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Use of nanotechnology in water purification

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ABSTRACT

Nanotechnology is expected to open some new aspects in water purification using atomic scale tailoring of materials. Green nanotechnology is the development of clean technologies, to minimize potential environmental and human health risks associated with the manufacture and use of nanotechnology products, and to encourage replacement of existing products with new nano-products that are more environmentally friendly. It has main goals like producing nanomaterials and nano-products without harming the environment or human health; thereby, providing solutions to environmental problems. This area could contribute to solutions for some of the major problems, such as ensuring a supply of safe drinking water for a growing population, as well as addressing issues in medicine, energy, and agriculture. Nanomaterials or products can clean hazardous waste sites, desalinate water, treat pollutants, or sense and monitor environmental pollutants. Nanoremediation of water offers the potential of novel nanomaterials for the treatment of surface water, groundwater, wastewater, and other environmental materials contaminated by toxic metal ions, organic & inorganic solutes, and microorganisms. The present market of nanotech-based technologies applied in water treatment consists of reverse osmosis, nanofiltration and ultrafiltration membranes. Among emerging products, one can name nanofiber filters, carbon nanotubes and various nanoparticles. This efficiency generally stems from the very high specific surface area of nanomaterials, which increases dissolution, reactivity and sorption of contaminants. Water filtration may be improved with the use of nanofiber membranes, which appears promisingly effective. Carbon nanotube-based membranes for water desalination and nanoscale sensors can identify contaminants in water systems. Electrospun nanofibers and nanobiocides show potential in the improvement of water filtration membranes. In this review, the unique physicochemical and surface properties of nanoparticles and the advantages have been discussed that these nanomaterials provide for engineering applications that ensure a supply of safe drinking water for our growing population.

Keywords: *Water purification, Carbon nanotubes, Nanoadsorbent, Zeolite, Nanofitration, Nanofiber, Nanosensor, Photocatalyis, Aquaporin, Self-assembly*

INTRODUCTION

There is a possibility of conflict between people because of increasing demand for potable water, supported by the world-wide water shortage of water resources. Water treatment can give a probable solution to overcome this problem to some extent. Water remediation is one of the major needs, which the world is facing today. Water contamination not only affects environment and human health, but it also has an impact on economic and social costs. There are various commercial and non-commercial methods to combat against this problem, which are growing day by day due to the fast growing advancing technology. Nanotechnology has also proved to be one of the finest and advance ways for waste water treatment. There are various reasons behind the success of nanotechnology and scientists are still working on further enhancement of its usage. Nanoparticles have very high adsorbing, interacting and reacting capabilities due to their small size with high proportion of atoms at surface. These can even be mixed with aqueous suspensions and thus, can behave as colloids. Nanoparticles can achieve energy conservation due to its small size, which can ultimately lead to cost saving. Nanoparticles have great advantage of treating water in depths and any other location, which is generally left out by other conventional technologies? Since water treatment by using nanoparticles has high technology demand, its usage cost should be managed according to existing competition in market (Crane and Scott, 2012). There are various recent advances on different nanomaterials like nanostructured membranes, nanoadsorbents, nanocatalysts, bioactive nanoparticles, biomimetic membrane and molecularly imprinted polymers (MIPs).

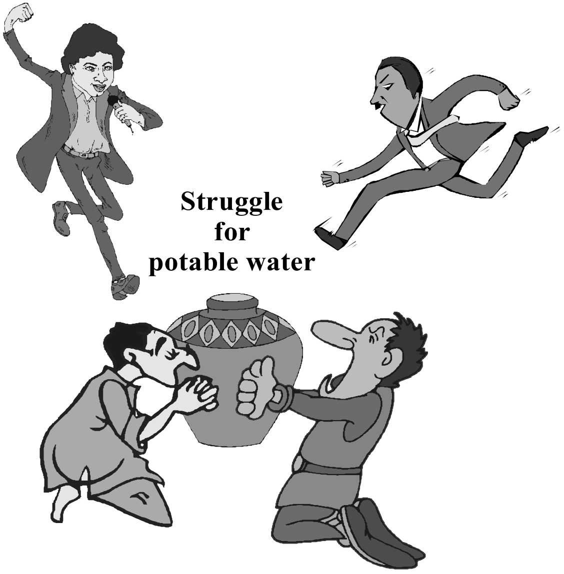

Figure 1. Scarcity of Water

ADSORPTION

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. Adsorption is a surface-based process, while absorption involves the whole volume of the material. The term sorption encompasses both these processes, while desorption is the reverse of it. Adsorption is a surface phenomenon. Nanoadsorbents show high rate of adsorption of organic compounds as compared to granular or powdered activated carbon. This is due to their large surface area and therefore, nanoadsorbents have great potential for more efficient, faster and novel decontamination processes aimed at removal of organic and inorganic pollutants like heavy metals and micropollutants. Adsorption-based techniques are simple and easy to use in water purification, which is an advantage over conventional desalination methods consuming more energy. Here, we will mainly focus on the following types of nanoadsorbents:

- Carbon-based nanoadsorbents i. e., carbon nanotubes (CNTs)
- Metal-based nanoadsorbents
- Polymeric nanoadsorbents
- Zeolites.

Carbon Nanotubes

One of the most heavily used materials for water purification filters is carbon, usually in the form of activated carbon i.e. carbon treated with oxygen. One of the problems with activated carbon is the disposal of adsorbed contaminants along with the adsorbent. Another concern is that its pores are often blocked during adsorption. Carbon nanotubes played a significant role to overcome such problems. Carbon nanotubes (CNTs) are tubular cylinders of carbon atoms that have extraordinary mechanical, electrical, thermal, optical and chemical properties. Nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of carbon, called graphene. Based on their manufacturing process, nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). CNTs possess highly assessable adsorption sites, an adjustable surface chemistry and a high specific surface area proving their potential for water treatment. Having a hydrophobic surface, CNTs need to be stabilized in aqueous suspension so as to avoid aggregation that reduces the active surface. CNT powders are incorporated in diverse commercial products ranging from rechargeable batteries, automotive parts, and sporting goods to boat hulls and water filters. In this field, Pan and Xing (2008) studied the adsorption mechanisms of organic chemicals on carbon nanotubes while Rao et al. (2008) used carbon nanotube to exhibit the sorption of divalent metal ions from aqueous solution.

Unlike many microporous adsorbents, CNTs possess fibrous shape and well developed mesopores, which contribute to the advanced removal capacities of macromolecular biomolecules and microorganisms. CNTs exhibit great efficiency in removal of cyanobacterial (microcystin derivatives) toxins from water systems (Upadhyayula et al., 2009). This review also considered CNT based adsorption filters for removal of contaminants from cost, operational and safety stand point. In addition to this, CNTs cause oxidative stress in bacteria and destroy their cell membranes exhibiting antimicrobial properties. During this chemical oxidation process, no toxic byproducts are produced, which is an important advantage over conventional disinfection processes.

Yang et al. (2013) reported that plasma-modified ultra long carbon nanotubes exhibit ultrahigh specific adsorption capacity for salt (exceeding 400% by weight), which is much higher than shown by activated carbon-based water treatment systems. This adsorption capacity of ultra long carbon nanotube-based membranes could be used in removing salt, as well as organic and metal contaminants. These ultralong carbon nanotube-based membranes may develop next-generation rechargeable, potable water purification appliances with superior desalination, disinfection and filtration properties.

Hashim et al. (2012) synthesized 3D macroscale carbon nanotube elastic solids by a boron-doping strategy during chemical vapour deposition. These sponge-like solids demonstrated high efficiency in removal of oil from contaminated sea water even after repeated use. Ahn et al. (2012) fabricated CNT membranes and used them for the purpose of desalination. Ji et al. (2009) used single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT) for removal of an antibiotic, tetracycline from aqueous solution. They compared a nonpolar adsorbate, naphthalene and two other carbonaceous adsorbents, pulverized activated carbon (AC) and nonporous graphite, with the adsorption efficiency of CNTs. The adsorption affinity of tetracycline decreased in the order –
Graphite/SWNT > MWNT >> AC.

