

Removal of pollutants from wastewater using alumina based nanomaterials: A review

Ramakrishna Mahesh^{*,†}, Khushi Vora^{**}, Madhu Hanumanthaiah^{**}, Anuradha Shroff^{**}, Pavan Kulkarni^{**},
Sridharan Makuteswaran^{*}, Suresh Ramdas^{**}, Hemanth Lakshmipura Ramachandrai^{***},
and Anjanapura Venkatarmanaiiah Raghu^{****,*****,†}

*Department of Chemistry, RV College of Engineering, Bangalore, 560059, India

**Department of Chemical Engineering, RV College of Engineering, Bangalore, 560059, India

***Samco Inc, Research and Development, Kyoto, Japan

****Department of Chemistry, Faculty of Engineering & Technology, Jain Deemed-to-be University, Bangalore 562 112, India

*****Faculty of Allied Health Sciences, BLDE (Deemed-to-be University), Vijayapura, 586103, Karnataka, India

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Abstract—Increasing urbanization and industrialization has led to a dramatic increase in demand for clean potable water. Nanotechnology is used in environmental applications to eliminate pollutants, pathogens, and other effluents from water. Nanomaterials have gained importance in sustainable development. Alumina (Al_2O_3) and its composites are generally used as nanomaterials because of high surface area, porous nature, large number of active sites, formation of meta-stable phase and hexagonal structure, which makes it a potential candidate for water treatment. The nano alumina can be coated on membranes and the composites can be used for purification of water, specifically for the removal of heavy metal ions, dyes and other microbes. The prime focus of the review paper is the treatment of water using alumina composites; the same can be extended to other applications like dye removal and desalination with some modifications.

Keywords: Water Pollution, Metal Oxides, Nano Alumina, Water Purification, Adsorption, Membranes

INTRODUCTION

Water pollution is the contamination of water to such an extent that it cannot be further used for drinking, bathing, washing, cooking and other purposes. Water pollution can be induced by both humans and naturally [1]. Almost 40% of world's population does not have access to safe drinking water [2]. However, the extent of development of a country, both economically and industrially, plays a crucial role in overcoming this issue [3]. The sources of water pollution due to human intervention include sewage disposal, oil spills, heavy metals effluents, deforestation, pesticides, herbicides and fertilizers. There is excess discharge of organic and inorganic pollutants, for example, dyes, oils, chemicals, runoff and other effluents from industries, which causes water pollution and can cause cancer in human beings [2]. Pollutant consumption can pose a serious threat to living beings. The most common diseases among humans are cholera, typhoid, dysentery and tuberculosis. Oil spilling is one of the major water pollutants, which causes serious threat to aquatic life that affects the food chain process [1]. There is huge challenge of centuries for cleaning the waste water generated from domestic, industrial and municipal waste [4]. While traditional processes like solvent extraction, activated carbon adsorption, and ordinary chemical oxidation are successful, they are usually expensive

and time-consuming. The development of new nanomaterials with enhanced affinity, capacity, and selectivity for heavy metals and other pollutants is an important area of research [5].

Nanomaterials play an important role in eliminating and resolving problems related to purification of water and improving the quality of water. The availability of providers who can deliver substantial quantities of nanomaterials at economically reasonable costs will be essential in the application of nanotechnology for water purification [6]. Nanomaterials fall between the range 1-100 nm [7]. Nanomaterials serve as the potential candidate for remediation of water pollution due to physical, biological and chemical properties [8]. These applications are divided into three categories: water remediation, sensing and prevention of pollution [5]. Nanomaterials have fascinating properties, like greater surface area, active sites, high surface free energy and quantum confinement [7]. The different types of nanomaterials, like nano-adsorbents, nanomaterials that are bioactive, bio-enzymes, membranes embedded with nanoparticles are being developed for water treatment to enhance filtration [9]. Thus, recent advances in the field of nanoscience may deliver solutions to eliminate/minimize water pollution [10].

Nano alumina has prospective applications like water remediation, filtration, ceramics, fire retardation, and capacitors due to its high surface area, mechanical strength, thermal stability, inertness to most acids and alkalis, adsorption capacity and non-toxicity [11, 12]. Alumina is a good adsorbent because of monolayer adsorption and pseudo-second-order kinetics [13]. In general, thermodynamic phases of alumina are alpha, beta and gamma phases. Alpha

[†]To whom correspondence should be addressed.

E-mail: maheshr@rvce.edu.in, gsraghu2003@yahoo.co.in

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alumina is a white powdered nanoparticle. It has lower specific surface area; it is resistant to high temperature and is chemically inert. It is the most stable form, hence used as ceramic material. Beta alumina has laminar hexagonal structure. Gamma alumina is used as a catalyst and an adsorbent due to its porosity [14]. Nano alumina has found its path as an adsorbent in water purification industries. It is also used as matrix to impregnate other materials into it for synthesizing nanocomposites [15].

In 2000, Salem et al. conducted experiments to study the kinetics of removal of color of the cationic dye (methylene blue) *via* oxidative mineralization with hydrogen peroxide supported alumina catalyst. Cu^{2+} , Co^{2+} , Mn^{2+} and Ni^{2+} ions were employed as supported alumina catalysts [16].

Gisi et al. reported a simple method to adsorb heavy metals in industrial plants using activated carbon based on their extensive review [17]. Rathi and Kumar focussed on the treatment of contaminants using solid and liquid-based adsorbents. They proposed that more than 90% contaminants can be removed merely by adsorption process. While others can be removed by nano based and magnetic adsorbents [18]. Iqadami et al. proposed an adsorption mechanism for the interaction of heavy metal ions like lead (II) into nano composites by two ways: Interaction between heavy metal ion and nano composites is purely electrostatic. Such interaction usually takes place between electron-rich nitrogen atoms of functional group within the molecule and heavy metal ion. These interactions were further confirmed from FTIR, EDX and SEM analysis. The interaction between amide and carboxylic and other groups was confirmed from FTIR bands at $3,425$ and $1,723\text{ cm}^{-1}$, respectively. EDX analysis results revealed the presence of desired elements on the surface of heavy metal ions on nanocomposites. SEM images of nanocomposites give an idea of more surface area of adsorbents which is more responsible for removal of pollutants from wastewater [19,20]. The metal oxides nanoparticles for different applications are summarized in Fig. 1.

