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Nano-remediation: Advance strategies to treat polluted water

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Abstract:

Our global environment facing highly critical situation due to rapid industrialization, excessive agriculture, domestic wastes and urbanization as well as population explosion in the limited natural resources. These things reflect the drastic changes in life style of the people that created anthropogenic stress on environment like water, air, soil contaminations. Ensuring reliable access to clean pollution becomes more and affordable water is one of the greatest global challenges of 21st century. As the world population increases (depletion of water resources) water pollution becomes more complex & difficult to remove. The development of cost-effective and stable materials and methods for providing the fresh water in adequate amounts is the need of the earth life, also water industry. Traditional water/wastewater treatment technologies remain ineffective for providing adequate safe water due to increasing demand (quality&quantity both) of water along with stringent health guidelines and emerging contaminants. By recent reports nanomaterials have gained special attention for environmental restoration of water/waste-water & removal of several typical pollutants (in-organic solutes, heavy metals, metal ions, water soluble complex organic compounds, natural organic matter, nitrate, pesticides, dyes and other pollutants). Nano-particles (NPs) possess many appealing properties that can be harnessed for environmental remediation. Their nano-scale size (1-100nm) offers them with appropriate dispensability and tunable reactivity (same with their shape). They can be dispersed appropriately. Under the right formulation and in the presence of stabilizing agents, NPs can travel just like water in soil, and when in the liquid phase, they quickly scan large volumes brownianly. Likely, their reactivity can be tuned to be enough to attack organic and inorganic molecules, but not enough to attack life forms. NPs can be designed to take advantage of their special physicochemical properties such as the presence of a higher surface area per unit of volume, which makes them very highly reactive (as compare to non-nano forms of same materials) towards targeted molecules. Due to their unique properties toward recalcitrant contaminants and implicational flexibility, its easy handling, low cost/maintenance and high efficiency, many nanomaterials are under active research and development. This literature about current research on different nanomaterials (nanostructured catalytic membranes, nanosorbents, nanocatalysts nanowires/tubes, and bioactive nanoparticles) and their application in water treatment, purification and disinfection is reviewed in the present article.

Keywords:*Nano-remediation, strategies,treatment, water, pollutant*

INTRODUCTION

Water is the most essential substance for all life on earth and a precious resource for human civilization. Reliable access to clean and affordable water is considered one of the most basic humanitarian goals, and remains a major global challenge for the 21st century. Our current water supply faces enormous challenges, both old and new. Worldwide, some

278 million people still lack access to improved drinking water sources (WHO 2012). It is urgent to implement to basic water treatment in the affected area (mainly developing country) where water and unconventional water sources (e.g. strong water, contaminated fresh water, brackish water, waste water and sea water) a new norm especially in historically water stressed regions. Furthermore, current water and waste water treatment technologies and infrastructure are reaching their limit for providing adequate water quality to meet human and environmental needs. Recent advances in nanotechnology offer leapfrogging opportunities to develop next generation water supply systems. Our current water treatment, distribution and discharge particles, which heavily rely on conveyance and centralized systems, are no longer sustainable. The highly efficient, modular, and multifunctional processes enabled by nanotechnology are envisaged to provide high performance, affordable water and waste water treatment solutions that less rely on large infrastructures nanotechnology- enabled water and waste water treatment promises to not only overcome major challenge faced by existing treatment technologies, but also to provide new treatment capabilities that could allow economic utilization of unconventional water sources to expand the water supply.Here, we provide an overview of recent advances in nanotechnologies for water and waste water treatment. The major applications of nanomaterials are critically reviewed base on their functions in unit operation processes. Nanomaterials are typically defined as materials smaller than 100 nm in at least one dimension. At this scale, materials often possess noble size-dependent properties different from their large counter parts, many of which have been explode for applications in water and waste water treatment. Some of these applications utilize the smoothly scalable size-dependent properties of nanomaterials which relate to the high specific surface area, such as fast dissolution, high reactivity and strong sorption. Others take advantage of their discontinuous properties such as super-paramagnetism, localized surface Plasmon resonance, and quantum confinement effect. These applications are discussed below on nonmaterial's function in unit operations processes.

