EVALUATION OF NANOTECHNOLOGY FOR APPLICATION IN WATER AND WASTEWATER TREATMENT AND RELATED ASPECTS IN SOUTH AFRICA

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by

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Executive Summary

Nanotechnology is the art, science and engineering for manipulating objects at the 1 - 100 nm scale. It involves design, synthesis, manipulation, characterization and exploitation of materials and devices with structures defined in terms of nanometers. Nanotechnology is not a single science but includes aspects of chemistry, physics, biology, material science, etc. Chemists, physicists, biologists, medical doctors, engineers and computer scientists typically form part of teams that work in the nanotechnology field.

Nanotechnology is generally regarded as a new generation of technology with the potential to revolutionise most facets of the world we live in. This includes virtually all aspects of our daily lives, including health and health care, the materials and equipment we use and the way they are manufactured, our environment and protection thereof. However, the 'revolution' will not happen overnight and very large investments in research and development and production will be required in the process.

Nanotechnology is an enabling technology that, potentially, could lead to cost-effective and high-performance water treatment systems. It has the scope and performance potential to generate technically and environmentally appropriate solutions to water related problems over a wide spectrum. In addition to improved treatment technologies, it offers the promise of cleaning up historic pollution problems. It has the potential for instant and continuous monitoring of water quality, but its biggest impact on the environment could be in pollution prevention through improved clean technologies for better conversion of materials and elimination of waste production.

Challenges that need to be resolved before nanomaterials could be successfully used on large scale in water treatment include safety evaluation, large scale production facilities, safe disposal of wastes and energy efficiency. These are major challenges that might cause major delays in the large scale application of nanotechnology in water treatment.

The main findings of an investigation into nanoscale research in South Africa (Pouris, 2007) is that it is driven by individual researchers' interests and it is in its early stages of development; the country's nanoscale research is below what one would expect in light of its overall publication output; the country's nanoresearch is distributed at a number of Universities with a sub-critical concentration of researchers.

From an initial survey of nanotechnology developments in the water field and problems in the South African water industry, the authors have compiled the following preliminary list of areas in which research on water-related nanotechnology could be initiated and existing South African efforts possibly be coordinated to address South African problem areas. Three general areas have been identified: (i) water treatment technology including development of improved membranes and development of activated filter media, (ii) development of real-time diagnostic tools for water quality assessment, (iii) development of membrane-based wastewater treatment technology.

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1. INTRODUCTION

1.1 What is nanotechnology?

Nanotechnology is a field of research and innovation concerned with building materials and devices on the scale of atoms and molecules. It is the art, science and engineering for manipulating objects at the 1 - 100 nm scale. It involves design, synthesis, manipulation, characterization and exploitation of materials and devices with structures defined in terms of nanometers (in at least one dimension) (Booker and Boysen, 2005). This refers to any substance that is engineered at the scale of a few atoms (about three to five) across. By manipulating substances at the atomic level, a substance can be altered so that it acquires different properties compared to the substance in macro or bulk form. A nanometre is one-billionth of a metre, 10^{-9}m or ten times the diameter of a hydrogen atom. At such scales, the ordinary rules of physics and chemistry no longer apply. This means characteristics such as colour, strength, conductivity and reactivity can differ substantially between the nano-scale and the normal size ranges.

Nanotechnology is hailed as a new generation of technology with the potential to revolutionise many facets of the world we live in. This includes virtually all aspects of daily life, including health and health care, the manufacturing and use of materials and equipment, the environment and protection thereof. It is said to be able to massively increase manufacturing production at significantly reduced costs. Products of nanotechnology will be smaller, cheaper, lighter yet more functional and require less energy and fewer raw materials to manufacture. However, the 'revolution' will not happen overnight and very large investments in research and development will be required in the process.

Nanotechnology is not a single science but includes aspects of chemistry, physics, biology, material science etc. Chemists, physicists, biologists, medical doctors, engineers and computer scientists typically form part of teams that work in the nanotechnology field. It is an enabling technology that, potentially, could lead to cost-effective and high-performance water treatment systems (Savage and Diallo, 2005). It has the scope and performance potential to generate technically and environmentally appropriate solutions to the water problem. Nanotechnology can be defined as having the following features:

- It involves research and technology development at the 1 nm–100 nm range
- It creates and uses structures that have novel properties because of their small size
- It builds on the ability to control or manipulate at the atomic and molecular scale

At the nano-scale the interactions and physics between atoms display 'exotic' properties that are absent at larger scale because at this level atoms leave the realm of classical physical properties behind and enter the realm of quantum mechanics.

Nanotechnology includes a bewildering array of activities including: molecular manufacturing, supramolecular and self assembly/organization; biomimicry; nanoparticles (e.g. Bucky balls and carbon nanotubes), nanospheres, nanocups and nanorods; nanobots (nanorobots); colloids, micelles, vesicles and nano-emulsions; clathrate complexes and intercalation compounds.

The National Science Foundation in the USA predicts that the global marketplace for goods and services using nanotechnologies will grow to $1 trillion by 2015, and there are already over 500 products being sold that claim they are made with nanoscale or engineered nanomaterials. These include products like self-cleaning windows, automobile paint, sunscreens, and tennis rackets. In the future, a marriage of nano- and biotechnology will likely create a whole new generation of

drugs, biomedical devices, and other solutions to some of our most challenging medical problems (Macoubrie, 2005).

1.2 Comparative size illustration

10^{0} m=1 m=1000 mm	Human length (~1.7 m)
10^{-1} m=10 cm	
10^{-2} m=1 cm	
10^{-3} m=1 mm=1000 μm	Sand filter grain (0.5 mm=500 μm)
10^{-4} m=0.0001 m=100 μm	Hair diameter (75 μm=75000 nm)
10^{-5} m=10 μm	Red blood cells (5000 nm=5 μm) *E.coli* (2000 nm= 2 μm)
10^{-6} m=1 μm=1000 nm	Visible colour (400-700 nm)
10^{-7} m=100 nm	Virus (50 nm) Pore size of UF membrane (50-200 nm) Colloidal particles (20-100 nm)
10^{-8} m=10 nm	DNA molecule (2 nm wide) Typical protein (3 nm diameter)
10^{-9} m=1 nm	Buckyball(1 nm)
10^{-10} m=0.1 nm=1 Ä	Hydrogen atom

1.3 Nanotechnology in South Africa

An interdisciplinary research field such as nanoscience requires substantial resources, both in terms of equipment and human resources with multi-disciplinary knowledge. This often prevents research groups from attaining sufficient critical mass to be effective. This situation is particularly relevant in South Africa where scientists and engineers are in high demand in all sectors of the economy.

