

Progresses in membrane and advanced oxidation processes for water treatment

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Abstract. At present water crisis is not an issue of scarcity, but of access. There is a growing recognition of the need for increased access to clean water (drinkable, agricultural, industrial use). An encouraging number of innovative technologies, systems, components, processes are emerging for water-treatment, including new filtration and disinfectant technologies, and removal of organics from water. In the past decade many methods have been developed. The most important membrane-based water technologies include reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), and nanofiltration. Beside membrane based water-treatment processes, other techniques such as advanced oxidation process (AOP) have also been developed. Some unconventional water treatment technology such as magnetic treatment is also being developed.

Keywords: water treatment methods; waste-water; membranes for water treatment; advanced oxidation process (AOP); nanoparticles; pollutants

1. Introduction

Water treatment consists of many processes to make water suitable for its application or returning to its natural state. Water treatment involves science, engineering, business, and art. The treatment may include mechanical, physical, biological, and chemical methods.

Water covers 70.9% of the earth surface, and is vital for all forms of life. On our planet, it is found mostly in oceans and other large water bodies, with 1.6% of water below ground in aquifers and 0.001% in the air as vapor, clouds (formed of solid and liquid particles suspended in air), and precipitation. Oceans hold 97% of surface water, glaciers and polar ice caps 2.4%, and other land surface water such as rivers, lakes and ponds 0.6%. A very small amount of the earth's water is contained within biological bodies and manufactured products. Nearly one third of all humanity relies only on groundwater.

Water pollution is a major problem in the global context. Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, like serving as drinking water, and/or a marked shift in its ability to support its constituent biotic communities, such as fish. Natural phenomenon such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of water. Each year,

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3.575 million people die from waterborne diseases like diarrhea, which could be easily prevented by treating the water (Slaughter 2010, World Health Organization 2008). In recent years the number of papers in journals, conferences, reviews dedicated to water treatment has risen exponentially. Shannon *et al.* (Shannon 2008) discussed highlights of science and technology being developed to improve the disinfection and decontamination of water, as well as efforts to increase water supplies through the safe re-use of wastewater and efficient desalination of sea and brackish water.

The specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens, and physical or sensory changes such as elevated temperature and discoloration. While many of the chemicals and substances that are regulated may be naturally occurring (calcium, sodium, iron, manganese, etc.) the concentration is often the key in determining what natural component of water is, and what contaminant.

Following are the main contaminants to pollute the water.

1. Salts
2. Metals
3. Chemicals
4. Radionuclide's
5. Emerging contaminants such as endocrine disruptor compounds (EDCs) and pharmaceuticals.
6. Biological species.

In petroleum refining, food processing, metals, chemical processing, and pulp and paper industries a large amount of water is used. The byproduct waste water contains toxic and hazardous materials which make the water polluted. Thus, this waste water neither fits to human consumption nor to agricultural sector. The expansion of industry to the developing world, in addition to local human contamination of fresh water supplies, is making it more difficult to maintain water quality.

Clean drinking water is essential to human and other life forms. Water purification is the removal of contaminants from untreated water to produce drinking water that is pure enough for its intended use, most commonly human consumption. Substances that are removed during the process of drinking water treatment include bacteria, algae, viruses, fungi, minerals such as iron and sulphur, and man-made chemical pollutants. The availability of drinking water has been progressively declining over the past few decades due to problems of urbanization, overpopulation, indiscriminate usage of water and water pollution. Because safe drinking water is essential to human health, the chemical and biological quality of our drinking water is of great importance. Although the presence of chemicals in our drinking water often creates concern about pollution and disease, chemically pure water does not in fact exist in nature. Water, which is known as the universal solvent, *always* contains a variety of chemicals and minerals.

The water that is used for drinking water treatment plants and for many industries is categorized, according to its source, as upland surface water, lowland surface water, groundwater, brackish well water, and seawater. The conventional water treatment processes are in excess of 100 years old and in most works foresheets would include coagulation followed by sedimentation to remove suspended solids and bulk organics, filtration through sand and disinfection with chlorine. More recently the need to remove micro-pollutants such as pesticides has seen the use of granular activated carbon and ozone at many European water treatment works. The sections below will introduce the main treatment processes and look at recent developments and possible alternative processes.

A number of devices are employed primarily for removing undesirable chemicals from water.

Many processes used for water treatment include filtrations, reverse osmosis, absorption, ion exchange, distillation, and advanced oxidation processes.

The objective of the present work is to review recent progresses in water treatment using membrane technology. Advanced Oxidation Processes (AOPs) are also highlighted due to many progresses made in the field since the discovery of semiconductor catalysts for water purification. In the last ten years, a tremendous progress has been made in other techniques for water treatment such as Membrane Bioreactor (MBR), activated carbon systems and ion exchange techniques (Theron 2010, Auffan 2007, Savage 2005, Yang 2006, Cicek 2003, Cao 2005), which are however beyond the scope of this article.

2. Water treatment by reverse osmosis, nanofiltration, ultrafiltration, pervaporation and membrane distillation; and membrane fouling

Filtration through sand has been used effectively for many years to remove particulate material in water including clays and silts, micro-organisms and precipitates of organics and metal ions. The process is based on particles colliding and sticking to the sand as the water flows past. Recent developments include novel filter media, and most significantly, membranes. Membranes are effective at removing key colloidal material as well as pathogenic organisms such as cryptosporidium. However, membranes are prone to fouling and this is a key developmental challenge.

Membranes are commonly used for the removal of dissolved solids, color, and hardness in drinking water. These days, membranes are also widely used in seawater desalination or water treatment. In these applications the membrane processes compete with conventional water desalinating or water treatment techniques, such as multistage flash evaporation or biological sewage treatment plants.

Recently many reviews have appeared in literature about the recent developments for water treatment based on synthetic membranes (Wenten 2002, Kashner 2009). Strathmann (Strathmann 2001) discussed the new developments in membrane technology for desalination of sea and brackish water and for treating industrial effluents.

