

Special Article - Wastewater Treatment

Influence of Nanoparticles for Wastewater Treatment- A Short Review

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In 21st century most important challenges in the global water situation, mainly resulting from worldwide population growth and climate change, require novel innovative water technologies in order to ensure supply of safe drinking water. The adaptation of highly advanced nanotechnology to traditional process engineering offers new opportunities in technological developments for advanced water and wastewater technology processes. The development of cost-effective and stable materials and methods for providing the fresh water in adequate amounts is the need of the water industry. Traditional water/wastewater treatment technologies remain ineffective for providing adequate safe water due to increasing demand of water coupled with stringent health guidelines and emerging contaminants. Nanotechnology-based multifunctional and highly efficient processes are providing affordable solutions to water/wastewater treatments that do not rely on large infrastructures or centralized systems. These advances range from the direct applications of synthesized nanoparticles as adsorbents for removing toxic contaminants or as catalysts for oxidative degradation of noxious contaminants in wastewater. Incorporation of nanoparticles with membrane separation technology, presents a composite photocatalytic membrane having immense potential to treat organic pollutants in effluents. Though a number of minerals, clays and agro wastes have been regularly used for the removal of metallic pollutants from water and industrial effluents, recently emphasis have been given on the application of nanoparticles and nanostructured materials as efficient and viable alternatives to conventional adsorbents. Because of their importance from an environmental perspective, special emphasis has been given to the removal of the metals Cr, Cd, Hg, Zn, As, and Cu. This review presents recent developments in field of nanotechnology for water and wastewater treatment emphasizing various nanomaterials, intrinsic properties, mechanisms, application spectrum; as well as advantages and limitations compared to existing processes, challenges and research needs for commercialization.

Keywords: Nanoparticles; Wastewater treatment; Nanotubes; Nano particles

Introduction

Water is the most vital substance in our life. Approximately, one-sixth of the world's population suffers from access to clean drinking water. The world is facing formidable challenges in meeting rising demands of clean water as the available supplies of freshwater are depleting due to (i) extended droughts, (ii) population growth, (iii) more stringent health based regulations and (iv) competing demands from a variety of users [1-3]. Therefore, an urgent stride is required to develop an innovative technology to provide clean and affordable water to meet human needs. Clean potable water is essential to maintain healthy life. In countries like India, 80% of the diseases are waterborne specially drinking water. Any water intended for drinking should contain fecal and total coli form counts of zero, in any 100 mL sample as recommended by the World Health Organization (WHO) [4]. Today a number of techniques are used for treatment of water i.e. chemical and physical processes such as treatment of chlorine and its derivatives, ultraviolet light [5], boiling, low frequency ultrasonic irradiation [6], distillation, reverse osmosis, water sediment filters

(fiber and ceramic), activated carbon treatment etc. Over the last few decades, nanotechnology is emerging as a rapidly growing sector of a knowledge-based economy due to unique physiochemical properties of nanomaterial. This technology gained a tremendous impetus due to its capability of reformulating the particle of metals into new nano-sized form. 'Nano' is derived from the Greek word for 'dwarf'. A nanometer is one billionth of meter (10^{-9}) and might be represented by the length of ten hydrogen atoms lined up in a row. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. Nanotechnology is a deliberate manipulation of matter at size scales of less than 100 nm (Figure 1) in at least one dimension meaning at the level of atoms and molecules as compared with other disciplines such as chemistry, engineering, and materials science. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions [7]. Their extremely small feature size is of the same scale as the critical size for physical phenomena for example, the radius of the tip of a crack in a material may be in the range 1-100

