Chapter 15

Rationally Fabricated Nanomaterials for Desalination and Water Purification

Rajendra S. Dongre

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.74738

Abstract

Rationally designed nanomaterials from synthetic/biopolymers like chitosan, zeolites, graphene, nanometal/oxides, zerovalent metal/magnetic iron, OMS and nanocarbon/carbon nanotube (CNT) utilized in desalination/purification are thoroughly discussed. Conventional desalination membrane/materials own inherent limitations; nevertheless, designed nanocomposite/hybrid/films address the new challenges/constraints and consequently aid the remediation of environmental/water pollution, thus denoting prospective nanotechnology/science. The morphology and chemical functionality of certain natural/synthetic polymers are altered/controlled rationally yielding advanced membranes/materials, for example, aquaporin, nanochannels, graphene and smart self-assemble block copolymer blends to cater futuristic desalination needs besides superseded conventional membrane limitations too. In a nut shell, advance nanotechnology via electrospinning, track-etching, phase inversion and interfacial polymerization yields structured composites/matrixes that conquer traditional barriers of conventional desalination and supplies treated/purified water. This review confers synthetic strategy and utility of nanomaterials that are procured via ordered/rational designing/self-assembly to be used in separation techniques including RO/FO antifouling membrane, superwet surface, oil-water/emulsion separation and multifunctional desalination nanodevices.

Keywords: nanomaterial, designing, chitosan, OMS, desalination, water purification, electrospun

1. Introduction

The ever growing population and economic expansion put potential crisis in supply, and the availability of fresh water as UN for the decade 2030 forecasts 40% high global water uptake hints intensifies water consumption [1]. Amid estimated 780 million that do not have access to safe water, UN reported that global populations will face water scarcity by 2050. Thus, obligatory purifications of existing polluted/unsafe water were achieved via desalination or any other techniques. Desalination via membrane technique was developed since 1960 which removes soluble salts and micro-pollutants that are not of concern in conventional treatments, nevertheless being expensive over conventional water purifications. It also has drawbacks like high costs/energy inputs, and greenhouse gas pollution puts constraints on the environment to discover rationally developed desalination materials. Conventional polyamide-based membranes own inherent drawbacks viz. limited permeability, less selectivity and low chemical stability, and affecting separation performance [2]. Nanotechnology aids in the design of smart/advanced materials/membranes via fabrication of one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanomaterials owing to improved efficiency for revolutionary desalination/water purification. Rationally designed nanomembranes trounce such demerits, for example, graphene membranes owing to exclusive features like tunable properties, extraordinary robustness, and advantageous leverage with a superior separation efficiency on par with CNT and biomimetic aquaporin membranes [3–5]. Fabricated 2-D membranes own fundamentally different separation capability due to peculiar features like punching nanometer/ultrathin pores, precisely controlled/manipulated shape/size super-strong impermeable monolayers, and facile industrial scale-up since they use cheap/biopolymeric feedstock/raw materials [6–9]. Certain nanomaterials such as 2-D graphenes, zeolites and molybdenum disulfides assembled via layer-stacking and own unique configurations with controlled interlayer spacing have fascinated research in making high-performance desalination membranes with advantages peculiarity like tangible manipulation for permeability and contaminant's selectivity. Further, 2-D materials innovatively converted into 3D nanomembrane to impart enhanced selectivity and minimized fouling, which find potential applicability in solar desalination devices [10]. Versatile pertinence of nanotechnology is exploited in fabrication of many superior organic and/or inorganic based nano-materials owing myriad functionality by virtue of inherent firm controlled shape and pore distribution with facile alterations in porosity, surface area: volume ratio, and optimized dimensions/shapes as designed prior to their synthesis. Desalination materials/membranes have been designed and developed via assorted methodologies reported in the study [6–12]. On the basis of structure, properties, and performance relationships, these smart nanomaterials are fabricated for water treatments [1–13], and so this review signifies/focuses on recent advances in synthetic strategy in its designing/fabrication besides purification applications.

1.1. Assorted techniques for desalination

1.1.1. Adsorptive separation and pervaporation

Desalination extracts/removes salts and mineral components from saline water [1–14]. It is an earliest form of treatment still popular throughout for the conversion of seawater (salinity due to dissolved salts at 10,000 ppm) to drinking water for addressing water scarcity. Desalinated water is better than river/groundwater, as it has less salt and lime-scale contents. This desalination technology has demanded the usage of assorted smart/fabricated materials involving through advancement in nanotechnology. Thermal-based desalination is achieved via adsorption onto fabricated porous silica surfaces owing to double-bond surface force affinity for pollutants, resulting in high permeability as demonstrated for seawater at a substantially lower cost than conventional membrane technologies [10–14]. Pervaporation is performed via a designed membrane owing to preferential higher affinity with one component with a faster diffusion rate responsible for the separation of oil-water/mixtures. Pervaporation technique is advantageous in desalination due to 100% salt rejections and low-energy consumption attenuated by combined membrane permeation and evaporation. Several sophisticated advanced membranes were synthesized, for example, polyvinyl alcohol-based membrane owing to peculiar features viz. excellent film formation, hydrophilicity, and hydroxyl-induced swelling accountable for the effective desalination/separation of pseudo-liquid blend/mixtures [13, 14]. Nanosilica in maleic acid-polyvinyl alcohol yielding composite membranes shows enhanced water flux/diffusion coefficient and 99.9% salt rejections as desired for an efficient desalination [10]. Polyethylene terephthalate grafted in styrene obtains a membrane for pervaporation with an improved toluene selectivity [15]. PEBAX matrix of 100-μm dimension obtained for working at 50°C feed water temperature showed enhanced diffusion and viscosity reduction ruled by vacuum and thickness, which vitally determines pervaporation performance [10]. Commercial coalescing water filtration and adsorptive difficult emulsion separations for oily contaminants were achieved via fabricated nanofibers found to get partially deactivated besides membrane fouling, thus increasing their treatment cost [1–15]. Coalescing filtrations break stable/difficult oil-water and surfactant emulsions [16–18] that are viable on a coalescing medium/material used, as large droplets downstream settlement require less residence time. In this context, electrospun nanofibrous-based membranes own a larger surface area, vitally enhancing its coalescing filtration performance [1].

1.2. Fabrication methods of nanomaterials/membranes

Assorted nanoporous membranes/materials yield via diversified synthetic techniques [19] including phase inversion, interfacial polymerization, track-etching, and electrospinning as described in the below section:

1.2.1. Phase inversion

Chemical stratification is performed to remove the solvent from liquid-polymer solution and converts homogeneous solution into porous solid membrane/films in a controlled fashion [1, 19]. This phase inversion is vastly reliant on both the types of solvent and polymers, besides accomplished via captivate precipitation and/or heat/vapor/evaporation-induced phase separations. Immersion precipitation and thermo-induced phase separation are applied for nanofiltration (NF), ultra-filtration (UF), and reverse osmosis (RO) membrane fabrications [10]. Membrane morphology and porosity are found to be controlled by the nature of solvent/oil-water mixtures. Phase inversion technique is used to yield superoleophobic poly(acrylic acid)-graft PVDF membrane that induces efficient desalination and major emulsion/oil-water separations.