Membrane separation processes are not new or even recent technology. The use of membranes for separation processes in a large scale started in 1960. In nineteen eighties, large filtration plants were already installed worldwide, and microfiltration, reverse osmosis and electrodialysis membrane processes were developed (Almendrala 2009). Membrane has the ability to reject various mineral salts, heavy metals, organic molecules, bacteria, parasites, and even viruses, while allowing the permeation or passage of water. Separation is based on the molecular size, shape or character of the species. Membranes may be as thin as a fraction of a micrometer or several millimeters thick. The ability of membrane to reject dissolved particles depends on the multitudes of pores, of incredibly small size, that penetrate its surface. The membrane pores can reject particles as small as 0.5 nm and allow water permeation with size equivalent to 0.298 nm. Membranes or synthetic membranes can be produced from organic materials such as polymers and liquids, as well as inorganic materials.

For water desalination by reverse osmosis (RO) many semipermeable membranes are made of different polymers. The commercial market consists primarily of thin-film composite polyamide formed into a spiral-wound configuration. The development of improved low-pressure membranes, large-diameter membrane modules, and non-fouling membranes has been important technology trends. Currently, a number of new material types; e.g. carbon nanotubes and nano fibers, are also in development.

A reverse osmosis treatment system usually consists of a semipermeable membrane, water storage tank and dispensing faucet. This system can remove inorganic chemicals and is often combined with an activated carbon filter to remove chlorine and organic chemicals. Reverse osmosis process is widely used for the removal of dissolved contaminants, as in the case of softening or desalination. Reverse osmosis is most commonly known for its use in drinking water production from seawater (desalination) and drinking water purification, removing the salt and other substances from the water molecules.

The first production of potable water from saline water was reported by Reid and Breton (Reid 1959) by using cellulose acetate (CA) membrane. In 1959, Loeb and Sourirajan found that heating a commercial CA membrane in water produced a desalination membrane. They pursued the study, which lead to the development of casting techniques that yielded anisotropic CA membranes, called the Loeb-Sourirajan (L-S) membranes with high flux and high desalination capacity (Loeb 1964). The mechanism of membrane formation was phase inversion (Kesting 1971) and the resulting membranes had a thin dense layer (less than 1 μm) on top of a thicker porous layer (Riley 1964).

The basis for modern RO and NF membranes was laid in the casting of CA solutions as well as annealing of the thin top layer, yielding different molecular weight cutoffs (MWCO) for the resulting membranes that extended from tight RO to UF, including the intermediate NF range (Lonsdale 1972).

In search for membranes that could give better results, in particular higher flux, composite membranes were prepared by coating a thin dense layer on top of a porous sub layer. Since the material of the top dense layer and the porous sub layer are different, these membranes are called thin film composite (TFC) membranes (Riley 1971). The search for better composite membranes was pursued by repagination and testing noncellulosic microporus support films. Polymers examined include polycarbonate, poly(phenylene oxide) and polysulfone (Kasher 2009). Polysulfone showed the best results and has remained a mainstay in composite membranes as the support material to this day.

Today's state-of-the art RO membrane technology for desalination provides excellent salt rejection (up to 99.8%) with a good recovery of potable water at the operating pressure below 600 psig. Over the course of the past 20 years the water permeability has increased by a factor of three and the salt passage has decreased by a factor of almost 20 (Wenten 2002, Rad 2009). This improvement is primarily due to the proper selection of monomers in the in-situ polymerization and the solvent additives in the organic phase. For example, addition of dimethylsulfoxide (DMSO) into the organic phase increased the surface roughness and the effective surface area, leading to the enhanced permeate flux without considerable loss of salt rejection. The combined results of AFM, XPS, and solid state NMR provided a robust explanation for the mechanism of flux enhancement of the aromatic polyamide TFC membrane, which would contribute to not only fundamental understanding of the process but also advanced designing of the so-called "tailor-fit" TFC membranes (Kwak 2001). Recent studies have also shown that membrane surface morphology and structure influence colloidal fouling behavior of RO and NF membranes (Wenten 2002, Kasher 2009, Rad 2009).

Due to increasing demand for water, both potable and for irrigation, coupled with a decrease in suitable water source, suppliers have to turn to alternatives. Seawater desalination or treatment of high saline, eventually contaminated surface waters have become standard. By using those alternative sources more trace contaminants start to appear in the final product. Among those is boron. Boron removal is a very serious matter in seawater desalination. WHO established boron concentration to be below 0.5 mg/L as a guideline value. Boric acid is a typical substance which is difficult to be removed by RO, since the size is as small as 0.4 nm in diameter. Henmi achieved the boron removal

of 94-95% by controlling the pore size of the RO membrane to 0.56-0.7 nm range, as proved by positron annihilation lifetime spectroscopy (PALS) (Henmi 2010).

Electron Research INC (Boulder, Colorado) developed a new family of polymers with a significantly different approach to polymer (semi permeable membrane) design. They claimed that these semi permeable membranes are 10-20 times more tolerant to oxidizers such as chlorine, stable to continuous contact with transition metals, good mechanical durability, and increased filtered water production at low pressures (up to 50% greater than comparable membranes) (Buschmann 2010).

Kumar *et al.* (Kumar 2007) developed a highly permeable and selective membranes based on the incorporation of the functional water channel protein Aquaporin Z (AqpZ) into a novel A-B-A tri-block copolymer. The vesicles were made of a block copolymer with symmetric poly(2-methyloxazoline)-poly(dimethylsiloxane)-poly(2-methyloxazoline) (PMOXA₁₅-PDMS₁₁₀-PMOXA₁₅) repeat units. The membrane showed significantly higher water transport than existing RO membranes used in water purification and desalination. In water productivity (permeability per unit driving force) of up to ~ 800 times that of pure polymer was observed when AqpZ was incorporated. The solute reflection coefficients of glucose, glycerol, salt, and urea were also calculated, and it was indicated these solutes were completely rejected. The productivity of AqpZ-incorporated polymer membranes was at least an order of magnitude larger than values for existing salt-rejecting polymeric membranes.