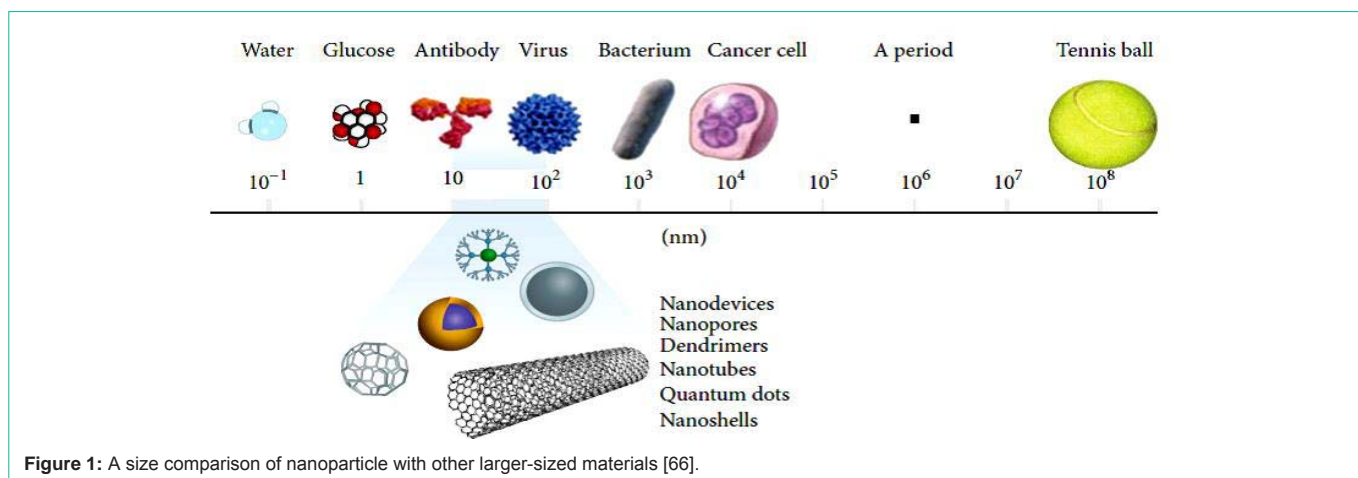


Figure 1: A size comparison of nanoparticle with other larger-sized materials [66].

nm. The way a crack grows in a larger-scale, bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable such as Choi et al. [8] describes the application of novel chemistry methods for the fabrication of robust nanostructured titanium oxide (TiO_2) photo catalysts. Such materials can be applied in the development of efficient photocatalytic systems with unique characteristics of high surface area ($147 \text{ m}^2/\text{g}$) and porosity (46%), narrow pore size distribution ranging from 2 to 8 nm, homogeneity without cracks and pinholes, active anatase crystal phase, and small crystallite size (9nm) for the treatment of water. These TiO_2 photo catalysts were highly efficient for treatment of dye industry effluent with complete mineralization of various dye components.

The several advances were made in the study of nano-scale structures. The term nano-technology was described by Taniguchi (1974) as “Nano-technology mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or one molecule” [9]. The tools and the methods for nanotechnology involve imaging, measuring, modeling, and manipulating matter at the nanoscale. Development of particles at the nanoscale level contributed extensively to the production, modification and shaping of structures that were used in different industrial, health and environmental applications [10-12]. Contamination of water with toxic metal ions [Hg(II), Pb(II), Cr(III), Cr(VI), Ni(II), Co(II), Cu(II), Cd(II), Ag(I), As(V) and As(III)] is becoming a severe environmental and public health problem [13]. To achieve environmental detoxification, various techniques like adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, oxidation and biosorption processes are extensively used. Nanostructured materials such as magnetic nanoparticle, carbon nanotubes, silver-impregnated cyclodextrin nano-composites, nano structured iron zeolite, carbon-iron nanoparticles, photocatalytic titania nanoparticles, nanofiltration membranes and functionalized silica nanoparticles can be employed in water treatment to remove heavy metals, sediments, chemical effluents, charged particles, bacteria and other pathogens. Nanoparticles, like nanosized zero valent ions when used as adsorbents, helps in pollutant removal/ separation from water as well as catalyze the chemical or photochemical oxidation process for effective destruction of persistent contaminants [14].

Table 1: Application of Nanotechnology in water and waste water treatment.