Jatto et al. carried out kinetic studies for the treatment of pollutants from brewery age industry using powdered based snail shell. They reported that snails are found to be potential due to large surface area and iron content responsible for coagulating property. They concluded that, among the proposed kinetic models, pseudo-second-order chemical seems to better in long run for treating heavy metals [19,21]. Baruah et al. have reported that titanium dioxide based nanocomposites were found to be more effective than indi-

vidual titanium dioxide nanoparticles in photo catalytic degradation of anthracene, which follows pseudo-first-order kinetics [22].

In 2010, Afkhami et al. demonstrated the capability and usefulness of newly modified alumina nanoparticles - immobilized- 2,4-dinitrophenylhydrazine adsorbent for removal of heavy metal ions in wastewater. They focused on removal of heavy metal ions like lead (II), chromium (III), cadmium (II), nickel (II), cobalt (II) and manganese (II). The adsorption behavior of analytes on DNPH-Alumina, as well as the experimental parameters for the removal process, were thoroughly examined. They concluded that the adsorbent used was a potential candidate for the removal of heavy metal ions [23].

In 2015, Masahiro et al. worked on photoinduced separation using alumina-based membrane for water filtration and desalination by sunlight. The water permeation was tested using azo-benzene modified anodized alumina membranes under visible and UV light. Since the dye molecules and a protein present in aqueous solutions were not involved in the photoinduced penetrated water, this membrane permeation was able to purify water solutions [24].

Raja et al. prepared ceramic MF membrane using drinking water treatment sludge, which is alumina- and silica-rich material. The prepared membrane was tested for suspension and textile effluents. The above membrane was successful in the removal of turbidity, reduction in COD and BOD. Thus, the research concluded that DWTS based membrane will be efficient in cleaning industrial waste water [25].

Based on the literature survey, it can be seen that the current study and research is focused on different metal oxides used for water purification, alumina advantages over other oxides, synthesis of alumina-based membranes, applications of membrane impregnated nano alumina in water treatment, etc. Although, nano alumina and other metal oxides are conveniently used for water treatment, researchers are searching for composite membranes for water filtration and purification. Several types of nanocomposite membranes were prepared to overcome the conventional nanomaterials. The prime review article enlightens the journey from conventional nanomaterials to recent advancement of nanomaterials used in water purification. The focus of the article is the synthesis of nano-alumina and composites of alumina, applications of the nano alumina and its composites in water remediation.

BACKGROUND OF METAL OXIDES FOR WATER TREATMENT

Metal oxides play an effective role in material science as a metal precursor. Metal oxides like TiO_2 , ZnO , CuO , and Al_2O_3 have shown

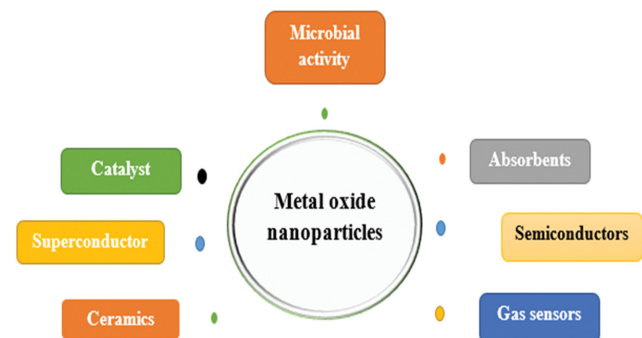


Fig. 1. Metal oxides nanoparticles for different applications [20].

Table 1. Surface area of metal oxide nano particles and nano composites

Name	Surface area (In m^2/g)	References
Iron oxide nanoparticles	7.6-22.4	[27]
Iron oxides-based nanocomposites	19.7-200.40	
Ti-O ₂ nanoparticles	49.5	[28]
Ti-O ₂ based nanocomposites	113	

unique characteristic properties at different nanoscale level for decontamination and disinfection purposes. Metal oxide nanoparticles have been used in medical, electronic and consumer products due to their stability and non-toxicity. The high surface area, tunable pore size, surface chemistry, low transluence in visible light, photo-degradation, photo-catalytic activity of nano adsorbents have made metal oxides more suitable for water treatment applications [26]. Iron based nano composites are more preferred in catalytic activity than iron nanoparticles because of large surface area [27]. Some of the surface areas of nano metal oxides and nanocomposites are given in Table 1.

1. Zinc Oxide (ZnO)

There are many technologies used to treat the wastewater for water management using various chemicals. ZnO nanoparticles have been used in water treatment for antimicrobial and disinfectant applications [29]. The mechanism involves the release of oxygen molecule from the ZnO surface, which causes damage to the fatal microorganism cell membrane and Zn^{+2} penetrate into the intracellular region, which causes the death of the microorganism. ZnO is stable, non-toxic in harsh conditions; therefore, it is used in water treatment applications [28]. The physical and chemical characteristics of ZnO have been studied and concluded that ZnO is a promising material due to non-toxicity, super oxidative nature, high surface permeable and high photocatalytic activity [30]. It occurs in two structures: wurtzite and zinc blende. Zinc oxide possesses the properties which make it an antimicrobial agent [29].

Huang et al. synthesized zinc oxide-activated carbon composite with good microbial properties. It proved to be efficient in reduction of *E. coli*-bacillus. After mixing with 500 L of water, the zinc oxide-activated carbon exhibited significant antibacterial activity and long service life by reducing *E. coli* by 91.18% [31].

2. Silver Oxide (Ag₂O)

Silver oxide is available in transparent forms with high purity, high surface area and particle size ranging between 30 and 70 nm. It can be synthesized using different chemical and physical techniques. Silver oxide nanoparticles are used commercially for antiviral, antimicrobial and antifungal applications. They are also used for wastewater treatment application to adsorb the organic pollutants and degrade the microorganisms present in water more effectively. Due to excellent performance of silver oxide, it can be used in water filtration processes [32].

