REVIEWS

Science and technology for water purification in the coming decades

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One of the most pervasive problems afflicting people throughout the world is inadequate access to clean water and sanitation. Problems with water are expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich. Addressing these problems calls out for a tremendous amount of research to be conducted to identify robust new methods of purifying water at lower cost and with less energy, while at the same time minimizing the use of chemicals and impact on the environment. Here we highlight some of the science and technology being developed to improve the disinfection and decontamination of water, as well as efforts to increase water supplies through the safe re-use of wastewater and efficient desalination of sea and brackish water.

The many problems worldwide associated with the lack of clean, fresh water are well known: 1.2 billion people lack access to safe drinking water, 2.6 billion have little or no sanitation, millions of people die annually—3,900 children a day—from diseases transmitted through unsafe water or human excreta[1]. Countless more are sickened from disease and contamination. Intestinal parasitic infections and diarrheal diseases caused by waterborne bacteria and enteric viruses have become a leading cause of malnutrition owing to poor digestion of the food eaten by people sickened by water[2,3]. In both developing and industrialized nations, a growing number of contaminants are entering water supplies from human activity: from traditional compounds such as heavy metals and distillates to emerging micropollutants such as endocrine disrupters and nitrosoamines. Increasingly, public health and environmental concerns drive efforts to decontaminate waters previously considered clean. More effective, lower-cost, robust methods to disinfect and decontaminate waters from source to point-of-use are needed, without further stressing the environment or endangering human health by the treatment itself.

Water also strongly affects energy and food production, industrial output, and the quality of our environment, affecting the economies of both developing and industrialized nations. Many freshwater aquifers are being contaminated and overdrawn in populous regions—some irreversibly—or suffer saltwater intrusion along coastal regions. With agriculture, livestock and energy consuming more than 80% of all water for human use, demand for fresh water is expected to increase with population growth, further stressing traditional sources. The shift to biofuels for energy may add further demands for irrigation and refining. Alarmingly, within 30 years receding glaciers may cause major rivers such as the Brahmaputra, Ganges, Yellow (which already at times no longer runs to the sea) and Mekong rivers, which serve China, India and Southeast Asia, to become intermittent, imperilling over 1.5 billion people during the dry months[4,5]. Even industrialized nations in North America and Europe, and those in Andean countries in South America, could see major disruptions to agriculture, hydroelectric and thermoelectric generation, and municipal water supplies from reductions in snowmelt and/or loss of glaciers[6,7]. In the coming decades, water scarcity may be a watchword that prompts action ranging from wholesale population migration to war, unless new ways to supply clean water are found.

Fortunately, a recent flurry of activity in water treatment research offers hope in mitigating the impact of impaired waters around the world. Conventional methods of water disinfection, decontamination and desalination can address many of these problems with quality and supply. However, these treatment methods are often chemically, energetically and operationally intensive, focused on large systems, and thus require considerable infusion of capital, engineering expertise and infrastructure, all of which precludes their use in much of the world. Even in highly industrialized countries, the costs and time needed to develop state-of-the-art conventional water and wastewater treatment facilities make it arduous to address all the problems. Furthermore, intensive chemical treatments (such as those involving ammonia, chlorine compounds, hydrochloric acid, sodium hydroxide, ozone, permanganate, alum and ferric salts, coagulation and filtration aids, anti-scalants, corrosion control chemicals, and ion exchange resins and regenerants) and residuals resulting from treatment (sludge, brines, toxic waste) can add to the problems of contamination and salting of freshwater sources. Moreover, chemically intensive treatment methods in many regions of the world cannot be used because of the lack of appropriate infrastructure.

However, even within central Europe there has been a movement towards reducing chemical treatment via engineered 'natural' systems for drinking-water production in order to reduce residual chemicals in the distribution systems[8]. Fortunately there is much more that science and technology can do to mitigate environmental impact and increase efficiency because current treatment methods are still far from natural-law limits in their ability to separate compounds, deactivate or remove deleterious pathogens and chemical agents, transport water molecules, and move ions against concentration gradients. Our expectation is that by focusing on the science of the aqueous interface between constituents in water and the materials used for treatment, new, sustainable, affordable, safe and robust

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methods to increase supplies and purify water can be developed and implemented to serve people throughout the world.

Here, we highlight some of the science and next-generation systems being pursued: to disinfect water, removing current and emerging pathogens without intensive use of chemicals or production of toxic byproducts; to sense, transform, and remove low-concentration contaminants in high backgrounds of potable constituents at lower cost; and to re-use wastewater and desalinate water from sea and inland saline aquifers, all of which hold great promise for effectively increasing water supplies. To realize these challenging goals, many open research questions need to be addressed. Our thesis is that research will enable improved disinfection, decontamination, re-use and desalination methods to work in concert to improve health, safeguard the environment, and reduce water scarcity, not just in the industrialized world, but in the developing world, where less chemical- and energy-intensive technologies are greatly needed.

Disinfection

An overarching goal for providing safe water is affordably and robustly to disinfect water from traditional and emerging pathogens, without creating more problems due to the disinfection process itself. Waterborne pathogens have a devastating effect on public health, especially in the developing countries of sub-Saharan Africa and southeast Asia[9]. Waterborne infectious agents responsible for these diseases include a variety of helminthes, protozoa, fungi, bacteria, rickettsiae, viruses and prions[10]. While some infectious agents have been eradicated or diminished, new ones continue to emerge and so disinfecting water has become increasingly more challenging. Viruses are of particular concern, accounting, together with prions, for nearly half of all emerging pathogens in the last two to three decades[9]. Enteric viruses received less attention in the past compared with bacterial pathogens (for example, *Vibrio cholerae*) and protozoan parasites (for example, *Cryptosporidium parvum*), partly because they were difficult to detect, and partly because free chlorine (the main disinfectant used worldwide because of its potency and low cost) was very effective in inactivating them. However, free chlorine is ineffective in controlling waterborne pathogens such as *C. parvum* and *Mycobacterium avium*. *M. avium* in particular is ubiquitous in biofilms within water distribution systems around the world, with remarkable resistance to chlorine at the high pH and low temperature of natural water. Indeed, ageing and deterioration of drinking water distribution systems and the associated growing of biofilms within them has emerged as a key infrastructure rehabilitation challenge: significant resources are needed to maintain and upgrade distribution systems. In the USA, where large numbers of such old systems exist, disinfectants are required to suppress pathogens within the system. Halogenated disinfection strategies for treatment and distribution systems produce toxic disinfection by-products (DBPs) such as trihalomethanes and haloacetic acids. Recent US disinfection regulations[11,12] require the control of *C. parvum* oocysts while minimizing the formation of certain DBPs, which might force some drinking-water utilities to discard free chlorine disinfection and implement alternative technologies.