Pouris (2007) investigated the state of nanotechnology in South Africa through a scientometric analysis of nanoscale research in South Africa during the period 2000–2005. The article identifies trends over time, major institutional contributors, journals in which South African authors publish their research, international collaborators and performance in comparison to four comparator countries (India, Brazil, South Korea and Australia). The major findings of the investigation are: nanoscale research in South Africa is driven by individual researcher's interests and it is in its early stages of development; the country's nanoscale research is below what one would expect in light of its overall publication output; the country's nanoresearch is distributed at a number of Universities with a sub-critical concentration of researchers.

A number of initiatives have been taken in South Africa to support research and development in the nano-science and nanotechnology fields:

(i) A National Nanotechnology Strategy was developed and published by the Department of Science and Technology.

The strategic objectives include the support of long-term nanoscience research, development of the required human resources and supporting infrastructure and to stimulate new developments such as advanced materials, nano biomaterials and advanced materials for IT technologies. In order to demonstrate the benefits of nanotechnology, the strategy makes provision for development of so-called Nanotechnology Flagship Projects. The following six focus areas were identified for the flagship projects:

- Water
- Energy
- Health
- Chemical and bioprocessing
- Mining and minerals
- Advanced materials and manufacturing

Success indicators for the strategy include:

- Impact of nanotechnology on the quality of life of previously marginalised sectors
- Commercial impact including direct investment and return on investment
- Rate of technology transfer of nanotechnology to existing industry
- Impact of nanotechnology based solutions on social upliftment and quality of life
- Quantity and quality of contributions to international journals
- Quantity and quality of intellectual property

(ii) A South African Nanotechnology Initiative (SANi) was formed in 2002 between twelve universities, four industrial councils and ten industrial companies.

(iii)A Nanotechnology Innovation Centre is in the process of being established on initiative of DST/Mintek, the water Research Commission and the Medical Research Council.

Most local universities have some ongoing research initiatives in the nanotechnology field. Mintek has been steadily developing the critical mass in nano-science and nanotechnology, specifically in the field of biomedical diagnostics. The resources that have been created are unique in South Africa and include a team of interdisciplinary researchers, ranging from drug researchers, chemists and chemical engineers, materials scientists to physicists. In addition, the characterisation infrastructure and capability is one of the most comprehensive on the continent (Van der Lingen, 2006).

1.4 Nano concerns

Concerns have been expressed over releasing nanoparticles and nanomaterials into the environment without a thorough understanding of pathways, reactions and eventual fate of such particles. Research has for example shown that nano-sized particles accumulate in the nasal cavities, lungs and brains of rats, and that carbon nanomaterials known as 'buckyballs' induce brain damage in fish.

The US-based Centre for Responsible Nanotechnology, have raised concerns about the following aspects of nanotechnology (UN Millennium project 2005):

- The toxicity of bulk material, such as solid silver, does not help predict the toxicity of nanoparticles of that same material.

- Nanoparticles have the potential to remain and accumulate in the environment.
- They could accumulate in the food chain.
- They could have unforeseen impacts on human health.
- The public has not been sufficiently involved in debates on the applications, uses, and regulation of nanotechnology.
- 'Grey goo': Tiny robots generated with nanotechnology could acquire the ability to self-replicate.
- If the rich countries are the main drivers of the development of nanotechnology, applications which benefit developing nations will be side-lined.
- Unless rapid action is taken, research into nanotechnology could progress faster than systems can be put in place to regulate its applications and their uses.

1.5 Conventional water technology on nano-scale

Conventional water and wastewater treatment employs a variety of physical-chemical and biological processes to produce drinking water and to purify wastewater. The bulk of the substances that have to be removed in drinking water treatment fall in the micro- and nano-scale range. This includes removal of:

- Monovalent ions such as Na^+ and Cl^- by means of reverse osmosis
- Hardness causing Ca^{2+} and Mg^{2+} ions by means of ion exchange, chemical softening and nanofiltration
- Organic contaminants that cause taste and odour problems by means of activated carbon adsorption
- Organic contaminants that might be harmful by means of oxidation (including catalytic oxidation) by ozone, ultra-violet irradiation, chlorine
- Colloids that cause turbidity by means of chemical coagulation or ultrafiltration
- Pathogenic viruses, bacteria and protozoa by means of disinfection or membrane processes

Although these processes function on the micro- and nano levels, they are normally not considered as nanotechnology since the materials and equipment that are used are produced conventionally. One could however, consider some of these processes as an ‘older generation’ of nanotechnology. Examples include the use of activated carbon adsorption with nanometre size internal pores and internal surface area of 1000 m^2/g or more for the removal of dissolved organic contaminants. The new generation nanotechnology materials include the use of carbon nanofibres, nanotubes and aerogels for adsorption. Potential advantages of the new technology could be better control of the formation of the internal pore structure and more effective and cheaper regeneration through imbedded catalysts for oxidation of adsorbed substances.

Another example is the use of membrane technology for removal of dissolved inorganic substances, e.g. reverse osmosis for sea and brackish water desalination, and nanofiltration and ultrafiltration for removal of colloidal and organic matter from water and effluents. Here too, the application is on the nano-level, but the manufacturing of the membranes employs conventional technology. The potential benefits of nanotechnology for the manufacturing of membranes could include aspects such as uniform pore size, thinner active layers with lower hydraulic flow resistance, modification of surface properties of the membrane material to resist fouling, inclusion

of active nanoparticles in the membrane material to facilitate separation of species, to resist fouling and to facilitate cleaning.

The fact that these processes function on the nano level presents a significant opportunity for the early introduction of nanotechnology in water treatment. It should be relatively simple (compared to development of new generation nanotechnology processes) to employ nanotechnology for the modification and improvement of existing materials and equipment such as reverse osmosis and nanofiltration membranes, activated carbon, ion exchange resins, etc. to be used in existing processes.

