Advancing Materials and Technologies for Water Purification

Mark A. Shannon and Raphael Semiat,
Guest Editors

Abstract

Worldwide, 1.2 billion people lack access to sufficient amounts of clean water, and 2.6 billion lack adequate sanitation. Also, industry relies on large quantities of water during manufacturing, which is then returned to the environment. Having adequate water supplies, and removing pathogens, chemicals, and other contaminants with high throughput at a low cost is a growing challenge around the world. This issue of *MRS Bulletin* examines how materials research, through the development of membranes, catalysts, nanoparticles, and other materials, is addressing these needs.

Introduction

Access to clean water is increasingly becoming the most important issue facing people around the world. Worldwide, 1.2 billion people lack access to sufficient amounts of clean water, and 2.6 billion lack adequate sanitation.[1] The combination of poor sanitation and unhealthy water quality accounts for the single largest cause of disease and death in the world.[2]

Clean water, according to the World Health Organization (WHO), is water that has less than the allowed concentrations of dissolved matter—a different amount depending on the constituent. Salted or polluted water contains suspended matter such as dust, algae, bacteria, viruses, and silt; organic matter such as solvents, fuel traces, pesticides, and herbicides; various salt ions above the recommended concentration; and heavy metals and more.

No other problem today is remotely close in magnitude to the need for clean water, and yet problems with water are expected to grow rapidly due to population growth imposing larger demands on the water supply for domestic use, agriculture, and energy. Moreover, water supplies are increasingly threatened due to the contamination of aquifers, the largest source of fresh water in the world, from toxic compounds to salts intruding from sea and saline sources. Salting and contamination of fresh water sources drives the need for new supplies of clean water and more extensive water treatment. As the glaciers on continents throughout the world disappear, major rivers that currently supply fresh water year-round may become intermittent, forcing the hunt for new supplies.[3,4] Current water purification methods in wide use employ chemically intensive treatment that is relatively expensive, increases stress on watersheds and the environment, and is not translatable to the non-industrialized world.

Water touches every aspect of human activity, from food, health, and the environment to local and global economies. Clearly, the staggering importance of water cries out for solutions to be found and enacted.

All is not bleak, however. Many current water treatment methods are far from the thermodynamic limits. Biological disinfection, decontamination, filtering, and ion transport stand as examples of optimized systems in energetically efficient, self-cleaning, and renewable purification. A hallmark of these systems is that the interaction of species in water occurs with solid, soft materials, rather than with other liquids, as is typical in the traditional homogeneous reactor treatment systems. Interactions, both passive and active, of materials with constituents in water at an aqueous interface, such as membranes, surfaces, and particles, govern the processes.

Recent water purification advancements include the development of heterogeneous methods to disinfect, filter, and transport ions. Emerging trends and new methods include

- Disinfection: a shift from chlorine and homogeneous oxidants to heterogeneous inactivation of pathogens on metal oxide catalysts;
- Decontamination: a shift from solution concentration and disposal to catalytic mineralization of toxic compounds;
- Biological contamination control: a change from trickle gravel filters and pond biodigestion systems, which use natural microorganisms to consume organic matter, to membrane-based systems for both aerobic and anaerobic digestion;
- Filtration: from gravity sand to manufactured filters; and
- Desalination: from thermal desalination to reverse osmosis.

The key issue addressed in this issue of *MRS Bulletin* is that these emerging heterogeneous processes are being developed to augment or replace homogeneous chemical treatment in unit mixing processes, and they give rise to the development of new materials, testing methods, and sensing modalities.

Development Drivers

Energy production is typically the single largest category driving the withdrawal of water from lakes, rivers, and aquifers. Vast quantities of water are used in mining, drilling, and refining of coal and oil; in cooling systems in the generation of electricity from hydro- and thermoelectric generators; and for the production of biofuels. Simply put, the increasing demand for energy is driving water use, and it will be very difficult for the world to sustain this growth without finding new ways of obtaining clean water.

Similarly, creating clean water consumes vast amounts of energy, for pumping (one of the largest uses of electric energy), desalinating, chemical production (chlorine, ammonia, ozone, etc.), and filtering. Rising energy costs are a strong driver in the development of new water purification methods.

With respect to materials development, the need to reduce energy consumption drives the development of new classes of membranes and filters. Increasing throughput for the same energy input increases efficiency, that is, increasing flux for the same pressure drop across a membrane or filter. While many materials are being synthesized with higher flux, fouling and scaling of membranes and filters

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are major inhibitors of throughput. Discovering materials and methods that reduce fouling and increase flux in total (including consideration of cleaning cycle and pretreatment) is an active area of new materials development.