VARIOUS NANO-TREATMENTS FOR WATER CONTAMINENTS

In terms of water\wastewater treatment, nanotechnology is applicable in detection and removal of various pollutants. Heavy metal pollution poses as a serious threat to environment because it is toxic to living organisms, including humans, and not biodegradable. Various methods such as Photocatalysis, Nanofiltration, Adsorption, and Electrochemical oxidation involve the use of TiO_2, ZnO, ceramic membranes, nanowire membranes, polymer membranes, carbon nanotubes, submicron nanopowder, metal (oxides), magnetic nanoparticles, nanostructure boron doped diamond are used to resolve or greatly diminish problems involving water quality in natural environment. Nanoparticles when used as adsorbents, nanosizedzerovalent ions or nanofiltration membranes cause pollutant removal/separation from water whereas nanoparticles used as catalysts for chemical or photochemical oxidation effect the destruction of contaminants present.

Scientists classified nanoscale materials that are being evaluated as functional materials for water purification into four classes namely, dendrimers, metalcontaining nanoparticles, zeolites and carbonaceous nanomaterials.

A. 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 [6]. Magnetic nanosorbents also helps in treating waste water and is proved very interesting especially for organic contaminants removal. 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. 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. Few advancements and applications of nanosorbents are given below(Nanosorbent Specialization/Treatment) :

1. Carbon-based nanoasorbents; Water containing nickel ions (Ni^{2+}). (high specific surface area, excellent chemical resistance, mechanical strength, and good adsorption capacity)

2. CaptymerTM Contaminants (perchlorate, nitrate, bromide and uranium) branched macromolecules forming globular micro particles

3. Regenerable polymeric nanosorbent; many organic and inorganic contaminants in wastewater

4. Nanoclays ; Hydrocarbons dyes and phosphorus

5. Carbo-Iron; The activated carbon for sorption while the elementary iron is reactive and can reduce different contaminants

6. Nano networks Complex; three-dimensional networks caused by the ion beam providing better efficiency

B. 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 [6]. 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 [6]. Silver (Ag) nanocatalyst, AgCCA catalyst, N-doped TiO_2 and ZrO_2 nanoparticles catalysts have been made which is highly efficient for degradation of microbial contaminants in water and are reusable as well. TiO_2-AGS composite is very efficient for Cr (VI) remediation in waste water due to the modification done in TiO_2 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. Waste waters with specific contaminants like traces of halogenated organic compounds (HOCs) can be selectively biodegraded using advanced nanocatalytic activities [8]. 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 amidoximefibres 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.

Palladium incorporated ZnO nanoparticles were found to be having very high photocatalytic activity for removal of E.coli from water which was studied through several analytical studies done using different concentrations of Pd in ZnO nanoparticles.

C. 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. Nanofiltration membranes are already widely applied to remove dissolved salts and micro-pollutants, soften water and treat wastewater [6]. The membranes act as a physical barrier, capturing particles and micro-organisms bigger than their pores, and selectively rejecting substances. Nanotechnology is expected to further improve membrane technology and also drive down the prohibitively high costs of desalination getting fresh water from salty water. 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 TiO_2 films and membranes under UV and visible-light irradiation. 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. 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[5]. 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. With the advancement in nanotechnology several novel nanostructured catalytic membranes has been with increased permeability, selectivity, and resistance to fouling. The techniques include bottom-up approaches and hybrid processes for enabling its multi functionality [6].

D. Catalytic Wet Air Oxidation(CWAO) using Nanoparticles: A great challenge in nanotechnology is to design highly selective catalysts comprising of an active site with the correct ensemble of metal atoms and other active components. The main advantage of nanocatalysts prepared in organic functional polymers is the easy tailoring via variation of the polymer nature. Such catalysts are characterized by high activityselectivity-stability. Here we report the synthesis of Pt, Pd, Ru, nanoparticles impregnated in hyper cross linked polystyrene matrix as efficient catalysts for CWAO of phenol. CWAO treatment of phenol compounds realized on the base of hyper cross linked polystyrene impregnated with platinum nanoparticles leads to high phenol conversion. Catalytic wet air oxidation of Oxalic Acid using Platinum catalysts in Bubble Column Reactor provides an efficient method of combustion at very low temperature as compared to thermal incineration [9].

E. Nanofibers: Nanofiber technology in combination with biological removal of toxic xenobiotics is the advanced method in industrial wastewater treatment process. Microbial biofilm formation can be greatly supported using nanofiber structures, and the whole system provides stable and accelerated biodegradation [5].Nanofibers carriers are examined on various parameters like cleaning efficiency of toxic compounds, stability of carrier and nanofiber layer, rate of carrier ingrowths by relevant microorganisms, disintegration of nanofibers and sorption properties. Each biomass carrier must meet the basic parameters (microorganism colonization ability, chemical and physical stability, surface morphology, maximum specific surface). The exceptional properties of nanofiber carriers are primarily the large specific surface, high porosity and small pore size.