1.2.2. Interfacial polymerization

A step-growth polycondensation occurs in immiscible solvents (aqueous solution, impregnates one monomer and organic solution containing a second monomer), for example, diamine and di-acid chloride solution yield polyamide membrane [1, 10]. This technique is used to fabricate ultra-thin films (10 nm to μm) to be used for RO and NF membranes [1–10]. A membrane skeletal morphology or a layer-by-layer build-up of a composite can be controlled by many factors like the type/concentration of monomer and solvents, and reaction time, besides posttreatment conditions [10, 19]. The study reported interfacial polymerization of diamine and acyl chloride onto cellulose nanocrystal layer yielding a triple-layered composite/membrane for nanofiltration/desalination [1]. Interfacial polymerized MCM-41-silica and graphene oxide onto polyamide surface yield ultra-films [10] that showed huge water flux and salt rejections in desalination.

1.2.3. Track-etching

Track-etching involves energetic heavy ion irradiation onto a substrate resulting in a linear-damaged track across irradiated polymer surfaces that yield nanoporous membrane [19]. This technique precisely augmented a pore-size distribution of nm to μm dimension and a pore density of $1–10^{10}$ cm^{-2} [10], for example, nanoporous silicon nitride membranes using porous nanosilicon templates [1, 10].

1.2.4. Electrospinning

Electrospinning technique uses high-voltage treatment to polymers that is outsized to overcome the surface tension of solution droplets, and the resulted charged liquid jet is then converted into ultrafine/nanofibrous at collection drums. The morphology and skeletal parameters like porosity, shape/size distribution, and ratios of the corresponding nanomaterials/membranes are controlled by adjusting the electric voltage and treatment conditions viz. polymeric solution's viscosity and flow of solution [19]. Illustrious nanofibrous PVDF and 2-D nanosheets (Ti3C2Tx MXene) are prepared for sieving cations and dyes from contaminated water [1, 10].

1.3. Myriad nanomaterials/membranes for desalination

Assorted nanoporous material-based membranes are categorized as inorganic, organic, and inorganic-organic hybrid as per the material compositions. Various inorganic membranes include Al_2O_3-, TiO_2-, ZrO_2-, SiO_2-, TiO_2-SiO_2-, TiO_2-ZrO_2-, and Al_2O_3-SiC-based ceramics, and 2-D matter like graphenes and carbon nanotubes. Organic membranes are obtained from polymers like polyvinyl alcohol, polyimide, polypropylene, polyethersulfone, cellulose acetate, cellulose nitrates, polysulfone, polyvinylidene fluoride, polyacrylonitrile, polytetrafluoroethylene, and biopolymers like chitin, chitosan, and so on. Chitosan-blended dendrimers showed highly efficient anionic dyes, heavy metals, and organic contaminants removal from water [1]. Hybrid membranes yield, using inorganic metal/metal oxide, carbon materials into a polymeric matrix [1–19].

1.3.1. Electrospun membranes

Electrospinning technique is found to control many parameters like porous tortuosity, pores size and/or shape deviations (straight or cylindrical) which are crucially reduced in nano-fibers synergistic amalgamation. Polystyrene-based nanofibrous smooth surface of 452 nm owns a peculiarity viz. uniform porosity with low tortuosity, no bead formation, and least surface roughness, establishing futuristic coalescing filtration media for oily emulsion separations.

Morphological/topographical features of such electrospun membranes can be altered by numerous methodologies namely molecular bonding, in situ polymerization, and dopants encroachment technology. Akin to surface modifications achieved via nanoparticle coating, chemical/heat treatments, grafting, and interfacial polymerization were found to be efficient in coalescing filtration across commercial treatments. During the last decade, electrospun technique utilizes myriad polymeric feedstocks for devising nanofibrous membranes for pressure/thermal-driven microfiltration (MF), UF, NF, forward osmosis (FO) and coalescing filtrations besides adsorptive desalination [19].

Electrospun membranes own 3D interconnected skeletons as critical for improved desalination media which is advantageous over traditional membranes in regard to the efficiency, price, and energy. Microporous polymeric progressive desalination membranes are fabricated via assorted techniques like film lithography, stretching, phase inversion, electrospinning owing to peculiarity viz. huge interconnective 3D porosity, adjustable pore-size distribution, high water flux, high surface area with molecular orientations and facile fiber-axis directional macroscales. These films/composites fascinated prominent field like water treatment/purification/separation, pressure-driven distillation, oil-water/marine oil spill cleanups, and RO/NF pretreatment feeds. Functionalized polymeric membranes can act as methanol fuel cell, separators for rechargeable lithium-ion batteries, pressure-retarded/driven/osmosis used for bacteria/fungus culture media/suspended particles micro-filtration, dye solutions, and ultra-filtration [1–19]. Tailored polyvinylidenefluoride-polyacrylonitrile nanofiber membranes are characterized for chemical adsorption, liquid filtration, and extraction of harmful chemicals from contaminated water. Nanochitosan owns fast adsorption kinetics, high arsenic sorption capacity, and facile arsenic and other such anionic removal [20–23]. Electrospun polystyrene-polydopamine/PDA fibrous cross-linked with β-cyclodextrin coating was found to overcome existing limitations for the removal of anionic pollutants from water compared to non β-cyclodextrin/mere PDA fiber [21, 22]. Biohybrid membranes from polyvinyl alcohol and hydrocolloidal natural gum yield via electrospinning remove assorted nanometal like Ag, Au, Pt, Fe_3O_4, and CuO from water [1, 21]. PVA/GK, amidoxime webs yield via methane plasma treatments and two-nozzle electrospinning, respectively, exhibited altered porosity and hydrophobicity besides elevated sorption capacity for the selective adsorption of uranium and vanadium, besides offering huge utility in tissue engineering and drug-delivery systems [1, 10, 19]. Self-assembly/phase separation techniques for nanomaterial synthesis control 3-D porosity without fiber orientation, while templating controls for fiber orientation over dimension arrangement using sacrificing agents [20]. Electrospinning fabricates tunable morphology and diameter in 1D to 3D nanofiber pores with a facile modification achieved via chemical grafting of rough surface [1, 19]. Chemical compositions, mechanical features, patterns, and membrane pore areas are dominant factors in desalinations that are attenuated by electrospinning, for example, polymethyl methacrylate fiber axis with 0.97-μm diameter found to affect cross-link adherence or extended orientation that ultimately regulates water flux. Thus, nanofiber augmented/controlled via electrospinning to manage fiber alignment yields aligned membranes for desalination utilities as shown in **Figure 1**. Still, many challenges require balancing the degree of orientation, nanofiber thickness, and productivity to be achieved by effective strategic controls like pore area, gap width, and orientation. Electrospinning coats nanofiber onto polymers/ceramic, imparting a high-specific surface and tunable porosity needs in separation [1, 19].

