. Further, the treatment of plant extracts modifies the surface nature of the nano alumina and the use of such modified surfaces in the extraction of pollutants from water is an interesting aspect to probe. Moreover, surface morphological studies are also to be undertaken to understand the nature of the groups present**s** on the inter surface and their affinities towards the polluting ions to account for the sorption nature.
5. The surface of alumina has functional groups like –OH, =O. The complexing nature of these groups towards polluting metal ions is an interesting research area. When the plant extracts are used as capping and stabilizing agents, the compounds in the extracts may modify the functional groups on the surface and thereby enrich the complexing/coordinating nature towards to pollutants. This advantage may be explored for wastewater purifications.
6. Cage like structures may be developed by admixing alumina with some other metal oxides in lieu of zeolites. Further, by incorporating phosphates in the matrix of Al_2O_3 , gel-like structures with controlled pore sizes may be developed. Thus developed cage like structure may be used for investigating the removal of pollutants by virtue of size (molecular exclusion).
7. In closed columns, the percolation of water through the nano-sized particles of Al_2O_3, occurs only under pressure head. This is the main disadvantage of these nano methods when applied in continuous mode. Hence, investigations are to be undertaken in developing films or beads embedded with the nanoparticles of Al_2O_3 and then using them as an adsorbent for the extraction of polluting ions from waste or contaminated waters.
8. Investigations are to be undertaken for preparing alumina doped with metal ions especially rare earths with an aim to enhance the sorption nature towards pollutants.

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