Promise of Nanomaterials for Water Cleanup

By J. Richard Schorr, PE, Ph.D.

The problem
New approaches are continually being examined to supplement traditional water purification methods. These need to be lower in overall cost, durable and/or more effective than current options for the removal of contaminants from water, either in-situ or in water purification systems. It is in this context that nano-enabled technologies are being considered. These consist of filtration materials that have enhanced performance arising from their high specific surface area and the abundance of surface-state electrons found in films and parts containing nanomaterials. These nano-enabled technologies will play a significant role in water treatment in the future.

Clean water is a requirement for a properly functioning society and, in parts of the world, demand is fast exceeding supply. While water is plentiful, clean water for human consumption is often limited. Global consumption of water is doubling every 20 years, more than twice the rate of human population growth. According to the United Nations, more than one billion people on earth already lack access to fresh drinking water. If current trends persist, by 2025 the demand for fresh water is expected to rise to 56 percent above the amount currently available. That, along with cleanup technologies constrained by capital and energy costs, combined with a growing population, is a recipe for conflict.1

What's nano?
Nanotechnology is the manipulation of individual atoms and molecules to create materials and devices with vastly different properties. Nano means one billionth; in this case a nanometer (nm). A nanometer particle contains only a few atoms. For comparison, a virus is typically 100 nm in size and a human hair is 70,000 nm thick.

Nanomaterials are available today in the form of activated materials like carbon or alumina. These materials have high surface areas; however, because of the fine pores, not all the water can easily reach the active surfaces and they are easily plugged. The small size of nanomaterials creates a major challenge. These fine particles or fibers cannot just be added to drinking water; rather, they must be incorporated into filtration media in ways that allow for the contaminants to readily come in contact with the active media. Attention is being given to the development of filters and media that can take advantage of the properties of nanomaterials for removal of contaminants from water.

Filtration media
The basis for the application of nanomaterials starts with lightweight porous ceramics that can be molded into simple or complex shapes using inexpensive processing methods where inorganic hydrogels are used to strongly bond additives together. Additives can include zeolites or iron-containing compounds. These porous ceramics have been sold for years in aquaculture applications for holding aerobic and anaerobic biofilms for the removal of ammonia, nitrates and nitrate contaminants. This itself provides a high surface area for colonies of bacteria. These products are used in systems where water is circulated and reused, such as in aquaculture, where water requires intensive and specialized treatment. These same ceramics, when prepared from iron-containing materials, have also been shown to be effective filters for water remediation.2

media tailored for water cleanup applications, such as the removal of metal ions (e.g. As and Pb), organics or phosphates. These base technologies are reasonably priced, highly effective and have significant potential for reducing a wide range of contaminants in water.
These can be made from nearly any fine-grained (even waste) materials and flexibility exists for controlling porosity without firing the ceramic. Pore sizes can be controlled from sub-micron to 250 microns or larger. An interconnecting pore network is formed that provides a high surface area for the growth of biofilms or nanomaterials. Typical surface area of these porous materials is 180,000 ft²/ft³, compared with a surface area of 10,000 ft²/ft³ for a typical sand filter bed. This provides a significant increase in active surface area. It is also a good platform for making filter materials tailored for a wide number of applications, including remediation and biofiltration.

Typical porosity of these ceramics is around 85 percent, which allows for easy water flow through the material without a hydrostatic pressure. They can also be provided as granules for replacement of other granular filtration media. Rigid, porous ceramics with a high surface area can be used in external systems and for in-situ use remediation. Blocks or granules of ceramic foam with open porosity can provide the same effectiveness as granules. Surface area, density and strength can be adjusted to withstand geostatic loads.

**Nano-enabled approach**

The typical surface area of these porous ceramics can be significantly increased through the growth of nanomaterials within the pores of this filter material, which can increase the surface area by 10 to 50 times, thus providing a very effective media for contact between the contaminant and the active filter agent.

This then greatly enhances the filtration media performance and can reduce the amount of active media needed. Active agents like manganese oxide can be used to change the valence state of metal ions in water (e.g. arsenic oxidized from the +3 to the +5 state), which can then be more easily removed by reaction with iron oxide to form a stable material. Iron oxide has also been used to break down organics, pesticides and such materials into non-hazardous compounds. Often, reactions are enhanced through the addition of other nano-materials, such as copper or copper oxide.

Coupled with application-specific nano-engineered agents, the resulting media can effectively remove phosphates, heavy metals, lead, arsenic and other pollutants as water flows through or into the porous filter media. This material is also being examined as a porous membrane support for deposition of nanostructured inorganic membranes that provide ultrafiltration. Thin membranes have been prepared with thicknesses well under 100 nanometers. These membrane filters can provide efficiency benefits and flow rates 100 times higher than conventional RO filtration membranes have been measured in the laboratory, thus reducing the waste of significant quantities of water used in the cleanup process.

