'Water, water, everywhere, Nor any drop to drink'?

With the world's population set to exceed nine billion by the end of the century, the demand for fresh water will become ever more acute. Applying nanotechnology to filter seawater in coastal areas could provide part of the answer, as **Jason Reese** explains

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Mass migration between continents; filthy and disease-ridden mega-cities; flare-ups of local wars and conflicts. These are some of the geopolitical tensions that may result from competition for water resources in the 21st century. The global population is projected to increase to about 9.5 billion by the latter half of this century and, at its peak growth rate, some 75 million people – more than the current population of the UK – will be added to the planet each year. Many of these individuals will live in so-called mega-cities – conurbations of more than 10 million people.

As a consequence of this population explosion, worldwide demand for water – for consumption, food production and sanitation – is anticipated to rise by a third by 2030. Scarcity of drinking water is already posing major problems for more than a billion people, mostly in arid developing countries. For example, China has 20% of the world's population, but only 7% of its water resources. And while demand increases, areas that currently provide fresh water may dry out. The possibility of 3–6 °C of climate warming and a redistribution of global rainfall patterns may leave some areas parched through long-term drought. As sea levels rise, another danger for coastal areas is that underground fresh-water resources will become contaminated with salt water. In Lagos, Nigeria, some of these aquifer sources have already been abandoned for this reason.

This grim picture of the future was painted in a report published earlier this year called *Population: One Planet, Too Many People?*, compiled by the UK's Institution of Mechanical Engineers. But the same report also points out that, on the planet as a whole, clearly there is no shortage of water. The supply-and-demand challenge is to get water in its appropriate form (pure water for drinking, and treated wastewater for less health-critical uses) to the right place and in the right quantities. However, all forms of water processing require energy, and so an increased demand for water will inevitably require more energy. Unless this can be sourced renewably, there is even a risk of accentuating the climate changes that exacerbate water-scarcity problems in the first place. Better water-resource management is certainly part of the answer, but to address some of the engineering challenges we can turn to physics and physical chemistry for solutions.

One unexpected recent finding that could help lay the spectre of global water shortages to rest is the "nearly frictionless" transport of water through carbon nanotubes. The most widely used type of water-purification plants require huge amounts of energy to force seawater through conventional filtration membranes; but membranes made of nanotubes could cut energy requirements by several orders of magnitude, making these plants a viable option for even the poorest countries.

At a Glance: Nanofluidics

- The predicted rise in the global population is likely to make fresh water increasingly scarce; this could be alleviated by finding better ways to remove the salt from our vast resource of seawater
- Desalination plants use porous filters; to design more efficient versions we can turn to nanotechnology, as conventional hydrodynamic behaviour changes dramatically at the nano scale
- Computer simulations of molecular flow have revealed that carbon nanotubes can transport water much more effectively than pores in a conventional filter
- Different approaches for how best to maximize the flow of water through nanotubes while blocking the salt ions are still being explored

Fresh water from the sea

Two important strategies for nations wishing to protect and grow their water resources are desalinating seawater and purifying industrially or environmentally contaminated water. Of course, these are not the only solutions to the water-scarcity problem, and many of the most water-stressed regions are far from the sea or at high altitudes. Nevertheless, generating pure water from the oceans for the use of coastal populations can relieve pressure on precious groundwater sources elsewhere.

The economics of desalination is complex. Worldwide, desalinated water can be generated at a cost of about \$0.45 per cubic metre. This is five times more expensive than fresh water extracted and processed from river or underground sources. The costs of desalination can be tolerated by high-income countries, but generally not by the low-income countries that are often the most susceptible to water stress and climate change.