Therefore, the effective control of waterborne pathogens in drinking water calls for the development of new disinfection strategies, including multiple-barrier approaches that provide reliable physicochemical removal (for example, coagulation, flocculation, sedimentation, and media or membrane filtration) along with effective photon-based and/or chemical inactivation. The 1993 outbreak of cryptosporidiosis in Milwaukee, Wisconsin, USA, in which approximately 400,000 people were infected and more than 100 died, was a wake-up call for the US drinking-water industry. They were reminded that relying exclusively on physicochemical removal, which can suffer from malfunctions arising from defects in manufacturing or operation, can have a devastating effect on public health.

The use of light from visible to ultraviolet (UV) to photochemically inactivate pathogens has recently seen a resurgence in interest, notwithstanding the historical use of sunlight to disinfect water. Sequential disinfection schemes such as UV/combined chlorine and ozone/combined chlorine are being considered by many drinking-water utilities as the inactivation component of their multiple-barrier treatment plants because, compared with free chlorine, both UV and ozone are very effective in controlling *C. parvum* oocysts. In addition, combined chlorine can provide a residual in distribution systems without forming high levels of regulated DBPs. However, changing disinfection technologies has raised new concerns because viruses, although effectively controlled by ozone, are resistant to both UV and combined chlorine disinfection. Moreover, ozone can form the DBP carcinogen bromate ion in water containing bromide ions, and combined chlorine can form other unregulated DBPs, for example, haloacetonitriles and iodoacetic acid[13,14], that may be more toxic and carcinogenic than those associated with free chlorine.

The situation in developing countries is similar. International agencies and non-governmental organizations have introduced the use of sunlight irradiation of water within PET (polyethylene terephthalate) bottles to kill pathogens, and are promoting the use of sodium hypochlorite for point-of-use disinfection of drinking water in rural areas (for example, the CDC SafeWater System)[15]. Although these initiatives have lowered the incidence of gastrointestinal disease, owing to the lack of adequate sanitation, the source waters in these areas contain ammonia and organic nitrogen that react with the sodium hypochlorite to form combined chlorine species that are ineffective in inactivating viruses. Furthermore, relatively high levels of toxic DBPs can form in the presence of high concentrations of organic matter associated with inadequate sanitation.

To develop alternatives to chlorine (free and combined) and UV disinfection for the control of waterborne viruses requires significant advances in understanding how viruses are inactivated by the benchmark (chlorine and UV) methods and by any new technologies. The goal is to match or improve on the positive aspects of chlorine and UV disinfection while avoiding the negative effects. To do so requires several questions to be answered. It is well established that both UV light and the free chlorine species hypochlorous acid (HOCl) react with various amino acids in the virus capsid proteins as well as with the nucleic acid protected by the capsid[16,17]. However, the actual limiting step (that is, the molecular target and its level of damage) responsible for inactivation is not yet known. Developing a process that targets that inactivation mechanism may create a new, safe, and robust disinfection method.

For example, many species of adenovirus—the waterborne pathogens with highest resistance to UV inactivation—use their fibre head (Fig. 1a) to attach to the amino-terminal D1 domain of the coxsackievirus-and-adenovirus receptor (CAR) of host cells[18]. Amino acid sequence alignments have shown that the hydrophobic side group of tyrosine and ionizable basic side groups of histidine and lysine in the fibre head associate with CAR amino acids (Fig. 1b) and thus play a role in the attachment of adenovirus to the host cell[19]. Consequently, oxidization of the phenolic group of tyrosine, and formation of reactive chloramines with the amino groups of histidine and lysine[20–23] could contribute to changing the conformation of the adenovirus head protein and inhibiting binding to receptors, thus effectively inactivating the virion. HOCl also reacts with nucleic acid and amino acid residues involved in many steps of the infection cycle of viruses, such as cell entry (endocytosis and endosomal lysis), intracellular trafficking and nuclear delivery, in the case of adenovirus[24]. Thus, even if the virus penetrates the cell, the infection cycle could be inhibited at some subsequent step. A potential problem with this strategy is that once inside the cell, the virion might manipulate the host cell to repair the damage and subsequently complete the infection cycle[25]. Consequently, disinfection processes that target the proteins responsible for attachment and penetration would avoid the unwanted possibility of genome repair.

A new generation of disinfection processes to control viruses should be capable of selective reactions with the key residues in

proteins responsible for binding to host cell receptor molecules. Heterogeneous processes are envisioned that would use complementary nanostructured and functionalized surfaces that mimic the structure and functionality of the receptors of target protein residues. These structures should have both high affinity and specificity and be relatively inert to the large amounts of organic matter ubiquitous in natural water. The surfaces of new materials could be designed with arrays of sites that serve to trap all waterborne viral pathogens via binding to host receptors.

A futuristic disinfection method involves the combined use of photons and engineered nanostructures. Although UV is effective for inactivating waterborne bacteria and protozoa cysts and oocysts, it is not very effective for viral pathogens. However, UV light is capable of activating photocatalytic materials such as titania (TiO_2), which are capable of inactivating viruses. Furthermore, new photocatalysts such as TiO_2 doped with nitrogen (TiON), or co-doped with nitrogen and a metal such as palladium, can be activated with visible light[26] (which could potentially inactivate viruses and other waterborne pathogens with much lower energy use than UV), or even with sunlight (for deployment anywhere with bright sunlight). Of particular interest are materials and systems that use low-cost visible lamp light and sunlight to achieve sufficiently high throughput. Low throughput rates have thus far limited adoption of photoinactivation. Throughput rates depend on factors such as incident light flux and wavelength, absorption length through water, geometry, reactor hydrodynamics, contact efficiency of species in water on the photocatalysts and, critically, the inactivation kinetics. Moreover, we need to improve our understanding of the mechanisms for the interactions of pathogens, in particular virions, with excited photocatalyst surfaces and adherent active moieties, such as hydroxyl radicals and superoxides. The physicochemical structure of such surfaces would need to be optimized for maximum selective affinity of target viral capsid molecular motifs.

