NANOTECHNOLOGY FOR WASTEWATER TREATMENT: IN BRIEF

I.J. El Saliby, H.K. Shon, J. Kandasamy and S. Vigneswaran
School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology, University of Technology, Sydney, Australia

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Summary

This chapter briefly deals with recent advances and applications of nanotechnology for wastewater treatment. Under the nanotechnology umbrella, a number of new procedures for producing nanomaterials ultimately used for the treatment of wastewater are presented. These techniques extend from the fabrication of membranes from nanomaterials to the use of catalysts for the decomposition of noxious compounds in water. Research advances for the use of metals, bimetallic nanoparticles, mixed oxides, zeolites and carbon compounds in wastewater treatment are also reviewed. Finally, the impact of nanotechnology on human health and the environment is briefly discussed.

1. Introduction

“Nano” is derived from the Greek word for dwarf. A nanometer is one billionth of a meter (10^{-9}) and might be represented by the length of ten hydrogen atoms lined up in a row. In nature, nanotechnology first emerged billions of years ago at the point where molecules began to arrange in complex forms and structures that launched life on earth. Through evolution, mutations and adaptation; plants were able to convert carbon dioxide using the energy from the visible range of sunlight to oxygen through a process known as “photosynthesis” (Roco, 1999). This transformation is still taking place in tiny structures called “chloroplasts” composed of several nanoscale “thylakoid disks” that contain a green pigment (chlorophyll). Another example of a natural nanotechnology is “chemical catalysis” through “catalysts” or in bioscience called "enzymes". Enzymes are biomolecules that catalyse chemical reactions (Smith et al., 1997) and sometimes they are considered as indispensable for the completion of specific reactions.

In 1867, James Clerk Maxwell was the first to mention some of the nano concepts in nanotechnology through a proposed experiment on a tiny entity known as Maxwell's Demon able to handle individual molecules. In the early 20th century, the first observations and size measurements of nano-particles using an ultramicroscope were made possible in a study of gold sols and other nanomaterials with sizes down to 10 nm and less (Zsigmondy 1914). Zsigmondy (1914) was the first to characterize particle sizes using the term nanometer and he developed the first system of classification based on particle size in the nanometer range. Several advances in the field of nanomaterial characterization were possible with Langmuir and Blodgett (1920s) who introduced the monolayer concept, and Derjaguin and Abrikosova (1950s) who conducted the first measurement of surface forces (Derjaguin, 1954). In 1959, Richard Feynman at an American Physical Society meeting at Caltech described a proposed process to manipulate individual atoms and molecules by using one set of precise tools (Gribbin, 1997). Since then, several advances were made in the study of nanoscale structures, but the term nanotechnology was first defined by Taniguchi (1974) as "Nano-technology mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or one molecule". The tools and methods for nanotechnology involve imaging, measuring, modelling, and manipulating matter at the nanoscale. In 1980s, nanotechnology and nanoscience got a boost with two major developments: the birth of cluster science and the invention of the scanning tunneling microscope (STM). Major current tools for nanotechnology measuring include many devices such as STM, scanning probe microscopes (SPMs), atomic force microscopy (AFM) and molecular beam epitaxy (MBE) (Roco 1999). Diagnosis 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.

Nanostructure science and technology is a broad research area that encompasses the creation of new materials and devices from nanosized building blocks (Hu and Shaw, 1998). Building blocks are used to make molecules that are arranged in nanostructures and nanomaterials with dimensions of 1 to 100 nm. This process is known as a "bottom up" approach where building blocks are arranged and then assembled to form larger size material. The formation of powder components (structural composite material) through aerosol techniques is a main example of this approach (Wu et al., 1993). Many other approaches are being used to synthesize and assemble nanostructures but the critical point remains in the control of the size and composition of nanocluster components and in the control of interfaces and the distribution of nanocomponents within the fully formed materials (Hu and Shaw, 1998).

