Nanomaterials and their Application in Waste Water Treatment: A Review

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Abstract—Water is considered to be one of the most precious resources for human civilization. Reliable access to clean, sufficient and affordable water has been a challenge of the modern era. Natural sources of water are shrinking at a rapid pace with an increase both in population and pollution. Organizations worldwide are struggling to match the increasing demand and deterioration in water quality. Industries are considered to be the major culprits for pollution as they not only consume a high percentage of water but also pollute the water bodies at a mass scale. Conventional treatment technologies have not been successful in eradication of this problem. An issue like energy consumption, high costs, ineffective treatment in aerobic conditions, etc. has provoked a need for advancements in technology.

Nanotechnology is not a new term and process and it has achieved remarkable feats in various fields in the past. Here we review the use of nanomaterials in the wastewater treatment process. It has been shown that nanomaterials due to the high surface area are very effective in the removal of various water contaminants like heavy metals, pathogens, organic and inorganic solvents, color from water. The discussion covers various classes of nanomaterials, comparison with existing process and finally barriers and research required for commercialization. By outlining these technological advancements to the physiochemical properties of nanoparticles, the current paper covers the advantages and limitations to capitalize on these exciting and unique properties for scaling up the wastewater treatment process.

I. Introduction

Water covers one-third of our planet's surface; unfortunately, most of it is saline and thus unusable for human consumption. Only 2.5% of the world's total water is fresh. In addition to its scarcity, increasing pollution of groundwater and surface water from a wide variety of industrial, municipal and agricultural sources has deteriorated water quality in these water resources. 785 million people lack even a basic drinking-water service, including 144 million people who are dependent on surface water (WHO, 2017). Therefore, the proper treatment of wastewater especially forms industries before its release is very important for our ecosystem. Conventional wastewater treatment technologies require high capital investment, operation and maintenance cost consumes high energy. Consequently, industries from developing countries find it difficult to afford such technologies and thus its compliance with environmental legislation and standards is relatively low.¹ To address these issues, many institutions are coming up with exciting research that can provide clean and affordable wastewater treatment technology. Over the past decade, nanotechnology has shown amazing results in various fields and its utilization in wastewater treatment would certainly alleviate this issue.² Nanotechnology is the manipulation of matter at the nanometer scale to create novel structures, devices, and systems. Unlike the parent material at nanoscale, materials show different physical, chemical and biological properties.³

This review explores some of the recent advances in the use of nanotechnology-enabled wastewater treatment approach in the removal of toxic metals, organic and inorganic compounds, pathogens and color. Use of nanoparticles such as TiO₂, ZnO, N₂O,AgO, CuO, SiO₂, Al₂O₃ and CeO₂, with potential risk to human and environment. Thus, the current paper also outlines limitations for scaling up and risks associated with the use of nanotechnology in wastewater treatment.

II. Current and Potential applications in wastewater treatment

A nanometer is one-billionth of a meter (10^{-9}) and could also be represented as the length of ten hydrogen atoms lined up in a row. At this scale, a material often possesses novel properties different from their parent counterparts. Nanostructure science and technology is a broad research area that encompasses the creation of new materials from nanosized building blocks.4 In this perspective, nanotechnology could be considered to be the most promising technology that could play an important role in resolving many of the problems involving water purification and quality.^{5,6,7} Most environmental applications of fall into three major categories:(1) nanotechnology environmentally friendly and/ or sustainable products(e.g. green chemistry or pollution prevention), (2) treatment and remediation of materials contained with hazardous substances, (3) sensors and detectors for environmental protection.^{8,9}

Nano-Adsorption

Adsorption is considered to be a polishing step for the removal of organic and inorganic contaminants in wastewater treatment. The efficiency of conventional adsorbents is limited by surface area or active site, lack of selectivity. Nanoadsorbents offer significant improvement with their extremely high specific surface area and tunable pore size and surface chemistry. Carbon nanotube (CNT) have shown higher efficiency than activated carbon on adsorption of various organic chemicals.¹⁰ In addition to organic removal, nanoadsorbents can also be effectively utilized for removalfor metal ions with fast kinetics through electrostatic attraction and chemical bonding.¹¹ Metal oxides such as zinc oxide, alumina, and iron oxide are suitable candidates for removal of heavy metals as they are effective and also low-cost absorbents. Magnetic nanoparticles (MNPs) are also employed for efficient and affordable removal of chemical pollutants. Contaminants such as arsenic or oil bind to MNPs, which are then subsequently removed using a magnet.¹² Tailored adsorbents called dendrimers are capable of removing both organics and heavy metals. Their interior shells can be hydrophobic for sorption of organics while the exterior branches are tailored (e.g., hydroxyl or amine-terminated) for adsorption of heavy metals. Dendrimers work on complexation, electrostatic interactions, hydrophobic effect, and hydrogen bonding.¹³ Their recovery is generally done by ultra filtration and regeneration by decreasing the pH to 4.

Photo-catalysis

Photocatalysis is a light-induced reaction which is enhanced by the presence of a catalyst. When light radiation falls on the surface of a metal, electrons absorb it and get excited. It is a useful pretreatment for hazardous and non-biodegradable contaminants to enhance their biodegradability. An ideal photocatalyst should be nontoxic, stable, inexpensive, easily available and highly photoactive.¹⁴ They can also be used as a polishing step to treat recalcitrant organic compounds.