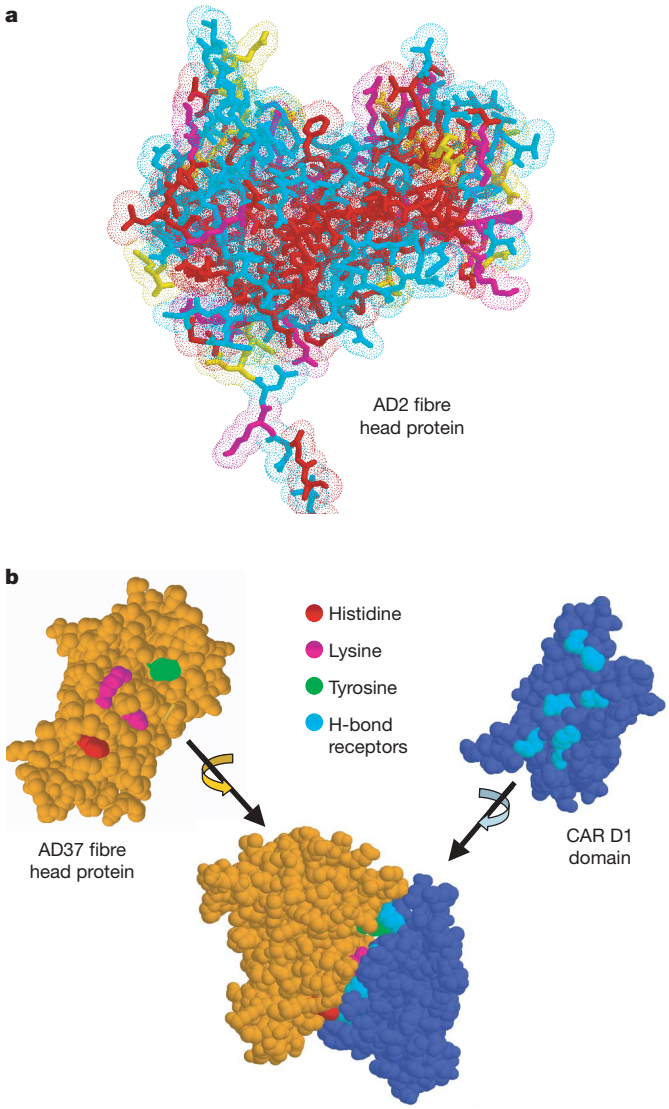

Figure 1 | Waterborne virus attachment head and receptor on host cell. **a**, Schematic of adenovirus-2 attachment fibre head showing amino acids with basic (magenta, orange, purple), acidic (yellow), and hydrophobic (red) side groups. **b**, Schematic of adenovirus-37 fibre head protein attaching to the D1 domain of the coxsackievirus-and-adenovirus receptor (CAR) on the host cell. Basic ionizable (histidine, lysine) and hydrophobic (tyrosine) side groups of AD37 amino acids and those in CAR D1 domain involved in hydrogen bonding are highlighted. The figure was developed with Protein Explorer[98] based on a structure described in ref. 99 (courtesy of Martin A. Page, University of Illinois).

Once these new materials are developed, they can be engineered into flow-through reactors for high-throughput systems. The configuration and associated cost of such systems could make them economically viable for applications ranging from large water-treatment plants supplying potable and non-potable water to point-of-use systems with segregated lines dedicated to human consumption and hygiene. Antiviral photocatalysts could be immobilized on fibres and foams of various materials[27–29], or incorporated into membranes[30]. Optical fibres could be used to bring photons into compact configurations such as monolithic reactors[31]. Reactors incorporating visible-light photocatalysts could be designed using sunlight as the source of photons[32,33], a configuration that would be particularly beneficial in developing countries. The resulting systems would provide a barrier against all pathogens by inactivating viruses and trapping any larger bacteria and protozoa cysts and oocysts with relatively high resistance to light and photocatalytic inactivation, all without producing DBPs or extensive use of chemicals.

Decontamination

The overarching goal for the future of decontamination is to detect and remove toxic substances from water affordably and robustly. Widely distributed substances, such as arsenic, heavy metals, halogenated aromatics, nitrosoamines, nitrates, phosphates, and so on are known to cause harm to humans and the environment. Two key problems are that the amount of suspected harmful agents is growing rapidly, and that many of these compounds are toxic in trace quantities. To detect their presence and remove them in the presence of safe and natural constituents that are 3 to 9 orders of magnitude more concentrated is challenging, expensive, and unreliable at present. Chemically treating the total volume of water to transform or remove a specific trace compound is also expensive and potentially itself harmful. Moreover, the treatment does not necessarily remove other harmful compounds, and safe constituents may interfere with the remediation. Thus, new methods to detect toxic compounds and decontaminate water are urgently needed.

The problems of detecting and accurately measuring toxic compounds in water and of selectively removing only these compounds are tightly linked. Both are affected by the particular combination of micropollutant classes (heavy metals, As(III/V), BTEX, pharmaceutical derivatives, agricultural chemicals, endocrine disrupters, and so on)[34] relevant to a specific water source. Furthermore, viable avenues for both detection and treatment are tied to the resource base available. Approaches to speciation of As(III/V) or elemental profiling relevant to western Europe are simply not an option for Bangladesh[35,36] or Benin[37]. Powerful methods of monitoring low concentrations of contaminants are invariably built around sophisticated laboratory instrumentation. It is extremely challenging to develop robust, low-cost, effective means of chemical sensing relevant to the water contamination problems of developing nations. Similarly, affordably treating toxic compounds in water, such as by

reducing As(III/V) concentrations to levels currently thought of as safe (<10 parts per billion), without producing toxic waste disposal issues has proved to be a major challenge. But although these goals are beset by severe technical difficulties, they also present exciting opportunities for the research community.

Speciation remains a challenging detection problem. For example, As(III) is estimated to be ~50 times more toxic than As(V), so both As(III) and total As must be measured. Anodic stripping voltammetry[38] has sufficiently low limits of detection (LOD = 1.2 $\mu g l^{-1}$) to be practical and is capable of measuring As(III) in the presence of large excesses of As(V). Alternatively, ion exchange separations may be combined with hydride generation atomic spectroscopy to measure As(III) and As(V) separately[39]. But neither method is suitable for untrained workers. These methods also demonstrate the related generic problem of the LOD dynamic reserve. The temptation, given that detailed dose–response data frequently do not exist (especially at low concentrations of toxic species), is to regulate to the existing analytical capabilities, which can create new problems. For example, if the total As concentration is regulated at a maximum contaminant level of 10 $\mu g l^{-1}$, then the 1.2 $\mu g l^{-1}$ LOD of As(V) represents only an eightfold dynamic reserve. It might not be possible to achieve a tenfold or greater dynamic reserve between the LOD and the maximum contaminant level using detection methods suitable for use by untrained workers to enhance human health.