Jiang et al. synthesized nano silver oxide aggregation by ion exchange method [33]. Under both artificial and natural light, the synthesis demonstrated excellent photocatalytic performance. These results showed that methyl orange decomposes fully in 4 min when exposed to near-infrared light and in 2 min when exposed to sunshine, artificial ultraviolet light, or artificial visible light.

3. Titanium Dioxide (TiO₂)

The organic pollutants present in wastewater can be degraded using metal oxides. Among that TiO₂ is most intensively used photocatalytic materials for the removal of contaminants in water. Titania has oxidizing power which makes it a good photocatalyst to degrade the waste present in wastewater such as pesticides [34]. The geometric structure of TiO₂ shows that it is a non-toxic, chemically stable material which can act as adsorbent due to high surface area and its versatility. TiO₂ semiconductor is an elegant metal precursor for different commercial purposes. The photocatalytic

activity of TiO₂ plays a vital role in degradation of organic pollutants in many wastewater filtration industries. Nanocrystal anatase is the most widely used form of TiO₂ for selective degradation. The hydroxylation reaction upon UV light illumination on TiO₂ semiconductor facilitates the removal of contaminants in water [35]. The superoxide radicals in doped TiO₂ favors degradation of pollutants and deactivation of microorganisms in wastewater. The modified Fe-TiO₂ doped gives better photocatalytic degradation efficiency of antipyrine present in wastewater [36]. The hydroxylation reaction takes place when UV light illuminates an aqueous solution of TiO₂ semiconductor along with electron-hole pairs formation. Holes and electrons generated react with water to form OH, H⁺ ions and [OOH, O²⁻] ions, respectively. Thus, all this reaction facilitates in formation of radicals that attack pollutants present in wastewater [37].

Based on the SEM-EDX analysis, Baruah and co-workers reported that nanocomposites have more area than do individual TiO₂ nanoparticles [22].

TiO₂ semiconductor has large scale application in wastewater treatment due to formation of active free radicals and partial water oxidation, which degrades the organic compounds and microorganisms in water [38]. Hasaan et al. conducted an experiment to test the *E. coli* bacteria degradation using photocatalytic titania nanoparticles with integrated nanofiltration system. Finally, they concluded that it depends on the reactor in which bacteria are incorporated and the concentration of the particles externally affects the bacteria deactivation [39].

4. Tin Oxide (SnO₂)

SnO₂ is an inorganic compound having strong oxidizing and photo-catalytic properties. It is an n-type semiconductor having a band gap of 3.56 eV which is more suitable as photocatalyst. SnO₂ is used in many industrial applications because of low electrical resistance, electrical conductivity, non-toxicity, chemical stability, porousness with high surface area. SnO₂ is used for oxidative degradation of contamination in wastewater. Metal oxide can be activated using the UV light, which cannot be activated by visible light to form the electron pairs from large band gap. The concentration of catalyst used for degradation of pollutants should be optimum, and if there is slight increase in concentration, it can lead to decrease in rate of degradation as photo-catalytic activity decreases. The pH and temperature also affect the photo-degradation. It is reported that metal oxide is active between 20 to 80 °C range of temperature [40]. Excess accumulation of SnO₂ (>200 ppm) as an adsorbent in water may adversely effects on human beings causing vomiting and diarrhea [41].

5. Copper Oxide (CuO)

CuO nanoparticles are very prominently used in wastewater purification for their antimicrobial and antimicrobial activity [42]. The CuO concentration in the purification process should be below 50 mg/L. A concentration of 3 mg/L is sufficient and increase in concentration may lead to decrease in removal of total organic carbon and flocculation capacity. A concentration of 1 mg/L exposure is enough for the reduction of chemical oxygen demand and ammonia in wastewater [43]. Naz et al. reported that small nanoparticles (size<50 nm) show more toxicity than bigger nanoparticles and experience cellular internalization [44].

6. Challenges and Gaps

Metal oxides have many applications commercially, but uncontrollable usage of these can lead to health hazards and environmental issues indirectly. For metal oxide, it is difficult to conclude which is the most efficient method of synthesis chemically regarding time of operation, concentration and chemical stability [26]. Large scale production of metal oxide can have high capital cost, energy input and manpower consumption and can also cause dispersion of nanoparticles in wastewater. There is need of a proper method to remove these materials after usage. Researchers have concluded that titanium is toxic when inhaled but size above 100 nm is not toxic above optimum concentrations. Recent report suggests that ZnO can get accumulated in the organs if concentration used is high in wastewater. AgO also gets accumulated in the organs and makes neurodegeneration, which may lead to brain damage. Research on alumina nanocomposite synthesis and reduction of toxicity of this nanoparticle is an economically viable method [45].

7. Alumina for Water Purification

Alumina is the most commonly found oxide of aluminium and is amphoteric in nature. Corundum (Fig. 2) is the natural form of alumina and can be prepared from Bauxite [13]. The crystalline forms of Alumina are: χ -, η -, δ -, κ -, θ -, γ -, ρ - and α -Alumina [46]. From the research papers, several observations were made that nano alumina plays a very important role in water purification by removal of the pollutants. Alumina is a good adsorbent because of monolayer adsorption and pseudo-second-order kinetics. Alumina is synthesized by different methods, such as *sol-gel*, solution-combustion, precipitation, microwave synthesis and hydrothermal method. Banerjee et al. [13] studied and reported that γ -alumina showed absorptive removal of orange G-dye and methylene blue from aqueous solutions. Nanostructured aluminium oxide has a wide range of application in catalysis field and absorption because of chemical and physical properties such as thermal stability, stiffness, hardness, oxidizing nature, electric insulation and non-toxicity [12]. Adsorption is the prominent method to remove metallic pollutants from effluent water, and from the studies its reported that nickel, cationic dye and sulfide which are hazardous to health and are removed using nanoparticles, and the removal of pollutants also varies with temperature, pH, adsorbent dose, contact time, initial concentrations and particle size [47]. Alumina nanoparticles/materials are used as membrane support or layer of membrane in water filtration due to high chemical, thermal and mechanical stability and operated to remove the lighter compounds in solution. Polycarbonate membrane possesses favorable antifouling property

in water treatment in combination with polyurethane and alumina [48].