At the nanoscale level, materials are characterized by different physical, chemical and biological properties than their normal size equivalents (Davies, 2006). For instance, materials as metals, metal oxides, polymers and ceramics, and carbon derivatives (carbon nanotubes and fullerenes) have a higher ratio of surface area to particle size at the nanoscale level. In other words, the surface area of particles increases with decreasing particle size and as such, nanoscale particles exhibit different optical, electrical, and magnetic properties from the properties exhibited by macroscopic particles (Shelley, 2005). These remarkable characteristics of particles at the nanoscale level possibly originated from the increase in the number of surface atoms with the decreasing of particle size.

Nanotechnology can easily merge with other technologies and modify, endorse or clarify any existing scientific concept, which is why it is so called a "platform" technology (Shmidt, 2007). The use of nanotechnology in the future is expected to expand into numerous industrial applications and help decrease production costs by reducing energy consumption, attenuate environmental pollution and increase the production efficiencies in developed countries. Moreover, nanotechnology may be a useful tool to address different social problems of developing countries' such as the need for clean water and the treatment of epidemic diseases (Fleischer and Grunwald, 2008). Nanoscience and nanotechnology may not provide all the solutions for the ever increasing problems of this planet but could help the sustainable development of many social communities.

Many potential benefits of nanotechnology have already been identified by many researchers in the environmental and water sector, medicine, and in several industry applications but the future nanotechnology might bring innovations that can answer many existing scientific questions (Theron et al., 2008; Fleischer and Grunwald, 2008; Savage et al., 2008). Hence, nanotechnology is going to play an important role in addressing fundamental issues such as health, energy and water (Binks, 2007). Major potential environmental benefits of nanotechnology were reported in the draft nanomaterials research strategy by Savage et al. (2008), including:

- Early environmental treatment and remediation
- Stronger and lighter nanomaterials
- Smaller, more accurate and more sensitive sensing and monitoring devices.

Additional benefits lay in the cost-effective use of renewable energy, low energy requirement and low waste generation devices, early disease detectors for preventive treatment, pollution control, and the prevention and remediation using improved systems.

2. Benefits of Nanotechnology in Water and Wastewater Treatment

2.1 Wastewater Treatment

Wastewater is any water that has been adversely contaminated by organic pollutants, bacteria and microorganisms, industrial effluent or any compound that deteriorated its initial quality. It can be sub-divided into: i) municipal wastewater (liquid waste discharged by domestic residences and commercial properties), and ii) industrial wastewater (liquid waste discharged by industrial and agricultural activities). Some of the factors that might affect the composition of wastewater are: land uses, groundwater levels, and the degree of separation between stormwater and sanitary wastes. The composition of municipal wastewater is usually less variable than industrial wastewater, the latter being highly affected by the type of industrial activity involved in the discharge of effluent water. In general, the organic composition of wastewater is estimated to consist of proteins (50%), carbohydrates (40%), fats and oils (10%), and trace amounts (e.g. μg/L or less) of priority pollutants, surfactants, and emerging contaminants. On the other hand, wastewater often contains 10^5-10^8 colony forming unit (CFU)/mL of coliform organisms, 10^3-10^4 CFU/mL fecal streptococci, 10^1-10^3 protozoan cysts, and 10^1-10^2 virus particles (Ellis, 2004).

Treatment of municipal wastewater has to take into consideration all the aspects related to water contamination and has to ensure that the product water is free from any substance that might adversely affect the health of humans and the environment. The treatment process in wastewater treatment plants is directly related to the composition of wastewater. Generally, conventional sewage treatment includes the following stages (Shon et al. 2007):

1. Preliminary treatment: to remove coarse and readily settleable inorganic solids with the size range of more than 0.01 mm.
2. Primary treatment: to remove the bulk of suspended solids including both organic and inorganic matter (0.1 mm to 35 µm).
3. Secondary biological treatment: to degrade the biodegradable binding organic matter and nutrients.
4. Tertiary treatment: to remove a portion of the remaining organic and inorganic solids and pathogenic microorganisms through a filtration step. This treatment is followed by chemical disinfection.