Beyond these quantitative issues lies the dichotomy between the capabilities for detecting target compounds and for identifying potentially troublesome non-target species. Even powerful multidimensional analytical methods, such as liquid chromatography-mass spectrometry (LC-MS), struggle to characterize waters containing significant amounts of non-target species. These compounds must often be pre-concentrated by factors of 10^2 to 10^3 and can only be assayed accurately in the presence of a small number of potential compounds whose liquid chromatography retention behaviour is known[40]. Such problems point to the critical need to develop molecular recognition motifs (sensor reagents) that can be combined with micro-nanofluidic manipulation[41] and data telemetry to accomplish single-platform chemical sensing having the requisite figures of merit to be competitive with bench-scale instrumentation. In this regard the recent combination of catalytic DNA (DNAzyme) in a micro-nanofluidic platform is of considerable interest. Functional DNA, obtained through *in vitro* selection, can be used to bind metal ions with high affinity (yielding parts-per-trillion LODs) and specificity (>10^6-fold over other cations)[42]. When synthetically elaborated with proximal fluorophore and quencher, the resulting molecular beacon construct (see Fig. 2) may be placed in microfluidic formats to achieve the double selection of a chemical separation followed by a highly specific molecular recognition event[43]. Significant opportunities exist to exploit the *in vitro* selection process to achieve similar performance characteristics for a wide range of micropollutants.

Biosensing strategies are also beginning to be applied to waterborne pathogens. For example, capillary waveguide integrating biosensors have been applied to detect waterborne *Escherichia coli* O157:H7, an enterohaemorrhagic bacterium[44]. However, given the large fraction of the contaminated-water death toll that is due to waterborne pathogens, there is enormous potential for future development of bio-based measurement schemes.

Detection and remediation of toxic compounds are inextricably linked, as treatment of anionic micropollutants demonstrates. Determination of the anionic constituents of aqueous systems remains among the most challenging analytical problems. Typically, anions are determined by ion chromatography coupled with conductance detection, which is universal but does not have the sensitivity required in all instances. Sensitivity can be grafted on through the use of LC-MS[45] at considerable added expense, although lowering the limits of detection from the ~5 $\mu g l^{-1}$ level to ~0.05 $\mu g l^{-1}$ may well justify the cost. On the remediation side, compelling research opportunities surround is the development of high-specificity synthetic anion transporters although these have thus far been focused on biomedical applications[46]—for particularly refractory micropollutant species, such as ClO_4^- and NO_3^-. Anions also illustrate the complexity of designing effective treatment/remediation strategies. For example, disinfection of water sources with ozone (O_3) is highly effective, but if the water contains significant amounts of Br^-, oxidation to the problematic BrO_3^- takes place[47], effectively substituting one water contamination problem for another.

Similar strategic considerations affect the treatment versus removal decision. Whether to treat water via a chemical or biochemical conversion of a micropollutant to an innocuous form, or to remove the toxic contaminant via adsorption, chelation and filtration, or another method is a decision that rests largely on matching the problem to the sophistication of the available technology and the resource base to support the use of the technology, as well as how far the target concentration is below the maximum contaminant level. The use of Sono filter technology at local wells in Bangladesh and reverse osmosis (RO) systems in central plants in the USA may both represent optimized solutions for As removal within the context of the local problem[48]. However, here, too, opportunities exist for research to make an impact.

The treatment protocols used widely and envisioned for the future all encompass a complex interplay of elementary steps such as transport, partitioning, reaction and conversion, and release. To this end, fundamental advances in understanding these processes will necessarily involve sophisticated modelling to assess the way in which the basic steps are coupled most effectively[49], and modelling-based predictions of potential removal activity[50]. Modelling is essential to optimize multi-step strategies—for example, the capture of As by monodisperse Fe_3O_4 nanocrystals followed by magnetic separation of the waste stream[51]—which are often the most effective, or perhaps the only, possible approaches.

Another critical problem involves unintended transformations of non-targeted pollutants. For example, treatment of wastewater with

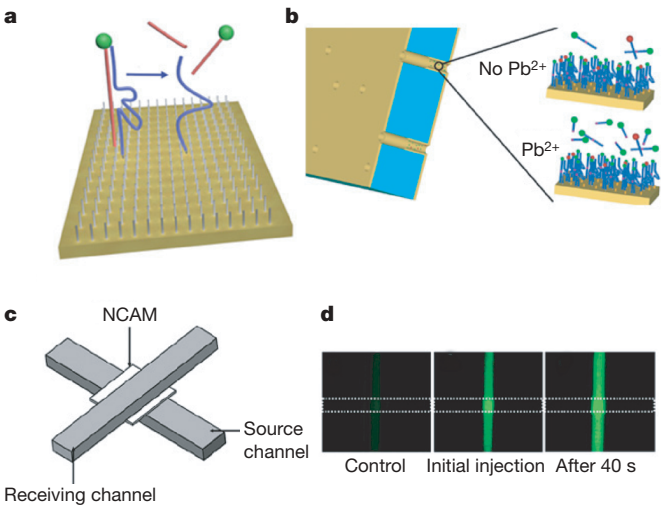

Figure 2 | Lead DNA sensor with a micro-nanofluidic device. Immobilized DNAzyme sensor and micro-nanofluidic devices for detection of Pb^{2+} by fluorescently labelled 17E DNAzyme. **a**, Schematic of immobilized DNAzyme showing catalytic beacon signalling of reaction on the surface, releasing fluorophore into solution for detection. **b**, Schematic of DNAzyme immobilized within the pores of a nanocapillary array membrane (NCAM) with inset showing the mode of ratiometric fluorescence signalling in the absence or presence of Pb(II). **c**, Schematic representation of orthogonal microfluidic channels separated by a NCAM flow gate. **d**, Fluorescence micrographs of the receiving channel before injection of Pb^{2+} sample into a receiving channel containing ~1 μM 17E DNAzyme, after initial Pb^{2+} injection and after 40 s of total injection time for a DNAzyme–NCAM microfluidic device.

Cl_2 or monochloramine can oxidize dimethylhydrazine to the suspected carcinogen *N*-nitrosodimethylamine (NDMA). These unintended secondary effects would seem to argue for separation over transformation strategies, but the relative cost and effectiveness of each approach needs to be considered on a case-by-case basis. A promising workaround focuses on exploiting biology to effect either transformation, such as the biodegradation of NDMA by monooxygenase-expressing microorganisms[52], or removal, as exemplified by the Fe-specific siderophile desferrioxamine-B produced by *Streptomyces pilosus*. Desferrioxamine-B exhibits stability constants in excess of 10^{26} for Th(IV) and Pu(IV), and so may be useful in actinide remediation strategies[53]. Of course, organism-oriented strategies must also be vetted to ensure that they do not introduce other undesirable secondary effects.

