RECENT ADVANCES IN NANOTECHNOLOGY-BASED WATER PURIFICATION METHODS

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ABSTRACT

Water and wastewater treatment is undoubtedly the most important topic in the field of environmental technologies. Membrane-based processes are the most widely applied technologies for drinking and ultrapure water production, desalination, wastewater treatment and water reuse. Intrinsic advantages of membrane-based processes include continuous, chemical-free operation, low-energy consumption, easy scale-up and hybridization with other processes, high process intensity (i.e., small land area per unit volume of water processed), and highly automated process control. However, the main disadvantages of the conventional membrane-based processes are related to short membrane lifetime, limited selectivity, concentration polarization, and membrane fouling. In particular, polarization and fouling of membranes require extensive physical and chemical pretreatment of feed water (e.g., chlorination, in-line coagulation, flocculent aid addition, and membrane filtration), recovery operation, extensive chemical cleaning, and frequent operator intervention. Recent advances in nanotechnology-based water purification methods (e.g., functional nanostructured materials, nanoadsorbents, nanocatalysts, etc.) can largely contribute to the improvement of conventional membrane-based water and wastewater treatment. Current issues related to nanotechnology-based methods for water and wastewater treatment, including nanoadsorbents, nanocatalysts and nanotechnology enabled membranes, among others, are critically reviewed [1,2].

INTRODUCTION

In recent years, the release of harmful pollutants to the environment, as a result of the massive exploitation of natural resources and the extensive use of chemicals, has received much attention because of their negative effects to human health. To this point, world-leading drinking-water industries focus their efforts on the development of novel technologies for the removal of various persistent pollutants (i.e., metals, disinfection by-products, pathogens, and synthetic or natural organic compounds) from water sources. Nanotechnology, offers the potential of long term solutions to increase energy efficiency and lower costs, through the adaptation of advanced materials that enable greater water quality and reuse. The unique properties of nanomaterials and their emergence with current water treatment technologies present great opportunities to revolutionize water treatment. On a mass basis, they have much larger surface areas than bulk particles. Nanomaterials can also be functionalized with various chemical groups to increase their affinity toward a given compound. They can also serve as highly selective and recyclable ligands for toxic metal ions, radionuclides, and organic and inorganic solutes/anions in aqueous solutions. Nanomaterials provide unprecedented opportunities to develop more efficient water-purification catalysts and redox active media due to their large surface areas and their size and shape-dependent optical, electronic, and catalytic properties. Among the nano-based materials, three categories show the most promising candidates in largescale application due to their commercial availability, low cost, and compatibility with the existing infrastructure, i.e., nanoadsorbents, nanocatalysts and nanotechnology enabled membranes [1].

NANOADSORBENTS

Nanoadsorbents are applied for the removal of inorganic and organic pollutants from water and wastewater. The unique properties of nanoadsorbents, such as small size, catalytic potential, high reactivity, large surface area, ease of separation, and large number of active sites for interaction with different contaminants make them ideal adsorbent materials for the treatment of water and wastewater. Carbon-based, metal-based (>99.5% purity) and polymeric nanoadsorbents, magnetic or nonmagnetic oxide nanocomposites, and zeolites are currently used as nanoadsorbents in the treatment of water [2].

Carbon-based Nanoadsorbents

Carbon-based nanoadsorbents, such as carbon nanotubes (CNTs) are explored as substitutes for activated carbon. CNTs are categorized as single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) depending on their structure (Figure 1 (a) and (b)). CNTs contain highly accessible adsorption sites due to their high specific surface area. Their surface chemistry can be modified accordingly. The hydrophobic surface of CNTs makes them form loose bundles/aggregates in aqueous medium. These aggregates have high-energy sites for the adsorption of organic contaminants in water. The reason for the adsorption of bulky organic contaminants by CNTs is the availability of larger pores in bundles and the presence of more accessible sorption sites. CNTs can also adsorb polar organic molecules because of diverse contaminant-CNT interactions in the form of hydrophobic effect, π–π interactions (with polycyclic aromatic hydrocarbons), hydrogen bonding (with acids, amines, alcoholic functional groups, etc.), covalent bonding, and electrostatic interactions (with positively charged organic contaminant molecules, such as antibiotics). Surface-oxidized CNTs using hydrogen peroxide, $KMnO_4$, and nitric acid are used in the removal of Cd^{2+} from aqueous solutions. The oxidation of CNTs can lead to high adsorption capacity for metal ions with faster kinetics. The surface of oxidized CNTs contains functional groups, such as carboxylic acid, hydroxyl, and carbonyls. These groups have good adsorbing capacity for heavy metal ions when the pH is above the isoelectric point of the oxidized CNT. Many other studies have been reported that CNTs are very good adsorbing nanomaterials for heavy metal ions, such as Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}. Furthermore, graphene and graphene oxide (GO) (Figure 1 (c) and (d)) have been applied in water purification. Many studies have been reported on the water treatment applications of GO in several states, such as pure state, surface modified, or incorporated in a hybrid composite or a membrane [2].