2. Current examples of nanotechnology/nanomaterials in water treatment

2.1 Nanostructured Membranes

Membranes are an important passive element in water treatment systems that concentrate and remove contaminants from water. Nanotechnology can aid tailoring of membrane thickness, pore size distribution, permeability, and surface chemistry. Membrane design via templating chemistry allows entirely new and more effective membrane architectures to be engineered and developed. An example would be reactive nanostructured ceramic membranes for remediation of organic waste in water.

Researchers at Lawrence Livermore National Laboratory and the University of California, Berkeley have experimentally demonstrated the predicted fast transport of water and gases through membranes containing carbon nanotube pores. The membranes could find a use in energy-efficient desalination or gas separations. Transport of gas and water through the nanotubes was much higher than predicted by classical diffusion or hydrodynamics models. The researchers believe the fast transport occurs because of the smoothness of the nanotube interiors or because of molecular ordering phenomena. They estimated the pore density at 2.5×10^{11} per sq. cm.

The nanotube membranes could offer a combination of high selectivity and high flow rate. Although the membranes have an order of magnitude smaller pore size, the enhanced flow rate per pore and the high pore density makes them superior in both air and water permeability compared to conventional polycarbonate membranes. (www.nanotechweb.org May 2006)

2.2 Nano Filters

Carbon nanotube filters have been developed that can remove nano-scale contaminants, e.g. 25 nm sized polio viruses and larger pathogens such as *E. coli* and *Staphylococcus aureus* bacteria (Anon, 2004).

Electrospun nanofibrous membranes have potential for pre-treatment of water prior to reverse osmosis or as pre-filters to minimize fouling and contamination prior to ultra- or nano-filtration (Gopal *et al.*, 2006).

Argonide Corporation developed a new nanofilter (Anon, 2005). This “Superfilter” is targeted primarily at purifying water and industrial solutions. The manufacturer claims superior performance for filtering particles from microns down to a few nanometres.

Nanofibres can be used in filter media, adsorption layers in protective clothing, etc. This is mainly due to their high surface area and porosity (Subbiah *et al.*, 2005).

Fibre diameter is the most important factors that control the performance of a filter medium separating dispersed liquid drops in an immiscible liquid-liquid mixture. Shin *et al.* (2005) show that adding nanofibres to conventional micron-sized fibrous filter material improves the separation efficiency of the filter media. A significant observation is that optimum performance is attained at minor additions of nanofibres, e.g. 1,6 mass % 250 nm diameter nylon 6 nanofibres to 5 μm diameter glass fibres in the filter (Shin *et al.*, 2005). Shin *et al.* (2005) also showed that addition of small amounts of polystyrene nanofibres (from recycled expanded polystyrene) significantly improved the coalescence performance of the filter medium.

2.3 Nanoscale catalysts

Nanoscale catalysts have potential for treating particularly challenging contaminants in water that must be removed down to a very low level. The catalytic particles may either be dispersed homogeneously in solution or deposited onto membrane or filter structures. These special catalysts are activated via either hydrogen or light (photocatalysts).

The production of metal oxide catalyst with nanoscale crystal sizes offers an attractive means of controlling catalytic behaviour in selective oxidation reactions. In an experiment conducted by Vidal-Michel (2003) the catalytic behaviour of MgO nanocrystal-supported vanadium was compared to that of vanadium supported on conventionally prepared MgO when conducting an oxidative dehydration reaction of butane. It was found that nanocrystals gave higher butane selectively for weight loadings of 5, 15 and 25%. It was hypothesised that the chemical nature of the support, specifically acid/base properties, was responsible for the differences noted in catalytic behaviour.

Gu *et al.* (2004) investigated the destruction efficiencies of nanoscale copper oxide and nanoscale nickel oxide for methanol. It was found that nanoscale CuO and NiO were highly active and stable catalysts for complete methanol oxidation at temperatures ~100°C lower than their microscale counterparts. The higher activity per gram of the nanocatalysts was attributed to their higher surface areas, which were roughly 2 orders of a magnitude higher than the microscale catalysts (Gu *et al.*, 2004).

Koper *et al.* (1993) investigated the ability of nanoscale CaO particles to destructively adsorb chlorinated hydrocarbons such as CCl_4 and $CHCl_3$. Thermodynamically the reaction is favourable, but kinetic considerations mandate the use of high surface area CaO, i.e. nanoparticles. Klabunde *et al.* (1996) also found that MgO and CaO nanocrystals are capable of destructively adsorbing organophosphorus compounds and chlorocarbons.

Environmentally hazardous and toxic acid catalysts such as H_2SO_4, HF, $AlCl_3$, $AlBr_3$, BF_3, etc., can be replaced with convenient, environmentally safe, and effective solid superacid catalysts: Olah *et al.* (1999) grafted superacid groups (e.g. fluoroalkylsulfonic acid and perfluoroalkylsulfonic) to suitable nanoscale carrier materials (e.g. fullerene with a size of about 1 nm or 100 to 50000 nm polystyrene beads). These products act as catalysts for a variety of reactions including substitution and addition reactions, polymerisation, hydrogenations and oxidation.

2.4 Nanoscale photocatalysts

Photocatalytic degradation of toxic chemicals that pose severe environmental pollution has been studied extensively in the past two decades. Most studies were devoted to the decontamination of air and water.

A typical target for photocatalysts is the removal of organo-chlorine compounds and organic aromatic contaminants, e.g. pesticides, from groundwater. Titanium dioxide (anatase or rutile), in combination with UV illumination, is capable of photo-oxidizing a variety of organic molecules. Yu *et al.* (2005) reviewed the utility of nano-photocatalysts for environmental pollutant degradation with such nano-photocatalysts. They cover treatment applications such as chemical industry effluents and wastewater from papermaking, refineries, dyeing plants and agriculture (containing pesticides).