The remarkably strong adsorption of tetracycline to the carbon nanotubes and to graphite can be attributed to the strong adsorptive interactions (Van der Waals forces, π-π electron-donor-acceptor interactions, cation-π bonding) with the graphene surface. In the same direction, Cong et al. (2013) reviewed the removal of antibiotics by carbon nanotubes.

Das et al. (2014) developed an appropriate water treatment technology that not only removed macro-, micro- and nano-pollutants but also desalinated water to a significant extent. The non-polar interior surface of carbon nanotubes (CNTs) strongly attracts the polar water molecules and rejects salts and pollutants. Self-cleaning functions, antifouling and low energy consumption have made CNT membranes extraordinary over the conventional ones. CNT-based membranes show great efficiency in terms of water permeability, desalination capacity, solute selectivity, antifouling, energy savings and scalability.

Amini et al. (2013) synthesized thin-film nanocomposite (TFN) membranes by interfacial polymerization for the forward osmosis (FO) application. They used amine functionalized multi-walled carbon nanotubes (F-MWCNTs) as an additive in aqueous solution of 1, 3-phenylendiamine (MPD) to enhance the FO membranes performance. Different concentrations of F-MWCNTs (0.01, 0.05 and 0.1 wt%) were added to the aqueous solution. The fabricated TFN membranes were characterized in terms of membranes structure and surface properties, separation properties as well as FO performance. They also compared these with traditional thin-film composite (TFC) membrane. It was observed that the surface hydrophilicity of TFN membranes was improved with increasing F-MWCNTs concentration in the aqueous solution. The TFN membranes exhibited high water permeability and acceptable salt rejection in the range of 0.01–0.1

wt% F-MWCNTs loading in comparison with TFC membrane. The most permeable TFN had a water flux (95.7 L/m^{2}h), which is nearly 160% higher than TFC membrane and it is an exceptional improvement in FO membranes.

Ahmed et al. (2013) demonstrated that coated nitrocellulose membranes with a nanocomposite containing 97% (wt%) of polyvinyl-*N*-carbazole (PVK) and 3% (wt%) of single-walled carbon nanotubes (SWNTs) (97:3 wt% ratio PVK:SWNT) achieve similar or improved removal of bacteria, when compared with 100% SWNTs coated membranes.

Corry (2011) carried out desalination of water through ion transport using functionalised carbon nanotubes. A range of different charged and polar functional groups were added to a 1.1 nm diameter CNT that was earlier found to be only moderately effective at rejecting ions. These CNTs were incorporated into membranes and simulations were conducted with a hydrostatic pressure difference to determine the ion rejection and flux of water. The results showed that the addition of charges at the entrance of the pore can help to prevent the passage of ions and any functionalisation reduced the flow of water through the membrane due to increased electrostatic interactions between the water molecules and the CNT. The performance of these membranes in the simulations was many times better than existing technology and thus, the inclusion of functionalised CNTs in desalination membranes has proved to be useful in achieving salt rejection and rapid water flow.

However, the direct use of unbounded CNTs can pose health risks to humans and ecosystems because they are difficult to separate from treated water. Wang et al. (2014) grew CNT arrays of hundreds of micrometers in length on nanometer-thin mineral discs with a negligible mass and volume, a structure which they termed carbon nanotube ponytails (CNPs). The layered double oxide (LDO) discs were slightly magnetic. This magnetization is sufficiently weak to prevent CNPs from aggregating under self-attraction but strong enough to be utilized for separation. Compared to individual CNTs, CNPs can be more effectively separated from water using gravitational sedimentation, magnetic attraction, and membrane filtration while retaining the ability to perform adsorption, disinfection, and catalytic degradation of contaminants in water. They used model pollutants like methylene blue, *Escherichia coli*, and *p*-nitrophenol, which showed that all the surfaces of individual CNTs in CNPs were accessible during water treatment.

CNT technology is promising, as it can possibly avoid difficulties of treating biological contaminants in conventional water treatment plants, and thereby, remove the burden of maintaining the biostability of treated water in the distribution systems.

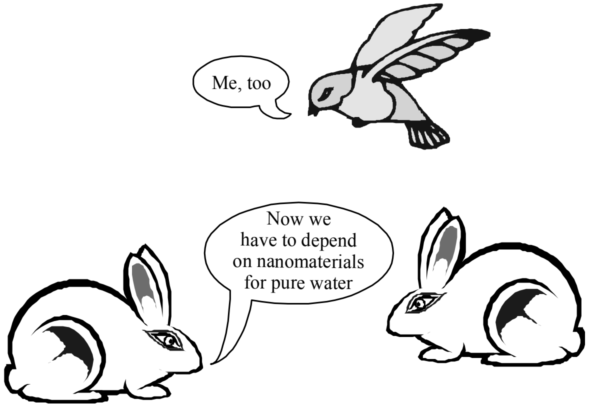

Figure 2. Dependence on nanomaterials

Metal and metal oxide based nanoadsorbents

Deliyanni et al. (2006) developed a novel, simple and cost effective method for the preparation of nanocrystalline iron hydroxides and oxyhydroxides. Different iron precursors were used and combined to form different volatile precipitating agents. They observed that the prepared product, akaganéite [beta- FeO(OH)], had high surface area and definite pore size distribution. The efficiency of the prepared material in the removal of heavy metal ions, which constitute priority pollutants like cadmium cations and arsenate oxyanions was also evaluated. Batch and column experiments were performed for the analysis of metal ions removal.

Seisenbaeva et al. (2015) prepared hybrid metal oxide adsorbents using anatase form of TiO_2 and employed it for removal of rare earth elements. Mesoporous nanorods of anatase were fuctionlized with imino-bis-methylphosphonic acid (IMPA, $NH(CH_2PO_3H_2)_2$) or aminoethylphosphonic acid (AEPA, $H_2NC_2H_4PO_3H_2$). Fang et al. (2014) used Mg/biochar, which is rich in magnesium nanoparticles and organic functional groups for removal and recovery of phosphorus from swine wastewater.

Ghosh et al. (2013) used superparamagnetic Fe_3O_4 nanoparticles bearing aminated β-cyclodextrin for the removal of pharmaceutically active compounds (PhACs), naproxen and carbamazepine and one endocrine disrupting compounds (EDCs) bisphenol A from aquatic environment. PhACs and EDCs have adverse effects on health and environment.

Kumar et al. (2011) developed a bi-metal (Fe and Al) doped micro- and nano-multi-functional polymeric adsorbents for the removal of fluoride and arsenic (V) from wastewater. The adsorption tests performed on Al/Fe-doped adsorbents showed significant loading of these ions. The equilibrium loading of fluoride on nanoparticles based adsorbents was determined as ~ 100 mg g^{-1} corresponding to the aqueous phase concentration range of 0–90 ppm, whereas that of arsenic (V) was determined as 40 mg g^{-1} corresponding to the range of 0–70 ppm. This methodology is a step towards developing multi-functional adsorbents for the removal of different types of solutes from wastewater.

Ray and Shipley (2015) reviewed the applicability of iron oxide (hematite, magnetite and maghemite), carbon nanotubes (CNT), and metal oxide based (Ti, Zn) and polymeric nanoadsorbents in waste water treatment. Du et al. (2011) studied the application of a novel sorbent, sodium titanate nanotube (STN) on partitioning of various divalent cations. Seven divalent cations, from alkaline earth, transition and post-transition groups, were used to determine the capacity and selectivity of STN. At pH 3±0.02 and 0.1 M ionic strength, STN displayed high capacity for Pb and Cd (1.27 and 0.39 mmol/g, respectively). The affinity of divalent cations was in the order –

Pb>>Cd>Cu>Zn>Ca>Sr>Ni

STN preferentially sorbed Cd over other metals (Zn, Ni, Ca and Sr), which coexist in industrial wastewater.