Finally, an ubiquitous problem in remediation strategies is the cost or use of critical components that are consumed in stoichiometric reaction, which spurs interest in catalytic treatment approaches to convert organic compounds to innocuous N_2, CO_2 and H_2O. Major anion pollutants such as nitrates and perchlorates are now removed via ion exchange resins or RO, leaving a deleterious brine to be disposed of. Next-generation remediation may use bi-metallic active catalysts to mineralize the brine, such as Pd-Cu/γ-alumina catalysed reduction of NO_3^- (ref. 54). Future efforts may include incorporating active nanocatalysts in a membrane barrier to transform anions at low concentrations in a hybrid process. The combination of modelling and experiments can reveal the mechanisms of these reduction reactions, helping to identify potentially transformative catalytic remediation strategies.

Re-use and reclamation

The overarching goal for the future of reclamation and re-use of water is to capture water directly from non-traditional sources such as industrial or municipal wastewaters and restore it to potable quality. Of all the water withdrawn from rivers, lakes and aquifers, the majority is returned to the environment. Agricultural and livestock users return the least at ~30–40%, whereas industrial users return ~80–90%, power generation returns considerably more at ~95–98%, and public and municipal users return ~75–85%. The rest is lost to the atmosphere or is consumed in biological or chemical processes. A large part of the cost of water for human use is pumping, transport and storage (particularly in developing countries whose citizens often spend substantial time acquiring water). Thus recovering water at or close to the point of use should be very efficient. However, unlike the decontamination of trace compounds just discussed, wastewater contains a wide variety of contaminants and pathogens, and has a very high loading of organic matter, all of which must be removed or transformed to harmless compounds.

Municipal wastewaters are commonly treated by activated sludge systems that use suspended microbes to remove organics and nutrients, and large sedimentation tanks to separate the solid and liquid fractions. This level of treatment produces wastewater effluent suitable for discharge to surface waters or for restricted irrigation and some industrial applications. Similarly, biological treatment via traditional trickling filters and aquacultures have been used extensively to reduce solids and remove ammonia and nitrites from water. Typically, these biological treatment systems are large with long water residence times. A technology now actively being pursued is membrane bioreactors (MBRs)[55–57]. This technology combines suspended biomass, similar to the conventional activated sludge process, with immersed microfiltration or ultrafiltration membranes that replace gravity sedimentation and clarify the wastewater effluent. MBRs can produce high-quality effluent that is suitable for unrestricted irrigation and other industrial applications.

MBRs have also the potential for use in developing countries to address the pressing need for improved sanitation[55]. Possible applications in developing countries include the direct treatment of raw sewage, particularly in rapidly growing megacities, and the extraction of valuable resources from sewage, namely clean water, nutrients (mostly N and P), and energy. The small footprint, flexible design, and automated operation of MBRs make them ideal for localized, decentralized sewage treatment in the developing world.

One of the growing applications of MBRs is as pretreatment for RO, which, when followed by UV disinfection (or, potentially, visible-light-activated photocatalysts), can produce water for direct or indirect potable use (Fig. 3). Current wastewater re-use systems use a conventional activated sludge process, followed by a microfiltration MBR pretreatment of the secondary effluent, which has high quantities of suspended and dissolved solids. The effluent water from the MBR still partially contains dissolved species and colloidial substances that act to foul the membranes of the subsequent RO system used as a final barrier to contaminants in the product water. Employing a 'tight' ultrafiltration membrane in the MBRs lets through fewer dissolved solids than does microfiltration, allowing the RO system to operate with significantly less fouling. Futuristic direct re-use systems envisioned involve only two steps: a single-stage MBR with an immersed nanofiltration membrane (obviating the need for an RO stage), followed by a photocatalytic reactor to provide an absolute barrier to pathogens and to destroy low-molecular-weight organic contaminants that may pass the nanofiltration barrier.

A major obstacle to the efficient application of MBRs in current or next-generation re-use systems is membrane fouling, particularly when it leads to flux losses that cleaning cannot restore[56,58]. Fouling in MBRs is primarily caused by microbe-generated extracellular polymeric substances, most notably polysaccharides, proteins and natural organic matter. The development of economical, high-flux, non-fouling membranes is therefore needed before viable MBR processes, as well as other membrane-based approaches for wastewater reclamation, can be achieved.

Fouling of polymer membranes is influenced by membrane chemistry and morphology. Polymers used in porous membrane manufacture have chemical and mechanical stability, but are generally hydrophobic in nature, and as a consequence are highly susceptible to adsorption of organic foulants. Commercial methods to reduce fouling largely involve graft polymerization of hydrophilic monomers on the membrane surface[59]. The resulting 'brush' of hydrated

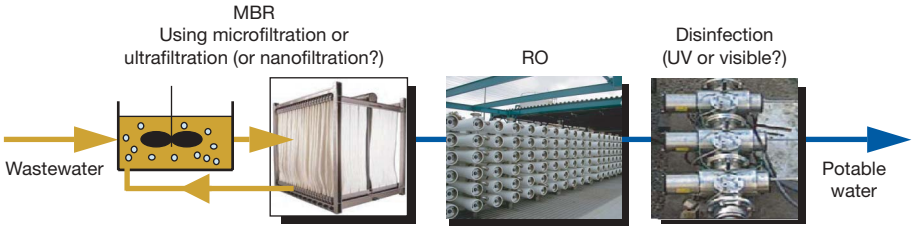

Figure 3 | Membrane bioreactor treatment system for direct conversion to potable water. Depiction of a next generation MBR-based treatment method that can potentially take wastewater from municipal, agricultural, livestock or other high-organic-content sources and convert it to potable water. Future methods may be able to omit the RO step with a nanofiltration membrane, and follow with a visible light disinfection step to ensure that all pathogens, including viruses, are inactivated.

chains serves as a steric-osmotic barrier to foulant adsorption, but reduces intrinsic permeability owing to partial blocking of surface pores, while internal pores may go unmodified and remain prone to fouling[60]. The extra manufacturing steps also add to membrane cost.

Alternative *in situ* approaches to membrane surface modification under development may generate more efficacious brush layers without the drawbacks of surface graft polymerization[61–64]. Comb copolymers, having hydrophobic backbones and hydrophilic side chains, function as macromolecular surfactants when added to membrane casting solutions[62], lining membrane surfaces and internal pores during the conventional immersion precipitation process used in membrane manufacture. Order-of-magnitude flux enhancements[63,65] and complete resistance to irreversible fouling by the three classes of extracellular polymeric substance foulants[65,66], recently demonstrated for such ultrafiltration membranes (see Fig. 4), offer substantial promise for decreasing operational costs of wastewater treatment through reduced membrane cleaning and replacement and increased process efficiency.