One way to remove salt from seawater is flash distillation – using heat to evaporate the water and then condensing the steam. Distillation plants can be built next to power stations so that they can make use of the

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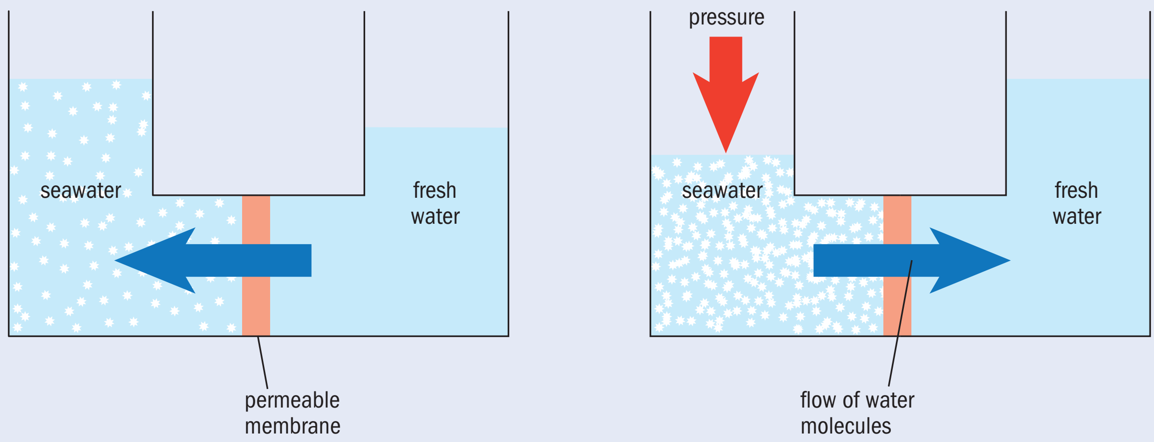
1 Osmosis and reverse osmosis



At desalination plants, seawater is filtered or distilled to produce fresh water. The most popular method of purification is "reverse osmosis". In osmosis (left), a solvent moves from a region of low solute concentration to a region of high solute concentration through a permeable membrane. In the set-up shown, that would mean losing fresh water to diluting seawater, which is not what is desired in desalination. In reverse osmosis (right), pressure is applied to the region of high solute concentration (seawater) to reverse the flow, producing more of the pure solvent (fresh water).

waste heat from the station's electricity generators. However, in locations where such co-generation is not possible, then "reverse-osmosis" plants are generally preferred. In fact, most desalination plants worldwide operate on reverse osmosis, including the one opened on the Thames at Beckton, London, in June 2010.

Osmosis is the natural movement of a solvent from a region of low solute concentration, through a permeable membrane, to a region of high solute concentration (figure 1). If a tank of seawater and a tank of fresh water are separated by a permeable membrane, water migrates from the fresh side to the salty side in order to equalize the solute concentrations, thus diluting the seawater. This natural transfer of solvent can, however, be slowed by pressurizing the more concentrated (salty) side, and can even be brought to a halt entirely by applying a threshold amount of pressure known as the "osmotic pressure".

In reverse-osmosis desalination plants, the solvent is, instead, forced to go in the other direction. Water is forced from the seawater side to the fresh-water side, so pure water is produced while the seawater is concentrated further. To make water potable, removing 95% of the salt and other minerals from seawater will suffice; the separation does not have to be complete. To achieve this an external pressure, above the osmotic pressure, is applied to reverse the flow of water through a polymer-based membrane. As the osmotic pressure of seawater is about 26 bar, industrial reverse-osmosis plants need to apply between 40 and 70 bar in order to achieve economical flow rates. The pumping requirements to produce these high pressures are the major source of operating costs and the energy intensiveness of reverse-osmosis plants.

While water flow in a pipe is a purely mechanical problem, at the nanoscale intermolecular forces need to be taken into account