Redondo *et al.* (Redondo 2003) discussed concepts for designing desalination plants using FILMTEC seawater reverse osmosis (SWRO) membranes.

Ameri *et al.* (Ameri 2004) modified PES hollow fiber membrane by heating and used them for water treatment process. The best results were obtained when the hollow fibers were heated at 150°C.

Susanto and Ulbricht (Susanto 2006) modified the surface of PES UF membranes via photo-graft copolymerization and obtained thin layer polymer hydrogel composite PES-based UF membranes. These membranes showed significantly lower humic acid (HA) fouling than commercial PES membranes with respect to adsorptive fouling as well as dynamic fouling.

A comprehensive study was made on desalination by direct contact membrane distillation (DCMD) using surface modified polymeric membranes. The surface of the membranes was made hydrophobic as a result of surface migration of surface modifying macromolecules (SMMs). The study includes membrane fabrication, transport mechanism and process optimization (Qtaishat 2008, 2009).

Yamaguchi *et al.* (Yamaguchi 2001) reported that hollow-fiber-type pore-filling membranes made by plasma-graft polymerization could be used for the removal of chlorinated organics from water via pervaporation technique. Laurylacrylate (LA) or *n*-butylacrylate (BA) grafted layers were formed inside the porous hollow-fiber substrate, and the pores were filled with the grafted chains formed by plasma-initiated graft polymerization. The hollow-fiber-type LA-grafted membranes showed extremely high separation properties: a 0.09 wt.% 1,1,2-trichloroethane (TCE) aqueous solution was condensed to 99 wt.% TCE in the permeate. The membrane also showed high separation performance for an aqueous dichloromethane (DM) solution.

Yoshida and Cohen (Yoshida 2004) removed the methyl *tert*-butyl ether (MTBE) from water via pervaporation using ceramic-supported polymer membranes. The membranes were created by the free radical graft polymerization of vinyl acetate onto a vinyl trimethoxy silane activated porous silica substrate. The resulting membranes consisted of poly (vinylacetate) chains terminally and covalently anchored to the membrane surface. These pervaporation membranes performed with separation factors ranging from about 68 to 577 at total permeate fluxes of 0.31-0.70 kg/m² h over feed concentrations of 74-7,400 ppm (0.01-1 %v/v).

Li and Sirkar (Li 2004) developed, using porous hydrophobic PP hollow fibers having three

different dimensions and two different wall thicknesses, membranes for desalination process via direct contact membrane distillation (DCMD). The outside surfaces of the fibers were coated with a variety of microporous plasma-polymerized silicon-fluoropolymer. The water vapor flux results obtained were highly encouraging and were as good as, if not better than, the best RO membrane performances.

The main hindrance in the application of membranes to the water treatment is the fouling. It is caused by the accumulation of organic/inorganic materials, as well as microorganisms, on the membrane surface or in its pores. Common foulants include;

i) calcium carbonate and calcium sulphate scales, ii) organic matter, iii) iron, iv) colloidal material, v) biofilm and microorganisms, vi) silica, and natural humic and fulvic acids. Other contaminants such as barium, strontium sulphate, calcium fluoride, aluminum silicate and manganese salts have been identified but are comparatively rare. Thus, fouling causes severe flux decline, deterioration of the membrane and reduction of the membrane rejection. There are many substances that may potentially cause fouling during water treatment (Peng 2005). Among those, natural organic matter (NOM) is believed to be the major foulant. However, monovalent and divalent cations and microorganisms are also considered as potential foulants.

Hong and Elimelech (Hong 1997) noticed that the NOM fouling rate was dependent on initial permeation rate, that is, the higher permeation rate resulted in the faster NOM fouling.

Peng and Escobar (Peng 2005) investigated the fouling behaviors of three different commercial membranes under various physical and chemical conditions to identify the dominant effects on the flux decline. Different reasons were given for different membranes. Feed bacteria concentration contributed to the initial fouling of a particular membrane. In another membrane, the initial fouling was significantly affected by the total organic carbon (TOC) content in the feed water arising from the initial accumulation of colloidal organic particles on the surface.

Mosqueda-Jimenez *et al.* (Mosqueda-Jimenez 2004) developed polyethersulfone (PES) based membranes for UF by blending surface modifying macromolecules (SMMs) in the casting solution, in an attempt to minimize the impact of fouling. Polyethylene glycol and its derivatives are well known as nonfouling material; however they loosen its resistance to fouling above 35°C (Harder 1998). Zwitterionic substances such as the *N,N*-dimethyl-*N*-(2-methacryloxyethyl)-*N*-(3-sulfopropyl)ammonium betain have been reported as a new family of nonfouling material and used in UF membranes (Susanto 2007, 2007a) as well as for modification of nonporous surfaces (Chen 2005, Holmlin 2001). Due to membrane's hydrophobic nature, it easily induces macromolecules to deposit (Blanco 2006). It is well known that increasing the membrane hydrophilicity can effectively minimize membrane fouling (Wang 2006). Charged membranes can also be used to reduce membrane fouling (Mulder 1992). Methods such as surface graft polymerization, chemical grafting, and radiation induced grafting have been developed in attempts to increase the surface hydrophilicity of membranes (Susanto 2007a, Shi 2007). UV radiation on polymeric surface for reducing the biofouling has also promising future (Goddard 2007).

Elimelech *et al.* (Elimelech 1994) measured the zeta potential of RO membranes by streaming potential analyzer. Results indicated that solution chemistry has a marked effect on the electrokinetic properties of RO membranes. It was also noticed that the zeta potential of RO membranes becomes more negative as the NaCl concentration in solution increases. It appeared that the zeta potential of RO membranes was strongly influenced by the presence of unreacted chemical substances or impurities on the membrane surface.