Dong Jang *et al.* (2004) considered the effect of particle size and phase composition on the photocatalytic performance of TiO_2 nanoparticles with respect to methylene blue, bacteria and ammonia gas. Degradation performance, with respect to methylene blue under black-light illumination, was directly proportional to the anatase content and inversely proportional to the particle size. The decomposition of bacteria and ammonia by TiO_2 nanoparticles under the illumination of fluorescent light showed a similar trend (Dong Jang *et al.,* 2004). Wang *et al.* (2002) showed that doped nano rutile has significantly higher photo catalytic activity than conventional rutile with respect to the photocatalytic degradation of methyl orange as model compound. Ding *et al.* (2000) found that silica-dispersed titanium (SiO_2-TiO_2) is also an effective photocatalyst for the removal of phenol. Ilisz *et al.* (2004) studied the degradation of 2-chlorophenol by a combination of photocatalysis (by TiO_2 nanoparticles) and clay adsorption.

Hariharan (2006) investigated the photodegradation of organic contaminants using the fluorescence emission characteristics of ZnO nano particles in aqueous solutions. The organic contaminants included aromatic solvents and other aliphatic and aromatic chloro compounds. It was found that ZnO nanoparticles outperformed other semiconductor systems and also acted as a non-specific sensor for the presence of the common contaminants in water.

ZnAl-layer double hydroxides show higher photocatalytic efficiencies than ZnO crystals towards the destruction of phenol in waste water (Patzkó *et al.*, 2005).

The performance of nano-sized photocatalysts is determined by their specific surface area (Cun *et al.*, 2002). Other factors affecting photocatalytic activity in coupled oxides such as ZnO/SnO_2 include the heat-treatment temperature, the pH of the reaction suspension and the presence of electrolytes, e.g. NaCl, KNO_3 and K_2SO_4 in the suspension (Cun *et al.*, 2002).

Hu *et al.* (2005) prepared ZnS nanoparticles using a low cost, self-assembly synthetic route. They found that the resultant ZnS photocatalytically degrades Eosin B.

Wilcoxon *et al.* (1999) used visible light and MoS_2 nanoclusters ($\phi < 10$ nm) as photocatalysts to effectively remove aromatic hydrocarbon and chlorinated hydrocarbon contaminants from water.

2.5 Nanoscale sorbents

General water treatment schemes can remove most of the waste from water. However, targeted treatment schemes are essential for near complete removal of highly toxic compounds. Catalytic remediation is not an effective removal option for heavy metal species, e.g. arsenic. Thus water treatment schemes focus instead on sorption onto either polymers or particle additives (Koh and Dixon, 2001).

Iron oxides are known to bind arsenic. Nanoscale hydrated iron(III) oxide (HFO) particles has a high sorption affinity towards arsenates and arsenites (Cumbal *et al.,* 2005). They used commercially available cation and anion exchangers as host materials for dispersing polymer-supported HFO nanoparticles within a polymer phase. The resulting polymeric/inorganic hybrid sorbent particles were subsequently used for arsenic removal under laboratory conditions. It was found that anion exchanger substrates provided substantially higher arsenate removal capacity than the cation counterpart.

Magnetite (Fe_3O_4) nanoparticles can provide a core system for aqueous arsenic removal. Iron oxide surfaces show preferential sorption of arsenic species, and in the right size range these magnetic particles can be removed from water via magnetic separation (Halford, 2006). A coating of oleic acid helps to prevent the particles from clumping together. Particle size (surface area) is important in arsenic remediation: 12 nm particles of Fe_3O_4 removed nearly all the arsenic from a solution while 300 nm particles removed only 30% (Halford, 2006). Vaclavikova *et al.* (2006) claim that nanoscale magnetic materials also adsorb heavy metal ions (Cu(II), Cd(II), Pb(II)) from aqueous solutions. Li *et al.* (2006) demonstrated that iron nanoparticles act as sorbent and reductant for the sequestration of Ni(II) in water.

Boumadiane *et al.* (1998) showed that water treatment with Zn-Al-Cl layered double hydroxides effectively removes chromate and dichromate ions. Álvarez-Ayuso and Nugteren (2005) showed that calcined hydrotalcite provided an effective system to treat chromium finishing wastewaters. The most stringent discharge limit for such industrial streams were achieved with between two and four consecutive removal cycles on C-HT at a dose of 2 g/l.

Nonionic organic contaminants (NOCs) such as benzene, phenol, and toluene from contaminated wastewater can also be effectively sorbed by organo-modified minerals (Koh and Dixon, 2001). Modified montmorillonite complexes are effective sorbents for NOCs such as phenol, benzene, and toluene in aqueous solutions and may have practical applications in wastewater purification (Koh and Dixon, 2001). Antibiotics, e.g. tetracycline and sulphonamide can be removed from water by micelles pre-adsorbed on montmorillonite clays (Polubesova *et al.*, 2006).

Klabunde *et al.* (2005) teach the removal of organosulphur contaminants from fluids using metal oxide sorption. The procedure comprises contacting the fluid containing organosulphur with mesoporous, nanocrystalline metal oxides, e.g. MgO, CeO_2, AgO, SrO, BaO, CaO, TiO_2, ZrO_2, FeO, etc. Stengl *et al.* (2003) found that nanoscale MgO particles, obtained from $Mg(OCH_3)_2$, converted solutions of sulphur mustard into non-toxic products.

Yuan (2004) discovered that allophane (a natural nanomaterial) is an effective sorbent of copper. He also found that a surface-modified smectite (i.e. a modified nanomaterial) is an excellent sorbent for naphthalene and 17β-estradiol.

Nanosized metal sulphide powders of Ag_2S, CuS, FeS, Ga_2S_3, In_2S_3, MnS, NiS, and ZnS can be used as liquid-phase and gas-phase sorbents for mercury (reference?).

2.6 Nanoscale particle reductants

Nanoparticles have potential in water and wastewater treatment and in air pollution control (Li *et al.*, 2006a). Important properties of such nano-based particles include particle size, structure, density and the intrinsic reactivity of surface sites (Li *et al.*, 2006a). Lu (2002) showed that biomineralization in the presence of natural minerals at the nano scale can lead to "self-purification".

Nanoparticles, especially nano-based iron materials, turn out to be remarkably effective tools for cleaning up contaminated soil and groundwater. Nano-based iron materials are much more effective than conventional iron powders. Owing to their smaller size they can be suspended in water and pumped straight to the contaminated site easily (Li *et al.*, 2006).