Industrial wastewater could be designated as the effluent produced from any industrial activity such as agriculture, food industry, iron and steel industry, mine and quarries, etc. The composition of industrial effluent can vary according to the activity in question. Therefore, the treatment is selective to ensure high quality filtered water with consideration of the cost involved in the filtration process. Wastewater from agricultural activities is high in organic compounds of animal and vegetable sources, microorganisms, and different chemicals used for the control of pest and diseases. It is not common to find agriculture effluent contaminated with heavy metals or petroleum derivatives. On the other hand, industrial wastewater originating from the metal processing industry, mines or chemical industries might be rich in heavy metals, organic and inorganic compounds as well as chlorinated by-products. Treating industrial wastewater could follow the same stages described for municipal wastewater treatment with modifications that might be integrated to ensure low concentrations of specific pollutants.

For the purpose of improving the above listed treatment processes, the use of nanomaterials is being researched to fabricate separation and reactive media which is of high quality in terms of reactivity and performance (Bellona and Drewes, 2007). Additionally, the use of nanomaterials and nanoparticles to bio-remediate and disinfect wastewater is gaining popularity (Hu et al., 2005; Mohan and Pittman, 2007). For instance, metal oxide nanomaterials such as TiO_2 are among the promising nano-catalysts that were tested successfully for their antimicrobial activity. Moreover, fullerenes (C60) as pollution tracers, are being used to provide contaminant-fate information to assist in developing water remediation strategies; magnetic nanoparticles are being developed to adsorb metals and organic compounds; and nanocatalysts are being explored to reduce pollution of oxidized contaminants (Hillie et al., 2006). Metal processing wastewater often contains hexavalent chromium species, Cr(VI), which are toxic and can act as carcinogens, mutagens and teratogens in biological systems (Dupont and Guillon, 2003). Metal industries are required to reduce the amount of chromium in their effluent to around 0.1 mg/L (Ayuso et al., 2003) before discharging it into the sewer system. Maghemite nanoparticles were studied by Hu et al. (2005) for their potential in removing and recovering chromium from wastewater. Hu et al. (2005) developed a new method by combining the adsorption ability of nanoparticles and the magnetic separation technique. The method was space-saving, cost-effective, simple, and environmental-friendly. Additionally, chromium was successfully removed from the wastewater and the nanoscale maghemite retained the original metal removing capacity after six adsorption-desorption cycles. The adsorption was pH dependent with optimal adsorption at pH 2.5. Industrial pollutants such as phthalates, alkylphenols, bisphenol-A, pharmaceuticals and many others could be removed from industrial wastewater by using nanofiltration. Nanofiltration is being integrated in many industrial effluent treatment plants to produce effluent with low concentrations of industrial pollutants (Bruggen et al., 2008). The use of nanotechnology to remove contaminants in water is widespread and many advances have already been achieved. A summary of recent advances in nanomaterial research for industrial wastewater treatment includes: the nanofiltration of biologically treated effluents from the pulp and paper industry (Manttari et al., 2006); the degradation of organic dyes using manganese–doped ZnO nanoparticles (Ullah and Dutta, 2008); the treatment of wastewater from molasses distilleries using nanosize pore membrane (Satyawali and Balakrishnan, 2008).

2.2 Water Treatment

Water purification using nanofiltration technology or through adsorption and catalytic degradation processes was made possible by the advances achieved and mysteries revealed in the quantum world. Worldwide, the need for clean water is increasing because of population increase, drought and the contamination of conventional water sources. WHO (2004) reported that 1 billion people are at risk because they do not have access to potable water and another 2.6 billion people lack access to clean water. The innovation of new technologies to increase the availability of clean water commenced 40 years ago (1960s) with the establishment of three membrane separation processes (Table 1): reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) (Sutherland, 2008). During the 1970s and 1980s, nanofiltration membranes (Loose RO) were developed as an intermediate filtration material between ultrafiltration and reverse osmosis (Eriksson, 1988). Membrane processes using different types of membrane are becoming increasingly popular for the production of drinking water from seawater, brackish water, wastewater, surface water and groundwater (Ventresque et al., 2000).