Overall, the membrane field has advanced immensely. Being economical, environmentally friendly,

versatile, and easy to use, membranes are a leading choice for water purification applications and should continue to be for many years to come.

3. Membranes based on nanotechnology

Nanotechnology, the engineering and art of manipulating matter at the nanoscale (1-100 nm), offers the potential of novel nanomaterials for the treatment of surface water, groundwater and wastewater contaminated by toxic metal ions, organic and inorganic solutes and microorganisms. Due to their unique activity toward recalcitrant contaminants many nanomaterials are under active research and development for use in the treatment of water (Theron 2010). For example, Cooper *et al.* (Cooper 2007) developed nanostructured material comprising defective carbon nanotubes, chosen from impregnated functionalized, doped charged, coated, and irradiated nanotubes for water purification. The water can be purified by contacting contaminated water with an activated nanostructured material. In the patent Cooper *et al.* (Cooper 2007) demonstrated that contaminants, such as salts, bacteria and viruses can be removed up to a level of at least 99.9% by using nano materials (carbon nanotubes).

In membrane processes, remarkable progresses have been made recently in the area of electrospun nanofiber membranes and nanoparticle impregnated membranes. Nanofibers have a much higher surface-to-volume ratio than conventional melt blown microfibers providing efficient separation of particulate. Electrospinning also offers opportunities to fine-tune the surface functionality through polymer chemistry. Electrospun nanofibers and nanobiocides have potential in the improvement of water filtration membranes. Bacterial load in water reduces the quality of drinking water due to biofouling of membranes. Several studies showed inhibition of these bacteria after exposure to nanofibers with functionalized surfaces. Nanobiocides such as metal nanoparticles and engineered nanomaterials are successfully incorporated into nanofibers showing high antimicrobial activity and stability in water (Rassaie 2007).

Nanofibers modified with plasma treatment or surface graft polymerization is an alternative approach for antifouling water filtration membranes. Nanofibers and nanobiocides may be the solution to ensure safe and easy access to drinking water. Research on the applications of nanofibers and nanobiocides in water purification, the fabrication thereof and recently published patents were discussed by Botes and Cloete (Botes 2010).

A good benefit of nanofibers with commercial success is that they can be fabricated into MF, UF, photocatalytic membranes, and membranes for membrane distillation. The nanofibrous MF and UF membranes are of particular interest as it shows high pollutant removal rate at low trans-membrane pressure (< 300 kPa). A commercial success of such fabricated MF and UF membranes has been demonstrated by Zhang *et al.* by using TiO₂ nanotubes/ nanowire (Zhang 2008, 2008a).

Sang *et al.* (Sang 2008) used nanofiber membranes prepared from chloridized polyvinyl chloride by high-voltage electrospinning process to remove the multivalent metal cations including Cu²⁺, Pb³⁺ and Cd²⁺ from the stimulated groundwater. The removals of these metal cations by several experimental methods, including static adsorption, direct filtration, soil-addition filtration, diatomic-addition filtration and micellar enhanced filtration (MEF) by using the nanofiber membranes was investigated. The experimental results showed that the rejections of copper in the simulated ground water by MEF can reach more than 73%; the rejections of lead more than 82%; and the rejections of cadmium more than 91%. It was indicated that MEF method can be used for the treatment of the

ground water containing Cu^{2+} , Pb^{3+} and Cd^{2+} with high efficiency.

Recently, scientists from Stellenbosch University in the Western Cape have developed and patented an inexpensive and effective filtering device for polluted water based on nanotechnology (<http://www.nano.org.uk/news/774>, Health 15.11, 2010). The filter, about the size and shape of a teabag, would be inexpensive and simple. The 'teabag filters' fit into the neck of a bottle and turns polluted water into clean water as you drink from it. The bag contains active carbon granules and is made from nanofibers treated with biocide, which kills bacteria rather than simply filtering them from the water. Each filter can clean one liter (one quart) of the most polluted water to the point where it is completely safe to drink. Once used, the filter can be disposed of and is biodegradable.

Yoon *et al.* (Yoon 2006) demonstrated a new type of high flux UF or NF composite membranes containing a thin layer of hydrophilic but water resistant chitosan coating, an asymmetric electrospun PAN nanofibrous mid-layer support and a non-woven poly(ethylene terephthalate) (PET) substrate. The interconnected porosity of the non-woven nanofibrous scaffold can be controlled partially by varying the fiber diameter (from about 100 nm to a few micrometers) through the electrospinning processing. For example, a membrane, containing an electrospun PAN scaffold with diameters from 124 to 720 nm, showed a flux rate an order magnitude higher than commercial NF membranes in 24 h operation, while maintaining the same rejection efficiency (>99.9%).

Feng *et al.* (Feng 2008) reported that polyvinylidene nanofiber membrane (PVDF) could be used in air-gap membrane distillation (AGMD) to produce drinking water (NaCl concentration <280 ppm) from a saline water of NaCl concentration 6 wt.%. This new approach may eventually enable the MD process to be comparable with conventional seawater desalination processes such as distillation and RO. The membrane flux was sufficiently high at temperature differences ranging from 25 to 83°C. In addition, the membrane was intact and unplugged after many days of operation.

The invention of (Khayet 2011) relates to copolymer (PVDF-co-F6PP) or homopolymer (PVDF) nanofibrous or nanostructured flat membranes for direct contact membrane distillation, which allows a considerable reduction in heat loss due to conduction and the polarization of temperatures and concentrations since said membranes have high permeate flows and which reduce the energy requirement of the direct contact membrane distillation (DCMD) process. The membranes are produced by means of electrospinning with solvents having different affinities with the polymer or copolymer used, thereby allowing the thickness of the membrane, the diameter of the nanofibers and the pore size of the membranes (empty space between nanofibers) to be controlled. The resulting membranes can be used in DCMD for different purposes, such as salt water treatment, wastewater treatment, or the production of distilled water or ultrapure water.