Huang et al. (2012) synthesized titanate nanoflowers through a hydrothermal treatment of anatase nanopowders in concentrated NaOH solution. These nanoflowers had large specific surface area and showed ability for the removal of heavy metal ions from water system. It was observed that titanate nanoflowers possess larger adsorption capacity and more rapid kinetics than titanate nanotubes/nanowires. They also showed high selectivity in the removal of highly toxic heavy metal ion i. e. Cd(II) than less toxic ions Zn(II) and Ni(II). Titanate nanoflowers are proposed as potential adsorbents for efficient removal of toxic metal ions.

Liu et al. (2013) studied the adsorption of four heavy metals (Pb^{2+}, Cd^{2+}, Cu^{2+} and Cr^{3+}) from aqueous solutions using titanate nanotubes (TNTs). The mechanism of ion-exchange between metal ions and H^+/Na^+ located in the interlayers of TNTs was observed. Binary or quaternary competitive adsorption indicated that the adsorption capacity (mmol g^{-1}) of the four heavy metals onto TNTs followed the sequence of –

Pb^{2+} (2.64) ≫ Cd^{2+} (2.13) > Cu^{2+} (1.92) ≫ Cr^{3+} (1.37)

It followed the reverse order of their hydration energies.

Chen et al. (2012) synthesized a novel bimetallic oxide adsorbent by the co-precipitation of Fe(II) and Ti(IV) sulfate solution using ammonia titration at room temperature. These were used for fluoride removal from drinking water. Fe—Ti adsorbent had a Langmuir adsorption capacity of 47.0 mg g^{-1}, which was much higher than that of either a pure Fe oxide or Ti oxide adsorbent. There was an interaction between Fe and Ti, where Fe—O—Ti bonds on the adsorbent surface and hydroxyl groups provide the active sites for adsorption, and Fe—O—Ti—F bonds were formed by fluoride adsorption. This Fe—Ti adsorbent was found to be efficient and economical for fluoride removal from drinking water. AiRong and Weng (2014) prepared graphene-based metal oxide nanocomposites and studied their application as adsorbents in water treatment.

Polymeric Nanoadsorbents

Pan et al. (2009) developed polymeric and polymer-based hybrid adsorbents for removal of inorganic pollutants like heavy metals from waters. They have focused on the preparation of these polymeric-based adsorbents, their physicochemical properties, adsorption characteristics and mechanism, as well as their application in water purification.

Poly(5-sulfo-1-aminoanthraquinone) nanosorbents were synthesized by a chemical oxidative polymerization of 5-sulfo-1-aminoanthraquinone by Huang et al. (2011). The polymerization parameters such as oxidant species, acid species, acid concentration, oxidant/monomer ratio, polymerization time, and temperature were studied to optimize the synthetic yield, structure, and multifunctionalities of the target nanoparticles. Various analytical and spectral techniques were used to study molecular structure, size distribution, morphology, and properties of the nanoparticles. It was observed that K_2CrO_4 (oxidant) and aqueous $HClO_4$ without any external stabilizers were an optimal combination for synthesizing the nanoparticles with a clean surface, large π-conjugation, narrow size distribution, intrinsic semiconductivity, blue fluorescence, and inherent self-stability. It was found that the nanoparticles, having a combination of five kinds of active groups, —NH—, —N═, —NH_2, ═O, and —SO_3H, with an appropriate specific area of 115.15 $m^2 g^{-1}$, exhibit very high removal percentage of lead and mercury of 99.6 and 99.8% at initial concentrations of even up to 200 mg L^{-1}. Ultrarapid initial adsorption rate of up to 10350 and 14140 mg $g^{-1} h^{-1}$ for Pb(II) and Hg(II), increased adsorbability order –
Zn(II) < Fe(III) < Cu(II) ≪ Ag(I) < Cd(II) < Pb(II) < Hg(II)

Removal of harmful heavy metal ions from wastewaters is becoming an ultrarapid technique using chelate nanosorbents.

The preparation, characterization and dye adsorption properties of nanocomposite (calcium alginate/ organophilic montmorillonite) (CA/OMMT) were investigated by Taleb et al. (2012). γ-Rays irradiation was used as an initiator for the polymerization of alginate and OMMT. Two textile dyes, acid green B and direct pink 3B, were used as model anionic dye. Factors affecting dye sorption, such as pH, sorbent concentration and temperature of each dye solution were studied. It was observed that the sorption of dyes by the nanocomposite was pH-dependent and maximum sorption was obtained at pH 2. It was concluded that the as-prepared adsorbents exhibited excellent affinity for the dye, and can be applied to treat wastewater containing anionic dyes.

Shirsath et al. (2011) carried out the synthesis of poly(acrylic acid)-bentonite-FeCo (PAA-B-FeCo) hydrogel nanocomposite via ultrasound assisted *in situ* emulsion polymerization. The strength and stability of hydrogel was increased by addition of exfoliated bentonite clay platelets and Fe–Co, which also assisted in the adsorption of organic pollutants. The response of the nanocomposite hydrogel was evaluated using a cationic dye, crystal violet under different temperature, pH, and cavitation environment. The optimum temperature was found to be 35°C and basic pH (optimum at 11) was responsible for the higher adsorption of dye due to dissociation of COO^- ions at higher pH.

A novel polyampholyte nanocomposite hydrogels (NH) was synthesized by Dalaran et al. (2011). The efficiency of the nanoadsorbent was studied by the removal of the indigo carmine from the aqueous solutions. Acrylic acid (AA), 2-(diethylamino)ethyl methacrylate (2-DEAEMA) and montmorillonite (MMT) were used as ionic monomers and inorganic component, respectively. In the preparation of NH, *in situ* free radical addition polymerization technique was used in the aqueous media. All NH were sensitive to pH. The indigo carmine adsorption rate of NH is faster than that of hydrogel. The pseudo-first-order adsorption mechanism was observed for indigo carmine adsorption from textile aqueous effluents.

Hydrogel nanocomposites having high amount of functional group, enhanced swelling ability, and improved mechanical properties were prepared by Kaplan and Kasgoz (2011) for removal of basic dyes from aqueous solutions. Acrylamide (AAM) and itaconic acid sodium salt (IANa) were polymerized using polyethyleneglycol (400) diacrylate as crosslinker in the presence of montmorillonite (MMT). The products were used as adsorbent for removal of brilliant cresyl blue (BCB) from aqueous solutions. It was found that the adsorption kinetics followed a pseudo-second-order kinetic model. These hydrogel nanocomposites had the potential to be used as novel, fast-responsive and high capacity adsorbent materials for the removal of cationic dyes, which is a serious problem, especially in textile industry.

Kumar et al. (2011) synthesized, characterized, and studied the application of bi-metals (Fe and Al) doped micro- and nanoparticles based adsorbents for the removal of fluoride and arsenic (V) ions from water. The adsorbents were prepared by suspension polymerization, where Fe and Al were incorporated during a polymerization step. A porous structure inside the materials was created by carbonization and activation of the bi-metals doped beads (~0.8 mm). The adsorption tests performed on Al/Fe-doped adsorbents revealed significant loading of those ions. This methodology is a step towards developing multi-functional adsorbents for the removal of different types of solutes from wastewater.