ElectrospunPolyacrylonitrile nanofiber mats are being used for heavy metal ion removal because of tremendous potential as a heterogeneous adsorbent for metal ions [4].

Depending on the type of polymer, nanofibers are durable, easily moldable and chemical resistant. The principal advantage of nanofiber materials is their comparability with the dimensions of micro-organisms, the surface morphology and biocompatibility, which allows for faster colonization of the nanofiber surface by the microorganisms [4] . An important advantage of the technology is the possibility of a bacterial biofilm buildup not only on the surface of the carrier but also closer to its center (inside the carrier), where the bacteria are much more protected against the toxic effects of the surrounding environment and shear forces during hydraulic mixing. In addition, penetration of substrate and oxygen to the microorganisms is also possible. High specific surface of the nanofiber layer allows to the bacteria great adhesiveness and as a result it simplifies the immobilization of microorganisms, especially in the initial stages of colonization of the surface carriers and also even during difficult emergency conditions (reducing the required regeneration time). After a longer period of colonization the microbial biomass grows naturally on the places without the nanofibers thus making the process of wastewater treatment more efficient. Fe-Grown Carbon nanofibers are being used for removal of Arsenic (V) in wastewater.

F. Membrane Filtration Technology Nano-filtration: It is a liquid separation membrane technology positioned between reverse osmosis (RO) and ultra-filtration. While RO can remove the smallest of solute molecules, in the range of 0.0001 micron in diameter and smaller, nanofiltration(NF) removes molecules in the 0.001 micron range. It refers to a membrane process that rejects solutes approximately 1 nanometer (10 angstroms) in size with molecular weights above 200[5]. Because they feature pore sizes larger than RO membranes, NF membranes remove organic compounds and selected salts at lower pressures than RO systems. It is also capable of removing bacteria and viruses as well as organic-related color without generating undesirable chlorinated hydrocarbons and tri-halomethanes. Nanofiltration is used to remove pesticides and other organic contaminants from surface and ground waters to help insure the safety of public drinking water supplies. Sometimes referred to as "membrane softening," NF is an attractive alternative to lime softening or zeolite softening technologies and since NF operates on lower pressure than RO, energy costs are lower than for a comparable RO treatment system. As such, nanofiltration is suited especially to treatment of well water or water from surface supplies such as rivers or lakes [5].

RETENTION AND REUSE OF NANOMATERIALS:

The retention and reuse of nanomaterials is a key aspect of nanotechnology enabled device design due to both cost and public health concerns. It can be usually achieved by applying a separation device or immobilizing nanomaterials in the treatment system. A promising separation process is membrane filtration which allows continuous operation with small footprint and chemical use. Ceramic membranes are more advantageous than polymeric membranes in photocatalytic or catalytic ozonation applications as they are more resistant to UV and chemical oxidants. The suspended particles in the receiving water are detrimental to reactor membrane hybrid systems as they can be retained by the membrane and significantly reduce the reaction efficiency [9]. Thus raw water pretreatment is usually required to reduce the turbidity. Nanomaterials also can be immobilized on various platforms such as resins and membranes to avoid further separation. However, current immobilization techniques usually result in significant loss of treatment efficiency. Research is needed to develop simple, low cost methods to immobilize nanomaterials without significantly impacting its performance. For magnetic nanoparticles/nanocomposites, low field magnetic separation is a possible energy efficient option [9] . Little is known about the release of nanomaterials from nanotechnology enabled devices. However, the potential release is expected to be largely dependent on the immobilization technique and the separation process employed. If no downstream separation is applied, nanomaterials coated on treatment system surfaces are more likely to be released in a relatively fast and complete manner, while nanomaterials embedded in a solid matrix will have minimum release until they are disposed off. For nanomaterials that release metal ions, their dissolution needs to be carefully controlled (e.g., by coating or optimizing size and shape). The detection of nanomaterial release is a major technical hurdle for risk assessment and remains challenging. Few techniques can detect nanomaterials in complex aqueous matrices and they are usually sophisticated, expensive and with many limitations [9].

PRIVILEGES OF USING NANOTECHNOLOGY:

(i) *Increased effectiveness* – Contaminants could be more effectively removed, even at low concentrations, due to the increased specificity of nanotechnology and the development of "smart" filters tailored for specific uses.

(ii) *Removal of new contaminants* – Contaminants that were previously impossible to remove could now be removed. This will be achieved through novel reactions at the nanoscale due to the increased number of surface atoms.

(iii) *Simplification* – Nanotechnology could radically reduce the number of steps, materials and energy needed to purify water, making it easier to implement widely in rural communities.