Various metal oxide nanoparticles are used in water purification because of high surface and porous nature to capture the pollutants and also by improving the filter capacity and mechanical strength of membranes including silver, SnO₂, etc [49]. There are several alumina nanocomposites which help and enhance the elimination of pollutants in effluents. Alumina/SiO₂, silver/mesoporous alumina nanoparticles, Copper/alumina, alumina and iron (III) oxide as nanoparticles with Nylon 6,6 and Poly(sodium-4-styrenesulphonate) as polymer matrix are some nano alumina composites [47].

8. Market Survey

According to a global survey, the aluminum oxide market was found to be worth 5.3 billion US\$ in 2022 and is further expected to achieve a value of US \$ 7.72 by 2028, resulting in a CAGR of 5.4% between the years 2022-2027. Nano-aluminium oxide that is unique in properties is available in various forms of powders or dispersions and is identified by different names such as gibbsite, bayerite and nordstrandite. They are found to have novel physiochemical characteristics that range from anti-bacterial to anti-fungal and also anti-corrosive, catalytic, and UV filtering properties which are mostly used in paints, cosmetics, domestic products, food industrial materials, therapeutic dressings, fabrics, and electronic devices. Increased investment in Research and Development, followed by the growth in various Al₂O₃ nanoparticles application sectors are attributed to its physical and chemical properties. Minimal quantities of nano aluminium oxides are found to help in improving the performance of the final products. Toxicity issues that are allied with usage of Al₂O₃ nanoparticles at higher concentration could greatly impede the market growth. At present, the water filtration and cosmetics industries form the major application segments of the nano Al₂O₃ market [50].

Based on processing technique, the global aluminium oxide nanoparticles market has been categorized into methods such as spray pyrolysis, precipitation, hydrothermal, micro-emulsion and *sol-gel* method. Increase in end-user industries such as automotive, pharmaceutical, and building and construction coupled with improved usage of aluminium oxide nanoparticles as an additive or catalyst are the reasons resulting in the rise in demand for these nanoparticles [51].

Further, in the global market, the demand for nano aluminium oxide has observed a significant growth due to unique properties that increases its level of applications in diverse fields. The various target industries of aluminium oxide nanoparticles are shown in Fig. 3.

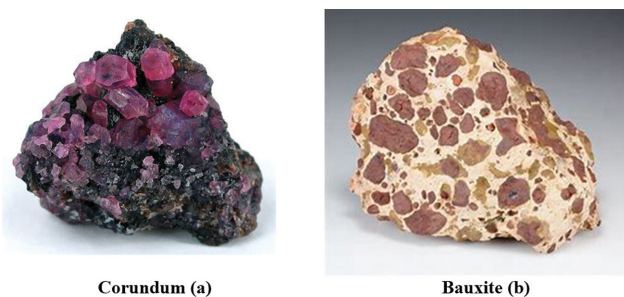


Fig. 2. Different minerals of Aluminium (a) Corundum, (b) Bauxite.

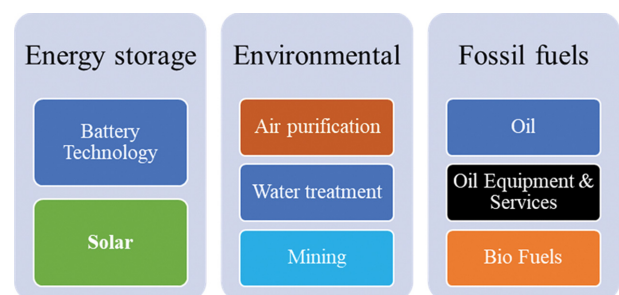


Fig. 3. Applications of Alumina in different Industries [12].

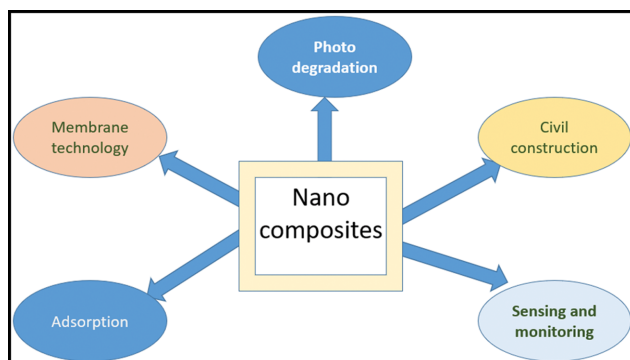


Fig. 4. Nanocomposites and their applications [55].

9. Background of Nanocomposites

Composites are a combination of one or more constituents having different properties integrated in a single material. Composites consist of reinforcement and matrix. There are several advantages of composites, which include specific strength, improved efficiency and flexibility [52]. Recently, a huge number of studies have been performed regarding metal oxides composites for water purification [53]. Various nanoparticles that have been used in the development of novel nanocomposite membranes for water treatment applications are silver oxide, titanium dioxide, zinc oxide, copper oxide, carbon nanotubes (CNTs), graphene oxide (GO), alumina (Al_2O_3), silicon dioxide, iron oxide, zirconium oxide, clay nanoparticles, and zeolites. Furthermore, several new types of nanocomposite membranes for a variety of filtration applications have recently been introduced [54]. The different applications of nanocomposites are given Fig. 4.

In the current scenario, it has become necessary to come up with new and emerging materials and technologies that are embedded with various properties like good mechanical strength, durability, thermal stability and corrosion resistance [56]. Metal oxides have high band gaps. In order to decrease the band gaps, composites are employed. Composites are classified into three main groups based on the material of matrix: Ceramic composites, metal composites and polymer composites [57]. The need of improvisation of the properties of composites led to the research in the field of nanocomposites. Among the categorized composites, polymer matrix and ceramic matrix composites have shown significant applications in medicine, engineering and water remediation. Nanocomposites have a large surface area, which makes them more efficient as compared to metal oxides [58]. Owing to the advantages like low cost, low density, better stability, and hardness, alumina is significantly used metal oxide in ceramic matrix composites [57].