Zou et al. (2014) used reverse atom transfer radical precipitation polymerization (RATRPP) and a surface imprinting nanotechnique for the preparation of core-shell silica-based surface molecularly imprinted nanoadsorbents (SMIP), which were then used to improve selective recognition and achieve the rapid removal of the antibiotic sulfamethazine (SMZ) from water. The SMIPs adsorbed more SMZ than non-imprinted nanoadsorbents, and they adsorbed much more of the template than other antibiotics, showing that the SMIPs had excellent selective recognition. Reusable SMIPs were potentially efficient nanoadsorbent for the selective and fast removal of antibiotic residues from aqueous environments.

Synthesis, modification and graft polymerization of magnetic nanoparticles for poly aromatic hydrocarbons (PAH) removal in contaminated water was done by Torabian et al. (2014) Magnetic nanoparticles (MNPs) were modified with 3-mercaptopropytrimethoxysiline (MPTMS) and grafted with allyl glycidyl ether for coupling with β-naphtol as a method to form a novel nano-adsorbent to remove two PAHs from contaminated water. Tests were performed on the adsorption capacity of the two PAHs on grafted MNPs. Factors applied to the tests were temperature, contact time, pH, salinity and initial concentration of PAHs.

Zeolites

Zeolites are microporous, aluminosilicate minerals, so commonly used as commercial adsorbents and catalyst. Zeolites occur naturally but are also produced industrially on a large scale. Zeolites and mesoporous silica nanoparticles are silicate or aluminosilicate nanomaterials with well-defined pore networks. Mesoporous silica nanomaterials have not been as extensively applied relative to zeolites due to the cost and reduced thermal stability (Lehman and Larsen, 2014)

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), and as traps for molecules so that, they can be analyzed. Zeolites are also widely used as catalysts and sorbents. Their well-defined pore structure and adjustable acidity make them highly active in a large variety of reactions (Vjunov et al., 2014). Barloková (2008) studied the removal of dissolved iron and manganese from water by using the natural zeolite–clinoptilolite mined in the territory of Slovakia.

Due to their high cation-exchange ability as well as the molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification processes in the past decades (Wang and Peng, 2010). Margeta et al. (2011) reviewed the development of natural zeolites for their use in water treatment systems.

Linde type A zeolite (LTA)-goethite nanocomposite was synthesized by Kugbe et al. (2009). Sodium orthosilicate solution was added to goethite, followed by addition of sodium aluminate and NaOH solutions at 100°C. The optimum condition for nanocomposite formation at the Si addition step was pH 10.0 and Si/Fe = 2.7. The final product consisted mainly of LTA and goethite crystals. Precipitation of silica on the surface of goethite was followed by the formation of Si-O-Fe bonds at the Si addition step, which contributed to formation of the LTA-goethite nanocomposite. The amount of adsorption of phosphate on the final product was more than 1.6 times the amount adsorbed on the mixture, indicating generation of synergistic effect in the LTA-goethite nanocomposite.

Zhan et al. (2010) worked on the removal of humic acid (HA) from aqueous solution by cetylpyridinium bromide (CPB) modified zeolite. This modification created more efficient sites for HA adsorption. The effects of various experimental parameters such as contact time, initial HA concentration, solution pH and coexistent Ca^{2+}, upon HA adsorption onto CPB modified zeolites were studied. The results revealed that natural zeolite had negligible affinity for HA in aqueous solutions, but CPB modified zeolites exhibited high adsorption efficiency for HA. A higher CPB loading on natural zeolites exhibited a larger HA adsorption capacity.

Valdés et al. (2009) compared experimental results on methylene blue (MB) removal systems based on ozone oxidation, zeolite adsorption, and simultaneous adsorption-oxidation using ozone in the presence of natural zeolite. It was observed that ozone oxidation combined with zeolite adsorption increased the overall MB oxidation rate with respect to ozonation process and zeolite adsorption. In presence of free radical scavenger, only a 25% of reduction on MB removal rate was observed in the simultaneous treatment, as compared with 70%, when ozonation treatment was used, showing that MB oxidation reactions take place mainly on the zeolite surface.

Mahlangu et al. (2011) designed and studied a cost-effective biosand filter. The biosand filter was modified with the addition of zeolites (clinoptilolite). The zeolites formed the largest part of the filter media, which comprised of four layers. The complete filter had six zones, which played a role during the filtration process. Results indicated removal of up to 80 calcium, 89 magnesium, 99 iron, 56 arsenic, 54 fluorides, 96 turbidity, 37 nitrates and 41% total organic carbon.

Nagy et al. (2011) studied the antibacterial properties of silver nanoparticles embedded within a zeolite membrane whereas Alvarez-Ayuso et al. (2003) studied the sorption behaviour of natural (clinoptilolite) and synthetic (NaP1) zeolites with respect to Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) in order to consider its application to purify metal finishing waste waters. The batch method employed using metal concentrations in solution ranged from 10 to 200 mg L^{-1} and solid/liquid ratios ranged from 2.5 to 10 g L^{-1}. Synthetic zeolite exhibited about 10 times greater sorption capacities (b(Cr) = 0.838 mmol g^{-1}, b(Ni) = 0.342 mmol g^{-1}, b(Zn) = 0.499 mmol g^{-1}, b(Cu) = 0.795 mmol g^{-1}, b(Cd) = 0.452 mmol g^{-1} than natural zeolite b(Cr) = 0.079 mmol g^{-1}, b(Ni) = 0.034 mmol g^{-1}, b(Zn) = 0.053 mmol g^{-1}, b(Cu) = 0.093 mmol g^{-1}, b(Cd) = 0.041 mmol g^{-1}), and therefore, appearing more suitable to perform metal waste water purification processes. This zeolite showed the same high sorption capacity values, when used in the purification of metal electroplating waste waters.

Zeolites P in sodium (NaP) and potassium (KP) forms were used as adsorbents for the removal of calcium (Ca^{2+}) and zinc (Zn^{2+}) cations from aqueous solutions (Yusof et al., 2010). The flame atomic absorption spectroscopy method was used to analyse the amount of Ca^{2+} and Zn^{2+} in aqueous solution before and after the adsorption by zeolites. This result also showed that zeolite KP adsorbed Ca^{2+} and Zn^{2+} more than zeolite NaP and proved that modification of zeolite NaP with potassium leads to an increase in its adsorption efficiency. Therefore, the zeolites NaP and KP could be used for water softening (Ca removal) and reducing water pollution/toxicity (Zn removal).

Ghadiri et al. (2010) synthesized surfactant-modified clinoptilolite-rich tuff for the removal of methyl tert-butyl ether (MTBE) from aqueous solutions. Clinoptilolite zeolite was treated with sodium chloride and then modified with hexadecyltrimethylammonium chloride (HDTMA-Cl) and n-cetylpyridinium bromide (CPB) to be used in different experimental conditions. The ability of raw or non-modified zeolite (NMZ) and surfactant-modified zeolites (SMZ) to remove MTBE from aqueous solutions was studied as a function of contact time, pH and concentrations of adsorbent and adsorbate, by means of a batch technique in aqueous system. The removal of MTBE from aqueous solutions by modified zeolites was found to be more effective than non-modified samples. Also, HDTMA-modified zeolite had more effective performance than CPB-modified zeolite.

Wingenfelder et al. (2005) reported on the removal of Fe, Pb, Cd, and Zn from synthetic mine waters by a natural zeolite. Pb was removed efficiently from neutral as well as from acidic solutions, whereas the uptake of Zn and Cd decreased with low pH and high iron concentrations. With increasing Ca concentrations in solution, elimination of Zn and Cd became poorer while removal of Pb remained virtually unchanged. The zeolite was stable in acidic solutions and disintegration was only observed below pH 2.0. Altare et al. (2007) investigated the regeneration and long-term stability of surfactant-modified zeolite for removal of volatile organic compounds from contaminated water. The unique ion exchange and adsorption properties, high porosity and excellent thermal stability of zeolites make them very suitable for many applications for water treatment processes.

Figure 3. Waters or tears- Choice is youtrs?