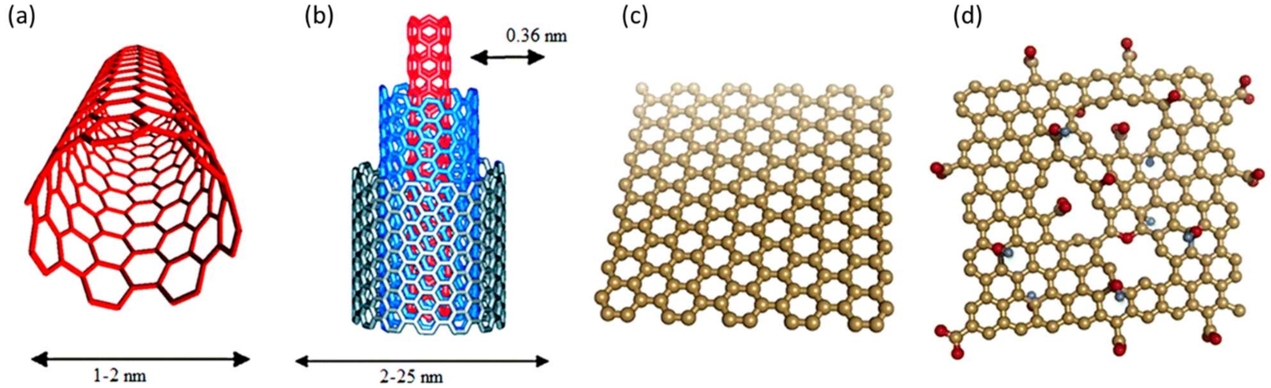

Figure 1. *Schematics of SWCNTs (a), MWCNTs (b), graphene (c) and graphene oxide (d)* [3].

Metal-Based Nanoadsorbents

Metal-based nanoadsorbents, such as iron oxide, titanium dioxide, zinc oxide, and alumina have several advantages, such as fast kinetics, high adsorption capacity, and are thus preferable nanomaterials for heavy metal removal. They are effective and low-cost materials. Metal-based nanoadsorbents can be regenerated by changing the solution pH. Also, after several reuses and regeneration steps, the adsorbing capacity of these nanoadsorbents is not altered [2]. The mechanism of the action is that the oxygen in metal oxides complexed with heavy metals dissolves in contaminated water. As the particle size decreases, the adsorption capacity increases several fold. This is because of the “nanoscale effect” of the magnetite, in which surface structure creates new adsorption sites for metal ions. Magnetic nanoadsorbents (MNPs), such as maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), and spinel ferrites (i.e., $M^{2+}Fe_2O_4$, where M^{2+}: Fe^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+}) are very good adsorbing materials for the collection and removal of toxic elements from contaminated water. Environmental benefits lie in their magnetic nature. They can be easily separated from reaction media by the application of an external magnetic field. Several reports are available in the literature for the application of these MNPs for the removal of a variety of elements, such as arsenic, chromium, cobalt, copper, lead, and nickel in their ionic forms. In addition, long reactive iron nanoparticles (10–100 nm) as reducing materials demonstrate effectiveness as detoxicants of chlorine containing compounds (pesticides, organic solvents, and polychlorinated biphenyls). Another metal oxide, TiO_2, has been studied for the removal of arsenic. Moreover, magnesium oxide (MgO) has been noticed due to its signaled removal properties against inorganic micropollutants, such as As(V) and heavy metal ions. ZnO nanoadsorbents have been also used to remove Zn^{2+}, Cd^{2+}, and Hg^{2+} ions from aqueous solutions.