Next-generation membranes offer further opportunities for improved contaminant retention or recovery of valuable constituents from wastewaters, without intensive chemical treatment and while reducing the need for subsequent decontamination. These advanced filtration processes require membranes with much narrower pore size distributions than those derived from immersion precipitation, in addition to fouling-resistant surface/pore chemistries[61,67]. Approaches under investigation include block copolymers, graft/comb copolymers, or lyotropic liquid crystals that self-assemble to form nanodomains that are highly permeable to water[68–71], or can be selectively removed to create nanopores for water passage[72,73]. Such nanostructured materials may be implemented as thin-film coatings on conventional ultrafiltration or microfiltration membrane supports[70,72,74], or on novel high-flux base membrane structures, such as electrospun nanofibres[75]. Recently, for example, rigid star amphiphiles with 1–2 nm hydrophobic cores and hydrophilic side chains were coated onto polyethersulphone ultrafiltration membranes to obtain nanofiltration membranes with comparable or better rejection of As(III) and water permeability several times greater than commercial nanofiltration membranes[76]. The commercial viability of this new class of thin-film composite membranes for water re-use hinges on the development of inexpensive coatings, chemistries and scalable processing methods that can reproducibly achieve the desired membrane structure and yield fluxes comparable to today's ultrafiltration membranes.

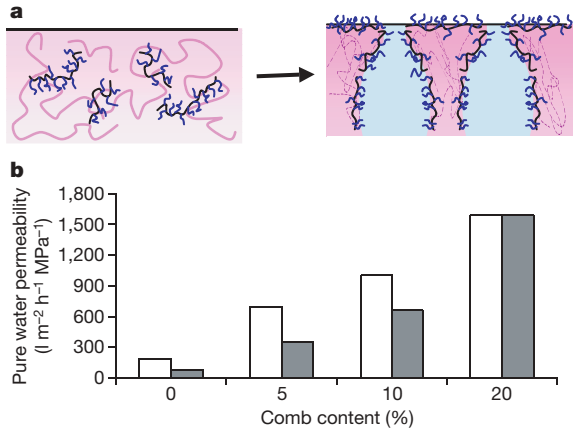

Figure 4 | Comb copolymer amphiphiles for fouling-resistant membranes. **a**, Schematic illustration of *in situ* approach using comb copolymer amphiphiles to modify ultrafiltration membrane surfaces and internal pores during membrane casting. **b**, Pure water permeability of polyacrylonitrile ultrafiltration membranes incorporating 0–20% comb copolymer additive having a polyacrylonitrile backbone and polyethylene oxide side chains. White bars show the initial pure water permeability, and grey bars show the pure water permeability after 24 h of dead-end filtration of 1,000 mg per litre of bovine serum albumin in phosphate buffered saline, followed by a deionized water rinse. Initial flux and flux recovery increase with comb additive content. Membranes exhibit complete resistance to irreversible fouling at 20% comb content (data from ref. 65).

Desalination

The overarching goal for the future of desalination is to increase the fresh water supply via desalination of seawater and saline aquifers. These sources account for 97.5% of all water on the Earth, so capturing even a tiny fraction could have a huge impact on water scarcity. Through continual improvements, particularly in the last decade, desalination technologies can be used reliably to desalinate sea water as well as brackish waters from saline aquifers and rivers.

Desalination of all types, though, is often considered a capital- [77] and energy-intensive[78] process, and typically requires the conveyance of the water to the desalination plant, pretreatment of the intake water, disposal of the concentrate (brine), and process maintenance. Estimated costs of pumping from sea intake to the desalination plant vary widely with geographical location, height and distance from the source water[77]. But so far, the total cost and increased environmental concerns have limited the widespread adoption of desalination technologies. Nevertheless, for a state-of-the-art RO system that uses as little as ~2.2 kW h of electrical energy to produce a thousand litres of drinking water inside the desalination plant, the total energy usage to desalinate water will be ~0.005 kW h l^{-1}, which includes the electrical plus modest conveyance energy needs. Putting this estimated energy use into perspective reveals that supplying even 50 litres a day per capita of drinking water at 0.25 kW h can be a small fraction of the daily energy required per capita (ranging from 3.2 kW h in China to 30 kW h in the USA) for living in a world with strained environmental resources (see http://telstar.ote.cmu.edu/environ/m3/s3/02needs.shtml).

The major desalination technologies currently in use are based on membrane separation via RO and thermal distillation (multistage flash and effect distillation), with RO accounting for over 50% of the installed capacity[77,78]. Conventional thermal desalination processes are inefficient in their use of energy and suffer particularly from corrosion, as well as scaling that also affects RO. Even where fuel is readily available and low-cost, high capital and operational costs limit adoption. Therefore, the market share of large conventional thermal desalination plants will probably decline. However, for family and very small community systems in remote locations, especially in the developing world, solar thermal distillation and humid air desalination technologies may find an increasing role, particularly in inland semi-arid areas with access to saline lakes and aquifers[79,80]. These thermal technologies may also find small-scale applications in locations without ready sources of energy, other than solar.

Although RO systems have a relatively low rate of energy consumption, they use high-cost electrical energy. RO desalination, however, can take advantage of low-grade heat energy to increase flux through the membrane for a given pressure drop. This thermally enhanced RO finds applications in locations where such heat energy is available, typically using waste heat from a co-located electrical power generation and RO desalination plant. We also envision hybrid desalination plants that would combine thermally enhanced RO and thermal desalination to lower electrical energy consumption per unit of product water further, while achieving higher water recoveries than can RO alone. Desalinating inland saline waters, which are present on most continents in quantities similar to fresh water, can also be used to increase water supplies, but disposal of the residual concentrate is a major problem. Hybrid desalination technologies that concentrate precipitates and salts while extracting the water with membranes can potentially process the brine. Two alternative desalination technologies currently under investigation, forward osmosis[81] and membrane distillation[82], can also use low-grade heat

energy and may be used alone, or as hybrid systems with RO, to achieve high water recoveries.

For large-scale desalination, RO has advanced significantly in the past decade, particularly owing to the development of more robust membranes and very efficient energy recovery systems. As a result, the reduction in energy consumption of RO desalination has been remarkable[77,78,83,84]. The specific (per unit of produced potable water) energy of desalination has been reduced from over 10 kW h m^{-3} in the 1980s to below 4 kW h m^{-3} (refs 78, 83). Any desalination system will be most energy efficient if it involves a reversible thermodynamic process, which is independent of the system and mechanisms used.