Research has shown that nanoparticles represent a new generation of environmental remediation technologies that could provide solutions to some of the most challenging environmental cleanup problems including water treatment (Auffan 2007). Nanomaterials have a number of key physico-chemical properties that make them particularly attractive as separation media for water purification (Savage 2005). Nanoparticles have much large surface areas than the bulk particles. Nanomaterials can be functionalized with various chemical groups to increase their affinity toward a given compound and can also serve as high capacity/selectivity and recyclable ligands for toxic metal ions, radionuclides, organic and inorganic solutes/ anions in aqueous solutions. In the near future, nanoparticles will help solve challenging water purification problems including; i) the desalination of brackish water; ii) the recovery of valuable and toxic metal ions from membrane concentrates thereby facilitating brine disposal; iii) the development of chlorine-free biocides; and iv) the purification of water contaminated by toxic contaminants such as perchlorate, pharmaceuticals, chiral

compounds and endocrine disrupting compounds. For example, Li *et al.* (Li 2008) reported that several antimicrobial nanomaterials such as chitosan, silver nanoparticles (nAg), TiO₂, and carbon nanotubes (CNTs) show promise as alternatives to traditional chemical disinfectants that are prone to generate harmful disinfection byproducts in water treatment. Some examples are shown below of membranes in which nanoparticles are impregnated.

The application of zerovalent metal nanoparticles to water treatment is a field of considerable interest. Incorporation of the nanoparticles in a membrane phase may simplify the engineering of nanotechnology based systems for water treatment.

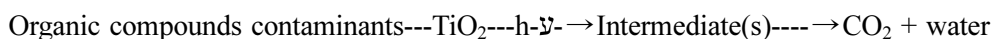
Tarabara (Tarabara 2009) discussed the recent progress in multifunctional nanomaterial-enabled membranes for water treatment.

Ritche (Ritche 2009) discussed how membrane supported nanoparticles are formed, as well as examined some unique aspects of these materials and their potential advantages for membrane water treatment.

4. Water treatment by advanced oxidation process (AOP)

The suitability of AOP for pollutant degradation was recognized in the early 1970s and much research and development work has been done to commercialize some of these processes. Klavarioti *et al.* (Klavarioti 2009) wrote a review on the recent techniques to remove residual pharmaceuticals from aqueous system by advanced oxidation processes. Comninellis *et al.* (Comninellis 2008) wrote an article in which they identified and discussed certain directions that seemed to advance R&D on advanced oxidation for water/waste water treatment.

Photochemical and chemical oxidation methods for the water treatment belong to a wide group of advanced oxidation processes (AOPs). The advantage of the AOPs for waste water treatment includes fast reaction rates and non-selective oxidation allowing the treatment of multiple contaminants at the same time. They also have the potential to reduce the toxicity of the contaminants and the total mineralization can be achieved. In the AOPs the main reactive species, typically hydroxyl radicals (OH^{*}), effectively degrade many refractory organic pollutants with high reaction rates. Other highly reactive transitory species are H₂O₂, O₂^{*}, O₃^{*}. Photochemical AOPs, which use UV radiation as an external source of energy, include UV and hydrogen peroxide (UV/H₂O₂). In AOPs, semiconductor catalysts such as TiO₂, ZnO, Fe₂O₃, CdS, GaP and ZnS are popular as heterogeneous photo-catalysts. Recently many reviews have appeared in literature about the developments in photochemical and chemical AOPs in water treatment (Vilhunen 2010). In AOPs where semiconductor catalysts are used, a series of chain oxidative-reductive reactions occur at the photon activated surface. Photo catalysis is based on the double aptitude of the photocatalyst to simultaneously adsorb both reactants and efficient photons. The liquid phase organic compounds are degraded to its corresponding intermediates and further mineralized to carbon dioxide and water according to the following scheme,



Gogate and Pandit (Gogate 2004) wrote a review on five oxidation processes operating at ambient conditions viz. cavitation, photocatalytic oxidation, Fenton's oxidation, ozonization and use of hydrogen peroxide for waste water treatment technologies.

Recently, Fatta-Kassinos *et al.* (Fatta-Kassinos 2010) discussed removal of xenobiotic compounds from water and waste water by advanced oxidation process. There are many ways to do water

treatment using AOP's technique as discussed below:

i) Photolysis: It involves the interaction of artificial or natural light with the target molecule and the induction of photochemical reactions which can lead to its direct degradation to intermediate products whose further decomposition eventually yields mineral end products. UV treatment has traditionally been employed for the disinfection of drinking water.

ii) Ozonization: Ozone is a strong oxidant that either decomposes in water to form hydroxyl radicals which are stronger oxidizing agents than ozone itself. Ozonization has been traditionally employed in drinking water treatment for odor and taste control and disinfection, as well as for waste water disinfection.

Andreozzi *et al.* (Andreozzi 1999) discussed the capability of exploiting the high reactivity of HO radicals in driving oxidation processes which are suitable for achieving the complete abatement and thorough mineralization of less reactive pollutants.

Esplugas *et al.* (Esplugas 2007) reported that ozonization (oxidation process) is a promising process to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals in water effluents.

iii) Fenton oxidation: Homogeneous oxidation with the Fenton reagent (Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst) occurs in the presence of the ferrous or ferric ions with hydrogen peroxide via a free radical chain reaction which produces hydroxyl radicals. It is considered to be a metal catalyzed oxidation reaction in which iron acts as the catalyst. Fenton systems are easy to handle and operate. This system is used to treat micro-pollution caused by residual pharmaceuticals in surface water as well as industrial effluents, e.g. hazardous hospital wastes or from drug manufacturing with increased organic loading.