Membrane type	**Pore size (nm)**	**Pressure (bar)**	**Product water**
Reverse osmosis	< 0.6	30 – 70	Pure water (PW)
Nanofiltration	0.6 - 5	10 – 40	(PW) and low molecular solutes
Ultrafiltration	5 - 50	0.5 – 10	All above and macromolecules
Microfiltration	50 - 500	0.5 - 2	All above and colloids

Table 1. Membrane type and characteristics (Adapted from Thorsen and Flogstad, 2006)

The impact of nanotechnology on the development of tools and techniques for water treatment will be more pronounced in the near future. As scarcity of natural water threatens the advancement and the social security of many communities around the world, it is expected that the solution will emerge from the exploitation of nanoparticles to make water recycling, seawater desalination and water remediation more efficient and cost effective. For instance, the use of nanofiltration membranes for treating water in rural areas of South Africa to provide drinking water was described by Smith (2006). The advantages of using nanofiltration relied in the direct humanitarian benefit from using nanotechnology and in the promotion of economical viabilities in rural communities. Therefore, the production of nanostructures, nanocomposites and modified nanostrucutres for water remediation will increase because of the need for producing clean water in fast and low energy consumption ways. Nanotechnology should be regarded as the tool to ensure the sustainability of social communities in different places. This is possible through the use of advanced filtration nanomaterials that enable desalination of seawater, recycling of contaminated water and the reuse of wastewater (Theron et al., 2008).

3. Application of Nanotechnology in Water and Wastewater Treatment

Nanotechnology is being applied in the production of water purification membranes. Recently, Theron et al. (2008) reported the following water filtration membranes produced from nanomaterials: i) nanostructured membranes from nanomaterials such as carbon nanotubes, nanoparticles and dendrimeres, and ii) nanoreactive membranes from metal nanoparticles and other nanomaterial. On the other hand, adsorption is considered as an effective, efficient and economic method to remove water contaminants (Jiuhui, 2008). Effective adsorbents include: i) activated carbon, ii) clay minerals and silicas, iii) zeolites, iv) metal oxides, and v) modified composites (Nouri et al., 2002; Zhang et al., 2005; Theron et al., 2008). The decomposition of organic compounds in water as well as the disinfection of water under UV light using TiO_2-mediated photocatalyst is gaining popularity as the effectiveness of the photocatalyst has been demonstrated by many scientific studies (Liu and Yang, 2003, Cho et al., 2005; Wei et al., 2008; Kumar et al., 2008).

Nanotechnology for water remediation will play a crucial role in water security and consequently the food security of the world. The applications of nanotechnology in the cleanup of contaminated water could be summarized by (Smith 2006):

- Nanoscale filtration techniques
- The adsorption of pollutants on nanoparticles
- The breakdown of contaminants by nanoparticle catalysts.

3.1 Nanomaterials and membrane filtration

Since sedimentation, flocculation, coagulation and activated carbon each remove a narrow spectrum of water pollutants, membrane filtration (UF, MF, NF and RO) have played a significant role in reducing pollutants and producing high quality pure water

(Strathmann, 2001). In the last two decades, the development of polymeric and ceramic membranes has positively impacted on the use of membranes. Nevertheless, membrane fouling is a major drawback in the membrane filtration process and poses a serious problem that challenges the viability of the use of membrane.