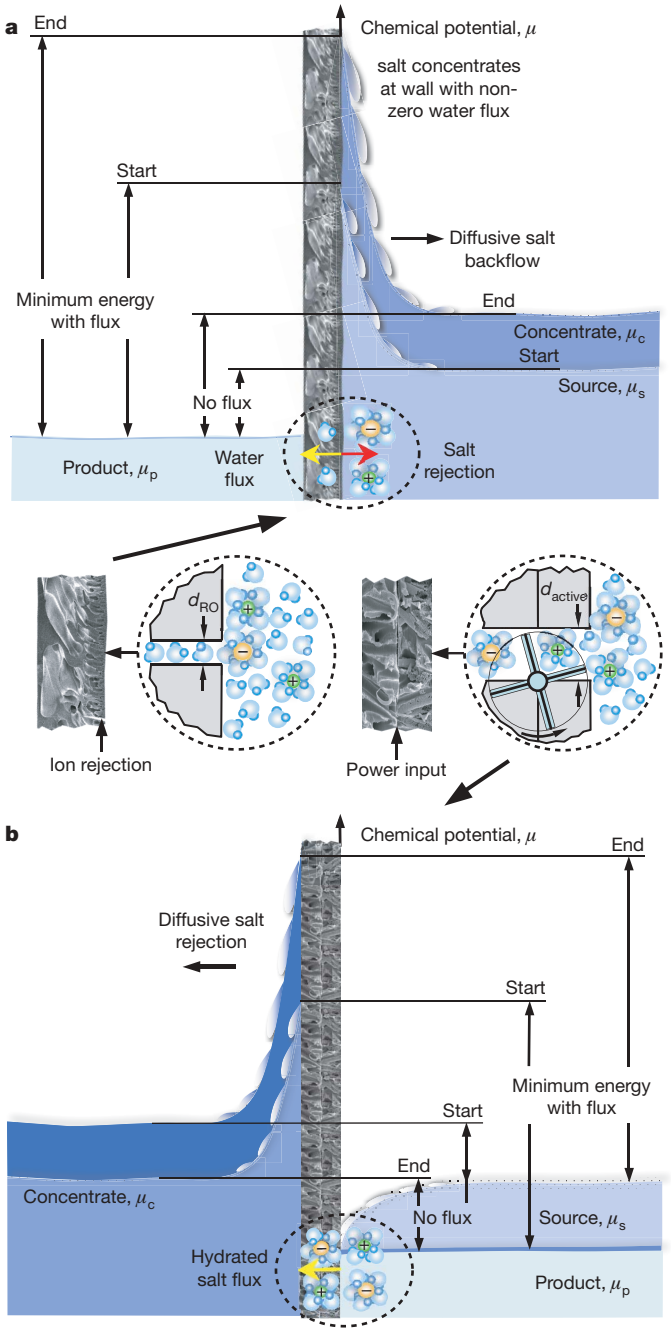

Figure 5 | Reverse osmosis and active desalination membrane processes. Concentration gradients in RO (**a**) and active (**b**) desalination membranes. The energy levels marked with 'start' and 'end' correspond to the evolution of each process. The darker blue colour denotes higher concentration. Insets depict different mechanisms of salt ion separation. The active process with energy input shows a conceptual strategy for overcoming the Born barrier with fixed charges.

From the free-energy change on removing a small amount of pure water from a mixture of water and salt, the theoretical lower bound of the energy needed for desalination can be estimated[85]. For zero per cent recovery, that is, the removal of a relatively small amount of water from a very large amount of sea water, the calculated theoretical minimum energy for desalination is 0.70 kW h m^{-3} of fresh water produced. This theoretical minimum increases to 0.81, 0.97 and 1.29 kW h m^{-3} for recoveries of 25, 50 and 75%, respectively, suggesting that further improvements in the energy efficiency of RO desalination are still possible.

Although RO is currently the state-of-the-art desalination technology, there are several challenges and opportunities that could result in additional reductions in the total cost per unit of product water. Among the major challenges of RO desalination are membrane fouling, relatively low recovery for sea water desalination (less than ~55%), which results in large volumes of concentrated brine, and relatively low removal of low-molecular-weight contaminants, most notably boron in sea water. Future RO desalination membranes will ideally have high water flux per unit of pressure applied, near-complete rejection of dissolved species, low fouling propensity, and tolerance to oxidants used in pretreatment for biofouling control. The total cost for RO involves three strongly interrelated components that depend upon region, source water, and energy sources: capital (infrastructure, equipment, membrane replacement), energy (thermal and electrical), and operation (pretreatment, post-treatment, concentrate disposal and cleaning). Lowering the flux to save energy may be offset by the consequent increase in capital costs. Increasing the permeability of the RO membranes decreases both capital and energy costs, but may increase the cost for pretreatment and cleaning. Improvements must be made in all three components to lower the total cost of the product water.

Recent work by the Affordable Desalination Coalition[78,84] has demonstrated a remarkably low specific energy of seawater desalination, at 1.58 kW h m^{-3}, under ideal conditions (that is, new membranes, no fouling, and low water flux) at 42% recovery. This value is relatively close to the theoretical minimum energy for seawater desalination at that recovery, suggesting that next-generation fouling-resistant RO membranes will be able to desalinate sea water with lower energy consumption. Asymmetric membranes depicted in Fig. 5 (a) currently used for RO have relatively large random pore size distributions. Therefore, the separation layer is thicker than ideal to ensure adequate salt rejection, reducing the flux rate. Desalination typically involves ions with small hydration diameter d_H, which require pores with a hydraulic diameter of $d_{RO} < d_H$ to exclude them, increasing mainly enthalpic energy requirements. The energy of desalination depends critically on pore diameters, and the chemical affinity of water and ions with the pore wall.

Approaching the theoretical minimum energy is impractical for desalination plants, because it would require huge facilities with high capital costs. Moreover, in real desalination processes, energy is lost because of inherent thermodynamic irreversibilities that arise from diffusion, viscous dissipation and flux-rate-dependent losses. To reduce the energy needed for desalination, the rate of entropy generation Φ must be minimized because the energy consumed by irreversible processes is $\sim T\Phi$, where T is the absolute temperature. Φ can be expressed as $J_v\Delta p + J_d\Delta\pi + J_a\Delta a$, where J_v is the total volumetric flux of water plus solute, J_d is the flux of solute relative to the water, Δp is the pressure difference from frictional losses ($\Delta p \propto J_v$), $\Delta\pi$ is the osmotic pressure difference across the membrane, and $J_a\Delta a$ is the entropy generation from any active ion pumping. The higher the flux, the higher the salt concentration will be at an RO barrier, increasing $\Delta\pi$ and Δp. Interestingly, for the same separation performance (that is, the same $J_d\Delta\pi$), if $J_a\Delta a$ is sufficiently small, the entropy generation using active membranes could be less than for RO for a water recovery of much more than 50%, because the fluid flux in RO will be higher than in active transport ($J_{v|RO} \gg J_{v|active}$), and the

diffusion of salts driven by concentration gradients will act in favour of the separation.