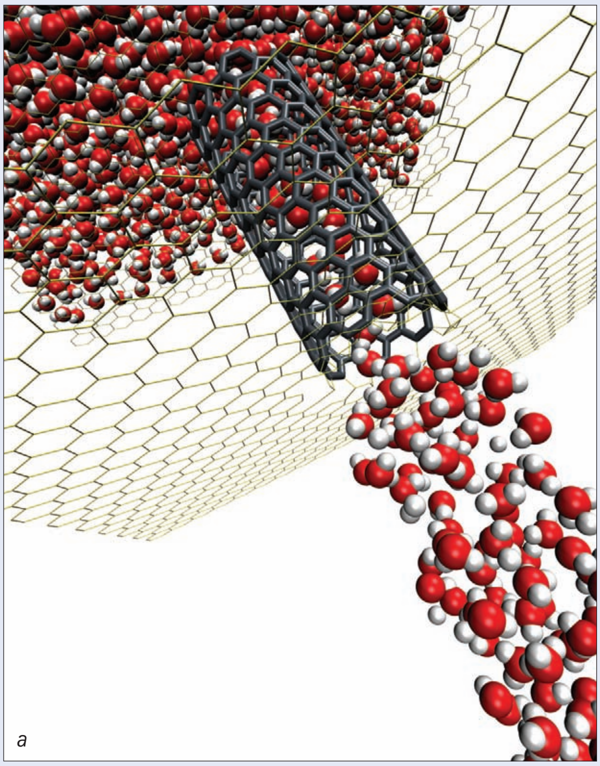
Nanotubes: not just small water pipes

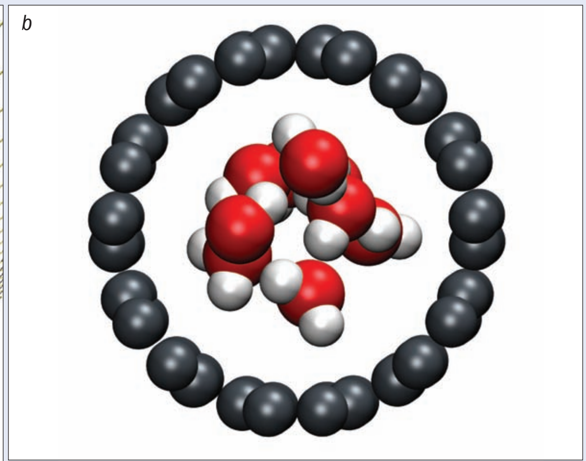
If a new material is found that can maximize water transport through the separating membrane, while at the same time rejecting dissolved ions and other particulates in seawater, reverse osmosis would be a much more efficient process. Simulating and designing such materials is one of the aims of my research group. We use a type of computer modelling called "non-equilibrium molecular dynamics" to simulate fluid flows at the molecular level, searching for nanoscale systems that let desirable molecules (namely water) pass through but reject those that are not (such as salt ions). While water flow in a pipe is a purely mechanical problem, at the nanoscale intermolecular forces need to be taken into account. Realistic simulations of these interactions for several hundred thousand up to millions of molecules, over periods of up to several nanoseconds, can only be achieved using high-performance computing.

Carbon nanotubes (CNTs) – essentially, sheets of graphene rolled into cylinders – have some remarkably useful properties that can be applied to desalination. In particular, the flux of water through them is unexpectedly large – much greater than is predicted by conventional hydrodynamic theory – and this finding has been supported experimentally.

Recent molecular-dynamics simulations indicate that the water permeability of a membrane of CNTs containing a realistic 2.5×10^{15} pores/m^2 will be more than 20 times that of modern commercial reverse-osmosis membranes. (This calculation is for (8,8) nanotubes, where the technical notation defines the position of the matched carbon rings during the roll-up of the graphene sheet.) For a CNT membrane with the theoretical maximum pore density of 5.8×10^{17} pores/m^2, the predicted performance improvement over standard membranes is 5000-fold. If these kinds of figures can be realized in practice, the cost/benefit analysis for large-

2 Molecular engineering





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Molecular-dynamics simulation of water molecules (red for oxygen and white for hydrogen atoms) transported through a short carbon nanotube (CNT) (grey) 0.95 nm in diameter, which is fixed between two graphene sheets (gold) to model a membrane. (*a*) Water being transported from an upstream (upper left) to a downstream (lower right) reservoir, as in a reverse-osmosis plant. The computational cost of molecular-dynamics simulations means the applied pressure difference along the CNT is here artificially set to 200 MPa – higher than it would be in reality – in order to see the dynamics of the water transport develop within a reasonable simulation time. (*b*) Cutaway showing how water molecules organize into a densely packed cylindrical shell when within a CNT.

scale desalination and other water-purification projects would be transformed.