Various semiconductor-based nanopolymers are reported for the photocatalytic degradation of organic contaminants present in wastewater, which include TiO₂, ZnO, ZnS, Zn–CeO₂, Si– Ti, and CdS-TiO₂.^{15,16,17}Titanium oxide is the most widely used semiconductor due to its low toxicity, chemical stability, low cost, and abundance as raw material. TiO₂ nanotubes were found to be more efficient than TiO₂ nanoparticles in the decomposition of organic compounds. Other than TiO₂, Palladium incorporated ZnO nanoparticles were also found with high photocatalytic activity for removal of E.coli from water.¹⁹ Composite photocatalytic membranes that combine the separation technology provided by the membrane process and the photocatalytic activity of catalysts were studied by several researchers.^{20,21,22,23}. Table 1 shows the various photo catalysts used in waster remediation.

Table 1: Examples of nanoscale semiconductor photocatalyst for		
use in water remediation		
Nanoparticle/	Pollutant	Reference
nanomaterial		
NanocrystallineTiO2	Metal ions	Pena et al. (2005)
Nitrogen (N)-doped TiO2	Azo dyes	Liu et al. (2005b)
Fe(III)-doped TiO2	Phenol	Nahar et al. (2006)
Supported TiO2 nanoparticles	Aromatic pollutants	Lópes-Munoz et al. (2005)
Silver-doped titanium dioxide nanoparticles	Bacteria	Liga et al. (2011)
Manganese-doped ZnO NPs	Methylene blue	Ullah and Dutta (2008)
Nanotubes Bi2O3	Chromium ions	Qin et al. (2012)
Bi2O3 and Au/Bi2O3 nanorods	Orange II dye	Anandan et al. (2010)
CeO2	Dyes	Zhai et al. (2007); Ji et al. (2009);
		Borker and Salker (2007)
Nanocomposite plasmonicphotocatalyst Ag-	Methyl orange	Wang et al (2011)
AgCl/CeO2		
Nano WO3	Escherichia coli	Gondal et al (2009)
Photocatalyst CdS coated with CdS nanoparticles	Dyes and phenolic compounds	Yang et al. (2009)
Zn Snanoporous nanoparticles	Eosin	He and Zhao (2005)

Membranes and membrane processes

Membranes provide a physical barrier for removal of undesired constituents based on size, allowing the use of unconventional water resources. They are the key components of water treatment providing a high level of automation, require less land and chemical use, and the modular configuration allows flexibility in design.²⁴

Conventional membrane technology has limitations of high energy consumption under pressure-driven processes. Membrane fouling adds to the energy consumption and the complexity of the process design and operation. Furthermore, it reduces the life of the membrane and its modules. The performance of membranes is largely decided by the material used. Incorporation of functional nanomaterials will enhance membrane permeability, fouling resistance, mechanical and thermal stability as well as render added functions for contaminant degradation and self-cleansing. Nanofiltration membranes are already widely used to remove dissolved salts and micro-organisms, soften water and treat wastewater.25 Various studies have been done regarding immobilization of metallic nanoparticles in membranes. Nano Ag has been doped on polymeric membranes toinhibit bacterial attachment and biofilm formation²⁶ on the membrane surface as well as inactivate viruses.²⁷Many biological membranes too are being tested for improving membrane performance owing to their

high selectivity and water permeability. Incorporation between Aquaporins(protein channels that regulate flux across membranes) from *Escherichia coli* to form amphiphilic tribloc polymer vesicles.²⁸

Barriers and research needs

While much attention has been focused on the development and potential benefits of nanomaterials in treatment processes, concerns have also been raised regarding their potential human and environmental toxicity. Indeed, studies have indicated that the selfsame properties of nanomaterials that make them attractive (e.g., size, shape, structure, and reactivity) may also cause them to be toxic. Therefore, a good knowledge of the bioavailability, mobility, and ecotoxicity of engineered nanomaterials is required to assess the environmental risks.²⁹ Evaluation addressing the long-term performance of wastewater treatment nanotechnologies is needed for comparison of nanotechnology-based systems and existing technology. Despite the superior performance, the adoption of innovative technologies strongly depends on the cost-effectiveness and the potential risk involved. The current cost of nanomaterials is prohibitively high with few exceptions such as nano-TiO2, nanoscale iron oxide, and polymeric nanofibers. Research is being carried out to bring about cost-effectiveness either by retaining and reuse of nanomaterials or by lowering purity of nanomaterials without significantly compromising efficiency.²³ These processes must be developed and investigated to ensure that nanomaterials are as safe as possible while reaching their full potential leading to a broader public acceptance, which is crucial for new technology adoption.

Conclusion

Current wastewater treatment methods can control the organic and inorganic wastes from water. But, these methods are energy-intensive and uneconomical because of the inability to completely purify water, as well as the inability to reuse the retentates. Moreover, nanomaterials can be engineered to efficiently harvest solar energy, which is freely available and thus can be used as a visible light photocatalyst to decontaminate water cost-effectively.

It is thus our belief that including nanomaterials with conventional treatment strategies will become an essential component of industrial and wastewater treatment systems in the future as more progress is made in terms of economically efficient and eco-friendly technology development. Also, update test methods and guidelines on harmful properties and exposure of nanoscale materials should be considered.

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