

Nanotechnology in Waste Water Treatment: A Review

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Abstract: Nanoparticles have a great potential to be used in waste water treatment. Its unique characteristic of having high surface area can be used efficiently for removing toxic metal ions, disease causing microbes, organic and inorganic solutes from water. Various classes of nanomaterials are also proved to be efficient for water treatment like metal-containing nanoparticles, carbonaceous nanomaterials, zeolites and dendrimers. The paper reviews recent advances on different nanomaterials (nanostructured catalytic membranes, nanosorbents, nanocatalysts, bioactive nanoparticles, biomimetic membrane and molecularly imprinted polymers (MIPs)) with their application in waste water treatment. Nanotechnology has lead to various efficient ways for treatment of waste water in a more precise and accurate way on both small and large scale.

Keywords: Nanoparticles, Polymers, Nanosorbents, Nanocatalyst, Water contamination.

Introduction

Water contamination is one of the major problems which the world is facing today. Water contamination not only effect environment and human health, but it has also impacts on economic and social costs. There are various ways used commercially and non- commercially to fight this problem which is advancing day by day due to technological progress. Nanotechnology has also proved to be one of the finest and advance ways for waste water treatment. There are various reasons behind the success of nanotechnology and scientists are still working on further enhancement of its usage. Nanoparticles have very high absorbing, interacting and reacting capabilities due to its small size with high proportion of atoms at surface. It can even be mixed with aqueous suspensions and thus can behave as colloid. Nanoparticles can achieve energy conservation due to its small size which can ultimately lead to cost savings. Nanoparticles have great advantage of treating water in depths and any location which is generally left out by other conventional technologies.

Since water treatment by using nanoparticles has high technology demand, its usage cost should be managed according to existing competition in market (Crane *et al.*, 2012)¹. There are various recent advances on different nanomaterials (nanostructured catalytic membranes, nanosorbents, nanocatalysts, bioactive nanoparticles, biomimetic membrane and molecularly imprinted polymers (MIPs)) for removing toxic metal ions, disease causing microbes, organic and inorganic solutes from water.

Nanosorbents

Nanosorbents have very high and specific sorption capacity having wide application in water purification, remediation and treatment process. Commercialized nanosorbents are very few mainly from the U.S. and Asia but research is on going on in large numbers targeting various specific contaminants in water. Few advancements and applications of nanosorbents are given below.

Table 1: Different specialization of nanosorbents

| S.No. | Nanosorbent | Specialization/Treatment |
|-------|-----------------------------------|--|
| 1. | Carbon-based nanosorbents | Water containing nickel ions (Ni ²⁺). (high specific surface area, excellent chemical resistance, mechanical strength, and good adsorption capacity) (lee <i>et al.</i> , 2012) ² |
| 2. | Captymmer TM | Contaminants (perchlorate, nitrate, bromide and uranium) branched macromolecules forming globular micro particles (Aquanano, n.d.) ³ |
| 3. | Regenerable polymeric nanosorbent | Many organic and inorganic contaminants in wastewater (Dunwell Group, n.d.) ⁴ |
| 4. | Nanoclays | Hydrocarbons dyes and phosphorus (Carrado <i>et al.</i> , 2009) ⁵ |
| 5. | Carbo-Iron | The activated carbon for sorption while the elementary iron is reactive and can reduce different contaminants (Helmholtz Centre for Environmental Research, n.d.) ⁶ |
| 6. | Nano networks | Complex three-dimensional networks caused by the ion beam providing better efficiency (Dongqing <i>et al.</i> , 2010) ⁷ |

Magnetic nanosorbents also helps in treating waste water and is proved very interesting tool especially for organic contaminants removal (Bull Mater, 2011)⁸. Since most of the contaminants are not of magnetic nature filtration aids are needed to absorb which is generally followed by magnetic separation. The nanosorbents used for magnetic separation are prepared by coating magnetic nanoparticles with specific ligands presenting specific affinity (Apblett *et al.*, 2001)⁹. Different methods like magnetic forces, cleaning agents, ion exchangers and many more are used to remove nanosorbents from the site of treatment to avoid unnecessary toxicity. Regenerated nanosorbents are always cost effective and promoted more for commercialization.

Nanocatalysts

Nanocatalysts are also widely used in water treatment as it increases the catalytic activity at the surface due its special characteristics of having higher surface area with shape dependent properties .It enhances the reactivity and degradation of contaminants. The commonly used catalytic nanoparticles are semiconductor materials, zero-valence metal and bimetallic nanoparticles for degradation of environmental contaminants such as PCBs (polychlorinated biphenyls), azo dyes, halogenated aliphatic, organochlorine pesticides, halogenated herbicides, and nitro aromatics (Xin *et al.*, 2011)¹⁰. The catalytic activity has been proved on laboratory scale for various contaminants. Since hydrogen is used in making active catalyst in large scale by redox reactions, there is need in reducing its consumption and maintain hydrogen economy by directly making catalysts in metallic form.