Table 1. *Nanoadsorbents in water treatment.*

Nanomaterials	Desirable Nanomaterial Properties	Enabled Technologies
Carbon-based	High surface area, highly accessible adsorption sites, diverse contaminant-CNT interactions, tunable surface chemistry, reusable	Contaminant preconcentration/ detection, adsorption
Metal-based	High specific surface area, short intraparticle diffusion distance, more adsorption sites, compressible without significant surface area reduction, easy reuse, some are superparamagnetic	Adsorptive media filters, slurry reactors
Polymer-based & Composites	Immobilized, synergistic effects of different materials, tailored (shell) surface chemistry for selective adsorption, reactive (core) for degradation, short internal diffusion distance	Nanoadsorbents, selective adsorbents, reactive nanoadsorbents

Polymer-Based and Composite Nanoadsorbents

Polymer-based nanoadsorbents gained great interest recently. They are used either as a system into which inorganic nanosized materials can be inserted or as a bed or template to prepare nanoparticles. The most important advantage of the polymer-inorganic composite nanoadsorbents is their high adsorption capacity and the excellent thermal stability over a wide range of pH. Furthermore, the resistance of polymeric groups and their linkages to acid and base hydrolysis is an additional advantage [2]. Particularly, the current research efforts are focused on functional polymers, possessing high selectivity and specificity and long-term stability, as well as the development of modern, efficient, environmentally friendly, and cost-effective water purification technologies.

One category of functional polymers that satisfies the above performance criteria, is the molecularly imprinted polymers (MIPs). In molecular imprinting, selected functional monomers and a cross-linker are co-polymerized in the presence of a specific-target molecule, acting as a molecular template, to produce a polymeric material of high specificity. The functional monomers initially form a complex with the template molecule through covalent or noncovalent interactions. Polymerization of the functional monomers with a bifunctional or trifunctional cross-linker results in the template's docking into the polymeric matrix. The template molecules are subsequently removed, revealing specific binding sites that are complementary in size and shape to the template molecule [4]. MIPs are a very promising class of functional polymers, exhibiting high affinity to target compounds. MIPs additional advantages include: high physical robustness and strength, resistance to elevated temperatures, inertness toward organic solvents, acids or bases. As a result, MIPs can withstand follow-up processing steps related to the removal of the template molecule (via a chemical process) and its repeated use and regeneration as a highly selective adsorption material in wastewater treatment applications. This means that MIPs can be reused several times in water and wastewater separation processes. This MIP property is a key factor in the overall reduction of wastewater treatment costs. Small and well-shaped molecularly imprinted polymer micro- and nanoparticles exhibit increased binding capacity due to their high specific surface area.

Thus, MIP micro- and nanoparticles have been widely used as adsorbing materials for the removal of endogenous estrogens, sulfonates, pharmaceuticals, synthetic dyes, polycyclic aromatic hydrocarbons, cyanotoxins, phenolic compounds, and organophosphate pesticides from polluted water sources. MIPs have been also used for the removal of metal ions, including Cd(II), As(V), Ag(II), Pb(II)-IIP, Zn(II), Zr(IV), multi-templated Pb-Zn-Hg, Hg(II), Li, and other heavy metals from environmental samples and wastewaters. Molecularly imprinted polymers have been also combined with other nanoparticles including magnetic particles and quantum dots. These advanced composite nanomaterials combine the high selectivity of MIPs with the specific properties of embedded nanoparticles. Thus, the composite nanomaterials can have high selectivity, high affinity, and rapid kinetics regarding the association/dissociation of the target analyte. CNTs, MCNTs, gold and silver nanoparticles, titanium oxide, and silica-based nanoparticles are typical nanostructured materials that have been used in the synthesis of composite MIPs. These nanostructured materials can be combined with MIPs in core-shell structures. These composite nanoparticles offer numerous advantages, including better control of the thickness and morphology of the thin MIP shell that largely facilitate the efficient removal of template molecules. Fe_3O_4 particles have been used in the synthesis of composite MIP materials that can selectively adsorb target pollutants from environmental samples [4].

NANOTECHNOLOGY ENABLED MEMBRANES

Membrane processes offer robust technologies that can be applied to produce potable water from both conventional surface/groundwater and impaired sources. Membrane technology has been accepted as an effective separation process for water treatment due to the reliability and efficiency of contaminant rejection, along with the flexibility provided through a range of membrane materials (ceramic: silica, alumina, titania, etc., polymeric: polyvinylidene difluoride (PVDF), polyamide (PA), polyether sulfone (PES), polysulfone (PSF), etc. and metallic: palladium, silver, etc.) and pore sizes (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)). However, like every other technology, there are drawbacks that need to be overcome to improve the membrane process performance. For instance, pressure driven membrane processes such as RO, NF, UF, and MF are prone to fouling during long-term operation. Fouling results in higher operating and maintenance costs due to limited recoveries, feed water loss and permeate quality deterioration, reduced service time, and premature membrane replacement. Non-pressure driven membranes such as forward osmosis (FO) and pressure retarded osmosis (PRO) have shown less fouling propensity; however, low permeation is a major limiting factor for such processes [5,6].