Type of Nanoparticle	Type of pollutants removed
Nano Scale metal Oxide	Heavy metals Radionucleides
Nano catalyst	PCB, Azodyes, Pesticides etc
Carbon nano tubes	Organic Contaminant
Bioactive nanoparticle	Removal of Bacteria, fungi
Biomimetic membranes	Removing Salts
Nano Structured catalytic	Decomposition of organic pollutant inactivation of micro organisms

Scientists classified nanoscale materials that are being evaluated as functional materials for water purification into four classes namely, dendrimers, metal-containing nanoparticles, zeolites and carbonaceous nanomaterials [15]. Above mentioned nanomaterials can be efficiently used in wastewater treatment and purification utilizing the unique features of nanotechnology. Nanotechnology has been considered effective in solving water problems related to quality and quantity [16]. Nanomaterials like carbon nanotubes (CNTs) and dendrimers are contributing to the development of more efficient treatment processes among the advanced water systems due their exceptional adsorption properties [17,18]. There are many aspects of nanotechnology to address the multiple problems of water quality in order to ensure the environmental stability. The most promising materials and applications are highlighted in Table 1.

Opportunities and challenges of using nanomaterials in the purification of surface water, groundwater and industrial wastewater streams is a matter of continuing concern. Apart from the conventional utilization pattern of the nano particles like, killing harmful organisms [19], repairing body tissue [20], and curing diseases; nanotechnology in future can be exploited in large scale water treatment plants being a cost effective and labor intensive process and a promising alternative to conventional water treatment practices. In short, the development of different nanomaterials like nanosorbents, nanocatalysts, zeolites, dendrimers, and nanostructured catalytic membranes have made it possible to disinfect disease causing microbes, removing toxic metals and organic and inorganic solutes from water/wastewater.

Strategies for Synthesis of Nanoparticles

Nano-sized materials spontaneously synthesized in nature being highly unstable, its synthesis processes are crucial to choose

for practical applications. Numerous techniques are used to fabricate different nanomaterial. Nanoparticles can be produced from larger structures (top down) by use of ultrafine grinders, lasers and vaporization followed by cooling. For complex particles, nanotechnologists generally prefer to synthesize nanostructures by a bottom-up approach by arranging molecules to form complex structures with new and useful properties. 'Layer by layer' deposition is a technique where the platforms for bilayer membranes that can be used for protein analysis can be fabricated by layering of sodium silicate and poly (allylamine hydrochloride) on gold followed by calcinations in a furnace. Lipid bilayers can fuse to the silicate layer and be used to detect specific proteins [21]. Rivero et al. [22] have reported synthesis of silver nanoparticles (AgNPs) with different shape, aggregation state and color (violet, green, orange) successful incorporation into polyelectrolyte multilayer thin films using the layer-by-layer (LbL) assembly. Zhao et al. [23,24] fabricated multilayer films containing silver nanoparticles and polycation poly (diallyldimethylammonium chloride) (PDDA) following similar techniques. During synthesis of biocompatible fibers, nanoparticle play crucial role in providing temporal stability. During that particular synthesis process (hydroxyapatite-aspartic acid/glutamic acid), crystallization is one the effective strategies. Gold nanorods and nanoparticles with other shapes were produced by incubation of dead oat stalks with an acidic aqueous solution of gold ions (Au III) [25]. Some living plants are also known to take up and sequester heavy metals (to prevent being poisoned by these metals) and these plants and its leaf and seed extract may also be useful in producing nanoparticles of metals also [26-28], which are all biomass reduction process of nanoparticle synthesis and micro-living cells have been harnessed to produce nanoparticles also known as microbial synthesis, for example, silver nanoparticles produced extracellularly by the fungus *Aspergillus fumigatus* [29]. Gold and silver nanoparticles can also be produced by other fungi and a number of bacterial species [30]. Major nanoparticle synthesis techniques belongs to two broad areas namely, gas phase synthesis and sol-gel processing. Nanoparticles with diameters ranging from 1 to 10 nm with consistent crystal structure, surface derivatization and a high degree of monodispersity have been processed by both gas-phase and sol-gel techniques. Initial development of new crystalline materials was based on nanoparticles generated by evaporation and condensation (nucleation and growth) in a sub-atmospheric inert-gas environment [31,32]. Various aerosol processing techniques have been reported to improve the production yield of nanoparticles [33,34]. In self assembly technique, manipulation of physical and chemical conditions such as pH, temperature and solute concentrations can induce self assembly of molecules to form fibrous nanostructures [35]. 'Polymerosomes' are special type of nanomaterials having immense potential in waste water treatment. Polymerosomes are synthetic vesicles which are self assembles tiny hollow spheres composed of block copolymeric amphiphiles, synthesized by self assembly technique. The presence of both hydrophilic and hydrophobic groups in polymerosomes creates layers along with an aqueous core in the copolymers which help in retaining variety of guest molecules at different pH values [36]. Hence, these hyper branched nano-sized copolymers are good promising tools for removal of organic wastes from water bodies.