(iv)*Reduced cost* – Substantial initial investment would be needed to incorporate or switch to nanotechnology–based water treatments.However,once adopted, these techniques could considerably lower water treatment costs over the long term.

(v) *Sensing and detection* – Nanotechnology is being used to develop small and portable sensors with enhanced capabilities for detecting biological and chemical contaminants at very low concentration levels in the environment, including in water.

(vi)*Increasing potable water supplies* – The development of low–cost portable filters, purifiers and other techniques could positively impact rural communities and informal settlements located close to industrial areas, where the accessible water is heavily contaminated.

(vii)*Desalination of sea water* – By removing the salt from seawater, another large sustainable source of potable water could be provided significantly more cheaply than existing techniques.

(viii)*Safety of industrial effluent* – New,more efficient and cost-effective techniques could be applied to protect the environment alongside industrial practices. For example, nanotechnology may be used by the mining industry to prevent the contamination of groundwater from inactive mines by cleaning of acid mine drainage sources.

CHALLENGES OF NANOTECHNOGY:

Besides its use in water treatment, nanotechnology may have unintended effects on human health and the environment. With more than 1100 nanotechnical products already available to consumers worldwide, nanoparticles may eventually interact with humans and the environment at different stages of the products life cycles. There are concerns that the same properties (size, shape, reactivity, conductivity) that make nanoparticles so useful to mankind can also make them potentially harmful to the environment and toxic to humans, especially if they enter and build up in drinking water supplies and the food chain. The concerns result from poor understanding of the fate and behavior of nanoparticles in humans and the environment, which are affected by biotic and abiotic factors. How this will affect their toxicity in the long term is unclear. For example, silver nanoparticles used in socks to reduce foot odour are being released during washing with possible negative consequences. The silver nanoparticles may then destroy beneficial bacteria which are important for breaking down organic matter in wastewater treatment plants. Also, recent studies have shown a similar response by the human body to some forms of carbon nanotubes as to asbestos particles, if inhaled in sufficient quantities. Extreme care needs to be taken with the use of nanotechnology in water treatment. Investigations to seek ways of removing nanoparticles from treated wastewater before discharge into the environment should be undertaken. Nanotechnology risk assessment research for establishing the potential impacts of nanoparticles on human health and the environment is crucial to aid in balancing the technology's benefits and potential unintended consequences.

No systematic investigations regarding the stability of nanomaterials in natural and engineered environmental systems have been carried out till date to the best of our knowledge. On a positive note, due to their extremely high potential in combination with the high specificity, nanoparticles can be developed into ideal candidates for water treatment and may contribute to solving future challenges in the area of water treatment technologies. Thus nanotechnology holds a lot of promise in the remediation of groundwater and for this there is further scope in research and development.

Scientific authorities acknowledge this as a massive challenge, since monitoring the huge volume of diverse nanoparticles being produced and used and their consequent impact is very difficult to track. A research platform should be currently established to investigate the environmental, safety and health related aspects of nanotechnology. The initiative comprises four pillars, namely human capital development, focused research, infrastructure development, and an inventory of nanoparticles in production. Other initiatives include the establishment of an Ethics Committee constituted by government, made up of stakeholder representatives to ensure the technology adheres to ethical principles.

It is important that nanotechnology is developed in a safe, responsible, acceptable, and sustainable manner. For this to happen, the entire life cycle of nanoparticles needs to be carefully considered from production to disposal, to allow an informed assessment of the potential human health and environmental impacts. This will mitigate the challenges faced by other technologies such as asbestos, DDT, and GMOs. Risk assessment of nanotechnology is currently starting at several universities and science councils and is expected to become an integral part of the nanotechnology research.

CONCLUSIONS:

Some key issues to be considered with regard to water and nanotechnology include:

Technology transfer – Developed water treatment technologies need to be transferred to specific target communities and must be relevant to the community needs, technical capability, and available infrastructure. The receiving communities have to take ownership both in skill and perceived benefit of the technology to be able to sustain it once there is no longer technical support.

Public understanding of nanotechnology – As with any emerging technology, public awareness and understanding of the technology and related issues are an integral component of responsible application. It is essential that factually based, credible information is communicated and that the public and other key audiences are engaged in relevant topics to ensure community preparedness for this technology.

"Buy–in" of the water sector – Since significant capital investment will be required to make the switch to nanotechnology-based water treatment, the involvement of the water sector, at all levels, is crucial.

Nanotechnology risk assessment – Long term acceptance of nanotechnology–based products and industrial applications by society is strongly dependent on the way risk concerns (real and perceived) will be investigated, communicated to the public, and managed

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