10. Alumina Composites and Nanocomposites

10-1. Zirconia/Ceramic Nanocomposites

Ceramic membranes have garnered considerable attention for water purification due to lower cost of operation and their promising performance in removing various pollutants. Zirconia can be used as adsorbent for the removal of heavy metals and hazardous contaminants. T-zirconia powder can be prepared using different synthesis methods like *sol-gel*, hydrothermal method, spray pyrolysis, thermal decomposition, microwave assisted synthesis and coprecipitation. Friktha et al. immobilized zirconia on ceramic mem-

branes and tested the removal of methylene blue dye from water and found it successful [59].

10-2. Nano Copper Oxide on Alumina

Recent studies on ceramic filters indicate that they are reliable for removing microorganisms like bacteria and protozoa but inefficient in removal of viruses due to smaller size. Removal of virus is necessary for the availability of clean drinking water. Viruses can be removed by introducing nano-filters under various forces like van der Waals, electrostatic and ionic interactions. Azam et al. discussed copper oxide efficiency in water purification by enhanced electrostatic adsorption and synthesized copper oxide-based alumina nanocomposites for virus removal using spray granulation technique [60]. Spray dried copper oxide-alumina and their granules are efficient in removal of MS2 bacteriophages. Hence, the nanocomposite can be the viable option for water filtration for real applications [61].

10-3. Alumina Modified Polysulfone Membrane

Industrial effluent which contains oil has become a significant reason for water pollution. There are many conventional methods for the separation of oil and water, for example, coagulation, ultrasonication and other biological methods. Membrane technologies are gaining popularity as a result of its consistent pollution removal without the generation of toxic by-products, particularly in water and also in sewage purification process [62]. Graphene oxide can be blended with membranes to improve the performance due to several properties like presence of several functional groups, anti-fouling properties and high permeability. Due to high thermal stability and chemical resistance, polysulfone modified nanocomposites membrane have proved to be efficient in water purification. Nguyen et al. prepared polysulfone/graphene oxide-alumina nanocomposite membrane using wet inversion technique. The results concluded the above membrane has potential applications in treating oily waste water and also enhancing anti-fouling properties [63].

10-4. Alumina-CNT Nanocomposite

Metal oxides like alumina, titania and zeolite are promising membrane materials for water purification due to hydrophilicity. Incorporation of nanomaterials into the membrane improves the permeability, porosity and surface area. Carbon nanotube has proved to be the efficient nanomaterial additive. Researchers have shown that multiwalled CNT are better compared to single walled CNT. Hussein et al. synthesized porous alumina-CNT nanocomposites using spark plasma sintering [64].

10-5. Carbon Based Ceramic Filters Coated with GO (Graphene Oxide)

Jankovsky et al. synthesized carbon-based foam filters by the Schwartzwald process using a two-step approach. This was coated with graphene oxide using dip coating technique [65]. Here, the graphene oxide was prepared by Tour method. The synthesized filters were used in purification of water by removing harmful metals like lead, zinc and cadmium ions. The sorption efficiency was found to be very high, hence making it a potential candidate for eradication of water pollution.

SYNTHESIS OF ALUMINA AND NANOCOMPOSITES

In recent years, numerous methods have been used for synthe-

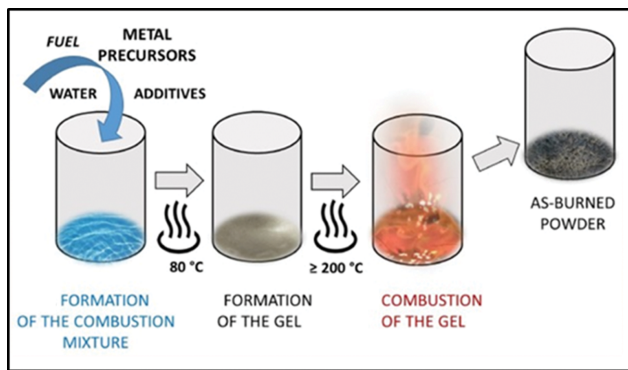


Fig. 5. Solution combustion synthesis metal oxide nano particles [69].

sis of nanoparticles, including the *sol-gel* method [59], vapor phase compression method, solvothermal method [64], hydrothermal method, mechanical alloying method or collision with high-energy pellets, plasma method, and electrochemical methods [67]. The next section discusses some of the methods to synthesize alumina nanoparticles and nanocomposites.

1. Solution Combustion Method

Solution combustion synthesis (SCS) is one of the commonly used methods for the synthesis of ceramics and composites for water purification, catalysis, electrocatalysis, etc. (Fig. 5) The advantages of SCS are easy availability of raw materials, less reaction time, less time required to achieve meta-stable state, cost friendliness and quality of product [68]. SCS is an exothermic redox reaction which involves a reaction between oxidizer and fuel in the presence of metal cations. Oxidizers preferred are generally metal nitrates, sulfates, etc. and fuels used are urea, glycine, citric acid and sucrose [69]. Chemical method to synthesize metal oxides is easy using fuels as oxidizers. Thermal process is a simple combustion and high temperature self-propagating method. Initially, calculated composition of metal nitrate and organic fuel are stoichiometrically dissolved in water to form aqueous solution followed by calcination at different temperatures. Slow cooling rate is required to obtain product at equilibrium. The structure and morphology of nanocomposites synthesized are analyzed by characterization techniques-XRD and SEM. Al_2O_3 , ZnO, Co_3O_4 are some of the products that can be synthesized using solution combustion method [70].