Mavronikola *et al.* (Mavronikola 2009) investigated the degradation and mineralization of the antibiotic amoxicillin by photo-Fenton reaction, mediated by artificial ultraviolet radiation (UVA) or solar irradiation. Amoxicillin was readily degradable by homogeneous-photo catalysis, converted to more stable intermediates as indicated by lower mineralization rate. The process was driven by solar irradiation which can be used for the water treatment.

Oturan *et al.* (Oturan 2000) described an indirect electrochemical method, named electro-Fenton' method, which was very efficient for the degradation of organic pollutants in water. Electro-Fenton's method was based on electro-catalytic generation of Fenton's reagent to produce hydroxyl radicals, which are very active toward organic compounds.

iv) Heterogeneous photocatalysts: Heterogeneous photocatalysis is based on the utilization of light along with a catalytic solid. Following are the main advantages of heterogeneous photocatalysis in water treatment:

1. Ambient operating temperature and pressure.
2. Complete mineralization of parents and their intermediate compounds without secondary pollution.
3. Low operating cost.

Heterogeneous semiconductor photo catalysis, using TiO_2 , ZnO , Fe_2O_3 , CdS , GaP and ZnS as the photocatalyst, is an emerging technology. Among above mentioned semiconductor photocatalysts, TiO_2 is a promising catalyst for water treatment. These heterogeneous catalysts demonstrated their efficiency in degrading a wide range of ambiguous refractory organics into readily biodegradable compounds, and eventually mineralized them to innocuous carbon dioxide and water. The heterogeneous photocatalysts are employed for almost all the pharmaceutical treatment. Ollis (Ollis 2000) surveyed the broad range of emerging potential applications for water treatment by light and catalyst utilization via periodic illumination and oxidant (ozone and peroxide addition). Achilleos *et al.* (Achilleos

2010) used UV-A/TiO₂ for the decomposition of diclofenac in water.

Zhang *et al.* (Zhang 2010) investigated photocatalytic degradation of chloramphenicol (CAP) using TiO₂ as a photocatalyst in a photo-reactor. The degradation rate of CAP approached 85.97 % under optimal conditions.

Ryu and Choi (Ryu 2008) used TiO₂'s photocatalytic activities in water treatment for phenols, organic acids, amines, chloro hydrocarbons, dyes, inorganic ions, etc. and studied their degradation or conversion rates in water.

Chong *et al.* (Chong 2010) wrote a review on the recent developments in photocatalytic water treatment. They predicted that a large scale photocatalytic treatment process with high efficacy, solar-driven and low site area requirements can be realized in the short future with rapid evaluation of different possible pilot plant configurations.

Heterogeneous photocatalysis is now reaching the preindustrial level. Several pilots and phototypes have been built in various countries. The solar photocatalytic treatment of pesticides is used in agriculture and in food industry (Hermann 1999).

Zhang *et al.* (Zhang 2003) developed a new type of tubular photocatalytic reactor using TiO₂ as photocatalyst for water purification. It would be expected that the reactor could be commercialized for its high efficiency in purifying polluted water and for its simple setup ensuring maintenance free.

Ray and Beenackers (Ray 1998) developed a new photocatalytic reactor for water purification. The reactor was made by using several hollow tubes coated on its outside surface with the catalysts. Light distribution system was inside the reactor through the absorbing and scattering liquid to the catalyst, and providing high surface area for catalyst per unit volume of reactor. The hollow tubes were employed as a means of light delivery to the catalyst. Bahnemann (Bahnemann 2004) reviewed the various solar reactors for the photocatalytic water treatment during the past 20 years.

v) Electrochemical oxidation: Electrochemical oxidation over anode made of graphite, Pt, TiO₂, IrO₂, Ti based alloys, boron doped diamond (BDD) electrodes in the presence of suitable electrolyte (NaCl solution) has been employed for the decomposition of various organic-containing effluents. In recent years, BDD anodes have received growing attention for pollutants oxidation as they exhibit significant chemical and electrochemical stability, good conductivity as well as they achieve increased rates of mineralization with very high current efficiencies (Comninellis 2008).

vi) Ultrasound irradiation: Ultrasound irradiation or sonolysis is relatively in early stage in water treatment and so far received less attention than other AOPs. Sono-chemical reactions are induced upon high intensity acoustic irradiation of liquids at frequencies that produce cavitation (typically in the range 20-1000 kHz). Thus, cavitation serves as a means of concentrating the diffused energy of ultrasound into micro-reactors with the simultaneous release of reactive radicals with each reactor serving as a hot spot. Ultrasonic degradation, mineralization and detoxification of anti-inflammatory drug diclofenac (DCF) in water were studied by Naddeo *et al.* (Naddeo 2010). It was reported that DCF conversion was enhanced at increased power densities and liquid bulk temperature, acidic conditions and in the presence of dissolved air or oxygen. Adewuyi (Adewuyi 2005) presented a critical review of the applications of ultrasound in environmental remediation focusing on the simultaneous or hybrid use of ultrasonic irradiation and photo-catalysis in aqueous solutions, namely, sonophotocatalytic oxidation processes. Pikaev (Pikaev 2001) discussed the radiation purification of polluted water and waste water.

vii) Sub-critical wet air oxidation (WAO): WAO is a thermo chemical process where hydroxyl radicals and other active oxygen species are formed at elevated temperature (200-300°C) and pressures (2-20 MPa) (Levec 2007). The process has great future for the treatment of wastewaters

with moderate to high organic content (i.e. 10-100 g/L COD).

viii) Coupling AOPs with other treatment processes: The concept of coupling AOPs as a pretreatment stage to enhance biodegradability and reduce toxicity with biological post-treatment has gained a lot of attention over the past several years. The use of combined photocatalysis and ozonization is an attractive route of the enhancement of the performance for both agents by means of the hydroxyl radical generation, a powerful oxidant agent that can oxidize completely the organic matter present in water (Agustina 2005).