Cohen (2006) reported that a promising approach to improve membrane performance, while mitigating fouling, is to structure the membrane surfaces at the nano- and molecular scale. Porous carbons have a great potential in adsorption and in membrane synthesis for water filtration as they are considered as "molecular sieve materials". Water filters from carbon nanotubes were synthesized by Srivastava et al. (2004). Those filters were re-usable and showed effective removal of bacterial pathogens (*Escherichia coli* and *Staphylococcus aureus*) and Poliovirus sabin 1 from contaminated water.

The nano-structure manipulation of nanofiltration membranes to produce a surface with salt rejection selectivity was achieved with Linder and Oren (2006). Membranes were prepared having above 70% rejection to NaCl and less than 40% rejection to $CaCl_2$ in single solution. This monovalent/divalent cation selection is very important to minimize membrane fouling by calcium carbonate or sulphate salts and to keep the Na to Ca ratio to a proper level for agricultural purposes. In a similar approach, the nanostructure surface modification of microporous ceramics was achieved by Wegmann et al. (2008) for the aim of efficient virus filtration. The procedure consisted of coating the internal surface area of highly porous elements with a colloidal nanodispersion of hydrated yttrium oxide. It was then heat treated to obtain an electropositive Y_2O_3 coated surface. Modified nanostructure filters were able to remove about 99.99% of 25 nm diameter MS2 bacteriophages from feed water of pH between 5 and 9.

Water filtration membranes fabricated from nanomaterials are already being promoted by water treatment companies. For instance, Agronide (Pittsburgh) has a product called "*NanoCeram*", which is a purifier that uses 2 nm diameter alumina nanofibres to remove 99.9999% of bacteria, viruses and protozoan cysts from water (Smith 2006).

The use of nanostructured material for improving membrane filters will gain more interest in the near future, because of unlimited benefits that accrue from producing membranes with superior performance in terms of organic and biological contaminants removal, with metal selectivity, that are resistant to fouling, durable and cost-effective.

Additionally, nanoreactive material has been used to synthesize membranes for use in water treatment. Nanoreactive membranes were able to decompose pollutants such as 4-nitrophenol (Dotzauer et al., 2006) and bind metal ions (Hollman and Bhattacharyya, 2004) in water solution. Polysulfonate ultrafiltration membranes impregnated with silver nanoparticles were found effective against *E. coli* K12 and *P. mendocina* bacteria strains and showed a significant improvement in virus removal (Zodrow et al., 2008). Additionally, the nanosilver impregnated membranes (nAg-PSf) were resistant to biofouling mainly because the attachment of bacteria to the membrane surface was prohibited by Ag^+.

Recently, TiO_2 nanowire membrane has been successfully fabricated with the capability of filtering organic contaminants from water with simultaneous photocatalytic oxidation

(Xiao et al., 2007). Nanowire membrane had uniform thickness, flexible, with nanowires of 20-100 nm in diameter (Figure 1). It showed similar photocatalytic activity as P-25 for decomposing humic acid in water and exhibited excellent anti-fouling ability Zhang et al. (2008).

Composite photocatalytic membranes that combine the separation technology provided by the membrane process and the photocatalytic activity of catalysts, were studied by several researchers (Molinari et al., 2000; Zhang et al., 2006; Yang and Li, 2008). TiO_2/Al_2O_3 composite membranes fabricated by following the extrusion method and sol–gel/slip casting method effectively decomposed Direct Black168 dye (82% removal) when photocatalysis is coupled with membrane separation (Zhang et al., 2006). Similarly, Yang and Li (2008) have successfully employed the extrusion method and sol–gel/slip casting method to prepare inside-out tubular TiO_2/Al_2O_3 composite membranes. They reported that the prepared tubular TiO_2/Al_2O_3 composite membranes degraded a great amount of the water pollutant of concern from the target wastewater that had a final permeate turbidity of lower than 0.75 NTU.