1-1. Fuel Amount

Along with fuel type, fuel amount also plays an important role in determining final properties of the product. Two important parameters are fuel-to-oxidizer ratio and fuel-to-cations ratio [69]. Shea et al. discussed the thermo-chemical concepts of propellant chemistry, which are based on elemental stoichiometry coefficient. The

equation for fuel-to-oxidizer ratio is given below as [71]. The significance of fuel to oxidizer ratio is given in Table 2.

$$\phi = \frac{\sum \text{Coefficient of oxidizing in specific formula} * \text{Valency}}{(-1) * \sum \text{Coefficient of reducing elements in specific formula} * \text{Valency}}$$

With respect to amount of fuel with respect to metal cations, a smaller amount of fuel is preferable as compared to metal cations, i.e., F/M ratio should be high in order to entitle complexation of cations by fuels [69].

1-2. Reaction Temperature

The temperature of reaction is also an important parameter for the synthesis of nanomaterials. Higher temperature during synthesis may result in reduction in size of pores and also surface area. Nitrates are most preferred hydrated metal salts as oxidizer, not only because of high oxidizing power of nitrate group but also good solubility in water and lower decomposition temperature. Among all the fuels, urea and glycine are most preferable due to lower cost and excellent coordination ability with nitrate groups. Urea has two amino groups, hence is more reactive as compared to the other fuels, whereas glycine has one -COOH group and one-NH₂ group, hence is reactive as compared to citric acid [72].

2. Hydrothermal Method

Siraj et al. synthesized boehmite by hydrothermal method at low temperature of 200-300 °C. They evaluated morphology and size by altering the pH of the solution from 2 to 10 pH in feed stock. In acidic condition, it was reported that particle structure was like a prolonged plate and in alkaline condition structure was like a rhombic plate [73]. Natarajan et al. reported that nucleation of the nanoparticles formed is directly proportional to the temperature. In this method, metal hydroxides are neutralized followed by hydrolyses and oxidation, which are two primary steps in this synthesis method [74]. Hakuta et al. synthesized alumina by dissolving aluminium nitrate into distilled water and with variation of pH from 1 to 12 by addition of NaOH or HNO₃. When heated at 400 °C and 30 MPa, particle size was found to be around 80 nm [73].

3. Sol-gel Method

Sol-gel method is a wet chemical method for the synthesis of metal oxide nanoparticles [58]. The phase change of a sol made from metallic alkoxides or organo-metallic precursors provides the basis for the *sol-gel* process. Sol, a solution with suspended particles, is polymerized at low temperatures to form a wet gel. The solvent is then removed from the gel by drying it, and then an appropriate heat treatment is applied. Rogojan et al. synthesized alumina using precursors AlCl_3 and aluminium triisopropylate from *sol-gel* method. The ethanoic solution (0.1 M) was prepared followed by addition of 28% NH₃ solution and was mildly shaken for 10 hours at 90 °C. The gel formed was left to mature at the temperature of 100 °C for 24 hours and finally was calcinated in a furnace at 1,000 °C and 1,200 °C [58]. The schematic representation of *Sol-gel* method is given in Fig. 6.

4. Sonochemical Method

Praveen et al. synthesized alumina using *sol-gel* method assisted sonochemical method. Initially, aluminum nitrate solution of 0.1 M was prepared in milli-Q-water maintained at 8 pH. Then the solution was ultra sonified at room temperature for 1 hour using Branson digital sonifier S-250D. After, sonification solution was aged,

Table 2. Significance of fuel to oxidizer ratio [59]

ϕ	Significance
=1	Balanced species
>1	Fuel rich mixture
<1	Fuel lean mixture

dried, washed and calcinated at 500 °C for 4 hours and finally aluminum oxide powder was formed [75]. Other metal nanocomposites synthesized by sonochemical methods are TiO_2 , ZnO , V_2O_5 , MoO_3 . In this method the initial solution is subjected to ultrasonic vibration causing compression and relaxation, which breaks chemical bond of the compound and finally crystals are formed at high

rate of cooling. This results in an increase in photocatalytic activity, surface area, porosity, faster reaction rate and uniform size distribution of metal oxide nanoparticles synthesized as observed by various research groups [51].

5. Vapor Phase Hydrolysis

Yoo et al. synthesized alumina using vapor phase hydrolysis. First,

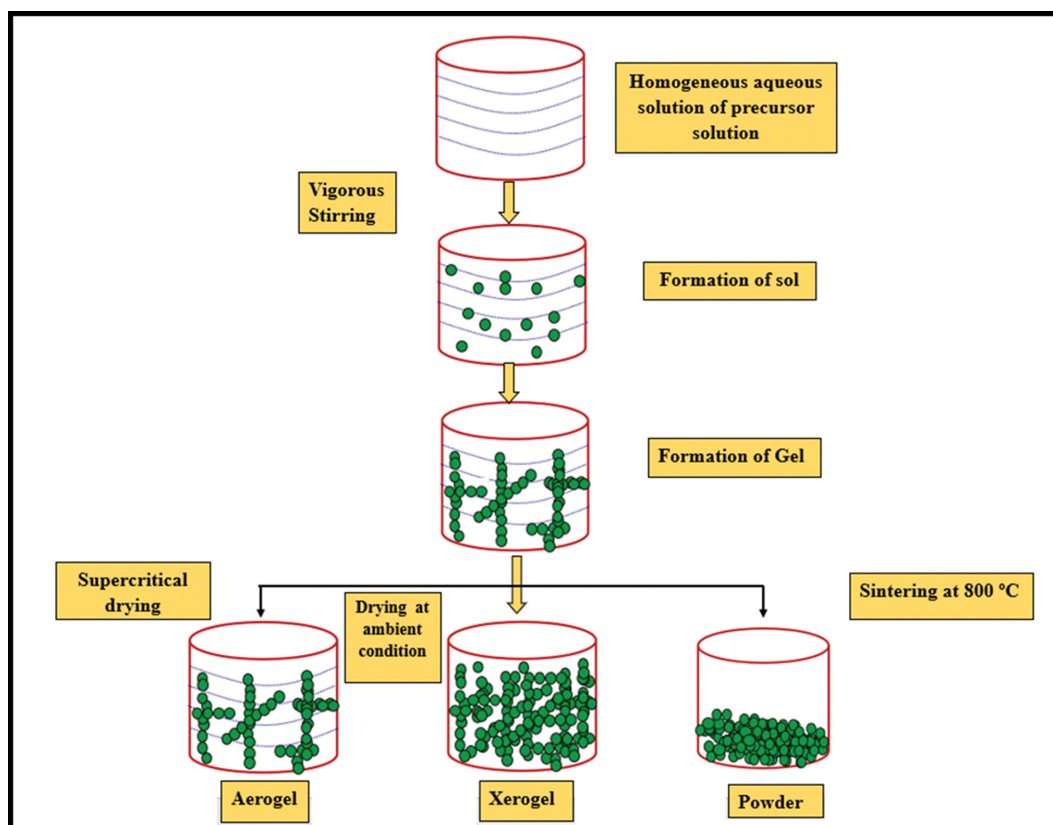


Fig. 6. Schematic representation of metal oxide nano particles synthesis by *sol-gel* [63].

