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Innovative Materials and Separations Science

Extended Abstract for Panel Presentation

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Fifty years ago, research and development funding through the U. S. Department of the Interior, Office of Saline Water was used to develop many of the water treatment technologies used today. These include reverse osmosis, electrodialysis, capacitive deionization, and some advanced thermal methods. Since that time, incremental advances to these methods have been made – for example, reverse osmosis is now significantly more energy efficient than it was decades ago; electrodialysis membranes are available that are monovalent ion selective; and multiple effect distillation can now be carried out without the severe corrosion and scaling problems that hindered the metals first used in its application. But there has not been a significant change in the nature of the technologies used for desalination and treatment of impaired waters. In a sense, several decades of advances in materials science, both in understanding separations science, and in the development of new materials, have not been applied to the area of water treatment.

The reason for this is simple: this area of technology development has not received significant R&D funding either through a renewed program in the United States or significant investments elsewhere in the world. Private industry has continued to make incremental technology improvements, but they do not have the resources or long-term interests to provide the next generation of technologies.

The most significant deficiencies of current technologies are their high energy use, and the lack of low-cost technologies for selective extractions to treat impaired water. For example, in spite of the seemingly straightforward nature of desalination – separating charged ions from uncharged water molecules - the most efficient current desalination technologies use 4 to 5 times more energy than the thermodynamic minimum for this process. As a result, half the costs for seawater desalination are energy costs. Thus there is a growing interest globally in the development of new technologies, in particular in countries such as China that have urgent needs for purified water, and the time is ripe for a renewed focus of R&D on water treatment.

One R&D area that seems promising is that of the general area of improved polymers, such as block copolymers, and functionalized and self-assembled surface layers on polymers. Current technologies for carrying out selective extractions, such as removal of nitrate or arsenate from water, use either a manufactured ion exchange resin that is selective for the target species, or a

sorbing media that has some affinity for the target species and is of such low cost that it can be disposed of after one use. With few exceptions, ion exchange resins of today are structurally very similar to those of 50 years ago. Most are polystyrene beads functionalized with sulfonate, carboxylate, or amine groups. The type of group and the degree of polymer cross-linking are varied in order to tune the polymer to favor ion exchange with the target species. This approach has limited ability to tune for selectivity. Perhaps the greatest improvement in ion exchange technology related to water treatment over the last 20 years is the Bi-Quat resin developed for perchlorate. The resin makes use of two distinct amine groups, one to promote the rate of ion exchange, the other to be selective for perchlorate. In any case, ion exchange as a process for treatment of impaired waters is by its nature labor intensive. Ion exchangers must periodically be regenerated, producing a secondary waste stream. What is clearly needed is a selective membrane based continuous process. Consideration should be given to the use of functionalized membranes that could combine selectivity with continuous operation.

Block copolymers may also have useful applications in water treatment. Block copolymers can be thought of as self-assembling ordered polymeric materials with length scales in the range of a few to a few hundred nanometers. If properly chosen, one of the two materials making up the polymer can be selectively removed (dissolved or oxidized), leaving a dense and highly monodisperse porous material. Such materials have significantly improved properties compared to the polymer materials commonly used in physical separations (micro- and ultrafiltration). Further performance improvements in terms of fouling resistance and selectivity could be achieved through functionalization and surface manipulations.

Non-membrane-based technologies that take advantage of nanoengineered conductive materials are another area that could give rise to new separations technologies. It is theoretically possible to separate ions using electrostatic fields and field gradients in the same way proteins are separated using dielectrophoresis. Because of the much smaller size of ions relative to proteins, the field gradients must be much larger, and the fields manipulated on a much smaller length scale. Such separations could be carried out for ions only if materials can be engineered on such small length scales. This would be the challenge for current technologies such as those used to produce nanolaminates and other nanoengineered materials. The advantages are that nothing would have to pass through a membrane, avoiding some of the problems with membrane fouling, and that such technologies might be tunable, and thus very versatile, through the use of externally applied fields.

Research on new treatment technologies should also take advantage of the current capabilities of first principles modeling. There are many potential applications. For example, in spite of the maturity of reverse osmosis, there is still debate on the nature of the fundamental mechanism of how reverse osmosis

membranes separate salt from water – the solution-diffusion model vs. the pore size exclusion model. *Ab initio* molecular dynamics is now sufficiently mature, and computers fast enough, to explore and hopefully resolve this issue. In these simulations the water molecules and ions are handled discretely (not as a continuum) which allows quantitative information on the structure of the electrical double layer, critical for modeling membrane transport in aqueous systems. Similar modeling approaches could be used to simulate the transport of ions through polymer membranes during electrodialysis in an effort to understand why this technology consumes even more energy than reverse osmosis for brackish and more saline waters.

Modeling capabilities are now sufficiently mature that they can be used to carry out discovery science that was once strictly experimental. For example, the permeability of carbon nanotubes to water was predicted by molecular dynamics calculations several years ago, prior to any measurements. The MD simulations predicted that the water would line up in hydrogen-bonded strings during transport through the 1-2 nm channels, and that as a result the tubes would have very high permeabilities – much higher than classical predictions. Recent experiments have confirmed these predictions, although they do not necessarily confirm the mechanism. Membranes of aligned carbon nanotubes are being considered for reverse osmosis. Because of their high permeability they could significantly lower energy costs for desalination.

Another example of the usefulness of MD simulations is the recent discovery that, contrary to predictions of the Gibbs equation, ions are not excluded from the air-water interface. MD simulations of a few years ago predicted that highly polarizable anions instead are selectively concentrated at the air-water interface. These predictions were later confirmed spectroscopically using the Advanced Light Source at Lawrence Berkeley Lab. This is significant because many toxic compounds of interest for water treatment are polarizable anions – e.g. nitrate, perchlorate, selenate, and arsenate. One can imagine some simple technologies that could be used to extract these species if the degree of concentration at the air-water interface is sufficiently high. Additional modeling could be used to develop and optimize these technologies.

Finally, membranes with the types of energy efficiencies and selectivities that we desire for water treatment already exist – as ion channels and aquaporins in the bi-lipid layers of cell walls. Over the last two decades, the structures and modes of operation of ion channels and aquaporins have received a lot of attention among biologists. For example, the discovery of the selectivity of the potassium ion channel resulted in a Nobel Prize in chemistry two years ago. The theory is that carbonyl groups attached to a protein framework at the outer ‘gate’ of the ion channel exactly mimic the octahedral coordination sphere of waters surrounding a potassium ion. A potassium ion approaching the ion channel can therefore pass from its hydrated state to a state inside the channel where its waters of hydration have been replaced by the oxygens in the carbonyl groups. There is

only a very small energy barrier to this transition because of the structural match. A smaller ion such as sodium, with a smaller hydration sphere, has a much bigger energy barrier to overcome and is therefore much less likely to enter the channel. The selectivity of the ion channel for potassium vs. sodium is much higher than the best available potassium ion exchange resin. It is clear that much can be gained from a better understanding of the selective membranes nature has developed and that this knowledge should be used to generate biomimetic technologies when possible.

In conclusion, there is tremendous current opportunity for researchers in academia, industry, the national labs, and private entrepreneurs to generate “next generation” water treatment technologies that significantly improve our ability to desalinate and decontaminate water.