Polymeric membranes remain a ubiquitous choice due to low relative cost, pore size range, configuration flexibility, and scalability. However, despite decades of research and development, polymeric membranes also remain plagued by long-standing operational issues such as fouling and challenging trade-offs between novel functionality and cost. As a result, while novel polymer chemistries and membrane fabrication techniques have been proposed in literature, few have been commercialized. Rather than rely entirely on novel polymer chemistries, the growth of the nanomaterials field has opened alternate, transformative avenues for membrane development, where a nanomaterial, when combined with a robust polymer platform, can result in a nanocomposite membrane with new or improved properties. Recent research attempts have focused on developing polymer-based nanocomposite membranes for sustainable water purification, aimed at enhancing fouling resistance and surmounting the trade-off relationship between permeability and solute rejection [6,7].

Figure 2. *Mono-component nanomaterial-based membrane (i.e., composed solely by nanoparticles, nanofibers and two-dimensional layer materials) and composite membrane (i.e., membrane together with carbon-based materials, polymeric and/or inorganic materials)* [5].

Among different nanocomposites, polymer-based nanocomposite membranes have driven considerable attention in recent years (Figure 2). Polymer-based nanocomposite membranes are fabricated by dispersing nanoparticles (NPs), nanotubes, nanofibers, or nanosheets into the polymer matrix via several techniques including phase inversion (PI), interfacial polymerization (IP), physical coating, electrospinning and cross-linking, self-assembly, layer-by-layer assembly, and chemical grafting. The incorporation of engineered nanomaterials including metal oxides (e.g., Al_2O_3, TiO_2, SiO_2, ZnO, MgO, Fe_2O_3, zeolite), metals (e.g., Cu, Ag), carbon-based nanomaterials (e.g., graphene, CNTs, carbon nanofibers (CNFs)), and polymer nanofibers (e.g., polyurethane, polylactic acid, polyethylene oxide) in polymer matrices imparts tunable physicochemical properties and unique functionalities to the membranes. Nanocomposite membranes have emerged as promising water purification technologies to overcome the limitations associated with conventional polymeric membranes by offering enhanced hydrophilicity, thermal and mechanical stability, permeability, targeted degradation, solute rejection, and magnetic, antimicrobial, and antifouling properties [5].

In particular, carbonaceous materials have been applied as an additive to polymeric membranes for water purification. Adding carbonaceous nanofillers like CNTs, CBF, graphene and GO to a polymeric matrix not only improves the mechanical, chemical and thermal properties of the membranes but also increases water purification performance. In particular, CNTs are fascinating in advanced membrane technologies for water purification since they provide low energy solution for water treatment. CNT-based composite membranes provide near frictionless water flow through them with the retention of a broad spectrum of water pollutants. The inner hollow cavity of CNTs provides also a great possibility for desalinating water. The high aspect ratios, smooth hydrophobic walls and inner pore diameter of CNTs allow ultra-efficient transport of water molecules. Furthermore, graphene-based macrostructures with 3D porous networks, such as aerogels, hydrogel, foams, frameworks, and sponges, have recently attracted considerable interest. These 3D graphene materials, consisting of micro-, meso- and even macroporous networks, can provide high surface area and fast ion/electron transport. Thus, the embedding of graphene in other membranes can improve the permeability and water flux with lower fouling. These exceptional properties have triggered extensive efforts to apply carbonaceous nanofillers in water desalination. Both CNTs and graphene have been successfully introduced particularly in membrane systems and received special attention for their exceptional capacities for the facile removal of charged ionic species from aqueous solutions in water desalination applications [8,9].

Table 2. *Nanostructured membranes for water treatment.*

Nanomaterials	Desirable Nanomaterial Properties	Enabled Technologies
Nanozeolites	Molecular sieve, hydrophilicity	High permeable thin film nanocomposite membranes
Nano-Ag	Strong and wide-spectrum antimicrobial activity, low toxicity to humans	Antibiofouling membranes
CNTs	Antimicrobial activity (unaligned CNTs), small diameter, atomic smoothness of inner surface, tunable opening chemistry, high mechanical and chemical stability	Aligned carbon nanotube membranes
Nano-TiO_2	Photocatalytic activity, hydrophilicity, high chemical stability	Reactive membranes, high performance thin film nanocomposite membranes