Silver (Ag) nanocatalyst, AgCCA catalyst, N-doped TiO₂ and ZrO₂ nanoparticles catalysts have been made which is highly efficient for degradation of microbial contaminants in water and are reusable as well (Shalini *et al.*, 2012)¹¹. TiO₂-AGS composite is very efficient for Cr (VI) remediation in waste water due to the modification done in TiO₂ nanoparticles leading to absorption band shift from UV light activity to natural light degradation. Specific interactions between hydrogen and the Pd based nanoparticles were proved (Kan *et al.*, 2012)¹². Waste waters with specific contaminants like traces of halogenated organic compounds (HOCs) can be selectively biodegraded using advanced nanocatalytic activities. The contaminants (HOCs) are first converted into organic compounds using nano-sized Pd catalysts which are followed by its

biodegradation in treatment plant. The nanocatalyst can be recycled back and reused due its property of having ferromagnetism which helps it to be easily separated.

The reductants for the reaction can be Hydrogen or Formic acid depending on the level of contamination (Hildebrand *et al.*, 2008)¹³. It has also been found that the nanocatalyst of silver and amidoxime fibres which is made by coordination interactions can be reactivated many times using simple tetrahydrofuran treatment and thus can be used efficiently for degradation of organic dyes (Zhi-Chuan Wua *et al.*, 2010)¹⁴.

Palladium incorporated ZnO nanoparticles were found to be having very high photocatytic activity for removal of E.coli from water which was studied through several analytical studies done using different concentrations of Pd in ZnO nanoparticles (Khalil *et al.*, 2011)¹⁵.

Nano-WO₃ having photo-catalytic activity for E.coli disinfection in water showed increased activity when used in conjunction with 355 nm pulse laser which is synthesized by sol-gel method (Khalil *et al.*, 2009)¹⁶. In situ remediation by using Palladium nanoparticles (PdNPs) as catalyst for the reduction of Cr (VI) to Cr (III) has been studied (Marcells *et al.*, 2009)¹⁷. Another approach for enhancing the effect is by combining nanosorbents with a catalyst for the combined sorption and degradation of contaminants. Nanocatalysis has proved to very efficient in water treatment.

Nanostructured catalytic membranes (NCMS)

Nanostructured catalytic membranes are widely used for water contamination treatment. It offers several advantages like high uniformity of catalytic sites, capability of optimization, limiting contact time of catalyst, allowing sequential reactions and ease in industrial scale up.

Several functions which include decomposition of organic pollutants, inactivation of microorganisms, anti-bio fouling action, and physical separation of water contaminants are performed by nanostructured TiO₂ films and membranes under UV and visible-light irradiation (Hyeok *et al.*, 2009)¹⁸. The N-doped “nut-like” ZnO nanostructured material forming multifunctional membrane is very efficient in removing water contaminants by enhancing photo degradation activity under visible light irradiation. It also showed antibacterial activity and helped in producing clean water with constant high flux benefiting the water purification field (Hongwei *et al.*, 2012)¹⁹.

Various studies have been done regarding immobilization of metallic nanoparticles in membrane (such as cellulose acetate, polyvinylidene fluoride (PVDF), polysulfone, chitosan, etc.) for effective degradation and dechlorination of toxic contaminants which offers several advantages like high reactivity, organic partitioning, prevention of nanoparticles, lack of agglomeration and reduction of surface passivation (Jian *et al.*, 2009)²⁰.

Nanocomposites films have been prepared from polyetherimide and palladium acetate and specific interactions between hydrogen and the Pd based nanoparticles have been studied proving the efficiency in water treatment. The metal nanoparticles were generated within the matrix by annealing the precursor film under different conditions using both in situ and ex situ method. This provides opportunities to design materials having tunable properties (Clémenson *et al.*, 2010)²¹.

With the advancement in nanotechnology several novel nanostructured catalytic membranes has been synthesized with increased permeability, selectivity, and resistance to fouling. The techniques include bottom-up approaches and hybrid processes for enabling its multi functionality (Volodymyr *et al.*, 2009)²².

Bioactive nanoparticles

Water pollution has caused lots of infectious diseases due to various contaminating pathogens. Many of the microorganisms acting as pathogens are antibiotic resistance and so it's very difficult to remove them from water. Recently the concept of bioactive nanoparticles has emerged which has given the alternative of new chlorine-free biocides (2008)²³.