Nanoscale zero-valent iron (Fe^0) is an effective particle reducer. When this metallic iron oxidises in the presence of organic contaminants, such as trichloroethane, trichloroethylene, tetrachloroethylene, or carbon tetrachloride, these organic compounds are broken down into simpler carbon compounds that are less toxic. Furthermore, the oxidised iron can transform heavy metals such a lead, nickel, or mercury to an insoluble form (Li *et al.*, 2006). Thus nano-iron particles have wide-ranging utility for removing chlorinated organics, heavy metals (e.g. arsenic, chromium and lead), and inorganics (Li *et al.*, 2006a; Tratnyek and Johnson, 2006). They are also effective alternatives for nitrate removal allowing denitrification of groundwater (Liou *et al.*, 2005). Lowry *et al.* (2004) found that nanoscale Fe^0 is capable of dechlorinating dissolved polychlorinated biphenyl (PCBs) congeners in water/methanol solutions. Liu *et al.* (2005) found that nanoscale Fe^0 particles are capable of dechlorinating trichloroethylene (TCE) plumes.

Nyer and Vance (2001) paint an optimistic picture for nano-scale iron as a treatment route for dehalogenation. Gillham (2003) points out potential difficulties and discusses the limitations of nano-scale iron technology for dehalogenation.

Schrick *et al.* (2002) studied the hydrodechlorination of trichloroethylene (TCE) to hydrocarbons using bimetallic nickel-iron nanoparticles. Henn *et al.* (2006) found that bi-metallic (iron and palladium) nanoscale particles suspension fosters the dechlorination of chlorinated volatile organic compounds in a non-aqueous phase. The degradation was largely due to abiotic degradation as the solvents were destroyed via anaerobic corrosion chemistry. Zhang *et al.* (2006) dechlorinated pentachlorophenol (PCP) by the Ni-Fe bimetallic nanoscale particles in aqueous solutions. Rapid and complete dechlorination of several chlorinated organic solvents and chlorinated aromatic compounds was achieved by using the nanoscale bimetallic particles. Application of ultrasound enhanced dechlorination efficiency from 46% in 30 min to 96%. Zhang *et al.* (1998) suggest that the base metal (Fe or Zn) within the bimetallic complex serves primarily as electron donor while Pd or Pt serves as catalyst.

2.7 Nanobiocides

Sunayama *et al.* (2002) propose that Cu-HT can be used as an alternative disinfectant to chlorine in a water purification system. Cu-HT possessed strong disinfection activities against Escherichia coli and phage Q β, whereas Zn-HT showed bactericidal activity against E. coli, Salmonella? aureus and phage Q β (Sunayama *et al.*, 2002). The remarkable disinfection activity of Cu-HT against phage Q β seemed to be based on the cooperative action of copper in Cu-HT and the direct contact of phage Q β cells to the hydroxyl layers on the surfaces of the Cu-HT particles (Sunayama *et al.*, 2002).

Buckyballs are effective bactericidal agents against both gram positive and negative bacteria with EC_{50} values of 1 mg/L, and ~ 10 nm.

Some nanoscale powders MgO and CaO carrying active forms of halogens such chlorine and bromine (i.e. $MgO.Cl_2$ and $MgO.Br_2$) possess antimicrobial properties. When these ultrafine powders come in contact with vegetative cells of *E. coli*, *Bacillus cereus*, or *B. globigii*, over 90%

are killed within a few minutes and spore forms of the bacillus species are decontaminated within several hours (Koper *et al.*, 2002).

Carnes *et al.* (2004) claims nanocrystalline oxides and hydroxides of Al, Ca, Ce, Mg, Sr, Sn, Ti and Zn as biocides for use as sprays, fogs, aerosols, pastes, gels, wipes or foams.

Silver ions and silver-based compounds, including silver nanoparticles, act as bactericidal nanomaterials (Morones *et al.*, 2005). The bactericidal properties are size dependent with nanoparticles with sizes 1-10 nm directly interacting with bacteria.

Silver can kill microbes even in bulk form but is more efficient as nanoparticles. Nanosilver also can be easily incorporated into a variety of products, such as food containers and shoe liners. That characteristic has made it the most common type of nanomaterial currently marketed to consumers. Nanosilver has also been added to bandages to speed healing.

Conventional materials, such as carbon or gold, exhibit unconventional properties when manufactured on a nanoscale. That is largely because the tiny particles have large surface areas relative to their small mass, which makes them very chemically reactive.

Carbon, for example, does not conduct electricity well in its bulk form but does so very well when spun into fibres a few nanometers in diameter. And though bulk gold hardly reacts with substances around it, nanoparticles of gold can destroy bacteria and other living cells.

The US Environmental Protection Agency has decided to regulate a large class of consumer items made with microscopic "nanoparticles" of silver, part of a new but increasingly widespread technology that may pose unanticipated environmental risks.

2.8 Environmental clean-up using nanoparticles

Nano remediation technologies may be classified as absorptive or reactive. Absorptive remediation removes contaminants (especially metals) by sequestration, whereas reactive remediation technology leads to the degradation of contaminants, sometimes all the way to benign products.

In situ nanotechnology remediation techniques treat the contaminants in place, whereas *ex situ* nanotechnology remediation techniques remove the contaminants to a more convenient location (Tratnyek *et al.*, 2006). *In situ* degradation of contaminants, when feasible, is often preferred over other approaches as it is likely to be more cost effective. It requires delivery of the treatment to the contamination. Nanotechnology has relevance in this regard owing to the possibility of injecting nanosized (reactive or absorptive) particles into contaminated porous media such as soils, sediments and aquifers. A variety of types of nanoparticles might be applicable to *in situ* remediation (for example non-ionic amphiphilic polyurethane or alumina-supported noble metals). However, nanoparticles that contain nanoscale zero-valent iron are attracting the greatest interest (Tratnyek *et al.*, 2006).

Self-assembly mesoporous supports (SAMMS) are prominent examples of a nanotechnology for contaminant remediation by adsorption. SAMMS are created by self-assembly of functionalised surfactant monolayers on mesoporous ceramic supports. This results in very high surface areas with adsorptive properties that can be tuned to target contaminants such as mercury, chromate, arsenate, pertechnate, and selenite (Tratnyek *et al.*, 2006).

Table 1 in the Appendix contains a list of companies involved in the research of the application of nanotechnology in water purification. Nanomaterials for water treatment include nanostructured porous membranes and nanoscale catalytic particles that remove and/or remediate waste.