NANOCATALYSTS

Metal nanoparticles and metal oxides have proven to be very good catalysts in oxidation reactions. They exhibit a strong catalytic activity through which pollutants are oxidized forming less toxic substances, or converted into ecologically acceptable final products. The main reasons for these properties of nanoparticles are their very small particle size (i.e., a large surface to volume ratio) and their high reactivity directly related to nanoparticle size. Nanocatalysts can be used effectively for the chemical oxidation of organic and inorganic pollutants in water following advanced oxidation processes. These processes are based on the formation of highly reactive radicals that react easily with the pollutants. Some nanocatalysts, applied in wastewater treatment in order to improve the process efficiency, are TiO_2, Pt, Fe, and Fe/Pd, Fe/Ni, Fe/Co. In particular, TiO_2 and ZnO, among others, are used for photocatalytic reaction aiming to disinfection and water purification. In a typical photocatalytic process, the semiconductor (e.g., TiO_2, ZnO) is irradiated by light with sufficient energy, thus, leading to reactive radical generations via initiating a series of reactions. A number of important advantages are exhibited including the ambient operating temperature and pressure, the complete mineralization of the pollutants and their intermediates into CO_2 and other inorganics, and the low operational costs. These important advantages fascinate researchers to extend nanostructured photocatalysts in water treatment applications.

CONCLUSIONS

Nanotechnology for water treatment is gaining momentum through a global perspective. Although many nanotechnology strategies are still in the laboratory stage, some have made their way to pilot testing or even large scale commercialization. Major practical challenges are the cost of nanostructured materials along with the difficulty in scaling up nano-based treatment processes for commercial use. In addition, health and safety issues around the use of nanomaterials have to be addressed in the domestic water industry, particularly with respect to the direct application of nanoparticles into the receiving natural bodies of water. Materials functionalized with nanoparticles incorporated or deposited on their surface have risk potential, since nanoparticles might leach into the environment where they can accumulate for long periods of time. As a result, nanomaterials can be embedded into various platforms (i.e., in the form of nanocomposites) to avoid leaching into the system. However, current immobilization techniques require further optimizations to mitigate the loss in efficiency. Research is, thus, needed to stabilize, as well as distribute nanoparticles throughout the hosting platforms without significantly impacting overall performance. Nevertheless, nanoengineered materials offer great potential for water innovations in particular for decentralized treatment systems, point-of-use devices, and heavily degradable contaminants.

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REFERENCES

[1] D.A. Gopakumar, A.R. Pai, D. Pasquini, S.-Y. Leu, H.P.S. Aul Khalil, S. Thomas (2019) Nanomaterials-State of Art, New Challenges, and Opportunities, Book Chapter in Nanoscale Materials in Water Purification, Elsevier Inc.

[2] K.R. Kunduru, M. Nazarkovsky, S. Farah, R.P. Pawar, A. Basu, A.J. Domb, (2017) Nanotechnology for Water Purification: Applications of Nanotechnology Methods in Wastewater Treatment, Book Chapter in Water Purification Nanotechnology in the Agri-Food Industry, Volume 9, Elsevier Inc.

[3] H. Sadegh, G.A.M. Ali, V.K. Gupta, A.S.H. Makhlouf, R. Shahryari-ghoshekandi, M.N. Nadagouda, M. Sillanpaa, E. Megiel, J. Nanostruct. Chem. 7 (2017) 1–14.

[4] O. Kotrotsiou, K. Kiparissides (2019) Water Treatment by Molecularly Imprinted Materials, Book Chapter in Nanoscale Materials in Water Purification, Elsevier Inc.

[5] Y. Ying, W. Ying, Q. Li, D. Meng, G. Ren, R. Yan, X. Peng, Applied Materials Today 7 (2017) 144–158.

[6] E.M.V. Hoek, M.T.M. Pendergast and A.K.Ghosh (2014) Nanotechnology-Based Membranes for Water Purification, Book Chapter in Nanotechnology Applications for Clean Water, Elsevier Inc.

[7] M.R. Esfahani, S. Aghapour Aktij, Z. Dabaghian, M. Dadashi Firouzjaei, J. Eke, L.F. Greenlee, A.R. Esfahani, A. Sadmani, N. Koutahzadeh, Separation and Purification Technology 213 (2019) 465–499.

[8] R. Das, M.E. Ali, S.B.A. Hamid, S. Ramakrishna, Z. Chowdhury, Desalination 336 (2014) 97–109.

[9] P. Liu, T. Yan, L. Shi, H.S. Park, X. Chen, Z. Zhao and D. Zhang, J. Mater. Chem. A 5 (2017) 13907-13943.