

EMERGING TECHNOLOGIES

REMOVAL OF BIOLOGICAL AND CHEMICAL CONTAMINANTS FROM WATER WITH SURFACE MODIFIED MINERALS

A proprietary nano technology has been developed by a research company^a that can transform low-cost materials, such as minerals or sand, into big-capacity, target-specific water purification technology for removal of biological and chemical contaminants from water. The proprietary nanocoated or surface-modified mineral adsorbents are capable of sequestering high concentrations of chemical contaminants, such as arsenic, lead, mercury, selenium, cadmium, and perchlorate, tetrachloroethylene (PCE), trichloroethylene (TCE), and methyl tert butyl ether (MTBE), as well as water-borne pathogens.

No single technology has proven effective at purifying raw water contaminated with pathogens, organics, and inorganics, much less at a price affordable to the majority of the world's population. The nano technology combines natural, high-surface area nano-porous minerals (zeolites and titania), which are low-cost substrates, and functionalized them with inexpensive nano-coatings such as ligands for metal removal and surfactants for pathogen and organic removal.

The nano-coated filter media for metal removal uses inexpensive ligand coatings capable of binding target metal contaminants. The bi-functional ligand is capable of binding multiple layers of

metal contaminants and dramatically increasing the amount of adsorbed contaminant to the point that the metal contaminant on the filter media can be recovered.

Heavy Metal Removal

Naturally occurring arsenic in the groundwater in Bangladesh, India, China, Vietnam, Pakistan, Nepal, Myanmar, and Cambodia have more than 700 million people at risk for arsenosis, which is the bioaccumulation of arsenic that over time can cause cancer and death. The primary heavy metals in water include lead, mercury, copper, zinc, nickel, chromium, and cadmium, along with arsenic.

A mono-functional ligand is covalently bound to the surface area of the substrate with a functional group on the other end specific for removing heavy metals. The substrate is functionalized to increase the adsorption capacity of the substrate as well as increase the selectivity for a class of contaminants, in this case, heavy metals. This functionalized nano-coated filter media is then exposed to ionized metal contaminants in water and removes the contaminants from so-

lution by bonding the metal, in the graphic shown below lead, to the functional group on the free end of the ligand.

In Figure 1, a high surface area substrate, in this case titania (TiO₂), is functionalized with a monofunctional ligand and exposed to lead in solution.

Additionally, the proprietary nanocoated filter media^b is capable of being regenerated *in-situ* without generating any waste stream by applying a fresh layer of the ligand nano-coating. The filter media is capable of being regenerated or re-charged in place and put back into service, treating eight times more contaminated water and loading eight times the amount of contaminants than any single use adsorbent media currently available.

The novelty of this design lies in the bifunctional ligand nature of the ligand coating. The ligand molecules are essentially "double stick"—one end is bound to the substrate, while the other end is free to bind contaminant. Once the surface of the media has been saturated with metal contaminant, it can then be regenerated or re-charged, in place, simply by applying a fresh layer of bifunctional ligand nano-coating. This allows

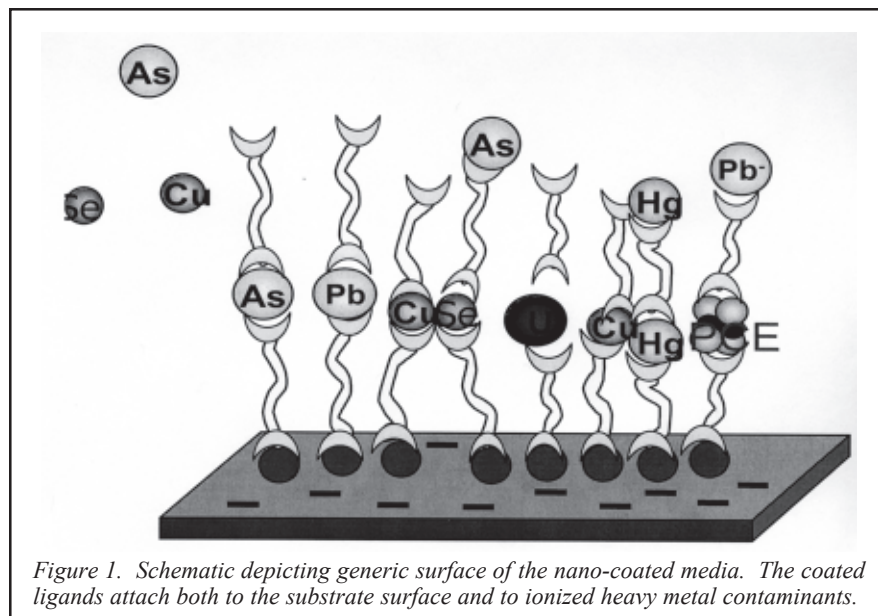


Figure 1. Schematic depicting generic surface of the nano-coated media. The coated ligands attach both to the substrate surface and to ionized heavy metal contaminants.