Methodology for Water Treatment

This section describes most promising technologies of waste

water treatment involving nanomaterials as key component.

Adsorption is one of the most well practiced techniques for water treatment. Use of nanomaterials as adsorbent in treatment of waste water is applicable in various forms like catalytic, absorptive, catalytic membrane, bioactive nanoparticles, biomimetic membrane, polymeric and nano composite membrane, thin film composite membrane etc. Various organic chemicals are absorbed more efficiently by using carbon nano tubes (CNT) than activated carbon [37]. Organic compounds which have carboxylic, hydroxyl, amide functional groups also form hydrogen bond with the graphitic CNT surface which donates electrons [38]. CNT have high adsorption competence for metal ions [39-41] and therefore is a good alternative for activated carbon. Nanoscale metal oxides like iron oxides like ferrous oxide, TiO_2 , Al_2O_3 are effective, low cost adsorbants for heavy metals and radio nucleides [42-44]. Dendrimers (polymeric nanomaterials) are capable of removing both organics and heavy metals [45]. Nano-adsorbents are used as powder, beads or porous granules loaded with nano-adsorbants.

Nanomembranes are a particular kind of membranes modified with nanofibres which utilized to remove microsize particles from aqueous phase with a high elimination rate with reduced fouling propensity [46]. Such membranes are used as pretreatment method used proceeding to ultrafiltration or reverse osmosis. Large number of studies on membrane nanotechnology has focused on creating multifunction membrane by adding nanomaterials into polymeric or inorganic membranes known as nanocomposite membranes. The addition of metal oxide nanoparticles including alumina, silica, zeolite and TiO_2 to polymeric ultra filtration membranes has been shown to amplified membrane surface hydrophilicity, water permeability, or fouling resistance [47]. Inorganic membranes containing nano- TiO_2 or modified nano TiO_2 have been used effectively for reductive degradation of contaminants, particularly chlorinated compounds [8,48]. The use of TiO_2 immobilized on a polyethylene support and a TiO_2 slurry in combination with polymeric membranes has proved very effective for degradation of 1,2-dichlorobenzene and pharmaceuticals, respectively [49,50]. Nanostructured composite of TiO_2 and Fe_2O_3 incorporated into ultrafiltration membranes successfully reduced the fouling burden and improved the permeate flux [51]. Alumina-zirconia-titania ceramic membrane coated with Fe_2O_3 nanoparticles was observed to reduce the dissolved organic carbon better than the uncoated membrane enhancing the degradation of natural organic matter [52,53]. Finally, ceramic composite membranes of TiO_2 and CNTs have resulted in enhanced membrane permeability and photocatalytic activity [54-56]. Antimicrobial nanomaterials such as nanosilver are doped or surface grafted on polymeric membranes to inhibit bacterial attachment and biofilm formation on the membrane surface [57,58]. It also inactivates viruses and can reduce membrane bio-fouling [59]. Developments of thin film nanomaterial membrane mainly focus on incorporating nanomaterials into the active layer of thin film composite membrane via doping in the casting solutions or surface modification. The effect of nanoparticles on membrane permeability and selectivity depends on the variety, dimension and quantity of nanoparticles added [60,61]. Many biological inspired membranes are highly selective and permeable [62]. The use of nanofibrous composites membranes for water/wastewater treatment is very limited and a stand-alone system (Figure 2) is proposed for