Membranes with a uniform pore distribution and a more permeable separation layer can potentially maintain or improve salt rejection while increasing the flux in RO. Recent research on the transport of water through hydrophobic double-walled carbon nanotubes is promising, demonstrating water fluxes that are over three orders of magnitude higher than those predicted from continuum hydrodynamic models (refs 86–89; also O. Bakajin, personal communication, 23 October 2007). The high flux may be due to the carbon nanotubes' atomically smooth, hydrophobic walls allowing considerable slip of water through the pores. The preliminary work of ref. 89 reported unusually high water flux through microfabricated membranes comprised of aligned carbon nanotubes ~3 μm long with an inner diameter of ~1.6 nm. Further measurements with these membranes reveal[90] salt rejection coefficients that match or exceed those of commercially available nanofiltration membranes, while exceeding their flux by up to four times. But such membranes may be difficult and costly to manufacture, prone to defect formation, and might have a high propensity for fouling given their hydrophobic nature.

The high performance of membranes based on carbon nanotubes[86,87,89], however, reveals an important pore characteristic shared by biological ion channels: hydrophobic pores ~1 nm in diameter. These cores allow the ion hydration shell to remain intact, thereby reducing the enthalpic translocation energy to be closer to the entropic loss for confining an ion in a pore. Decreasing the pore diameter much below 1 nm creates a large free-energy barrier, which arises from stripping the hydration shell off the ion and water molecules that need to overcome a Born energy barrier. Modifying the surfaces of the membrane, as discussed for nanofiltration membranes, can alter the surface properties, and thus potentially decrease the energy barrier.

Technological challenges to incorporating carbon nanotube materials include the functionalization of the mouth of the pores to increase selectivity and potentially reduce hydrophobicity at the surface, integration of the active layer with robust support substrates, scaling up the fabrication of the ion channel and carbon-nanotube-based membranes and increasing the pore density per area of the active layer, and decreasing the cost of membrane fabrication. Still, the costs of such membranes could eventually be affordable with future improvements in carbon nanotube synthesis and membrane processing.

Aquaporins (water channels) and ion channels of biological cells have also motivated the search for alternative approaches to engineering membranes with high water flux and selectivity[91,92]. *De novo* synthesis of ion channels[93] and the development of low-molecular-weight anion transporters is an emerging topic in supramolecular chemistry[94]. Based on an array of aligned carbon nanotubes with hollow graphitic cores embedded within a solid polymer film, the first biomimetic protein channel controlled by the same mechanism of phosphorylation/dephosphorylation that occurs in nature has also been recently reported[95]. However, much work remains to incorporate these futuristic materials into large-area membranes at competitive costs.

Even if a perfect membrane could be created, with no pressure drop required for complete salt rejection, the increase of flux rates for RO is ultimately limited by the concentration polarization layer at the membrane (see Fig. 5a), which constitutes an additional impedance to fluid flow. The higher the flux of water, the higher the gradient in solute concentration on the rejection side. The polarization impedance can be reduced via tangential fluid flow, but can never be eliminated. What is worse, the transmembrane chemical potential difference increases along the direction of the tangential flow (from 'start' to 'end' in Fig. 5a), while the transmembrane pressure difference decreases because of pressure losses, resulting in additional irreversible losses with higher fluxes.

To see how active systems might compare to RO systems, we can extrapolate from the energetics of existing ion channels. Biological channels transfer 10^7 ions per pore per second, and measurements corroborated by systematic computer simulations reveal that the free-energy barrier for biological potassium channels is 2–5 kcal mol^{-1} (depending on the type of K^+ channel), which corresponds to a specific energetic requirement of 2.55–6.4 kW h m^{-3} of water produced from sea water with a salt concentration of 32,000 parts per million. For potassium ions, the lower bound is near the current energetic costs for RO, but is still much higher than the theoretical minimum. However, these channels are ion- and charge-specific, and there is a significant energetic cost for the exclusion of the other ions. If active nanopores of dimensions greater than 1 nm are created that pass a multiplicity of anions and cations, as depicted in Fig. 5b, the energetics can potentially drop by more than a factor of two below that of biological channels.

Bio-inspired systems for active transport provide another route towards improving the energetics of desalination. In contrast to conventional desalination whereby water is 'pushed' through an RO membrane by a pressure gradient, or in electrodialysis whereby hydrated anions and cations are forced through their respective ion-selective membranes by electrokinetic action, active ion separation involves pumping of both hydrated anions and cations through the same membrane via modulation of pore potentials, against a chemical potential, leaving desalinated product water. As Fig. 5b illustrates, membranes that actively 'pull' hydrated ions through the barrier reverse the direction of the concentration polarization layer, and should not suffer the same decrease of performance with increasing flux as does RO. Nature also provides a solution to the problem of lowering the cost of overcoming electrostatic barriers in engineered systems, which typically involve dielectric membranes. The Born energy barrier[96] to move an ion of charge q from water to the low-dielectric-constant membrane ($\varepsilon \approx 2$ for typical biological membranes) is $\Delta G \approx q^2/d_H(1/\varepsilon - 1/80)$. This barrier can be offset by the energy liberated if the penetrating ion meets a counter-ion buried inside the membrane ($\Delta G' = -q^2/\varepsilon d_H$), or by the pump, as depicted in the insets of Fig. 5. It has been suggested[97] that for biological ion pumps the energy cost of burying the counter ion is paid for by actively manipulating charged groups in the proteins within the pumps. However, whether passive or active, high-permeability membranes with high resistance to fouling are needed, as well as new strategies for synthesizing membranes with multiple functions to screen small molecules, and to resist stresses and chemical degradation.

Conclusion

The work highlighted here, plus the tremendous amount of additional research being conducted on every continent that could not be mentioned, is sowing the seeds of a revolution in water purification and treatment. We believe that advancing the science of water purification can aid in the development of new technologies that are appropriate for different regions of the world. That said, the sheer enormity of the problems facing the world from the lack of adequate clean water and sanitation means that much more work is needed to address the challenges particular to developing nations, which suffer a diversity of socio-economical-political-traditional constraints, and require a broader approach incorporating sustainable energy sources and implementing educational and capacity building strategies. Consortiums of governments at all levels, businesses and industries, financial and health organizations, water and environment associations, and educational and research institutions need to focus increasing attention towards solving these water problems. While better water resource management, improved efficiencies, and conservation are vital for moderating demand and improving availability, it is our belief that improving the science and technology of water purification can help provide cost-effective and robust solutions.

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