Along with increasing throughput to decrease energy per unit volume, there is a growing interest in removing trace concentrations of toxic compounds from water. To decontaminate water of specific compounds, often the entire water stream is treated chemically, increasing the amount of chemicals used in the purification process. Since water can have up to parts per thousand of harmless, potable constituents, treating all the constituents to reduce toxic compounds to parts per billion and below is naturally expensive. To decrease costs and reduce the amount of energy used requires increasing the specificity and selectivity of the purification process, so that only the targeted compounds are removed or transformed to harmless compounds. Heterogeneous purification lends itself inherently to doing so via specific adsorbents and catalytic materials. Along with better removal and transformation materials, better methods to sense species with high specificity (by achieving a low number of false positives) and selectivity (high discrimination) with respect to interferents (compounds that prevent the detection of the target specie) are also needed to enable detection and mitigation of toxic compounds. Measuring trace contaminants robustly in the presence of a high background of aqueous constituents at a low cost is often one of the more difficult problems that face chemists and materials scientists. Perhaps surprisingly, water also often has extremely high variability in contamination at different locations, particularly in groundwater, and even at different times in the same location. There are thousands of potential compounds in water. If one only needs to treat water when the compounds of interest are present, water quality can be improved at lower costs.

Historically, when people speak of safe water, they are thinking of pathogen-free water. Thus, disinfecting water from microbes, viruses, and emerging agents such as prions (disease-causing proteins) that sicken people is an extremely important driver. Powerful oxidants mixed homogeneously through the solution to inactivate pathogens is the current standard treatment modality.

However, there are drawbacks to chemical treatment that are driving the development of new materials and methods for disinfection. Disinfection byproducts produced by the oxidants with constituents within the water, such as nitrosoamines and polyaromatic halogens, are themselves very toxic and/or potent carcinogens. There are also protozoan parasites, such as *Cryptosporidium parvum* oocysts and *Giardia lamblia*, and viral agents that cluster within natural organic matter that are resistant to oxidation, necessitating very high concentrations of oxidants and/or long residence times in order to sufficiently disinfect the water. Filtering is then needed to separate these agents via size exclusion, which, depending on the size of the pathogen (tens of microns for protozoa, but only tens of nanometers at most for viruses) require different filter pore sizes, and thus pressure drop and energy usage. Other techniques to heterogeneously inactivate pathogens without depending on filtering by size and shape are being developed, including targeted absorption with enhanced flocculants and photocatalytic oxidation with metal oxides, such as titania compounds.

Nanoparticles, such as those shown in Figure 1, for adsorbing and mineralizing organic pollutants to harmless compounds, such as nitrogen, oxygen, carbon dioxide, and water, are being actively researched to provide a less chemically intensive alternative to advanced oxidation. Nanocatalysts are thought to work by the transfer of chemical or photon energy to form an electron–hole pair within the catalyst. When the hole comes in contact with water at the surface, according to current theories a highly reactive hydroxyl radical is thought to form, which has the capacity to oxidize hydrocarbons. Similarly, if an electron comes into contact with an oxygen molecule at the water/catalyst interface, a super oxide (such as the fast-acting O_2^-) can form, which can subsequently reduce carbon–oxygen and nitrogen moieties that are often present in organic matter. These oxidation/reduction reactions can act to mineralize organic complexes, as well as highly toxic polyaromatic and halogenated compounds. A nice offshoot of these techniques is that they can also oxidize proteins and lipids on the surface and vesicles of pathogens that the catalysts come in contact with, thus inactivating the pathogen in water.

In all of these heterogeneous purification methods being developed, fundamental studies are needed to advance the materials science underlying these technological advancements. Even after nearly 200 years of study of aqueous solutions, a great deal of scientific study of the aqueous/material interface is still needed to be able to better design materials for a given