Although the CNT manufacturing process produces mostly multiwalled nanotubes, in that they comprise multiple concentric tubes of graphene, we use single-walled CNTs in simulations because they are a simpler model of the inner tubes of multiwalled CNTs. While their diameters are on the nanoscale, CNTs can be manufactured up to several millimetres in length, which will be needed if a nanoscale-structured membrane is going to be thick enough to be robust for industrial applications. To make such a membrane, CNTs of the appropriate length can be set in a vertically aligned array, supported by a polymeric substrate, and their ends opened (as they are usually synthesized with their ends closed off by fullerene caps).

The surprising behaviour of flows at the nanoscale (called "nanofluidics") can only be understood if we recognize the limitations of our macroscale conception of fluids. Conventional fluid dynamics was developed in the 19th century to be independent of the molecular structure and configuration of the fluid that is flowing. But water in CNTs that are 2 nm diameter or less does not flow in the same way as water in a mains pipe.

It may seem surprising that water molecules will enter and fill up such a narrow and hydrophobic tube at all, but molecular-dynamics simulations show that filled CNTs are energetically preferred: the CNT acts to structure the water molecules for the lowest potential energy. For example, water molecules within a (7,7) CNT, which has a diameter of 0.95 nm, are organized into a cylindrical shell with a density reaching nearly four times that of the water outside the CNT (figure 2).

Our simulations also show that, for the same pressure difference end to end, the longer the CNT, the greater the flow rate along the nanotube, relative to hydrodynamic predictions. This is most likely because longer CNTs act to structure the encapsulated water even more efficiently, and with greater densities. In smaller-diameter (6,6) CNTs, the water molecules even arrange themselves in single file. It is as chains of molecules, suspended by intermolecular forces in the centre of the nanotube, that water is transported nearly frictionlessly along it. Conventional hydrodynamics cannot hope to capture such behaviour.

Chemical gatekeepers

The amazing fluid-transport properties of CNTs conjure up new possibilities for future flow-system technologies. But CNT membranes have an additional property that makes them particularly useful for desalination: they are highly efficient at repelling salt ions. Sodium and chloride ions in solution are surrounded by hydrating water molecules (figure 3). In order for them to squeeze into a CNT – which we do not want in desalination – they would first have to shed their water molecules. The large "dehydration energy" required to separate the ions from their water partners makes this difficult to achieve. In fact, this is why a (7,7) CNT blocks more than 95% of salt ions, which would bring seawater to potable standard. An (8,8) CNT does better in one respect, in that it passes nearly 70% more water than a (7,7) CNT under the same conditions, but the (8,8) CNT is not quite suitable for drinking-water applications because it blocks only 85% of salt ions.

However, it is difficult to synthesize CNTs of a single small diameter reliably. The usual method of catalytic chemical vapour deposition produces CNTs with a range

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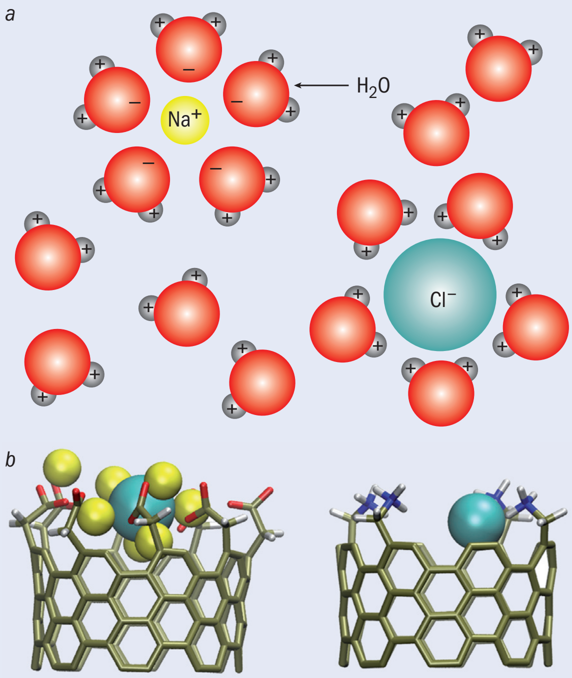
3 Molecular sorting