MEMBRANE PROCESSES

Nanofiltration Membranes (NF membrane)

Nanofiltration is a recent membrane filtration process mostly used with low total dissolved solids water such as surface water and fresh groundwater, with the purpose of softening (polyvalent cation removal) and removal of disinfection by-product precursors such as natural organic matter and synthetic organic matter (Letterman, 1999). Nanofiltration is also becoming more widely used in food processing applications such as dairy for simultaneous concentration and partial (monovalent ion) demineralization.

NF membrane exhibits properties between those of ultrafiltration (UF) and reverse osmosis (RO), both charge and size of particle play important role in NF rejection mechanism. Simpson et al. (1987) described NF as a charged UF system whereas Rohe et al. (1990) referred it as low pressure RO system. However, NF has advantages of lower operating pressure compared to RO, and higher organic rejection compared to UF. Physical sieving would be the dominant rejection mechanism for the colloids and large molecules, whereas solution diffusion mechanism and charge effect of membrane play the major role in separation process for the ions and lower molecular weight substances.

Macoun (1998) presented the NF rejection mechanisms into the following five steps –

(i) Wetted surface – In this step, water associates with the membrane through hydrogen bonding and the molecules, which form the hydrogen bonding with the membrane can be transported.

(ii) Preferential sorption/Capillary rejection – Here, the membrane is heterogeneous and microporous, and electrostatic repulsion occurs due to different electrostatic constants of solution and membrane.

(iii) Solution diffusion – The membrane is homogeneous and non-porous; solute and solvent dissolve in the active layer of the membrane and the transport of the solvent occurs due to the diffusion through the layer.

(iv) Charged capillary – In this step, the electric double layer in the pores determines rejection. Ions of same charge as that of membrane are attracted and counter ions are rejected due to the streaming potential.

(v) Finely porous – The membrane is a dense material punctured by pores. Transport is determined by partitioning between bulk and pore fluid.

Some benefits of water treatment through nanofiltration membrane are:

- Lower operating costs,
- Lower energy cost,
- Lower discharge of wastewater than reverse osmosis,
- Reduction of total dissolved solid (TDS) content in slightly brackish water,
- Reduction of pesticides and VOCs (organic chemicals),
- Reduction of heavy metals,
- Reduction of nitrates and sulfates,
- Reduction in turbidity, color and tannins,
- Hard water softening,
- Chemical-free (i.e., does not use salts or chemicals), and
- Water pH after nanofiltration is typically non-aggressive.

Han et al. (2013) prepared ultrathin (≈ 22–53 nm thick) graphene nanofiltration membrane (uGNMs) by chemically converted graphene (CCG) sheets for water purification. The uGNMs have well packed layer structure and high retention (> 99%) for organic dyes and moderate retention (≈ 20–60%) for ion salts. The rejection mechanism of this kind of negatively charged membranes was studied. The integration of high performance, low cost, and simple solution-based fabrication process of uGNMs promises great potential application in practical water purification.

Shon et al. (2013) reviewed the applications of nanofiltration membranes (NF) for water and wastewater treatment. NF has replaced reverse osmosis (RO) membranes in many applications due to lower energy consumption and higher flux rates. Park et al. (2012) synthesized new and ion-selective nanofiltration (NF) membranes based on polyvinylidene fluoride (PVDF) nanofibers and hyperbranched polyethylenimine (PEI) as building blocks. These new nanofibrous composite (NFC) membranes consisted of crosslinked hyperbranched PEI networks supported by PVDF nanofibrous scaffolds that were electrospun onto commercial PVDF microfiltration (MF) membranes. Positively charged NF membranes could be operated at low pressure with high water flux and improved rejection for monovalent cations. The effects of crosslinker chemistry on membrane properties (morphology, composition, hydrophobicity, and zeta potential) and membrane performances (salt rejection and permeate flux) in aqueous solutions (2,000 mg L^{-1}) of four salts (NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$) at pH 4, 6, and 8 was investigated. NFC–PVDF membrane with a network of PEI macromolecules crosslinked with trimesoyl chloride had a high water flux (~30 L m^{-2} h^{-1}) and high rejections for $MgCl_2$ (~88 %) and NaCl (~65 %) at pH 6 using a pressure of 7 bar. PVDF nanofibers and hyperbranched PEI are promising building blocks for the fabrication of high performance NF membranes for water purification.

Zinadini et al. (2014) prepared a novel polyethersulfone (PES) mixed matrix nanofiltration membrane containing graphene oxide (GO) nanoplates by the phase inversion method. The effect of the embedded nanosheet on the morphology and performance of the fabricated new membranes was investigated in terms of pure water flux, dye removal and fouling parameters. The GO membranes had higher dye removal capacity than the unfilled PES. Fouling resistance of the membranes assessed by powder milk solution filtration revealed that 0.5 wt% GO membrane had the best antibiofouling property and the highest mean pore radius, porosity, and water flux. The prepared GO nanocomposite membrane showed reusability during filtration.

Yin and Deng (2015) fabricated a new class of membranes by combining polymeric materials with nanomaterials. The advanced nanocomposite membranes could be used for specific water treatment applications by tuning their structure and physicochemical properties (e.g. hydrophilicity, porosity, charge density, and thermal and mechanical stability) and introducing unique functionalities (e.g. antibacterial, photocatalytic or adsorptive capabilities).

Wu et al. (2013) prepared multi-walled carbon nanotubes MWNTs/polyester thin film nanocomposite (TFN) membranes by interfacial polymerization of triethanolamine (TEOA) and trimesoyl chloride (TMC) on the polysulfone (PSf) supporting membrane. The effect of MWNTs concentration and surfactant species in the aqueous phase as well as the reaction time of interfacial polymerization on the membrane properties were investigated. The MWNTs/polyester TFN membrane exhibited a good long term stability.

Gehrke et al. (2012) developed multilayer coating systems and applied them on a new nanocomposite filter resulting in high photocatalytic activities with maximum photon efficiencies of 0.0733. The coating layer do not have a negative influence on the permeate flux. Titanium dioxide nanoparticles were used for nanocoating. It reduced the fouling potential of membranes and destroyed water contaminants.

Mukai and Mizuno (2014) prepared iron ferrocyanide-supported nanofiber membrane for purification of cesium-contaminated water. The nanofiber membrane, made up of polyacrylonitrile (PAN), was used as a base material of the functionalized membrane. Nanofiber membranes were immersed in the dispersions of iron ferrocyanide with various concentrations and pH values.

Hang et al. (2014) synthesized mixed-matrix membranes for water treatment. These can be prepared by incorporating nanoparticles into membrane matrix. A number of nanomaterials were used as potential water transport channels and to modify the structure and surface properties of the membrane thin film layers. Mixed-matrix membranes (MMMs) can benefit from the high performance of both; the organic matrix and inorganic fillers, which are believed to be the next generation of novel membrane materials.

Self-Assembling Membranes

Self-assembly is a process, in which a disordered system of pre-existing components forms an organized structure or pattern as a consequence of specific, local interactions among the components themselves, without external direction. Self-assembled membranes are of vital importance in biological systems e.g. cellular and organelle membranes, however, more focus is being put on synthetic self-assembled membranes as an alternative for lipid membranes and for lithographic methods. More investigations move towards self-assembly processes because of the low cost preparations, structural self-regulation and the ease of creating composite materials and tunable properties. The fabrication of self-assembling membrane materials is of interest due to their use in delivery vessels, size selective separation and purification, controlled-release materials, sensors and catalysts, scaffolds for tissue engineering, low dielectric constant materials for microelectronic devices, antireflective coatings and proton exchange membranes for polymer electrolyte membrane fuel cells.