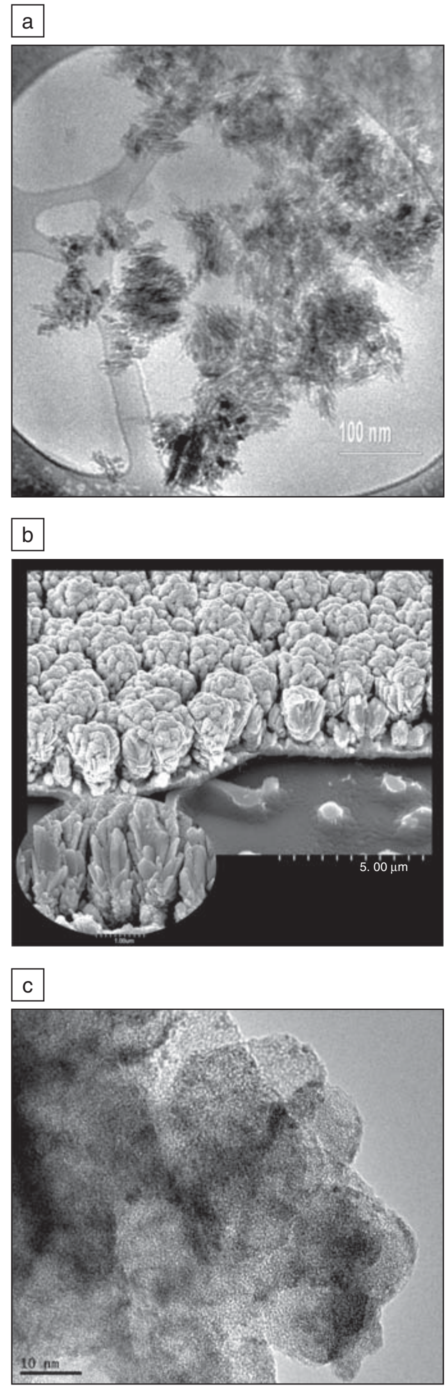

Figure 1. (a) Cryo-TEM image of a cluster of needle-like iron(III) oxide-based nanocatalysts for advanced oxidation of organic pollutants.[5] (b) SEM image of a bed of tantalum pentoxide (Ta_2O_5) photocatalysts for oxidizing organic pollutants and inactivating pathogens. (c) TEM image of nanoparticles of Ta_2O_5 on larger (micron-sized) silica particles for enhanced photo-oxidation of organic pollutants and pathogens.

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system. New methods are needed to characterize the interactions, including the physical and chemical properties and the resulting structure–property relationships of the materials, to determine, for instance, how the solute is partitioned by membranes from the solution. With knowledge gained, synthesis of membranes and filters can be guided, such as changing of pore size, surface charge, and proton donating/accepting (pK_a) tendencies of the material in water. The integration of these materials into systems also needs to be analyzed, as well as the source water and any pretreatment required, such as shifting of the pH to be above the pK_a of the material to deprotonate the surface, leaving a negative surface charge if that is desired.

Integrating the membrane and filtration systems into the modules that hold them (examples of which are shown in Figure 2) is critical. Modules strongly affect cost and performance, and determine in large part the extrinsic defects that dominate performance. Currently, many modules employ a spiral-wound design for membranes that promotes scaling along the contacts between the membranes and the spacers. This scaling may be avoided by new types of hollow-fiber membranes made from improved polymers, which have significantly higher transfer area per unit volume of the pressure vessel. The membranes also serve as spacers between adjacent membranes. Proper integration of materials in structures that can enhance throughput and reduce pressure vessel size and cost are necessary. This will further save equipment, volume, and plant area, thereby reducing water production costs.

Articles in Issue

In this issue of *MRS Bulletin*, there are five articles that cover a range of materials issues in water purification that we just discussed. The first article (Vainrot et al.) talks about the rapidly growing use of reverse-osmosis membranes in desalination to increase water supplies by desalinating seawater at lower energy and cost than previous processes. It also describes the use of microfiltration and ultrafiltration membranes in water treatment, for instance, to reduce high biological solids content via membrane bioreactors, thus enabling reuse of water. The second article (Kaur et al.) presents the increasing use of fibrous filter media for separating out a wide range of particles in the source stream; the next generation of nanofibrous media for smaller particle size separation; and functionalized media for enhanced adsorption of specific classes of molecules in solution. The third article (Cahill et al.) presents materials characterization techniques being employed on reverse-osmosis and nanofiltration membranes to better understand how these materials interact with aqueous species to improve treatment systems. The fourth article (Wernette et al.) discusses new materials and devices being developed to sense and quantify trace contaminants in water, in particular for onsite and