Silver nanoparticles (AgNPs) can be synthesized extracellularly by bacteria *Bacillus cereus* which is having very high antibacterial potential. The silver resistant strain was exposed to different concentrations of silver

salt (AgNO_3) 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.*, 2011)²⁴.

MgO nanoparticles and Cellulose acetate (CA) fibres with embedded Ag nanoparticles are very effective biocides against Gram-positive bacteria, Gram-negative bacteria and bacterial spores (Nora *et al.*, 2005)²⁵.

Current and emerging nanotechnology approaches for the detection of microbial pathogens will aid microbial and pathogen detection as well as diagnostics.

Biomimetic membrane for water treatment

Biomimetic membranes are developed by Albuquerque-based Sandia National Laboratories and the University of New Mexico. It represents a new and advanced way for water purification based on its specific design and fabrication (2011)²⁶.

The invention uses self-assembly and atomic layer deposition tuned nanopores which generally gives high-flux desalination. The membranes remove impurities like salt and others from water with applied pressure powered by electrical energy. The nonporous bio mimetic design enables high salt rejection and faster water flow at lower driving pressures generally used is around 5.5 bars. The process basically uses reverse osmosis principle with doubled efficiency due to its low pressure requirement.

Tremendous improvement was found in water purification with cost effectiveness due to this innovative functionalization which combines use of nano-fabrication techniques and inspiration from protein channels in biological membranes. Some of the molecular design principles of natural porous systems were transcribed into robust synthetic porous membranes.

The technology uses pressure driven water filtration. Some of the advantages of this technique are advancements, reduced cost, better water flux and improved efficiency with high salt rejection (Jeffrey *et al.*, 2011)²⁷. A biomimetic membrane can be prepared by vesicle fusion on a dense water-permeable support, such as an NF membrane. The process uses electrostatic stitching principle by maximizing attraction and minimizing repulsion between head groups. Biomimetic membrane should have high permeability and selectivity with chemical stability (Kaufman *et al.*, 2011)²⁸. Chemical stability can be provided using various synthetic biomimetic analogues like of aquaporins, carbon nanotubes etc. Many more advancements are expected from this technology in coming years.

Molecularly imprinted polymers (MIPs)

Molecularly imprinted polymers have recently emerged as one of very fine techniques for various biological, pharmaceutical and environmental applications. The high selectivity of the polymers is due to its synthetic procedure where a template molecule is linked to suitable monomer(s) having functional groups by covalent, semi covalent or non-covalent bonds providing subsequent specific binding sites to the MIPs. The left imprint after the removal of template from polymer helps in recognizing properties of the MIP and are generally called binding sites.

Molecular imprinting is basically a process of free radical polymerization of a functional monomer and a cross linker. It works very selectively and has great potential to act as absorbents. It has been used for detection and treatment of water pollutants even at very low concentrations (Caro *et al.*, 2006)²⁹.

Molecularly imprinted materials can be also used in combination with catalysts forming novel composite adsorbent or catalyst systems. The use of MIPs is advantageous over commonly used sorbents due to nature of being or performing selective extraction. MIP nanoparticles are encapsulated in nanofibres using electrospinning method that can be used for various pollution control applications including water treatment (Costas Kiparissides, 2010)³⁰.

Molecularly imprinted nanospheres (nano MIPs) are also developed for the specific adsorption of micro pollutants from hospital waste water by using mini-emulsion polymerization technique which is very complex but can run in a single reaction chamber resulting in particles with size (50 nm-500 nm). Magnetic

core can be introduced to allow the final separation of the nano MIPs and more important of the recognized pollutants from waste water (Tino *et al*, 2009)³¹.

Conclusion

Nanotechnologies have made great improvements for handling water contamination problems and will clearly make further advancements in future. Nanotechnology based treatment has offered very effective, efficient, durable and eco friendly approaches. These methods are more cost-effective, less time and energy consuming with very less waste generations than conventional bulk materials based methods. However certain precautions are to be taken to avoid any threat to human health or environment due to the nanoparticles.

The technology should be cost effective and friendly with ease in establishment and use. BCC research has concluded, in a report from 2011-12, that the total market for emerging nanotechnology products used in water treatment, including nanosorbents, will be only around €80 million in 2015. One can see that the large scale commercialisation of nanosorbents is to be expected only after some additional 10 years of applied research (Boehm, 2009)³². For the success of proper commercialization of nanotechnology based water treatment several technical, economical and social challenges has to be tackled properly.

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