1.3.2. Advanced nanomaterials

Novel nanocomposites, films, hybrids, matrixes, and membranes were fabricated via constitutional morphological alterations to owe substantial water flux/permeability and salt rejection sought in desalination [1, 19]. Lucratively, R & D has designed nanoporous materials that accede to high water flux to keep salt/other contaminates away, thus paving the path for futuristic overwhelmed desalination. Single-layer nanoporous sulfur-coated molybdenum (MoS_2) sheets exhibited 70% higher water flux than graphene RO membranes due to unusual features like a fish-bone/hourglass architecture owing to a nozzle subnanoporosity withstanding necessary water pressure/volumes and robustness as energetic and economic than other counterparts [24]. Certain single-layer nanosheet (pore area of 20–60 Å^2), MFI-zeolite, polymeric high-flux RO, and graphene membranes owing to nanofiltration are significant due to vital modulated parameters like porosity, velocity distributions, permeation, and water density imparting 90% ion rejection with huge water transportation than conventional membranes [24]. Modern nanotechnology aids in designing opportunistic energy-efficient membranes/sheets/mats for efficient desalinations, for example, few A^0 to several nanoporous dimensionally drilled resultant molecular sieves/membranes that *control mass transportations* [1, 19]. B*oron nitride-doped carbon nanotubes and* single-atom-thick *graphene* are augmented for assorted hydrated ions/salt rejections performance than conventional zeolitic membranes in desalination [1]. Hydroxyl functionality gets altered via

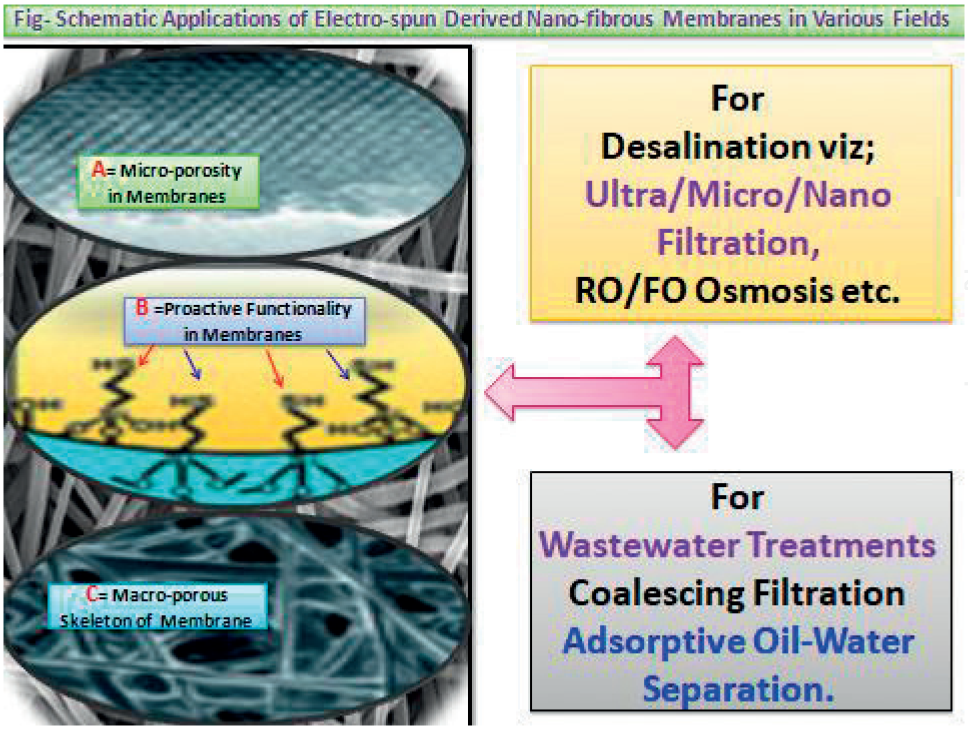

Figure 1. Schematic application of electrospun nanofibrous membranes in various fields.

chemical treatment, for example, graphene nanopore provides hydrophilic sites with enhanced water flux achieved via precise nanopore edges with tunable properties and hydrophilicity in certain advanced desalination [19, 24]. Chemical vapor deposition is combined with focused electron beam to get sculptured single-layer assorted metal dichalcogenide ($MoSe_2$, $MoTe_2$, WS_2, WSe_2)-based membranes that carry effective ion separations as a function of pore size, chemistry, geometry, and hydrostatic pressure [1]. Mechanistic separations via reverse osmosis and capacitive deionization utilized many nanomaterials including zeolites, carbon nanotubes, and graphene to develop highly efficient and capable futuristic desalinations [1, 19, 24]. Advanced designing of nanomaterials paved new avenues and ability to manipulate nanomaterials like carbon nanotubes, nanowires, graphene, quantum dots, super-lattices, and nanoshells [1, 24]. Nanotechnology enables unique nanofabrication that controls macroscopic nontortuous ~1-nm pores specifically designed in MCM, carbon nanotubes, and graphene to offer well-designed size-selective, filtration membranes superior to conventional polymeric membranes (rigidity owing to size-selective nondesign porosity) for desalination [1, 19, 24].

1.3.3. Zeolites

Aluminosilicates are commonly termed as zeolites that possess 3–8-nm pore dimensions found to control morphological features that are well exploited for adsorption/ion exchangers in water treatments. Molecular dynamics stimulates a tight pore distribution as vital for absolute salt rejections and high water permeability, for example, ZK-4 molecular sieve-based RO membrane (4.4-nm) solvates salt and allows the passage of water to flow [1, 25, 26]. Mordenite-coated α-alumina zeolite (MFI, 5.6-nm) RO membranes exhibited hydrophobicity and lowers salt/ionic transport due to fabricated interstitial-defective surfaces so as to control major ion transportations. Zeolites/molecular sieves can be directly coated onto ceramics and incorporated via laser-induced fragmentation to yield RO/FO membranes, for example, Linde-zeolite-A (4.4-nm) interfacial-embedded composites [25, 26] as shown in **Figure 2**. Further rising of zeolite weight % was found to enhance water permeability and salt rejections in resultant membranes compared to experimental thin-film membranes (without zeolite). Zeolite-coated membrane permeates high salt/water throughout since specific transport limits intrinsic pores, and it is difficult to establish its exact role in water transport and salt rejection [10, 25, 26].

1.3.4. Nanocarbons

Assorted nanocarbon materials get vast popularity due to their specific morphology, physicochemical properties, and varied significant utilities. Thus, carbon-based materials are developed as nanoparticles, nanoonions, peapods, nanofibers, nanorings, nanowires, nanotubes, and fullerenes, owing to extensive analytical explicabilities. Intrinsic surface defects of nanostructured carbons were found to affect their stability, and mechanical and physicochemical properties, which further aids in rationally designed requisite materials like zero-dimensional fullerenes and diamond clusters, 1-D nanotubes, 2-D graphenes, 3D nanodiamond (<1 μm), and ultra-hard fullerite [1, 19, 24]. Nanocarbon materials have special advantages viz. facile functionality alterations, high carrier capacity, hydrophilic/hydrophobic incorporations besides high chemical stability [1, 15, 24].