Phillip et al. (2010) prepared self-assembled nanoporous membranes containing monodisperse pores of 24 nm diameter using poly(styrene-b-lactide) block copolymers. These thin films were used as water filtration membranes. Qiu et al. (2013) prepared nanoporous membranes by combining the self-assembly of an amphiphilic block copolymer (PS-b-P4VP) with nonsolvent-induced phase separation. This membrane was found to be composed of a thin layer of densely packed highly ordered cylindrical channels with uniform pore sizes perpendicular to the surface on top of a non-ordered sponge-like layer. The self-assembled membrane obtained a water flux of more than 3200 L m^{-2} h^{-1} bar^{-1}, which was in an order of magnitude higher than the water fluxes of commercially available membranes with similar pore sizes. This membrane was compatible in size-selective and charge-based separation of biomolecules (proteins).

Green et al. (2015) synthesized functional membranes by the self-assembly of inorganic, polymeric or hybrid nanoparticles. Two types of such membranes were studied, those possessing size and charge selectivity suitable for ultrafitration, nanofiltration and chemoselective separation, and those possessing proton or lithium transport properties suitable for fuel cell and lithium battery applications, respectively.

Nanoporous structures were obtained by the self-assembly of polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymers (BCP), where thick films, cylindrical microdomains were oriented normal to the substrate and air interfaces, and in the interior of the films, the microdomains were randomly oriented. Continuous nanopores that penetrated through the film were readily produced by a simple preferential swelling of the PMMA microdomains.

The confined swelling and rapid contraction of PMMA microdomains generated well-defined uniform pores with diameters of 17.5 nm. The size selectivity and rejection of Au nanoparticles (NPs) for these ultrafiltration (UF) membranes were demonstrated, suggesting an efficient route to tunable, noncomponent-degradative UF membranes (Ahn et al. 2014).

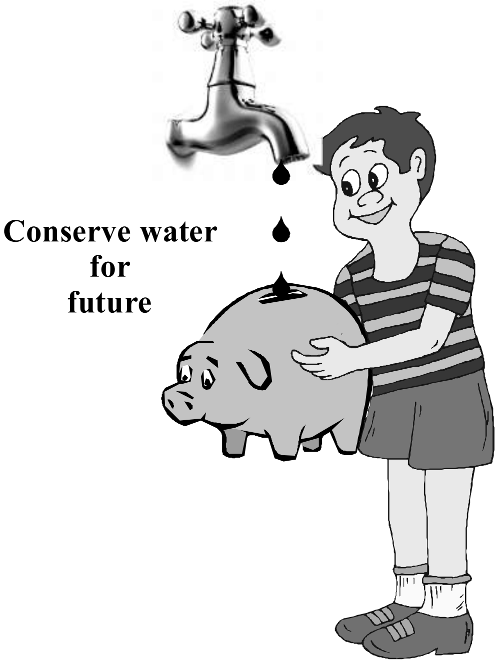

Figure 4. Conservation of water: A necessity of the day

Nanofiber Membrane

Faccini et al. (2015) developed efficient carbon nanofibrous (CNF) membranes for NP filtration from aqueous solutions. Free-standing carbon nanofiber (CNF) with different fiber size distribution ranging from 126 to 554 nm in diameter were produced by electrospinning of polyacrylonitrile (PAN) precursor solution, followed by thermal treatment. To increase the specific surface area and flexibility of the CNF, tetraethoxyorthosilicate was added. The resulting membranes were flexible and mechanically strong enough to withstand filtration under pressure or vacuum. The experimental results of filtration showed that the fabricated membranes could efficiently reject nanoparticles of different types (Au, Ag, and TiO_2) and sizes (from 10 to 100 nm in diameter) from aqueous solutions. It is worth mentioning that the removal of Ag NP with diameters as small as 10 nm was close to 100% with an extremely high flux of 47620 L m^{-2} h^{-1} bar^{-1}.

High flux, low pressure, thin film nanocomposite (TFNC) ultrafiltration membrane based on a polyacrylonitrile (PAN) nanofibrous substrate coupled with a thin hydrophilic nanocomposite barrier layer was prepared by electrospinning technique combined with solution treatment method (You et al. 2013). It was used as an ultrafiltration media to separate an oil/water emulsion. Yoon et al. (2009) fabricated high quality polyethersulfone (PES) nanofibrous membranes that were particularly useful for water purification by mixed solvent and oxidation processes. It possessed suitable strength, wettability and permeability, where the size, inter-fiber adhesion and hydrophilicity of electrospun nanofiber were controlled.

Huang et al. (2013) increased the strength of electrospun nanofibrous membranes (ENMs) for water purification using solvent vapour. A post-treatment approach was used to improve the mechanical properties of two commonly used membrane polymers: polyacrylonitrile (PAN) and polysulfone (PSu). This post-treatment involved exposing ENMs to the solvent vapor, where the mechanical strength was improved by the solvent-induced fusion of inter-fiber junction points. The treated membranes showed significant enhancement on tensile strength and Young's Modulus while high porosity and water permeability were retained.

Taha et al. (2012) prepared novel NH_2-functionalized cellulose acetate (CA)/silica composite nanofibrous membranes by sol-gel combined with electrospinning technology. Tetraethoxysilane (TEOS) as a silica source, CA as precursor and 3-ureidopropyltriethoxysilane as a coupling agent were used in membrane preparation. The composite nanofibrous membranes exhibited high surface area and porosity. The membranes were used for Cr(VI) ion removal from aqueous solution. The maximum adsorption capacity for Cr(VI) was estimated to be 19.46 mg g^{-1} and it could be regenerated by alkalization. Thus, the composite membrane prepared from biodegradable raw material has potential applications in the field of water treatment.

Li et al. (2013) fabricated PA6@Fe_xO_y composite nanofibrous membrane by electrospinning technique combined with hydrothermal strategy. PA6@Fe_xO_y nanofibrous membrane exhibited excellent performance for the removal of Cr(VI). The adsorption capacity could reach 150 mg Cr g^{-1} nanofibrous membrane, which was much higher than the previously reported values of some nanomaterials. Electrostatic adsorption led to the adsorption of Cr(VI) and redox reaction reduced Cr(VI) to Cr(III), which is much less toxic. Therefore, the PA6@Fe_xO_y composite nanofibrous membrane could be a good candidate for removing Cr(VI) from wastewater.

Polyethylene oxide (PEO)/Chitosan nanofiber membrane was prepared by the electrospinning technique. This nanofiber membrane was used for the adsorption of nickel (Ni), cadmium (Cd), lead (Pb) and copper (Cu) from aqueous solution (Aliabadi et al. 2013). The homogeneous electrospun nanofibers with the average diameter and surface area of 98 nm and 312.2 m^2g^{-1} were obtained, respectively. The sorption selectivity of lead, copper, cadmium and nickel onto the membrane was in order –

Pb(II) < Cd(II) < Cu(II) < Ni(II)

The adsorption of metal ions onto the PEO/Chitosan nanofiber membrane was feasible, spontaneous and endothermic. The reusability of nanofiber membrane for the removal of different metal ions was also determined after five sorption–desorption cycles.

Feng et al. (2008) carried out the production of drinking water (NaCl concentration < 280 ppm) from saline water of NaCl concentration 6 wt. % by air-gap membrane distillation (MD) using polyvinylidene fluoride nanofiber membrane. This was the first attempt to use electro-spun nanofiber membrane in MD. The MD process can compete with conventional seawater desalination processes such as distillation and reverse osmosis.

Bai et al. (2015) fabricated heterojunctioned architectures functionalized membrane using hydrothermally treated electrospun TiO_2 nanofibers in an alkaline $Sr(NO_3)_2$ precursor solution in an electronic oven. TiO_2 on the fiber surface was partially dissolved into Ti^{4+} to react with Sr^{2+} in favor of the nucleation of $SrTiO_3$ on TiO_2 nanofibers, and thus, a heterojunction was formed between $SrTiO_3$ and TiO_2, which improved photocatalytic activity. A multifunctional membrane was created by functionalizing the surface of commercial cellulose acetate (CA) membrane with heterojunctioned $SrTiO_3/TiO_2$ nanofibers. This newly structured membrane exhibited excellent water purification performances in a concurrent photocatalytic membrane filtration system under the irradiation of UV light.