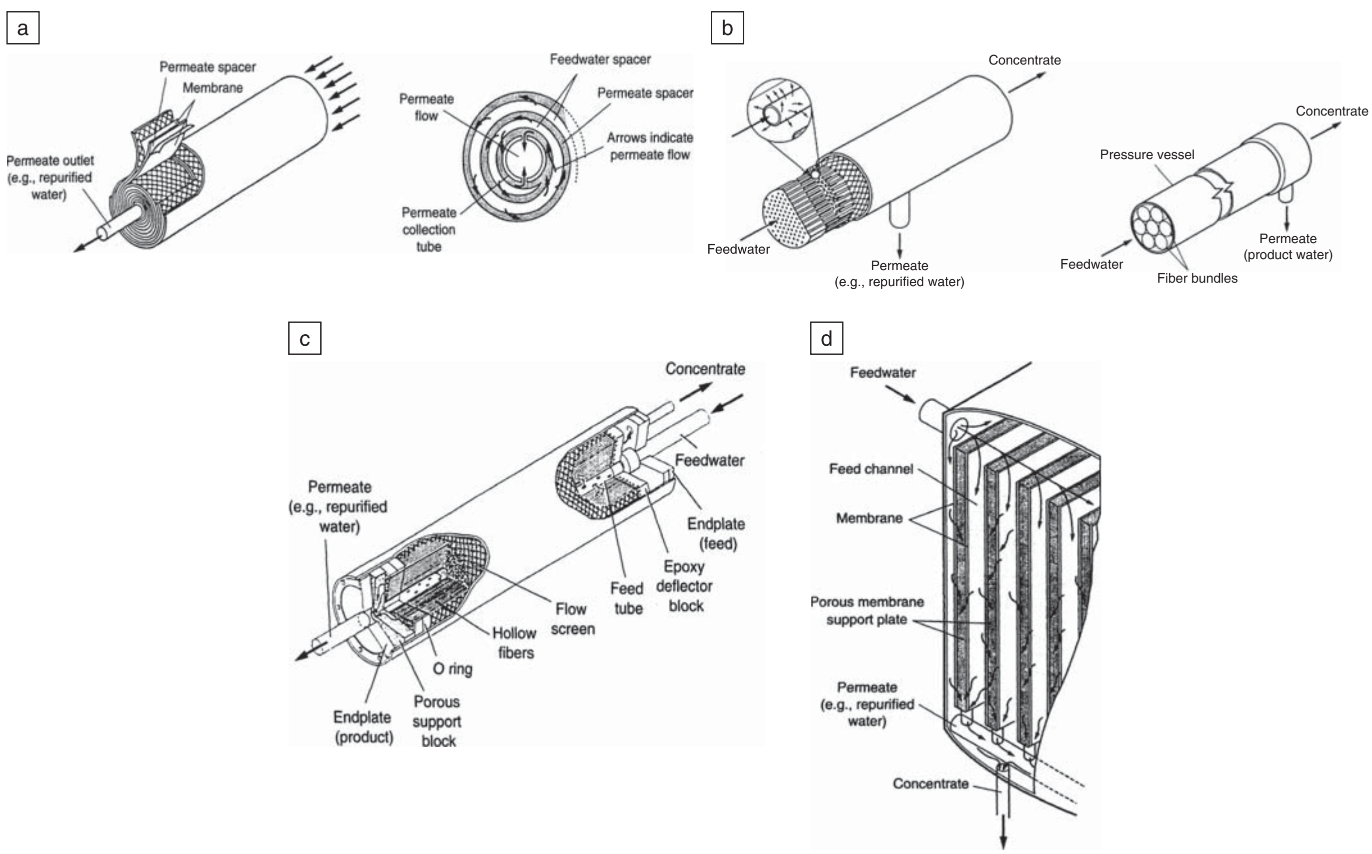

Figure 2. Schematic views of different types of membrane elements and modules, highlighting many of the materials/structure/systems issues that dominate water purification modalities in terms of cost and robustness. (a) Spiral-wound membrane and its system configuration. (b) Hollow-fiber membrane and its system configuration. (c) Elements and materials within a hollow-fiber module, highlighting the number of places where extrinsic defects and joints can cause crossover and reduced performance. (d) Similar module for flat plate membranes, which while often lower in cost than cylindrical modules, do not sustain high pressures and thus are not suitable for many current reverse-osmosis and nanofiltration systems. (From Reference 6.)

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real-time applications that can permit targeted decontamination of specific species when they are present. Finally, the fifth article (Cygan et al.) delves into the molecular basis for designing and synthesizing advanced and next-generation materials for heterogeneous purification of water for desalination, decontamination, and disinfection applications.

While these articles are not comprehensive and only touch on some of the advancements being made in materials and systems for water purification, they highlight many exciting new developments, approaches, and methodologies being pursued with materials science at the core. It is our hope that readers of *MRS Bulletin* will find many of the ideas and developments exciting as well, and that researchers throughout the world will bring their intellects, expertise, and ideas to bear in helping to solve the most pressing problem facing the world in the upcoming decades: water.

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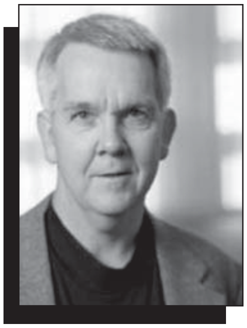

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faces, ultrafast and strongly driven transformations in materials, and the development of new experimental tools for the measurement of heat transfer and thermophysical properties.

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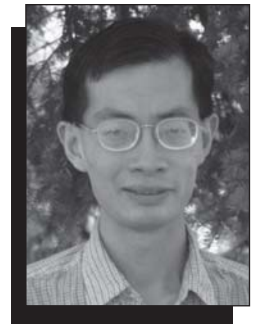

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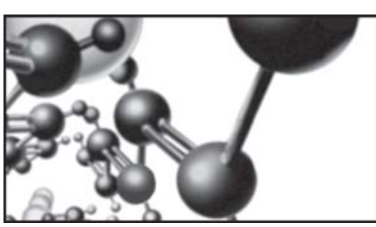
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