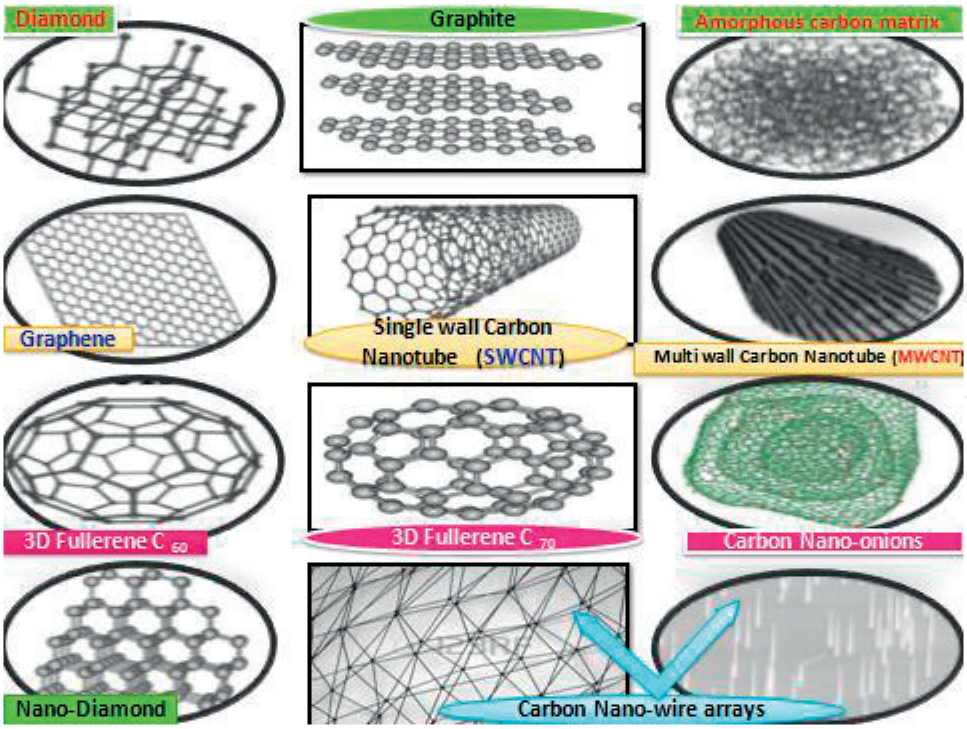

Figure 2. Some nanocarbon materials used in desalination/water purifications.

Allotropic carbon nanotube (CNT) contains rolled-up/cylindrical graphite layers arising as fascinated structural materials due to excellent thermal-electrical conductance, strength, and adsorption properties [1, 12]. CNTs are characterized as single-walled and multi-walled based on the built-up route. A high specific area and elevated available adsorption sites of CNT aid its adaptable surface chemistry. Hydrophobic CNT surfaces are benignly stabilized to avoid persistent contaminant adsorption/aggregation and for preconcentration/detections [15, 19] besides metals/ions too adsorbed onto CNTs through electrostatic attraction and chemical bonding. CNT-based desalinations are facile for point-of-use water purification, for example, plasma-modified ultra-long CNT-based membranes own specific enhanced salt, organic, and metal adsorptions compared to conventional carbon [19]. Futuristic techniques can equip with CNT so as to achieve superior desalination, disinfection, and filtration. USA developed CNT-boron sponges to separate oil-water/emulsion besides oil spills removal aiding oil remediation [1]. Less CNT amount is available in mitigations of degradable antibiotics/pharmaceutical contaminants in point-of-use purification systems [19]. Facile, cheap, and compatibility features of CNT, nanometal, and zeolite nanomaterial-based pellet/bead are utilized for arsenic removal from water [1, 22]. Electrochemically active CNT-based membrane can remove salt, proteins, virus, dyes, and phenol from water [1]. Advanced nanotechnology controls carbon nanotube diameter [19] that aids fabrication of CNT-coated high flux RO membrane owing to labile hydrophobicity and surface roughness [13–17]. Rapid mass transport occurs in CNT-coated polystyrene/silicon nitride membranes that are designed via carboxylation offering high salt ions rejection due to salt anionic and carboxyl repulsions. Some CNT composites owe a low surface area of 210 m^2/g than the activated carbon of 1500 m^2/g; instead, the adsorptive capacity is more due to ordered nanoporosity, which enhances the adsorption of pollutants

[1]. Graphene is utilized potentially in the fabrication of RO/FO membrane fabrications [1] due to high breaking strength and impermeability aiding to create tunable pore size and ultrathin high flux membranes akin to molecular sieves. Molecular dynamic and impregnation techniques simulate the designing of pores (3–25 nm) in ordered carbon, subterminal pores in CNT that allows facile ionic transportation within electrolyte interfaces [20, 21]. The porosity of nanocarbon, CNT, and graphene can be tailored to direct specific adsorption/ultrafast ion transports vital in separation/desalination [1, 19].

1.3.5. Nanometal/metal oxides

Nanometals/metal oxides owe peculiar features like high specific surface area, short intraparticle diffusions, and facile compressibility, which are devoid of activated carbon; hence they are preferred for use in the remediation of metals, arsenic, radionuclides, and organics [1, 19]. Nanometal/oxide gets easily compressed into porous pellets, bead, and powder, for example, Solmete-X, Inc., USA, commercialized nanoselective resin *Arsen-Xnp* from nanoiron oxide-coated organic polymer for the removal of arsenate from water. Nanozerovalent iron adsorbs chlorinated polycyclic aromatic hydrocarbons and perchlorate from water due to its high specific surface area than granular iron [30]. Magnetic nano-Fe_3O_4 separates arsenic from contaminated water [1] besides being injected directly into systems as it gets easily removed by increased osmotic pressure in FO osmosis [1, 19]. Nanosilver-coated TiO_2 has high stability and low toxicity availability in disinfectants in water treatments [19]. Assorted properties, applications, and approach of nanomaterials in treatments [19] are summarized in **Table 1**.

1.3.6. Rationally designed composites/hybrid/biomimetics

Rational designing is done to get ultra-thin, dense active membranes/composites which own less salt rejections and ambient water flux utilized in much FO/RO desalination [1]. Nanomaterial's intrusion in contemporary polymeric skeleton offers extra physical/permeable barriers so as to attain two bulk phases as utilized in promising oil-water separations and desalination [1, 19]. Nanomaterial matrix/blend, for example, nano-SiO_2, CNT, aquaporin-rapped polyamide, and polysulfone-zeolite's superior sieving fabricated myriad smart membranes [25] (**Figure 1**). Functionalized multi-wall carbon nanotube (MWCNT) polyamide-based RO membrane reported 200% water flux with at par salt rejection, amplified water flux [1–17], high hydrophilicity, and thermal stability [27]. Mesosilica MCM-41 incorporated polyamide-based RO membranes augmented water permeability/flux [16]. Biomimic amphiphilic tri-block vesicles enclosed aquaporin-Z and interfacial polymerize RO/FO mem brane impart complete salt rejection and 800 times water flux for seawater desalinations [15, 17]. Conventionally intense polarized membranes own depleted water flux and operation efficiency as serious issues in RO/FO separations [1]. Smart nanosupported bottleneck RO/FO membranes are proficient due to nanoporosity, low tortuosity, high mechanical strength [17], and huge water flux than conventional under similar conditions. Zeolite/nanosilica-polysulfone hydrogel (10 nm) was found to alleviate conventional membrane clogged owing [1, 15] to water flux enhancement and anti-fouling mitigation as achieved due to anti-adhesive surface hydrophilicity [15]. Grafted polyethylene glycol-based RO/FO membrane has great