**Applications**

**Arsenic and lead removal**

Arsenic is a serious contaminant that needs to be lowered in many sources for drinking water. While methods exist, they are often cost prohibitive. Nanomaterials have a great potential as a more cost-effective filtration media, either used with existing filter beds or in separate filter beds, to reduce arsenic to acceptable levels. The Safe Drinking Water Act reduced acceptable arsenic levels from 50 to 10 µg/L and several thousand communities in the US exceed this level, as well as many groundwater sources that require POU filters.

It has been shown that a combination of nano manganese oxide fibers combined with nano iron oxide is exceptionally effective at removal of arsenic (and lead) from water. This technology is now being used with the porous ceramic media to provide a very cost-effective approach to utilizing these nanomaterials, which rapidly remove arsenic and lead from water. Small column tests of this media with very short empty-bed contact time (EBCT=0.5 min.) using NSF/ANSI Standard 53 challenge water containing 50 ppb arsenic is most promising.

Figure 1 shows a comparison of the arsenic breakthrough bed volume compared with a commercial benchmark media GFH (granular ferric hydroxide). In all three water pH conditions, the...
MnO₂/Fe₂O₃ media containing nanofibers demonstrated higher breakthrough bed volume than the GFH media that were tested side by side. In addition, this media was almost equivalent in efficiency for the removal As(III) and As(V). As(III) is much more toxic and harder to remove than As(V); however, this media allows for pre-oxidation of As(III) to As(V) prior to sorption of the As(V) thus eliminating the need for a pre-oxidation step, which also reduces the amount of byproducts generated during pretreatment. There was only one system design. This testing was done using 50-mesh granular particles in a column, through which challenge water was passed. The media can also be provided as a solid porous cylinder or plate. There was no prefiltration or backwashing performed for these tests; however, if groundwater was used or if the water is chlorinated, it is feasible that particulates could accumulate in the bed that will require backflushing.

Besides removing As(III) and As(V), the nano iron-based media also demonstrated very high Pb(II) adsorption capacity.

**Abiotic reductive dehalogenation**

Iron (and zinc/other metals) in the zero-valence state are very effective for dehalogenation of chlorinated solvents, particularly trichlorethane. Porous ceramics containing nanomaterials of iron oxide or iron can provide an effective product for remediation. Water flowing through a permeable wall is used to break down chlorinated solvents, such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Granulated porous media was used in a controlled barrier to break down these compounds in groundwater.

**Adsorption of heavy metals**

Ferrous and or metal oxides can also adsorb heavy metals and radionuclides. Sometimes, combinations of metal and oxides are needed. Deposition of zeolite-type structures in the pores of the ceramic can provide a caging process that allows significantly high surface area without blocking the pores.

**Bioremediation of groundwater**

Bioremediation involves the use of bio-organisms that destroy contaminants in water coming in contact with the organism. Cell-Pore™ is an outstanding carrier for bio-organisms because of its high surface area (1,000 times higher than plastic media). Properly designed systems with appropriate operating conditions, such as oxygen, nutrients, etc. can make very effective use of high concentrations of bio-organisms without fouling.

**Phosphate removal**

Porous ceramics with high surface area containing iron/iron oxide have been shown to be as effective as higher-cost products such as activated alumina, while continuing to remove phosphate for significantly longer periods.

**Conclusion**

An increasing use of nanomaterials will be seen in the coming decade because of the significant contaminant removal potential that exists for improving the effectiveness of water purification systems. The key to successful introduction will be development of affordable systems. One approach is to use a porous ceramic media containing the active nanomaterials. This approach has been shown in the laboratory to be effective for arsenic, lead and phosphate removal as well as the breakdown of some organic contaminants. Field trials are needed to observe the long-term advantages and practical-use applications of these nano-media products.

**References**

1. The wars of the next century will be about water. Ismail Serageldin, Vice President of the World Bank


Comparison of breakthrough curves for As(III) and As(V) for nano-media at pH 7.5 and at EBCT 0.5 min (Initial As(III)/As(V) concentration 50 µg/L)

Dr. J. Richard Schorr, President and Founder of MetaMateria (now a subsidiary of NanoDynamics, Inc.), has nearly 30 years’ experience in developing and applying advanced materials. Previously, he was CEO of Orton Ceramics, held senior management positions at Battelle and Liebert and was Vice President for Research and Engineering at Advanced Refractory Technologies. Schorr is a distinguished alumnus of Ohio State University College of Engineering and was awarded the Meritorious Service Citation by the College. He is a graduate of the Columbus Leadership Program; has served on a number of boards, including Ohio Fuel Cell Coalition and the Edison Materials Technology; is a Registered Professional Engineer and Fellow of the American Ceramic Society; was past President of the National Institute of Ceramic Engineers and North Central Community Mental Health Services; and has been the recipient of numerous community and professional awards.

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- NanoDynamics is a fully integrated technology and manufacturing company utilizing nanoscale engineering and materials to address some of the world’s biggest challenges. The company’s research and business units, including ND Innovations, ND Materials, ND Products, MetaMateria Partners and ND Life Sciences, provide nano-enabled solutions in the fields of energy, automotive, water processing, life sciences, electronics, advanced materials and consumer products. Headquartered in Buffalo, N.Y., NanoDynamics is delivering the power of nanotechnology to the global marketplace.

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