3. THE ENVIRONMENTAL IMPACT OF NANOWASTE

New and potential impacts of nanomaterials pose a new threat that must be considered as a matter of urgency. Nanomaterials are becoming increasingly common in manufactured goods and are frequently found in products such as cosmetics and other household products. Although nanotechnology brings advanced products and scientific advances to this generation, little scientific information is currently available on the fate of nanomaterial in water and wastewater treatment plants, whether they are present in biosolids or effluent, or their potential impact on the treatment processes

The reality is that not much is known about nanotechnology's potential long term health and environmental effects and the state of knowledge about the actual risk of nanotechnology is incomplete (Friedman *et al.*, 2005).

Substantial literature exists detailing the effects of incidentally produced aerosols on living systems, particularly through inhalation exposures. Virtually nothing is known about the eco-toxicology of nanostructures and nanoparticles produced through liquid phase routes. The rate of nanoparticles movement through water has important implications for efficiency but also for the environmental threat they may pose.

Historically fine particle pollution is closely connected to mining and industrial activities with respect to specific materials, such as coal, asbestos, man-made mineral fibres, and more recently ambient particulate matter (Borm, 2004). Risk factors include the length of exposure, concentrations, particle size and the nature of the particle surface (Borm, 2004).

There is a growing concern over the threats posed by nanowaste on human health and on the environment (Mraz, 2005; Amato, 2004). Materials can behave differently at the nanoscale compared to the way they do in bulk. This potential difference is the reason why some nanoparticles can produce toxic effects even if the bulk substance is non-poisonous. The concern about tiny nanoparticles is further exacerbated by the possibility that they may absorb other toxic substances and thereby become more dangerous. Thus they may convert themselves into toxic materials with the capacity to travel farther through air or water (Amato, 2004).

Free or unconstrained nanoparticles and nanotubes are a greater potential risk than those fixed within a composite or a coating. Should the nanoparticles enter the human body through inhalation, ingestion, or adsorption through the skin, they are able to move around and enter cells more easily than larger particles (Dowling, 2004).

The effect of nanoparticles in the environment, when they come in contact with micro-organisms, is a topic of great concern (Amato, 2004). Water polluted with minute amounts of Bucky balls (C-60 molecules) halt the growth of bacteria and cause brain damage in fish (Mraz, 2005). Even trace amounts can kill half of the human liver and skin cells (Mraz, 2005).

Mraz (2005) is concerned by the fact that it is currently impossible to track the fate of nano particles in the environment. However, Bundschuh *et al.* (2005) developed a Nano-Particle Analyzer (NPA) based on Laser-Induced Breakdown Detection (LIBD). It selectively generates and detects plasma events on colloids in aquatic media. Consequently, the method can be used for

online-monitoring of both non-biological and biological particulate content of water. This makes the technique useful for tracking contamination of pure water by process chemicals or biological matter e.g. in biomedical industry or for example during the purification, transport and storage of drinking water.

Toxicological testing of engineered nanomaterials is in its infancy. Much of what has been observed regarding biological responses to nanomaterials, actually comes from studies in the biomedical and pharmacological sciences, exploring the potential use of nanomaterials in the treatment and prevention of disease. According to Sweet *et al.* (2006) significant absorption of nanomaterials through the skin is unlikely. Furthermore an adequate study on the ingestion and subsequent absorption of nanoparticles has not been done but it is expected that smaller nanoparticles can diffuse faster within the intestine, but surface charge and endocytosis are also likely to be important determinants of gastrointestinal absorption.

Dagani (2003) reports conflicting data regarding adverse affects at the blood brain barrier of potential drug-carrying nanoparticles. Some of the nanoparticles, e.g. carbon nanotubes pose health risks. Nanoparticles appear to be capable of damaging lung tissue in mice and carbon nanoparticles can cause brain damage in fish (Wilsdon, 2004).

Helland *et al.* (2004) conclude that nanoparticles cause more toxic effects in the lungs than bigger particles and can translocate within the environment and the body. However, nanoparticles are likely to cause different impacts to human health, occupation health and the environment, depending on the size, shape and chemical composition of the nanoparticle. Thus there's great uncertainty about what the actual risks of nanoparticle to human health and the environment are.

According to Colvin (2003) nanomaterial exposures and health effects are unlikely to pose any substantial risk to public health given the current prevalent exposure routes and the limited scope of their use. However as the quantity and types of engineered nanomaterials used in society increases, the potential for unintended environmental consequences will also increase. Furthermore, since there's a relative lack of data on engineered nanoparticles, the approach when dealing with the topic of nanoparticle health effects must rely on a patchwork of distantly related information: from pulmonary particle toxicology, a well-developed field of medical research, to biomaterial compatibility studies. Studies aiming to develop nanomaterials for biotechnology can be used to glean more specific information concerning nanoparticle clearance and bioavailability.

Since little is known about the resulting impact on the ecosystem, Dowling (2004) recommends that the use of free manufactured nanoparticles, in environmental applications such as cleaning up contaminated land, should be prohibited until appropriate research on the interaction between the environment and the nanoparticles has been done.

4. THE SOUTH AFRICAN WATER SITUATION

4.1 Introduction

The water resources and water supply systems of South Africa are under mounting pressure both with respect to water quantity as well as with respect to water quality. On the quantity side demands on water sources are increasing at an accelerating rate due to population growth as well as from increasing industrial activities. The rapid rate of urbanisation since independence causes ever-increasing demands for treated water in urban areas, resulting in the need to upgrade and expand water supply systems on a continuous basis to meet these demands.

The accelerating growth in our economy also results in an increasing water demand for power generation and industrial and mining activities. Available raw water supplies are limited and due to increases in demand for treated water, raw water of relatively poor quality has to be used in many cases to meet the growing demand. This often requires advanced treatment processes to produce water of acceptable quality for domestic and industrial use. The fact that most treatment works only employ conventional treatment processes underlines the vulnerability of water supply systems to produce water of the required quality. The water supply problems are in many cases exacerbated by a shortage of suitably trained and experienced staff to manage and operate treatment water plants.