SN	Nanoporous materials	Characteristics		Applications
		Useful properties	Adverse properties	
1	Nanofiltration (RO/FO)	Reliable, automated, charge-based repulsion, high selectivity, low pressure, costly	High energy, costly, membrane jam, concentrated polarization, few nanoscale pore dimensions	Water hardness, color, odor reduction and heavy metal removal, sea water desalination, wastewater
2	Nanocomposite membranes	Large hydrophilicity, water permeability/flux, thermal/mechanical robust, fouling resistant	Leakage of nanoparticle, bulk nanomaterials needed for oxidation, and composite dependency	Reverse osmosis and removal of micropollutants, bionanocomposite membrane utility
3	Self-assembled membranes	Homogeneous nanoporosity, tunable designed/tailoring	Applied on laboratory/small scales	Ultra-filtrations, process scale-up.
4	Nanocarbon membranes	High porous, high permeable, bacteriosidal, superhydrophobic, tailored electrospun and sustain high salinity, hydrophobic. Survive filtration under high pressure/vacuum	Pore blockages/chocking, leakages of nanofibers	Ultra-filtrations, filters, cartridges, nanofiber composite membranes in water treatments and high-performing direct contact membrane distillations
5	Aquaporin membranes	Assort molecular transportation, highly selective, tailored to dense polyfilm, mechanically stable, regenerative/self-healed	Low pressure desalination, mechanical weakness	Low pressure desalination, biomimetic membrane for RO and FO filtrations, and surface imprint and embed membrane filtrations
6	CNT: carbon nanotubes	Assessable adsorption sites, vast reusability, high cost, health risk	Production cost is very high, own health risks	Degradation of antibiotics, organic, pharmaceutics and own high specific salt adsorption
7	Dendrimers/dendrons (arborol cascade species)	Water-soluble bifunctional (inner hydrophobics and outer hydrophilic absorptions), encapsulate molecules, reusable, bioactive mimics, handy toxicity, nontoxic	Dendrimer production steps are complex and multistage processes	Organic and heavy metal removals, biodegradable, biocompatible, for example, chitosan/dendrite-based
8	Zeolites/aluminosilicate	Highly microporous molecular sieves, lodge variety of cations, selective molecule sorts at size exclusions, control ion release, regular molecular porosity	Reduction in active surface through immobilization	Water disinfections, ion-exchange beds in water purification/softening, solar thermal collector, adsorptive refrigeration
9	Nanozerovalent iron (1–100 nm)	Permeable reactive barrier to filter out contaminants, high specific surface area, and nZVI high mobility/reactivity	Stabilization is needed, that is, surface modifications	As permeable reactive barriers, sediment cap, groundwater remediation like PCB and PAH degradations

SN	Nanoporous materials	Characteristics		Applications
		Useful properties	**Adverse properties**	
10	Nano-TiO_2	High reactivity, stable, durable, toxic, needs UV activation, controllable nanosizes controlling by process conditions like calcinations	Removes suspended fine particles, needs ultraviolet activation	Water disinfections, antifouling processes
11	Metals magnetic nanoparticles/alloys	Nanoparticle manipulations via magnetism/magnetically tunable colloidality and shows superparamagnetism, highly recyclable, easy magnetic separation, own very large surface to volume ratio and biocompatible	Stabilization is needed to enhance its potential	Environmental remediation, cation sensors, nanobeads adsorbents in water treatments, groundwater remediations
12	Nanometals/ nanometal oxides	Short intraparticle diffusivity, tunable pore size/surface chemistry, compressible, abrasion resistive, magnetic, reusable	Needs variant nanodopant to enhance capturing potential by interconnections	Heavy metallic anion removal, filters, slurry reactors, palates, powders

Table 1. Characteristics of the utility of nanomembrane/materials in water treatment processes.

surface tensions, which are utilized for more wetability for hydrophobic foulants [1]. Certain smart nanomembranes, for example, graphene oxide-coupled polyamide, nanosilver-coated polysulfobetaine and polypeptide-grafted single-walled carbon nanotube owing peculiar features viz. bendable size/porosity, high defect density, irreversible bacterial cell adhesion, and antibacterial activity exploited in antimicrobial RO/FO and desalination [1–20].

Thus, nanotechnology improved flux efficiency via ordered pore/size/shape variations and physical barrier/selective charge-base repulsion as requisite for specific/establish emulsion separation/desalination [1–20]. Argonide corporation-USA developed nanoceram interlinked nanofibrous of 2–100 nm diameter and surface area of 300–600 m^2/g to work as an electropositive filter cartridge [27]. Cellulose polymers tailored on nonwoven glass sheets are utilized for ultra-filtration of dirt, bacteria, viruses, and proteins [18]. Certain nanomaterials like fluorocarbon-coated tetramethyl orthosilicate and polyurethane/polylactic acid/polyethylene oxide-coated bio-films' superior features have exploited in desalination due to its mechanical strength, hydrophobicity, biocompatibility, and nontoxicity [1–19]. Biomimetic membranes akin to a*quaporin* are embedded in polymeric matrix/nanofilters [20] to withstand 10 bar high pressures and huge water flux of >100 $L/(hm^2)$ involved in brackish water desalination. Nanotechnology aids in the fabrication of specific aquaporin-based membranes competitive with conventional membranes withstanding under all critical conditions like operating pressures of reverse osmosis, high temperature, acidic/alkaline range, and fouling-based corrosion [1]. Nano-Al_2O_3/TiO_2 zeolite, CNT, photo-catalytic, and nanobimetallic incorporation improve hydrophilicity, raise water permeability, enhance foul resistance, and elevate mechanical and thermal stability which impart high water permeation in RO/FO membrane desalination [1, 20]. Carbon intrude nanopolymeric matrices-based semi-permeable membranes raised the hydrophilicity and increased water permeability/salt permeation as utilized for reverse osmosis [1]. Trimesoyl chloride-metaphenylenediamine interfacial-coated polyethersulfone yields nano-NaX zeolite with 40–150 nm dimensions catering to effective RO/FO membrane [25, 26]. Nano-H_2O Company-USA has commercialized *Quantum-Flux/WO-2006/098872-A3* matrix owing to more permeable efficiency with low fouling and no clogging for membrane-based reverse osmosis [27]. Such coated matrix membranes maintained a surface profile that carries immobilization of potential harmful nanoparticles, for example, P25-Evonik robust membrane [1, 27]. Smart material-based membranes overcome inherent conventional material limitations and address global challenges of water scarcity besides combating environmental pollution [1–20]. Molecular designing of CNT and aquaporin membranes highlighted surface modification and interfacial interactions with enhanced fouling resistivity as shown in **Figure 3**.

1.3.7. Multifunctional nanodevices

Advancement in nanoscience aids in the design of proactive/flexible synchronous and synergistic functionality in desired water treatments as achieved via nanodevice concepts like Fenton nanofiltration and self-floated solar device using well-ordered CNT, nanogold-derived hydrophobic membranes [1, 17]. Polypyrrole-coated stainless steel-based hydrophobic membranes enhance water evaporation than natural solar heating/point-of-use seawater desalination [44]. Molecular simulation theoretically designed smart nanomaterials/devices/systems for best ground-breaking solutions to the existing desalination/purification problems [1, 19].