Yang *et al.* (Yang 2009) for the first time provided a novel advanced oxidation process based on sulfate radical ($\text{SO}_4^{\bullet-}$) to degrade organic pollutants in waste water: microwave (MW)-activated persulphate oxidation (APO) with and without active carbon (AC). They predicted that MW-APO is a new catalytic combustion technology for destruction of organic contamination even for high concentration in waste water.

Chang (Chang 2001) discussed plasma pollution control technology for water treatment. Bhaumic *et al.* (Bhaumic 2004) used an advanced oxidation process (AOP) technique by using H_2O_2 , O_3 and UV light to destroy bacteria and to eliminate bacterial contamination in the production of ultrapure water (UPW). In their study they used porous hydrophobic polypropylene (PP) membrane module.

Nanotechnology has also an effect on AOP. For example, Chen *et al.* (Chen 2003) fabricated a novel composite reactor and studied towards the degradation of organic pollutants in water. In the reactor, a UV lamp was installed to provide energy to excite nano TiO_2 , which served as photocatalyst, leading to the production of hole-electron pairs, and a three-electrode electrolysis system was used to accumulate H_2O_2 which played an important role in the degradation process.

In 2009, BioNano International, an international nano-technology company with its head office in Singapore, had developed a revolutionary waste or polluted water treatment system based on their proprietary nano-bubble technology to revive water ecosystems. BioNano's water system can produce 200,000 nano-bubbles with the diameters ranging from 50 -15,000 nm at extremely high pressure and temperature through reaction of air and water producing cluster of radicals. These clusters of radicals produced by BioNano's proprietary water treatment system decompose organic substances, oxidize heavy metals, neutralize stubborn chemical substances in waste or polluted water, and in the process, the suspended substance is attached to the nano-bubbles and floats to the water surface for removal. The suspended substance can subsequently be decomposed by micro-organisms in the water or be collected as fertilized soil for agriculture use. At the end of the treatment process, the water ecosystem is restored.

5. Enzymes in waste water treatment

A large number of enzymes from a variety of different plants and microorganisms have been reported to play an important role in an array of waste water treatment applications (Karam 1997). The purpose of an enzyme is to break down an organic matter. Enzymes are biological catalysts that regulate the multitude of chemical reactions that occur in a living cell, whether it is plant, animal or microbial. Enzymes that have been isolated from their parent organisms are often preferred over intact organisms containing the enzyme because the isolated enzymes act with greater specificity. They are better standardized, easier to handle and store, and the enzyme concentration is not dependent on bacterial growth rates (Nicell 2003). Several enzymes belonging to the class of oxidoreductases are used for the treatment of phenolic contaminants. One of these, horseradish

peroxidase (HRP) catalyzes the oxidation of a variety of aqueous phenol and aromatic amines with H_2O_2 to their respective radicals. These highly reactive compounds undergo further non-enzymatic reactions leading to the formation of insoluble polymers that can be separated from the solution by sedimentation or filtration. Considerable research has been conducted during the past three decades to investigate the new possibilities offered by enzymes in waste water treatment (Wagner 2003).

Biological waste water treatment processes can be classified as either aerobic or anaerobic. These two biological treatment processes are each characterized by groups of micro-organisms and their associated enzymes. Hydrolytic enzymes secreted by these micro-organisms are vital for the rate limiting step of hydrolysis in the treatment of highly polymeric substrates present in sewage sludge (Burgess 2008).

Organic matter in waste water sludge consists of lipid, carbohydrates and protein molecules, and is often very complex. Complex, big molecules can not penetrate the cell membrane and are therefore not directly available as substrates for the microorganisms to digest. Microorganisms in the sludge produce enzymes to degrade these substrates to smaller molecules which then enter the cells and are digested. The microorganisms which produce these enzymes are obligate or facultative anaerobes (Gurg e Cirne 2006, Davidsson 2007, 2007a).

Heat treatment has been used by Yan *et al.* (Yan 2008) for the reduction of excess sludge. This is a relatively simple process. On heating, protease-secreting bacteria emerged and the activity of protease increased. Ultrasonic treatment can improve the aerobic digestibility of sludge, and therefore lead to enhanced sludge reduction (Yu 2008). Yu and co-workers reported that ultrasonic pre-treatment enhanced the activities of various enzymes and promoted the shift of extracellular proteins, carbohydrates and enzymes from the inner layers of sludge flocs to the outer layers, leading to increased contact and interaction between these components and more active aerobic digestion.

Cation-binding agents such as sodium tripolyphosphate (STPP), citric acid or ethylenediaminetetraacetic acid was used to improve the solubilisation of sludge (Wawrzynczyk 2008). The cation –binding agents are believed to disrupt the adsorption of enzymes to the sludge matrix via polyvalent metal ions, thereby liberating the trapped or bound enzymes from the sludge structure.

A number of researchers have shown the advantages of enzyme addition or pretreatment on the conditioning of wastewater solids (primary sewage sludges) and enhancement of the degree of dewaterability of anaerobically digested biosolids (Ayol 2005, Ayol and Dental 2005, Roman 2006).

Sesay *et al.* (Sesay 2006) investigated enzyme hydrolysis as a mild and effective means of extracting extracellular polymers from mixed culture activated sludge flocs. Alpha-amylase, cellulose and proteinase were used for enzyme hydrolysis. Enzymatic extraction of the extracellular polymers was found to be quite rapid.