Aquaporin Membranes

Aquaporins are water channel proteins in biological membranes that have extraordinary water permeability and selectivity. They play an important role in osmoregulation in living organisms (Borgnia et al. 1999). These proteins have exceptionally high water permeability (~ 10^{10} water molecules/s), high selectivity for pure water molecules, and a low energy cost, which make aquaporin-embedded membrane well suited as an alternative to conventional RO membranes.

Zhong et al. (2012) prepared planar biomimetic membranes consisting of aquaporin Z (AqpZ) upon cellulose acetate membrane substrate functionalized with methacrylate end groups. A selective layer was formed upon the substrate by vesicle rupture of triblock copolymer (ABA) vesicles and UV polymerization for nano-filtration (NF). The AqpZ:ABA ratio was varied from 1:200 to 1:50 and its effects on nanofiltration performance were elucidated. It was found that the NF membranes comprising AqpZ:ABA ratio of 1:50 can give an impressive water permeability of 34 LMH bar^{-1} and NaCl rejection of more than 30%.

A novel and simple method was introduced to prepare an aquaporin Z (AqpZ) based biomimetic nanofiltration (NF) membrane with a relatively large membrane area of 28.26 cm^2 (Li et al. 2014). The proteoliposome integrated with AqpZ, was fully encapsulated into the selective layer through crosslinking of a polyelectrolyte with the membrane substrate made by poly(amide–imde) (PAI). The water flux of the AqpZ based membrane was around 50% higher than the mutant one. At optimal preparation conditions, the AqpZ based membrane could offer a water flux of 36.6 $Lm^{-2}h^{-1}$ with $MgCl_2$ rejection of 95% at 0.1

MPa. AqpZ could maintain its activity even under harsh environmental conditions of thermal treatment at 343 K for 2 h.

Sun et al. (2013a) designed and fabricated nanofiltration membrane by immobilization of AqpZ-reconstituted liposomes on a polydopamine (PDA) coated microporous membrane. Amine-functionalized proteoliposomes were first deposited via gentle vacuum suction and subsequently conjugated on the PDA layer via an amine-catechol adduct formation. Due to the existence of a polymer network within the lipid bilayers, the membrane could sustain hydraulic pressure of 5 bar as well as strong surface agitation in nanofiltration tests, indicating a relatively stable membrane structure. In comparison with membrane without AqpZ incorporation, the membrane with AqpZ-to-lipid weight ratio of 1:100 increased the water flux by 65% with enhanced NaCl and $MgCl_2$ rejections of 66.2% and 88.1%, respectively. With AqpZ incorporation, the vesicle immobilized membrane exhibited high productivity water purification.

Wang et al. (2015) prepared a biomimetic nanofiltration (NF) membrane by immobilizing an aquaporin Z (AqpZ)-incorporated supported lipid bilayer (SLB) on a layer-by-layer (LbL) complex polyelectrolyte membrane to achieve excellent permeability and salt rejection with a high stability. The polyelectrolyte membranes were prepared by LbL assembly of poly(ethylenimine) (PEI) with positive charges and poly(sodium 4-styrenesulfonate) (PSS) with negative charges alternately on a porous hydrolyzed polyacrylonitrile (H-PAN) substrate. AqpZ-incorporated 1,2-dioleloyl-*sn*-glycero-3-phosphocholine (DOPC)/1,2-dioleoyl-3-trimethylammo-nium-propane (chloride salt) (DOTAP) vesicles with positive charges were deposited on the H-PAN/PEI/PSS polyelectrolytes membrane surface. The resulting biomimetic membrane exhibited a high flux of 22 $Lm^{-2}h^{-1}$ (LMH), excellent $MgCl_2$ rejection of 97% and NaCl rejection of 75% under an operation pressure of 0.4 MPa. Due to the attractive electrostatic interaction between SLB and the polyelectrolyte membrane, the biomimetic membrane showed satisfactory stability and durability as well as stable NF flux and rejection for at least 36 h.

Xie et al. (2013) developed a new innovative method to overcome membrane fragility by using aquaporin Z membranes incorporated into self-assembled polymer vesicles and surface imprinting onto a substrate membrane. This novel membrane was well controlled nano-structured selective layer that exhibits high mechanical strength and stability during the water filtration process. The water purification performance was significantly improved by using the AQPz-vesicle-imprinted membrane in either nanofiltration or forward osmosis mode.

Kim et al. (2013) studied the mass production of aquaporin Z for biomimetic water purification membrane. Aquaporin Z (AqpZ), widely spread in *Escherichia coli* cell membrane, showed higher water permeability than conventional membranes. Application of those exceptional properties as water purification membrane material seems promising.

Wang et al. (2013) designed and synthesized a mechanically robust and highly permeable aquaporin Z biomimetic membranes. The membrane is formed by cross-linking AqpZ-embedded block copolymer vesicles, followed by immobilizing vesicles on the membrane support via covalent binding, and then stabilizing through an optimized layer-by-layer polydopamine (PDA)–histidine (His) coating process. As compared with commercially available HTI membranes, the AqpZ-embedded vesicular membrane showed an order-of-magnitude increment in water flux (17.6 L m^{-2} h^{-1}) with high salt retention (91.8%) when using 6000 ppm NaCl as the feed and 0.8 M sucrose as the draw solute in the forward osmosis operation.

The Aqp embedded layer-by-layer (LbL) membrane demonstrated a water permeability of 6 L $m^{-2}h^{-1}$ bar^{-1} and $MgCl_2$ rejection greater than 95%. In comparison with the control LbL membrane without embedding any liposomes, the newly designed mixed matrix membrane improved the water permeability by 60% because of the presence of Aqps. The AqpZ-incorporated membrane was also tested for glutathione separation at various pH levels. The rejection rate of glutathione was greater than 93% at pH values ranging from 4 to 9. Since the LbL approach provided the Aqp embedded biomimetic membrane with satisfactory stability and separation performance, it makes the large scale fabrication of AqpZ-incorporated membranes feasible and practical (Sun et al. 2013b).

PHOTOCATALYST

Photocatalytic oxidation is an advanced oxidation process for removal of trace contaminants and microbial pathogens. It is a useful pretreatment for hazardous and non-biodegradable contaminants to enhance their biodegradability. Baruah et al. (2012) used nanostructured zinc oxide for water treatment. Kottegoda et al. (2013) fabricated an efficient reactor system using renewable solar energy for purification of pollutants dissolved in drinking water. A novel glass tube based prototype reactor was constructed by coating nano-titanium dioxide (TiO_2) inside the glass tubes. The nano-TiO_2 was deposited on the bottom surface of the clear glass tubes and is connected in parallel, increasing the surface area. The reactor was exposed to sunlight and the contaminated water was passed through the reactor. The photocatalytic activity including antibacterial activity was tested using methylene blue and the bacterial culture of *Escherichia coli*. The reactor system was found to be effective in decontaminating the tested organic entities. The reactor module could be used to purify water for drinking purpose and can be fixed on top of roofs for exposure to sunlight.

Li et al. (2008) evaluated several natural and engineered nanomaterials having strong antimicrobial properties including photocatalytic production of reactive oxygen species that damage cell components and viruses (e.g. TiO_2, ZnO and fullerol) and compromising the bacterial cell envelope (e.g. peptides, chitosan, carboxyfullerene, carbon nanotubes, ZnO and silver nanoparticles), interruption of energy transduction (e.g. silver nanoparticales and aqueous fullerene nanoparticles), and inhibition of enzyme activity and DNA synthesis (e.g. chitosan). They also reviewed the antimicrobial mechanisms of several nanoparticles, discussed their merits, limitations and applicability for water disinfection and biofouling control, and highlighted research needs to utilize novel nanomaterials for water treatment applications.