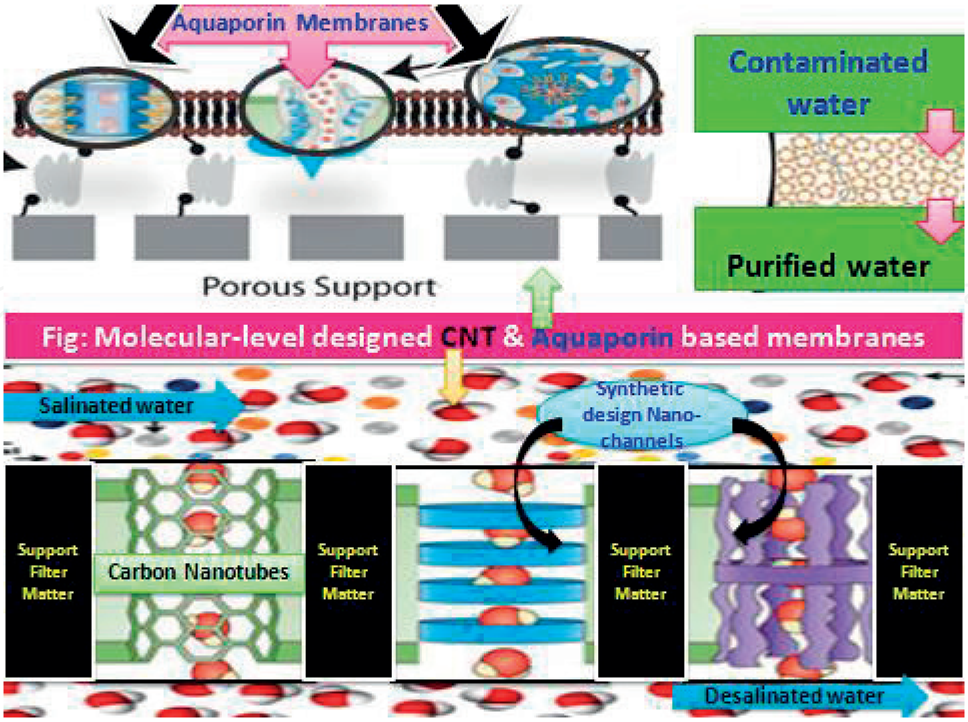

Figure 3. Molecular-level designed CNT and aquaporin-based membranes.

1.3.8. Ordered mesosilica

Ordered mesosilica (OMS) are designed via eco-friendly synthetic paths to offer controlled pore-size network as explored in industrial applications [28]. Kuroda-Mobil Oil Company in 1990 had prepared ordered mesosilica with huge surface areas of >1000 m^2/g and a controlled porosity of 2–20 nm via amphiphilic co-polymeric pore/structure directing agent/precursor [1, 28]. Eco-sustainable mesosilica has achieved via greener syntheses from raw feedstock, and thus sol-gel is preferred [28]. Research on various applications of OMS (last decade) is given in **Figure 4**.

OMS has an ordered chemical/structural/textural distinctiveness which permits to exhibit pollutant adsorption selectivity in water purifications/desalinations [29]. Conventional petroleum-derived surfactants are replaced by renewable amphiphilic polysaccharides that impart an efficient porosity and a high pore volume in resultant OMS [28, 29]. Hydro-soluble polyionic micelles afford wide-ordered porosity needed for oil-water/emulsion separations as targeted OMS applicability differs by means of porosity and template removal/thermal calcinations/chemical extractions [1, 29]. Calcination temperature vitally shrinks shape/size, porosity, and morphology and affects micro-skeleton of OMS as mentioned in **Table 2**.

OMS manufacturing is expensive due to costly precursor usage like silicon-alkoxide/TEOS, so, it is developed in a more eco-synthetic way for large scale [28, 29]. Environmental impacts are lessened if biomass/recycled waste silica sources are used viz. fly/rice husk's ashes extracted silica. Several templating surfactants are recognized for lyotropic liquid crystalline phase formations. However, classical surfactants are substituted by new hydro-soluble/dissociable and recoverable porogens. The ecodesigned industrial ordered meso-silica synthesis

Figure 4. Research publications on various field applications of mesoporous silica (last decade).

Silica solids	Particle shape	Size dimensions	Pore-size ordering
MTAB-MSN	Spherical	50–100 nm	Low-stretched mesoporous channels
CTAB-MSN	Spherical	70–100 nm	Well-ordered mesoporous channels
STAB-MSN	Rod-like	100–500 nm length 50–75 nm width	Well-ordered mesoporous channels
DDAB-MSN	Irregular	80–100 nm	Ink-bottle porosity
TDTHP-NS	Spherical	100–500 nm	Microporosity

Table 2. Shape, size, pore-order morphology, and microskeletons in mesosilica.

which uses assisted self-assembly path for removal of template own profound impacts on surface, chemical and textural properties of OMS and thus affects their synthetic applications [29]. Calcination and solvent extraction eliminate organic templates during synthesis, and numerous template removals are studied to lessen process time and solvent usage. Assorted varied surfactants vitally fix sustainable synthetic paths as shown with waste generation (E-factor = kg waste/kg product) in **Table 3**.

These developed sustainable OMS syntheses rely on the choice of silica precursor, environmental impact, byproduct, and cost [29]. Green chemistry synthesis aspects escort silica from natural mineral deposits, biomass, or industrial wastes, and constitute huge resources that are commercially compared in **Table 4**.

Nomenclature	Surfactant used	Structure	E-factor [30]
MCM-41/48: mobile composition of matter	Alkyltrimethyl ammonium salt $C_nH_{2n+1}N^+(CH_3)_3X^-$ (with *n* = 12, 14, 16 or 18 and X = Cl or Br)	*P6mm*, hexagonal for MCM-41 and *Ia3d*, cubic MCM-48	41.9/21–2.0 and 45.3/1 = 45.3
FSM-16[a] Folder sheet mesoporous	Alkyltrimethyl ammonium $C_nH_{2n+1}N^+(CH_3)_3X^-$ (with *n* = 12, 14, 16 or 18 and X = X or Br)	*P6mm*, hexagonal	31.9/10
HMS Hexagonal mesoporous silica	Uncharged amine surfactant $C_nH_{2n+1}NH_2$	Wormhole framework structure	29.9/12
SBA-15 and 16 Santa Barbara amorphous	P123 and F127, respectively	*P6mm*, hexagonal and *Im*3*m*, cubic, respectively,	16/2.3–7.0
KIT-6[b] Korea Advanced Institute of Science and Technology	P123	*Ia3d*, cubic	25/4–6.2
FDU-1[c] FuDan University	Polyethylene oxide-polybutylene oxide-polyethylene oxide tri-block copolymer B50-6600 ($EO_{39}BO_{47}EO_{39}$, Dow)	*Fm*3*m,* cubic	—
COK-12[d] Centrum voor Oppervlaktechemie & Katalyse	P123	*P6m*, hexagonal	—

[a] FSM-16 yield from layered silicate kanemite

[b] KIT-6 by tri-block copolymer ($EO_{20}PO_{70}EO_{20}$)-butanol.

[c] FDU-1 in NaCl salt.

[d] COK-12 in citrate/citric acid surfactant, E-factors are found to be lower than nanomaterials and bulk chemicals.

Table 3. Ordered mesoporous materials, used surfactant, and their crystallographic structure.

Origin	Type	Advantages	Drawbacks
Natural	Natural clays, diatomite/kieselgur, siliceous sedimentary rock and minerals, besides zeolite	Copious economical amicable, mesoporous materials without the need of organic surfactants rather than metal cation impurities, residual natural lignins are helpful	Polycondensation is uncontrolled under neutral/acidic conditions, strong acids and high temperatures needed purification
Synthetic	Silicon alkoxides Si(OR)4, for example, TEOS, TMOS, besides soluble silicates, for example, sodium silicate, colloidal and fumed silica	Silicon alkoxides, uniform oligomers impart highly organized mesostructure at any pH, facile and cheap protocol, water as solvent	High energy input and expensive procedures, toxic precursors, needs catalysts and organic solvents only, byproduct alcohol during hydrolysis. Silicate oligomers with varied degrees of polymerization, polycondensation is uncontrolled under neutral/acidic conditions

Origin	Type	Advantages	Drawbacks
Recycling wastes	Industrial ashes, for example, coal, rice husk, and packaging resin waste, glasswares	Plentiful cheap and nontoxic, acidity conferred by residual metal ions within matrix besides waste disposal solutions	Has lower surface area and pore volume than other precursors, porous silica material regenerations as hard templates used for nanocasting

Table 4. Comparison of different silica sources for the synthesis of silica-based mesoporous material.