Table 3. Advantages and limitations of common synthesis methods

Methods	Advantages	Limitations
Hydrothermal method [73]	Effective method increases photo catalytic degradation of the pollutants. Generate nanomaterials which are not stable at elevated temperatures.	Need expensive autoclaves Blockage of reactor
<i>Sol-gel</i> method [58]	Possibility of Low temperature synthesis High purity products are obtained Production efficiency is very high Complex shapes like wurtzite are possible Uniformity is maintained in prepared compounds	Catalyst is required to increase rate of reaction Solution can be toxic
Sonochemical method [76]	Cost effective method Time of operation is very less	Low yield Inefficient energy
Solution Combustion method [68]	Cost effective Easy availability of starting materials Energy saving Time of operation is less Meta-stable state is achieved during synthesis	Compound may decompose at high temperature.
Gas-Phase Condensation [77]	Versatile in nature Scalability is possible	The agglomeration of the particles needs to be prevented.

AlCl_3 was hydrolyzed with water with molar ratio of 4.5 and the resulting particle was calcinated at $1,200^\circ\text{C}$. The particle size 40-200 nm particles were obtained and there was weight loss of 40% due to volatility and densification. The morphology of this particle can be controlled using hydrolysis and calcification [76]. The advantages and limitations of common synthesis methods are given in Table 3.

6. Treatment of Water/Wastewater Using Alumina

Nanomaterials have been an area of extensive research and development due to their characteristics such as enhanced adsorption and catalysis along with increased reactivity, which results because of its nanoscale size. Nanomaterials have also shown effective results in removal of different pollutants from wastewater and have been accepted as a suitable material for different water purification techniques. Different types of nanomaterials like nanoparticles of metals with zero valence (like Ag, Fe, etc), metal oxide nanoparticles, carbon nanotubes, nanocomposites, can be used for different water purification methods [78].

Nanofiltration is nowadays seen as the most efficient as well as an eco-friendly method for water treatments, and therefore many further developments and research are being done for this. Two most important characteristics are that they have very large surface area compared to other macro materials and their chemical affinity can be increased towards their target compounds by enhancement using different reactor groups. Nanomaterials are suitable for removal of a wide variety of pollutants like organic and inorganic pollutants, biological and chemical contaminants, microorganisms, cations, and heavy metals [79].

Metal oxide nanoparticles due to their exceptional characteristics like high capacity for metal selectivity and high removal capacity, proper pore size distribution, and good mechanical rigidity, are considered as potential candidates for research in wastewater treatment. Different metal oxides like nanosized manganese oxide, zinc oxide, aluminum oxide, titanium oxide, and ceramic oxides are being used [2].

There are a number of techniques for water filtration like adsorption, chemical and biological treatments, membrane separation, ion

exchange methods (Fig. 7), and each method is used for different types of water pollutants [2].

7. Adsorption

Adsorption is one of the most preferred methods for water purification, where nanoparticles are used to adsorb pollutants from wastewater and the nanoparticles are further removed from the treated water. It has several advantages like being useful for removing a number of pollutants, low cost, is highly effective and is easy to operate. Several metal oxides like titanium, aluminium and Iron oxides are found to be highly efficient materials for this technique along with lower costs. Also, adsorbents made of nanomaterials are highly porous and have an effective active surface area, which results in increased interaction between the adsorbate and adsorbent. Such metal oxide nano-adsorbents are highly studied and have been effective in removal of heavy metals from wastewater. Also, use combinations of metal oxides [80].

Cervera et al. evaluated the application of activated alumina and chitosan as adsorbents for the removal of heavy metal ions. The Cr (III) and Cd (II) used as ion models for heavy metal removal from aqueous solutions by adsorption onto alumina and chitosan have shown that 10 g of solid and shaking for 30 min could be sufficient for a significant reduction of polluted wastes. Wet residues range from 500 g to around 11 g; therefore, stocking capacity is increased by a factor of 50, lowering the cost of garbage disposal in a similar manner. Results concluded that chitosan is more environmentally friendly than alumina. Other researchers tried to make composite of alumina/chitosan and concluded it to be a better option [81]. Gupta et al. worked on the removal of arsenic using aluminum oxide nanocomposites. It was noted that approximately 90% of arsenic could be eliminated from groundwater maintained at a pH of around 6.5 with the use of aluminum oxide nanoparticles [3].

8. Ion Exchange Method for Water Purification

Ion exchange is similar to reverse osmosis and can be used for water softening. There is a strong interaction that occurs between functional group of the charged pollutants and the ion exchange resins, that helps in successful elimination of contaminants from water. Ion exchange membranes that are fabricated with polymeric