Chen et al. (2003) prepared a new composite reactor for the degradation of organic pollutants. In the reactor, a UV lamp was installed to provide energy to excite nano TiO_2. As TiO_2 is a photocatalyst, it led to the production of hole–electron pairs, A three-electrode electrolysis system was used to accumulate H_2O_2, which played an important role in the degradation process. The reactor was evaluated by the degradation process of rhodamine 6G (R-6G), and the data obtained in the experiments showed that the combination of the photochemical and electrochemical system raised the degradation rate of R-6G greatly. The prepared reactor was also utilized to treat polluted water from dyeing and printing process. After continuous treatment for 0.5 h, chemical oxygen demand, biochemical oxygen demand, quantity of bacteria and ammonia nitrogen of the polluted water were reduced by 93.9%, 87.6%, 99.9% and 67.5%, respectively, which indicated that this method is quite effective for organic dyes degradation.

Yang et al. (2012) designed a novel functionalized nano-TiO_2 loading electrocatalytic membrane reactor (ECMR) for oily wastewater treatment. The oil removal rate increases with a decrease in the liquid hourly space velocity (LHSV) through the ECMR. The COD removal rate was 100% with a LHSV of 7.2 h^{-1} and 87.4% with a LHSV of 21.6 h^{-1} during the treatment of 200 mg L^{-1} oily water. It suggested that the synergistic effect of electrocatalytic oxidation and membrane separation in the ECMR plays the key role**.**

Byrne et al. (2002) investigated the photocatalytic and electrochemically assisted photocatalytic degradation of formic acid in a one-compartment photoelectrochemical cell incorporating nano-crystalline TiO_2 electrodes prepared by the immobilisation of Degussa P25 on tin oxide coated glass. Formic acid was degraded at the TiO_2 photoanode and copper metal was recovered at the copper mesh cathode with a high efficiency.

Cheng et al. (2010) studied different kinds of nano-semiconductors such as ZnO and TiO_2 as photocatalysts for the removal of bacteria such as *Escherichia coli* from water using UVA radiation from fluorescent lamp, cold cathode lamp and light emitting diodes (LED). The effectiveness in removal of *E. coli* by UVA and UVC was also compared. UVA cold cathode lamp had the highest removal efficiency of *E.Coli*. The comparative studies on the effectiveness of different kinds of nano semiconductors in the removal of pathogens from water were also studied, and it was found that nanoscale ZnO was more effective than nanoscale TiO_2.

Chaturvedi et al. (2012) synthesized silver (Ag) nanocatalyst, AgCCA catalyst, N-doped TiO_2 and ZrO_2 nanoparticles for degradation of microbial contaminants in water. Heidarpour et al. (2010) used nano silver-coated polypropylene water filter for microorganism removal. Silver nanoparticles were deposited on cylindrical polypropylene water filter by physical vapor deposition method using a modified Balzers machine. Membrane filter method was used for enumeration of bacteria. At a flow rate of 3L h^{-1} filtration all of the *Escherichia coli* cells were killed after 5 h, when the input water had a bacterial load of 103 colony-forming units (CFU) mL^{-1}. The inductively coupled plasma/mass spectrometry (ICP/MS) was used to determine any trace amount of the silver nano particles left in the water sample after filtration.

Brunet et al. (2009) compared the photoactivity and antibacterial properties of C60 fullerenes and titanium dioxide nanoparticles. The generation of reactive oxygen species (ROS) by aqueous suspensions of fullerenes and nano-TiO_2 (Degussa P25) was measured both in ultrapure water and in minimal Davis (MD) microbial growth medium. Fullerol (hydroxylated C60) produced singlet oxygen ($^1O_2$) in ultrapure water and both $^1O_2$ and superoxide ($O^{-\bullet}$) in MD medium, but hydroxyl radicals ($^{\bullet}OH$) were not detected in either case. PVP/C60 (C60 encapsulated with poly(N-vinylpyrrolidone)) was better than fullerol in generating singlet oxygen and superoxide. Bacterial (*Escherichia coli*) toxicity tests proved that, unlike nano-TiO_2 which was exclusively phototoxic, the antibacterial activity of fullerene suspensions was linked to ROS production. Nano-TiO_2 was more efficient for water treatment involving UV or solar energy, to enhance contaminant oxidation and for disinfection. However, fullerol and PVP/C60 were useful as water treatment agents targeting specific pollutants or microorganisms that are more sensitive to either superoxide or singlet oxygen.

Bai et al. (2010) assembled a novel TiO_2 nano-thorn membrane for concurrent filtration and photocatalytic oxidation to remove pollutants in water. This membrane had hierarchical porous and multifunctional properties, which provide these advantages: (i) Producing water with high quality; (ii) Increasing water flux; and (iii) Eliminating membrane fouling.

Sivalingam et al. (2003) prepared 8–10 nm pure anatase phase titania with 156 m^2 g^{-1} BET surface area by solution combustion method. This catalyst was used for the photocatalytic degradation of various dyes such as heteropolyaromatic dye (methylene blue), anthraquinonic dye (alizarin S), and azoic dyes (methyl red, congo red, and orange G). The effect of catalyst loading, initial concentrations of the dyes, pH, and transition metal doping on TiO_2 was investigated. The photoactivity of the combustion synthesized titania was higher than commercial TiO_2 (Degussa P-25) for both UV and solar exposure.

Figure 5. An impossible task for future

NANOSENSORS

Nano-materials have potential to act as sensor components due to their unique physical, chemical and electrical properties. Such sensors are valuable for water quality monitoring. Sensors based nanoparticles have optical properties to develop sensitive and selective detectors for pollutants. New sensor technologies that combine micro- and nanofabrication technology to create small, portable, and highly accurate sensors to detect chemical and biochemical parameters in water have been developed by Hillie et al. (2006). Nanosensors consisting of different nanomaterials such as CNTs both single-walled and double-walled, nanowires (V_2O_5, SnO_2, ZnO, etc.), quantum dots, nanocantilevers, and metal nanoparticles (Ag, Au, Cu, etc.) were used for this purpose.

Detection technology for water purification would allow people to quickly find out, what the contaminants are, without having to send samples to laboratories for testing. Nanosensors can detect single cells or even atoms, making them far more sensitive than larger components. Single- and double-walled carbon nanotubes can detect chemicals in water (Vedala et al. 2004). Cui et al. (2001) used boron-doped silicon nanowires to create highly sensitive, real-time electrically based sensors for the detection of biological and chemical species. Magnetic nanosensors were used to detect smaller particles with sensitivity in femtomole range (0.5–30 fmol) such as mRNA, proteins, enzymatic activity, and pathogens (Perez et al. 2004). Water quality analysis could be carried out by using nanosensors as these were used for the detection of *E. coli* and other indicator bacteria. Nanosensors save time and money for the detection of microbes in water samples. Taurozzi and Tarabara (2007) assembled silver nanoparticle array on track etch membrane support as flow through optical sensors for water quality monitoring. These silver nanoparticle arrays were assembled on the surface of polycarbonate track etch membranes using 3-aminopropyltrimethoxysilane as the chemical linker. These assembled arrays were submonolayer and regular. The nanoparticle-modified membranes were characterized in terms of their hydraulic and optical properties and were evaluated as flow-through surface-enhanced Raman scattering (SERS) sensors for water quality monitoring.

Nanotechnology has opened many avenues for water purification and water quality monitoring. Time is not for off, when conventional treatment technologies will be almost replaced by these nanomaterial based techniques in coming few deades.

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Conflicts of Interest

The authors declare no conflict of interest.