Eco-designed OMS synthesis focused on assisted self-assembly involving assorted [28, 29] treatments via precipitation, liquid phase reactions, solid recovery, washing, and drying as shown in **Figure 5**.

1.4. Major smart materials/membranes for desalination and oil-water/emulsion separations

Nanomaterial-aided modus operandi have simulated membranes especially designed onto advanced nanostructures like CNT, graphene, graphene oxide and reduced graphene oxide for desalination [1, 19]. Graphene/graphene oxide/rGO showed unique performance and promising direction in futuristic water treatment/desalination [1–20]. Such stimulated membrane penetrates water via nanometer pores in single-layer graphene and offers salt nanofiltration with enhanced permeability than conventional RO [17, 19]. Graphene oxide membrane exhibits

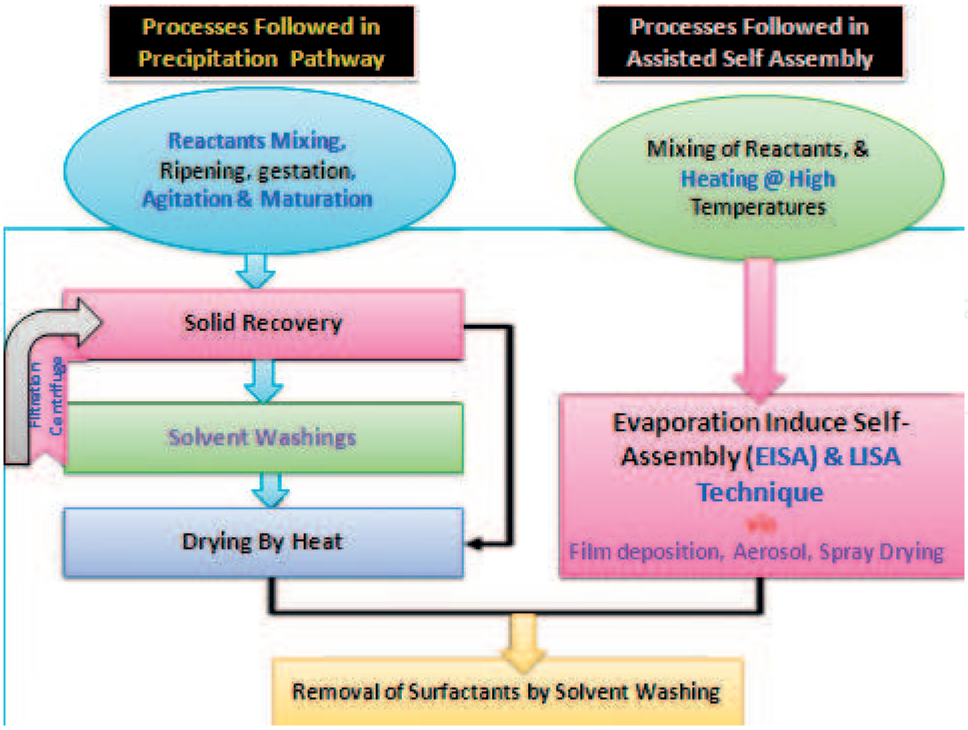

Figure 5. Steps involved in precipitation and assisted self-assembly routes for OMS synthesis.

anomalous liquid fast permeation into capillary high pressure created inside inter-layers and used for seawater desalinations as it contains varied ions including Na^+, K^+, Mg^{2+}, and Cl^-. Such ultrafast transportation via precise casing imparts single/double-layered graphene as enthusiastic representative in desalination [18] which has 100% LiCl, NaCl, and KCl salt rejections than traditional membranes [17–19]. Akin, two-dimensional inorganic matrixes like MXenes possess atomic-layered skeletons with controllable compositions as potential nanofiltration membranes. Nanofiltration assembly/devices were developed with specified and smartly designed nano-TiO_2, CNT, and noble-metals and Fenton agents [1, 19].

Oil-water separations are required if fuel spillage especially gasoline/diesel/petrol during transportation failures releases oil in aqueous systems to pose environmental hazardous, and thus emulsion separations are highly sought [1, 19]. Interface science and bionic knowledge have developed some 2-D membranes via surface micronanohierarchical structure grafting so as to impart unique/super-wetting characters viz. superhydrophobicity, superoleophobicity, and superamphiphilicity to be utilized for oil-water separation [1, 15]. Bio-inspired spatial hierarchical polytetrafluoroethylene-coated stainless steel mesh has self-cleaned superhydrophobic surfaces that impart a water contact angle of >150° and a diesel contact angle of ~0° and responsibly perform excellent oil-water separations [15]. Such hydrogel-coated mesh is superior due to extraordinary water passage selectivity over oil, thus preventing oil-material contacts and avoiding membrane clogging caused by viscous oils besides allowing gravity-driven separation. Surface chemistry designed membranes like polyvinylpyridine-polydimethylsiloxane-polyurethane sponges, grafted polyacrylic acid, and sodium silicate-TiO_2 stainless steel mesh have irreversible encapsulation of low-surface-energy species, flexible wet-ability, and toggled superoleophilicity as benefited for emulsion/oil-water separation [15].

1.5. Futuristic nanomaterials for desalination

Advanced nanotechnologically designed/engineered nanoadsorbents, nanometals, nanomembranes, and photo-catalysts have vulnerable flexibility and adjustability with water treatment systems encompassing assorted micro-pollutants [1]. The compatible existing water treatment processes can be integrated simply in conventional modules. Nanomaterials are advantageous due to their ability to be integrated to various multifunctional membranes that enable both particle retention and contaminant mitigations compared to conventional materials used in water technologies [20]. Auxiliary usages of nanomaterials impart higher process efficiency and higher sorption rates. However, in order to minimize the health risk of nanomaterial’s usage in water treatments, several regulatory norms need to be prepared for being adaptable to mass/large-scale utility. Still, nanostructured materials have offered potential innovations in serious contaminants degradation, decentralized water treatments, and point-of-use devices [1–20]. Nanotechnology assists in wastewater treatments for the mitigation of pathogens, organic and inorganic, heavy metals, and other toxic contaminants using nano-ZnO RO/FO nanofilms and polyrhodanine-encapsulated magnetic nanoparticle that are removed by contaminants up to ppb level [19]. There emerge innovative technologies in nanoscience; yet, many challenges posed by water purification need to be resolved by future scientists.