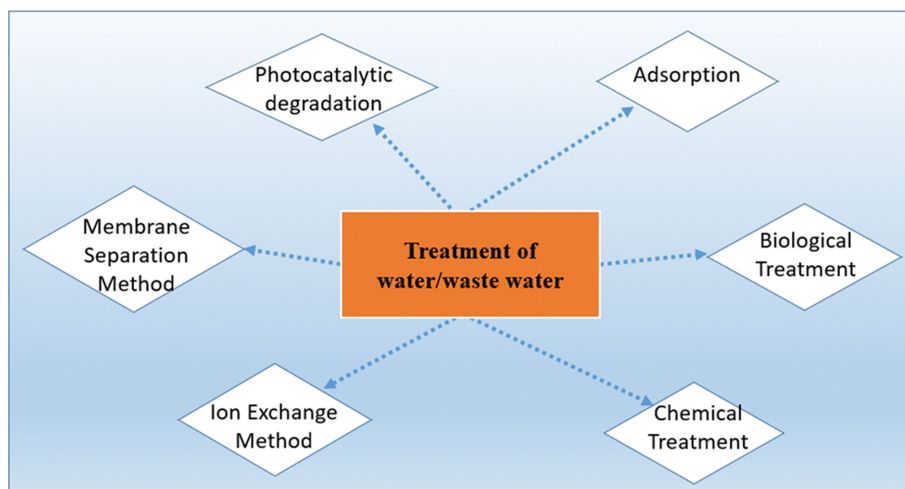


Fig. 7. Applications of nanocomposites in water purification and recycling.

materials have shown high chemical stability and efficiency; therefore, combining polymers with inorganic metal oxides results in a membrane with high stability, high ion exchange capability along with good selectivity for metal ion [2].

Aliaskari et al. demonstrated a study for the removal of arsenic ions from drinking water using activated alumina via ion exchange method. They evaluated the activated alumina system for the reduction of arsenic concentrations by monitoring the results weekly and biweekly. They also studied the residuals obtained during the treatment process [82].

9. Membrane Separation

Membrane separation is one of the important techniques for water purification that, depending on the molecule or the pore size, the membrane acts as a barrier between the pollutants and purified water. It is a helpful method in industries as well for removal of pollutants generated by industries. The advantages are high efficiency, low operation cost, easy to use and set up, and the efficiency can be enhanced more by using nanoparticles in the membranes [80]. Nanoparticles of different types can be introduced into the functional membranes, that partially allows water molecules to pass through them, where 2D membranes have been found to be highly beneficial for water treatment compared to other commercial membranes made from polymers [83].

Sunil et al. used new Al-Ti₂O₆ nanoparticles and polysulfone composite membranes. Precipitation method was used to make Al-Ti₂O₆ and diffusion-induced phase separation was used to make membranes with various Al-Ti₂O₆ compositions. Heavy metal ions such as arsenic, cadmium and lead were effectively removed by the proposed membrane. This work entails the most cost-effective, budget-friendly and simple scientific way for obtaining heavy metal ions in aqueous solution [84].

10. Biological Treatment of Water

Nanomaterials, along with treatment of organic and inorganic pollutants, also are useful for purifying wastewater from the presence of microorganisms, i.e., antibacterial activity. For removal of microorganisms and dyes, the metal oxide nanoparticles being used depends on various factors like size, structure, aggregation [26]. In the case of biological treatment of water, many factors like temperature, content of water, and aeration also affect the water treatment process. Also, due to dependence on microbes in such methods, their activity must be maintained for efficiency in treatment of water. The bacterial cell wall, in particular, is critical for the preservation of the bacteria's original state [85]. Different gram-positive and gram-negative bacteria adsorption mechanisms are produced by cell membrane components. The bacterial cell wall, in particular, is critical for the preservation of the bacteria's original state. Different gram-positive and gram-negative bacteria adsorption methods are produced by cell membrane components. Unlike gram-negative bacteria, gram-positive fungus has more unfavorable stress on cell wall surface, which may store nanoparticles [26].

Yahyaei et al. synthesized silver/ordered mesoporous alumina via *sol-gel* and photogeneration combined method for the removal of pollutants, specifically dyes. It also shows great response towards gram-positive and gram-negative bacteria. Antibacterial activity of nanocomposite against *E. coli* and *S. aureus* was also tested and was concluded to be an excellent nanomaterial for both chemical

and biological treatment of water [86].

11. Photocatalytic Degradation of Pollutants in Wastewater

Photocatalysis is known to be one of the improved technologies for water treatment, which is more like a natural form of purification with the help of solar light, and a metal transition complex initiates the treatment [87]. Using titanium oxide and zinc oxide-based nanomaterials, phenols like di-nitro and amino phenol can be photodegraded intensively and widely in wastewater. Also, BMO nanocomposites can be used to remove hazardous aromatic phenols from polluted water [88]. It is considered to be an effective approach when compared to other conventional approaches that does not require much energy consumption and does not leave any toxic or less biodegradable products as residue. Numerous metal oxide-based photocatalysts has attracted substantial consideration in the degradation of highly toxic and non-biodegradable compounds. Metal oxide polymer nanocomposites are advantageous in water treatment owing to extraordinary characteristics like optical properties, non-toxicity, cost effectiveness, and high stability in case of both photo and chemical corrosion [2]. There are very few literatures for photocatalytic degradation of pollutants using alumina and composites. Researchers can study and evaluate the same.

CONCLUSION AND FUTURE PROSPECTS

Alumina based composites and their water pollution control applications played a major role in this review paper. Synthetic methods and applications pertaining to control water pollution were discussed. In particular, different metal oxides used as nanomaterials, alumina advantages over others, synthesis of alumina and composites. In the recent years, pure alumina-based research to reduce water pollution and also for their filtration applications is a wide range of study, and hence this proved to be one of the efficient solutions to reduce the global problem of availability of potable water. The efficiency was proven to be lower for alumina due to wide band gap and resulted in the emergence of composites of alumina. Among the various composites, the most popular is the membrane impregnated alumina/mixed matrix membrane due to higher surface area and porosity. Several synthetic methods which constituted a crucial role on alumina and composites were discussed. On comparison, we can conclude that *sol-gel* and solution combustion method as the best process for achieving highest purity. Importance of alumina as an adsorbent has been explored, thus becomes the future scope.

The outcome of this review emphasizes usage of low cost, eco-friendly bio-based adsorbents along with alumina based composites for removal of heavy metals from industrial waste water. Furthermore, it is suggested to scale up the usage of bio-based nano-adsorbents to industrial scale. Finally, detailed studies are required, including kinetic and thermodynamics approach for the separation of nano adsorbents from aqueous medium.

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