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(*a*) In a salt solution, sodium (yellow) and chloride (blue) ions are surrounded by hydrating water molecules. In order to slip through the smallest diameter carbon nanotubes (CNTs), the ions would first have to shed their water partners, and the energy required to do this means it does not happen very frequently. Larger-diameter CNTs let more water through but at the cost of letting more ions through too. The ions can, however, be repelled using chemical gatekeepers (*b*) such as COO^- (left) or NH_3^+ (right) groups positioned at the CNT inlets. Whether the CNTs have these gatekeepers or not, the build-up of ions around the inlets to the CNTs will be a problem. If they are not periodically removed, perhaps by chemical flushing or electrical-field pulsing of the membrane, they can be expected to reduce the membrane efficiency substantially.

of diameters. The unwanted CNTs can be separated out using density-gradient ultracentrifugation, but this adds to the complication, costs and timescales of a manufacturing process that, if it is to be used for practical desalination, will need to be done on an industrial scale.

If reliably manufacturing the smallest diameter CNTs is a problem, perhaps attaching chemical groups to the ends of larger CNTs – "functionalizing" the nanotubes – can offer an alternative route to efficient salt rejection? An (8,8) CNT has a diameter of 1.09 nm, large enough for Na^+ ions to slip through, even when surrounded by their hydration shell of five water molecules. But charged or polar groups, such as COO^- or NH_3^+, attached to the CNT inlet could be used to repel or trap passing ions, acting as controllable molecular "gatekeepers" (figure 3).

The exciting potential is clear, and is a very real and socially progressive use of nanotechnology

While molecular-dynamics simulations show that salt rejection is then almost total, the downside is that functionalization reduces the area of the CNT inlet, and introduces new interactions with the water molecules. Together, these reduce the water flux to around a fifth of that through an unfunctionalized CNT. At present, it seems that the best compromise between maximizing both water flux and salt rejection is achieved by narrower and unfunctionalized CNTs.

Steps towards a water-stress-free world

There are other issues still to be resolved. Can we use multiwalled CNTs in efficient membranes, rather than single-walled tubes, as their manufacture is substantially easier? Do nanotubes made out of materials other than carbon, such as boron nitride, promise the same or different desalination performance? What are the health and safety issues if some of the nanotubes break loose from the membrane and end up in the drinking water? Do nanotubes selectively filter components of gases in the same way as liquids? Can a nanotube membrane be used to cost-effectively extract gold, uranium and other important elements that seawater carries in addition to sodium and chlorine?

To answer these questions, the 21st-century engineer will have to get used to counterintuitive fluid-flow behaviour at the nanoscale that has previously been the preserve of the physicist or physical chemist. Molecular simulations have highlighted some remarkable fundamental behaviour, which needs to be carefully verified and explored experimentally. For the engineering design of a complete reverse-osmosis system the macroscopic flow characteristics should also be examined, because the fluid interactions with the CNTs at the molecular level will affect the macroscopic flow behaviour, and vice versa. A new research programme between the University of Strathclyde, Daresbury Laboratory and the University of Warwick, running from 2011 to 2015 and funded by the UK's Engineering and Physical Sciences Research Council, is intended to develop multiscale computational tools to tackle this kind of problem. One of the programme's aims is to understand the through-cycle performance of a desalination process that depends fundamentally on effects at the molecular level, including the optimum design of the nanotube membrane and the surrounding macroscale flow infrastructure.

The holy grail of reverse-osmosis desalination is combining high water-transport rates with efficient salt-ion rejection. While many questions still remain, the exciting potential of membranes of nanotubes to transform desalination and water-purification processes is clear, and is a very real and socially progressive use of nanotechnology. Understanding the unconventional fluid dynamics at the nanoscale is key to innovating in these visionary applications. Nanofluidics is a rich area for research and development, in which molecular simulations can guide and stimulate the experiments that will hasten the adoption of new technologies to address the health, energy and climate challenges that the world faces over the next 40 years. ■

More about: Nanofluidics

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