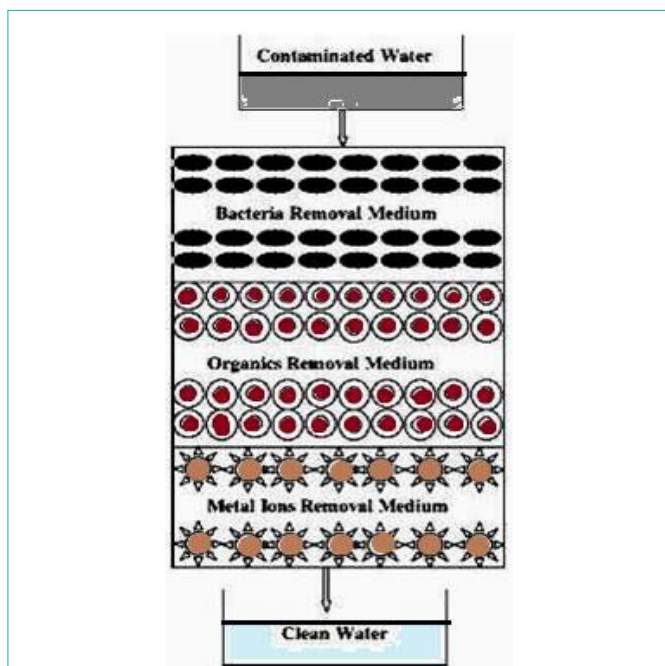


Figure 2: Schematic of a proposed composite nanofibrous media/membrane filters for complete removal of contaminants from wastewater [67].

removing all types of contaminants including bacteria/viruses, heavy metals and ions, and complex organic compounds.

Nanocatalysts are also effective in removing contaminants from water streams due to unique physical and chemical characteristics. Due to high surface to volume ratio and shape dependent properties, nano catalytic substances like zero-valent metal, semiconductor materials and bimetallic nanoparticles are widely used in water treatment as they increase the catalytic activity at the surface. It enhances the reactivity and degradation of environmental contaminants such as organochlorine based pesticides, halogenated herbicides, azo dyes, polychlorinated biphenyls and nitro aromatics [63]. The catalytic activity of nanomaterials and reusability of this particle (silver nanocatalyst, N-doped TiO₂ and ZrO₂ nanoparticles) has been proved on laboratory scale for various contaminants with efficient removal of microbial contaminants in water [64].

Bioactive nanoparticles are also important class of materials having immense potential for waste water treatment. Silver nanoparticles can be biosynthesized extracellularly by bacteria *Bacillus cereus* which is having very high antibacterial potential. This strain was exposed to different concentrations of silver salt AgNO₃ and studied with the help of various analytical instruments like High Resolution Transmission Electron Micrography (HRTEM), X-ray diffraction (XRD), and Energy Dispersive spectroscopy (EDS). Prakash et al. [65] have reported MgO nanoparticles and Cellulose acetate CA fibers embedded with Ag nanoparticles effective against both positive and negative bacteria and spores.

Conclusion

While nanotechnology is considered to be the new era by many scientists, information related to the subject remains largely unknown to many of the folk's because of novelty of the technology. In future the

nano materials will be used in large amount for the purpose of water purification and treatment. Therefore this eureka will be considered as great milestone in the 21st century. MNPs (metal nanoparticles) were powerful tools to remove heavy metal from drinking water with high efficiency and low significant toxicity. MNPs are therefore suitable for the removal of various heavy metals like Arsenic (As). Compared to other disinfection technologies, MNPs disinfection is cost-effective and easy to operate, with bright future for its engineering application. The features of MNPs address the challenges of drinking water safety in rural areas of developing countries where are lack of resources and appropriate technology in water treatment. It is particularly suitable for small scale water treatment systems serving a population of between 500-1000 people and is an ideal emerging technology to provide clean water to these areas.

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