Sessile communities of bacteria encased in extracellular polymeric substance (EPS) are known as biofilms and causes serious problems in various areas. Enzymes are highly selective and disrupt the structural stability of the biofilm EPS matrix (Ullrich 2009). Various studies have focused on the enzymatic degradation of polysaccharides and proteins for biofilm detachment since these are the two dominant components of the EPS. Due to the structural role of proteins and polysaccharides in the PES matrix, a combination of various proteases and polysaccharases may be successful in biofilm removal. The biodegradability and low toxicity of enzymes also make them attractive biofilm control agents. The activity, stability and efficiency of immobilized enzymes can be improved by reducing the size of the enzyme carrier. Nano-scale carrier materials allow for high enzyme loading per unit mass, catalytic recycling and a reduced loss of enzyme activity. Moreover, enzymes can be stabilized by producing single-enzyme nanoparticles consisting of single-enzyme molecules surrounded by a

porous organic-inorganic network of less than a few nanometers thick. All these new technologies of enzyme stabilization make enzymes even more attractive to other biofilm removal and control agent (Cloete 2010).

Lewis *et al.* (Lewis 2011) demonstrated that through the integration of nanostructure materials, enzymatic catalysis, and iron-catalyzed synthetic membrane, free radical reactions within pore-functionalized synthetic membrane platforms are able to conduct oxidative reaction for toxic organic degradation and detoxification of water without the addition of expensive harmful chemicals. Lewis *et al.* (Lewis 2011) utilized two independently controlled, nanostructured membranes in a stacked configuration for the generation of necessary oxidants. These include biocatalytic and organic/inorganic/(polymer/iron) nanocomposite membranes. The bioactive (top) membrane contains an electrostatically immobilized enzyme for the catalytic production of one of the main reactants, hydrogen peroxide (H_2O_2) from glucose. The bottom membranes contains either immobilized iron ions or ferrihydrite/iron oxide nanoparticles for the decomposition of hydrogen peroxide to form powerful free radical oxidants

6. Unconventional water treatment process; magnetic water treatment

As well, microwave (MW)-assisted reactions have gained popularity as indicated by a large number of publications (Kappe 2004). The applications of MW energy to enhance environmental waste treatment have also been growing (Abramovitch 1999, Jones 2002, Xia 2003, Bo 2008).

In recent years magnetic separation technology has received considerable attention for its separation capability of suspended particles, nanoparticles, oil waste, heavy metals and organics in waste water treatment (Lo 2007). The basics of the magnetic aggregation and separation are that magnetic particles are aggregated with pollutants in the water, and then separated from water by magnetic force with applied magnetic field.

Magnetic water treatment is a proposed method of reducing the effects of hard water, as an alternative to water softening. Electromagnetic water conditioners are a relatively new invention. The idea is that by passing water through a magnetic field, the calcium and magnesium ions are altered in such a way that they lose their ability to cause scale formation (Coey 2000, Baker 1996). This has a number of benefits; although the water is not technically soft, it has the useful properties of soft water, and that is, it will not cause limescale in the pipes thus increasing heating efficiency and lengthening the lifespan of any clothes washed in the conditioned water. Calcium is an important dietary element, so the fact that conditioned water still retains its calcium content is an added benefit.

When water runs through a magnetic field, the calcium carbonate will precipitate as aragonite rather than the usual calcite. For example, Kronenberg has published an article (Kronenberg 1985) and stated the following: *'The crystallization mode of the water's mineral content was found to change from a dendritic, substrate-bound solidification habit to the form of separate disc-shaped crystals after the water had moved through a number of magnetic fields. The former scarcity of crystallization nuclei in the water had been turned into an abundance of nucleation centers in the water. The reduction of the number of the substrate-bound crystals has been used as a quantitative measure of the magnetic effect'*.

Mitsuhashi *et al.* (Mitsuhashi 2003) developed a superconducting High Gradient Magnetic Separation (HGMS) system to remove endocrine disrupters (EDCs) from water. EDCs are exogenous chemicals,

which influence the normal hormone functions in an organism. Lo *et al.* (Lo 2007) described a method of magnetic aggregation and separation that can reduce the turbidity of raw water of different initial turbidity and from different areas at different pH values. Oder (Oder 2005) illustrated the application of magnetic fields to dewatering and desalting of California crude oil. It was claimed by them that the magnetic fields of the order of few hundred gauss are sufficient to achieve 90% separation of water from water/oil emulsions of interest. The agnetostatic demulsification found a wide range of applications. Isogami *et al.* (Isogami 2011) made patent application on magnetic separation and waste water treatment apparatus.

7. Future research on water treatment

No one processes of treatment equipment manages all contaminants. All treatment methods have limitation and often water quality requires a contaminant processes.

With the proven success of membranes in the water treatment arena, membrane technology continues to advance. Major problems still needing attention are membrane fouling and membrane chemical stability. Reduced fouling would make membranes even more cost effective by extending their operational lifetime and lowering their energy requirements. Work in this area has focused on surface modification of membranes and increasing the pretreatment of the feed water before it reaches the membranes. In addition to waste water treatment and desalination, new applications of membranes for water purification are being pursued. Air stripping is one of the most effective technologies for removing volatile organic compounds (VOCs) from aqueous solutions, although the presence of surfactant poses some unique challenges. A process for removal of organics from aqueous solutions by membrane stripping needs more work concerning membrane material (hydrophobic).

Both AOPs and the use of nanofibers have shown great potential in treating pollutants at both low and high concentrations. Carbon nanotubes (CNTs) are emerging technology in water purification system, particularly with respect to its potential for the removal of arsenic, fluoride, heavy metals and toxic organic components. CNTs have great future in the field of water purification owing to their unique thermal, electrical and mechanical properties.

TiO₂ photocatalysis membrane separation technology is a relatively new and advanced process for water and waste water treatment with great potential. However, further investigations are needed in terms of the development of loading methods and the control of payload capacity. Studies related to modified TiO₂ and TiO₂ with different morphologies (such as TiO₂ nanotube, TiO₂ nanowire, etc.) should be conducted.

Magnetic or electrostatic scale control technologies can be used as a replacement for most water softening equipment. Specifically, conventional chemical softening processes such as lime or lime soda softening, ion exchange, etc., for the control of hardness, could potentially be replaced by non-chemical water conditioning technology. However, this technology needs more study.

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