A similar situation exists with respect to urban and industrial wastewater treatment and disposal. The volumes of wastewater to be treated increase in relation to higher water usage and this in turn places greater demands on wastewater treatment systems. The result is often that inadequately treated effluents are discharged to water courses causing continuous deterioration in the quality of many water resources. Industrial and mining effluents also continue to increase in volume and in complexity due to the presence of new and diverse types of contaminants in industrial effluents. In addition, the load of diffuse (non-point) pollution on water sources is increasing due to poor sanitation in many informal settlements and from diffuse runoff from agricultural, mining and industrial activities.

4.2 Water quality problems

The quality of most of our inland raw water sources continues to deteriorate as a result of the discharge of treated effluents into these sources. This gives rise to eutrophication resulting in excessive algal growths which have severe negative impacts on water quality such as production of algal toxins and odour-causing substances as well as production of precursors that produce halogenated by-products (e.g. trihalomethanes) upon chlorination. The presence of algae in raw water also causes problems in the physical removal processes employed to separate algae from water during treatment.

Discharge of treated effluents into water sources has other negative quality effects as well related to the presence of different contaminants in the treated effluents. These include contaminants such as heavy metals and other inorganic contaminants. However, the biggest concern is the presence of various types of organic contaminants in effluents that are not adequately removed by conventional treatment processes from wastewater and that are also not removed effectively during drinking water treatment. These include substances such as medication and lifestyle product residues, endocrine disruptors, pesticides, solvents and many other types. Some are suspected to have negative health effects even at very low concentrations and advanced processes are therefore required to remove these potentially harmful contaminants to very low concentration levels.

It is evident that conventional approaches, conventional treatment technologies and conventional water supply philosophies are not adequate to solve these mounting water supply and water quality problems. New approaches and technologies are needed.

4.3 The potential role of nanotechnology

Advances and developments in the field of nanotechnology could be such a ‘package’ of technologies that could in future play a significant role to prevent and/or solve many of the current water supply and water quality problems. It seems that a window of opportunity has opened and

that a number of exciting developments in this field holds great promise for improved treatment technologies, for water quality assessment and for other environmental applications.

It is the view of the authors that South African scientists and engineers cannot afford not to be actively involved in research and development in the nanotechnology field (specifically water related research) in order to be part of global R&D efforts and therefore to be in a position to benefit from developments and be able to direct research that could serve to ameliorate South Africa's water problems.

A very large body of literature already exists on various aspects of nanotechnology in general including advances on research and development on water-related nanotechnology. Most of the publications are on the laboratory developmental level and it may be a number of years before such processes and techniques are available commercially. However, there are a number of developments that could see implementation in the near future.

South African scientists and engineers have a long history of excellence in research and development in the water field. Examples include the development of water reclamation technology (Windhoek), development of biological nutrient removal technology (Badenpho, UCT), application of desalination technology to treat industrial effluents (Eskom, Sasol), development of membrane manufacturing technology (University of Stellenbosch) and many others. The window of opportunity referred to above presents an opportunity and challenge to South African scientists to become involved in this exciting field. Since nanotechnology is a multi-disciplinary field, it presents an ideal opportunity for South African scientists in different institutions to collaborate by developing R&D expertise on different aspects of nanotechnology in coordinated programs in the water field.

The energy and water industries are very closely related. Up to a third of the cost of a desalination plant is energy for high pressure pumps to force water through membranes. If desalination is to make a substantial difference in providing fresh water to coastal communities, the problems of energy efficiency and renewable energy have to be solved, in both of which nanotechnology can play a role.

5. DISCUSSION

As pointed out above, nanomaterials can already be harnessed to enhance existing water treatment processes. Replacing existing materials and equipment such as activated carbon and reverse osmosis and nanofiltration membranes by nanotechnology modified or produced materials can lead the way for more advanced (or second generation) nanotechnology processes. In view of concerns expresses over the safety and fate of nanomaterials and nanowaste in the environment, it can be expected that entirely new (second generation) materials such as nanobiocides will require long periods of testing before safety approvals are obtained for large scale application.

Renowned participants in a discussion on the 'Project on Emerging Nanotechnologies' sponsored by the Woodrow Wilson International Centre for Scholars identified several scenarios for the future of nanobased water technologies (www.nanotechproject.org March 2007). In the near term, participants said they expected to see new techniques for remediation of water pollution. Many exploratory projects have already been launched with research grants from the U.S. Environmental Protection Agency (EPA) and the NSP. One of the most promising examples is zero-valent nano-iron, which is being tested for use in removing solvents from pumped groundwater. Another new method may prove valuable for cleaning up polluted lakes and

streams. Titanium dioxide nanoparticles could potentially be sprinkled into a contaminated body of water, where they would be activated by sunlight to degrade PCBs and dioxins.

In another decade or so, nanotechnology is expected to have an impact on water treatment, beginning with nanosorbents and bioactive nanoparticles that could be integrated into existing purification systems. These first hybrid technologies would eventually be replaced by entirely new kinds of devices that use nanotechnology to improve the efficiency of filtration, remove more kinds of contaminants and add functions, such as water-quality sensors. Research groups are currently investigating a wide variety of nanomaterials - including carbon nanotubes, zeolites, dendrimers and metal-oxide nanoparticles - for use in such devices. Ultimately, a single membrane might be made to perform multiple tasks - for instance detect, separate out and detoxify a contaminant. If researchers could develop a suit of smart membranes that perform many different filtration tasks, water-treatment plants could mix and match them to address specific needs. To achieve this, participants said, basic research to develop new and improved catalysts and membranes should be pursued over the long term.

Because nanosize particles have a high surface area and can be chemically tailored, many show great potential as sorbents which can remove specific contaminants from water. Nanotubes have been shown to take up lead, cadmium and copper more effectively than activated carbon. Some nanoparticles also act as potent catalysts and could be used to render pollutants harmless. Nanosize iron, for example, can detoxify organic solvents, such as trichloroethylene. Other nanoparticles that are bioactive, such as silver and magnesium oxide, can kill bacteria and might be used in place of chlorine to disinfect water.

Nano-engineered membranes and filtration devices could be used to detect and remove viruses and other pollutants that are difficult to trap using current technologies. For instance, a preliminary technique employs imprinted polymer nanospheres to detect pharmaceuticals - a kind of pollution coming from households that is difficult to spot in waterways and was only recently discovered. Such nanoscale sensors might be helpful for real-time monitoring of these pollutants at wastewater treatment plants and industrial sites. Eventually, "smart" membranes with specifically tailored nanopores might be designed to both detect and remove such pollutants. With greater ability to filter out unwanted materials, industrial wastewater - and even the ocean - could become available to boost the supply of clean water.