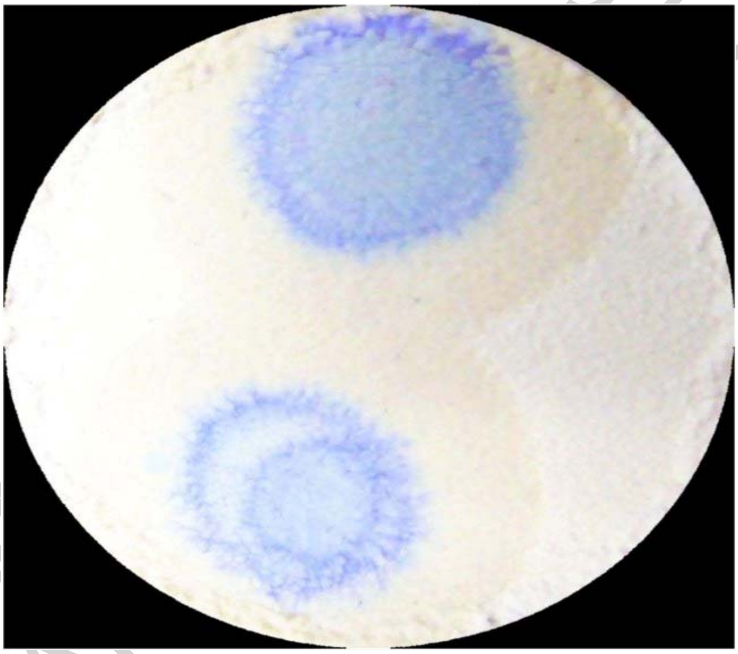

Figure 1. TiO_2 nanowire membrane with simultaneous photooxidation potential

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Biographical Sketches

Ibrahim El Saliby is currently a PhD student in the School of Civil and Environmental Engineering at the FEIT, UTS. He is working on the development of new filtration membranes from metal nanomaterial. He holds an Engineering diploma in plant production from the Faculty of Agricultural Sciences at the Lebanese University (2000), and a master degree in plant sciences from the Faculty of Agricultural and Food Sciences at the American University of Beirut (2002). As an expert in plant propagation and production, especially of native wild Lebanese plants, he was the plant production coordinator in IBSAR production team at the American University of Beirut from 2002 to 2007. He joined the FEIT staff at UTS in February 2007 for studying the ways to improve the photocatalytic activity of titania produced from the incineration of sludge.

Dr H.K. Shon is currently a UTS Chancellor’s postdoctoral research since 2006. His research interests include membrane processes and new analytical methods for wastewater treatment and reuse. He has made significant contributions to the understanding of membrane fouling in wastewater treatment processes.

Dr J. Kandasamy is Senior Lecturer in the Faculty of Engineering University of Technology, Sydney, Australia. He obtained his PhD from University of Auckland., New Zealand where is also obtained his Bachelor in Civil Engineering and Masters in Civil Engineering. He has worked in the New South Wales Government as a Senior Engineer for 15 years and has wide industry knowledge.

Dr S. Vigneswaran has been working on water and wastewater treatment and reuse related research since 1976. During the last twenty years, he has made significant contributions in physico-chemical water treatment related processes such as filtration, flocculation, membrane-filtration and adsorption. His research activities both on new processes development and mathematical modeling are well documented in reputed international journals such as Water Research, American Institute of Chemical Engineers Journal, Chemical Engineering Science, Journal of American Society of Civil Engineers, and Journal of Membrane Science. He has also been involved in a number of consulting activities in this field in Australia, Indonesia, France, Korea, and Thailand through various national and international agencies. He has authored two books in this field at the invitation of CRC press, USA, and has published more than 230 papers in journals and conference's proceedings. Currently a Professor of the Environmental Engineering Group at the University of Technology, Sydney, he was the founding Head of and the founding Co-ordinator of the University Key Research Strength Program in Water and Waste Management. He is coordinating the Urban Water Cycle and Water and Environmental Management of the newly established Research Institutes on Water and Environmental Resources Management and Nano-scale Technology respectively.