1.6. Conclusions

Rationally designed smart nanomaterials provide myriad scientific and technology growth to desalination/water purification. Still, biomaterials must be explored in this perspective that owes high permeation and low salt rejections in futuristic desalination. Thus, advanced nanotechnology aided commercially viable products/solutions that enhance/replace existing desalination/purification. Certain functionalized nanoporous biopolymeric membranes were found to cater to inherent challenges. Bio-polymer cross-linking fixes usual instability and imposes functionally cost-effective nanoporous biomaterials to be used in desalinations. Overall, rational fabrication highlighted "*design-for-purpose*" unlike *trial-and-error approach* starts with scientific perceptions by knowing inherent barriers, and thus the conceptual design of nanomaterial is proposed, as fed back to desalination problems for thorough usage in water treatments. Nanomaterials' performance must unambiguously be defined in water purifications and need redesigning under failure conditions with "thinking-outside-the-box" prospective as confronted by desalination. Till now, nanomaterials' rational designing offered more unprecedented opportunities for solving desalination challenges in a sustainable manner. A prospective-ordered designing should owe few aspects namely molecular dynamics/simulation tools to extend problem definition and theoretically needs more multi-functional/all-in-one nanomaterial for effective desalination/water purifications. Therefore, progressive and versatile nanomaterials/devices, which can work under ambient conditions with paramount desalinations/water purification performance, are expected in the near future. Such design-sophisticated material surfaces reversibly counter stimuli via innovative and promising exterior/interior changes and eminent environmental adaptability which displayed myriad functions viz. interfacial pollutant adsorption, omniphobic slippery coatings, responsive particle-stabilized emulsions, and self-healed surface membranes. This chapter described the strategic and valuable rational-designing idea for assorted biomimetic membranes/materials owing to environmental utilities.

Acknowledgements

The author is thankful to the Head, Department of Chemistry, R.T.M. Nagpur University, Nagpur, for laboratory facilities and to the Vice Chancellor, Nagpur University, Nagpur, for the sanction of a research project under University Research Project Scheme, No. Dev./RTMNURP/AH/1672 (9), dated 24 September 2016.

Author details

Rajendra S. Dongre

Address all correspondence to: rsdongre@hotmail.com

Department of Chemistry, R.T.M. Nagpur University, Nagpur, Maharashtra, India

References

[1] Li R, Zhang L, Wang P. Rational design of nanomaterials for water treatment. Nanoscale. 2015;**7**:17167-17194. DOI: 10.1039/C5NR04870B

[2] Eijkel JCT, van den Berg A. Nanofluidics: What is it and what can we expect from it? Microfluidics and Nanofluidics. 2005;**1**:249-267

[3] Humplik T, Lee J, O'Hern SC, Fellman BA, Laoui T, Wang EN. Nano-structured materials for water desalination. Nanotechnology. 2011;**22**(29):1-19

[4] Han JY, Fu JP, Schoch RB. Molecular sieving using nanofilters: Past, present and future. Lab on a Chip. 2008;**8**:23-33. DOI: 10.1039/b714128a

[5] Sint K, Wang B, Kral P. Selective ion passage through functionalized graphene nanopores. Journal of the American Chemical Society. 2008;**130**:16448-16449. DOI: 10.1021/ja804409f

[6] Murad SM, Lin JC. Using thin zeolite membranes and external electric fields to separate supercritical aqueous electrolyte solution. Industrial and Engineering Chemistry Research. 2002;**41**:1076-1083

[7] Jeong B et al. Interfacial polymerization of thin film nano-composites: A new concept for reverse osmosis membranes. Journal of Membrane Science. 2007;**294**:1-7

[8] Wang HZ, Huang ZP, Carnahan D. Reversible transformation of hydrophobicity & hydrophilicity of aligned carbon nanotube arrays & buckypapers by dry processes. Carbon. 2010;**48**(3):868-875

[9] Ji L, Zhu D. Mechanisms for strong adsorption of tetracycline to carbon nanotubes: Comparative study using activated carbon & graphite as adsorbents. Environmental Science & Technology. 2009;**43**:2322-2327

[10] Qu X. Applications of nanotechnology in water treatment. Water Research. 2013;**47**: 3931-3946

[11] Li LX et al. Ordered mesoporous carbons synthesized by a modified sol-gel process for electrosorptive removal of sodium chloride. Carbon. 2009;**47**:775-781

[12] Striemer CC et al. Charge- and size-based separation of macromolecules using ultrathin silicon membranes. Nature. 2007;**445**:749-753

[13] Hajeh M, Laurent S, Dastafkan K. Nanoadsorbents: Classification, preparation, and applications (with emphasis on aqueous media). Chemical Reviews. 2013;**113**:S7728-S7768

[14] Li J-J, Zhou Y-N, Luo Z-H. Smart fiber membrane for pH-induced oil/water separation. ACS Applied Materials & Interfaces. 2015;**7**:19643-19650

[15] Liu H, Gao S-W, Cai J-S, He C-L, Mao J-J, Al-Deyab SS, Lai Y-K. Recent progress in fabrication & applications of superhydrophobic coating on cellulose-based substrates. Materials. 2016;**9**(3):124

[16] Lee A, Elam JW, Darling SB. Membrane materials for water purification: Design, development, and application. Environmental Science: Water Research & Technology. 2016; **2**:17-42

[17] Lalia BS, Kochkodan V, Hashaikeh R, Hilal N. A review on membrane fabrication: Structure, properties and performance relationship. Desalination. 2013;**326**:77-95

[18] Dervin S, Dionysiou DD, Pillai SC. 2D nanostructures for water purification: Graphene and beyond. Nanoscale. 2016;**8**:15115-15131

[19] Wang Z, Ciacchi LC, Wei G. Recent advances in nanoporous membranes for water purification: Review. Nanomaterials. 2018;**8**(2):65

[20] Davis ME. Ordered porous materials emerging application. Nature. 2002;**417**:813-821

[21] Diallo MS, Goddard WA. Dendrimer enhanced ultrafiltration. Recovery of Cu(II) from solutions PAMAM dendrimer with ethylenediamine core-terminal NH_2. Environmental Science & Technology. 2005;**39**:S1366-S1377

[22] Aredes S, Klein B, Pawlik M. The removal of arsenic from water using natural iron oxide minerals. Journal of Cleaner Production. 2012;**29-30**:208-213

[23] Torrey JD et al. Oxidation behavior of zero-valent iron nanoparticles in mixed matrix water purification membranes. Environmental Science: Water Research & Technology. 2015;**1**(2):146-152. DOI: 10.1039/c4ew00068d

[24] Lin SC, Buehler MJ. Mechanics and molecular filtration performance of graphyne nanoweb membranes for selective water purification. Nanoscale. 2013;**5**:11801

[25] Humplik T, Wang EN. Framework water capacity & infiltration pressure of MFI Zeolites. Microporous & Mesoporous Materials. 2014;**190**:84-91

[26] Gehrke I, Geiser A, Somborn-Schulz A. Nano-techn innovations for water treatment. Nanotechnology, Science Applications. 2015;**8**:1-17. DOI: 10.2147/NSA.S43773

[27] Porada S et al. Direct prediction of the desalination performance of porous carbon electrodes for capacitive deionization. Energy & Environmental Science. 2013;**6**:3700

[28] Corine G'r, Reboul J, Bonneb M, Lebeau B'n'd. Ecodesign of ordered mesoporous silica materials. Chemical Society Reviews. 2013;**42**:4217

[29] Fernandes FM, Coradin T, Aimé C. Self-assembly in biosilicification and biotemplated silica materials: Review. Nanomaterials. 2014;**4**:792-812

[30] Sheldon RA. E factors, green chemistry & catalysis: Odyssey. Chemical Communications. 2008;(9):3352-3365. DOI: 10.1039/B803584A