6. RECOMMENDATIONS

There are a number of areas in the water field in which active nanotechnology research is currently being pursued. Most of these areas are relevant to South African conditions and it would appear appropriate that South African scientists could become involved in them. However, since relatively large financial investments are required to establish facilities for nanotechnology R&D, it would be essential to focus on priority areas and to coordinate research in order to possibly share facilities and eliminate duplication.

From an initial survey of nanotechnology developments in the water field and problems in the South African water industry, the authors have compiled the following preliminary list of areas in which research on water-related nanotechnology could be initiated and existing South African efforts possibly be coordinated to address South African problem areas. Three general areas have been identified: (i) water treatment technology including development of improved membranes and development of activated filter media, (ii) development of real-time diagnostic tools for water quality assessment, (iii) development of membrane-based wastewater treatment technology.

6.1 Treatment technology

New developments in water treatment technology point to the replacement of conventional processes by relatively simple single step automated processes such as membrane processes. This approach has the advantage that plant operation can to a large extent be automated to make it less dependent on operating staff and better quality water can be produced by these processes. In view of the problems being experienced in water supply systems in South Africa, it seems appropriate that this area should be identified as one of the priority areas for development and application of nanotechnology.

There are a number of possibilities that can be pursued in this area and it would be necessary to define specific aspects in greater detail:

- Application of nanotechnology to develop improved membranes (or adapt/modify/apply available membranes) for water treatment. This could include development of membranes with specific characteristics for rejection/retention/separation of different species. It could include development of membranes with well defined pore structures to improve hydrodynamic flow conditions, resulting in reduced flow resistance and reduced energy requirements. It could include membranes with surfaces containing nanoparticles to improve fouling resistant properties and that can be cleaned and restored effectively.

- Application of nanotechnology to develop/adapt nanoparticles for use in water treatment systems, e.g. filter media coated with (or incorporating) nanoparticles to kill micro-organisms. Such a passive disinfection system will have great advantages over chemical disinfection systems. It would be possible to engineer it into a failsafe disinfection system. Furthermore, there would be no formation of harmful disinfection by-products.

- Similarly, filter media coated with (or incorporating) nanoparticles could be developed/adapted to adsorb harmful organic substances and/or oxidise harmful organics.

- Development of multi-media filtration technology in which different layers of nanomedia could be used to perform different functions.

6.2 Diagnostic tools

Development of nanotechnology based diagnostic tools that can be used for real-time drinking water quality assessment. Such techniques have already been developed to almost practical level. Detection of viruses, bacteria and parasites in real-time is needed rather than culture-based techniques that could provide information in days. Specifically the detection of pathogenic protozoa such as *Cryptosporidium* in drinking water is a need that could be addressed by such developments.

6.3 Membranes for wastewater treatment

As is the case with water treatment, developments in wastewater treatment also point to the increased use of membranes. Although the type of membranes used for this purpose is different to that used in water treatment, the approach towards using nanotechnology for development of improved membranes is similar and the same expertise is required for both areas.

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Appendix A

Table 1: Organizations involved in nanotechnology related water research

Organization	Research focus	Country	Contact details
CBEN	Cost-effective and high-performance water treatment systems using nanomaterials and nanocatalysis for remediation of environmental pollutants	USA	http://cben.rice.edu
INNI	Nanotechnology research with applications in water purification.	Israel	http://www.nanoisrael.org/default.asp
National Centre for Environmental Research (EPA)	Exploratory Research on the application of nanoscale science, engineering, and technology to environmental problems	USA	http://es.epa.gov/ncer/rfa/archive/grants/01/futures.html#Part%201:%20Exploratory%20Research%20on%20the%20Application%20of
NNI	Environmental, health and safety R&D	USA	http://www.nano.gov
NSTI	Nanotechnology-based drinking water-filtering and purification technology for advanced health benefits	USA	http://www.nanosprint.com/workshop/2005/index.html
Peres Centre for Peace	Nanotechnology in the service of desalination, remediation and protection of water	Israel	http://www.peres-center.org
CRN	Environmental impact of nanotechnology in water purification	USA	http://crnano.typepad.com
PLoS Medicine	Lists information about organisations involved in nanotechnology research	Not given	www.plosmedicine.org
Meridian Institute	Comparisons of conventional water treatment technologies with nano-based treatment technologies	USA	http://www.merid.org.
ESAA	Nanotechnology in the environment industry: Opportunities and trends	International	www.esaa.org
NIOSH	Implications and applications of nanotechnology in occupational health and safety	USA	http://www.cdc.gov/niosh/homepage.html
Nanotechnology	Environmental and water-	Australia	www.investaustralia.gov.

Australia	treatment related nanotechnology research		au
University of Aberdeen	Nanotechnology for sustainable water purification	Scotland (UK)	http://www.abdn.ac.uk/mediareleases/release.php?id=230 or go to: http://www.dti.gov.uk/files/file28138.pdf
Woodrow Wilson International Centre for Scholars	Strategies for addressing the risk of nanotechnology in the environment	USA	www.wilsoncenter.org/nano or www.nanotechproject.org
Impart-Nanotox	Objective: Prevent knowledge of the health and environmental implications of nanoparticles from lagging behind the technological advances.	UK	http://www.impart-nanotox.org/impartnanotox/impart_summary.html
MacDiarmid Institute for Advanced Materials and Nanotechnology	Concerned with high quality research and research education in materials science and nanotechnology	New Zealand	http://www.macdiarmid.ac.nz
Science Metrix	Purpose: Evaluation of science, technology and innovation (STI) for economic development and the advancement of knowledge	Canada	http://www.science-metrix.com/eng
Tekes	Public funding organisation for research and development in Finland	Finland	http://tekes.fi/eng/
Nanotechnology now	Lists companies producing nanomaterials		http://www.nanotech-now.com/ or in the saved files: nanotechnology companies
HM government (UK government report)	Researching the potential risks posed by engineered nanoparticles	UK	http://www.defra.gov.uk/