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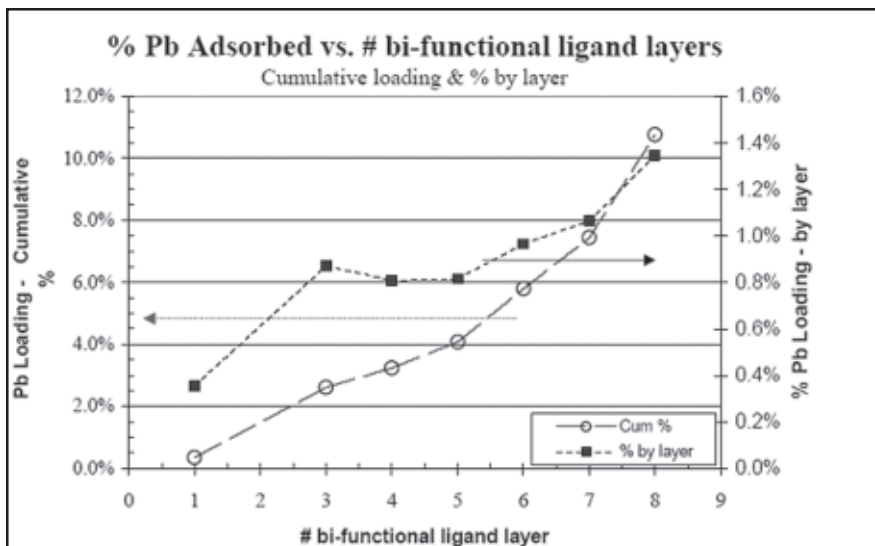


Figure 2. The eight layers of adsorption with a cumulative adsorption loading of 11% by weight.

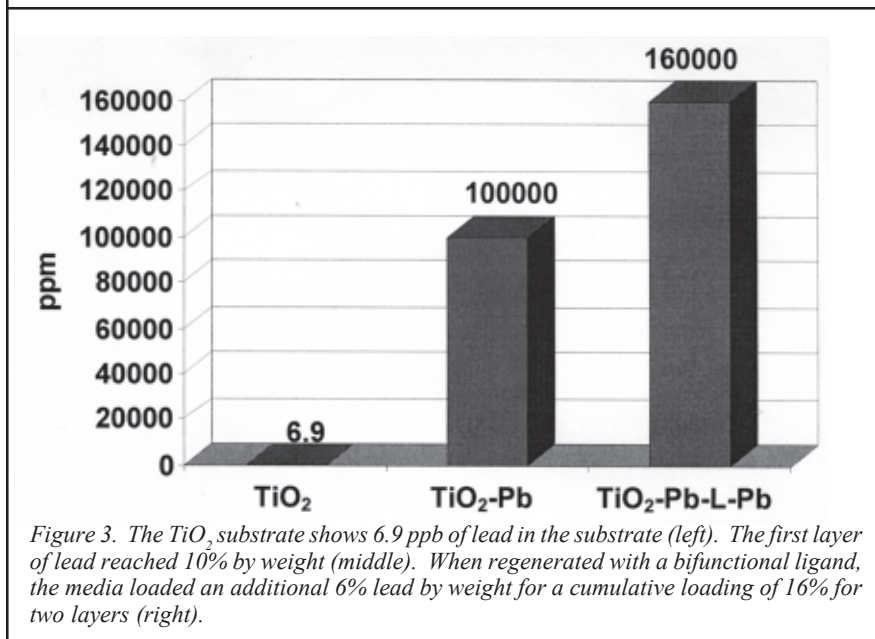


Figure 3. The TiO₂ substrate shows 6.9 ppb of lead in the substrate (left). The first layer of lead reached 10% by weight (middle). When regenerated with a bifunctional ligand, the media loaded an additional 6% lead by weight for a cumulative loading of 16% for two layers (right).

for construction of multiple ligand and contaminant layers (Figure 1). In this manner, a total adsorption of eight times greater than currently available adsorbents can be realized.

Figure 1 shows a schematic of the generic surface of the nano-coated media. The nano-coating ligands attach both to the surface of the substrate and to ionized heavy metal contaminants. After one-layer of contaminant is bound, the media can be regenerated of “re-charged” *in-situ* with application of a second layer of nano-coating, providing a fresh surface for another layer of incoming contaminant.

The research company’s technology

relies on surface nano-coatings to dramatically increase the adsorption capacity of low-cost mineral substrates. By applying an organic mono and bi-functional ligand with a specific functional group to a high surface area substrate, we have created a target specific adsorbent media capable of adsorbing 8 times the contaminants of conventional adsorbing media. Figure 2 shows eight layers of adsorption with a cumulative adsorption loading of 11% by weight. The research company’s filter media is capable of loading 0.4 milli-mole of metal per gram of substrate.

The bi-functional ligand has two receptor sites for target species, each capa-

ble of attaching a target contaminate at either end; the molecular structure prevents both sites from adhering to the same substrate. In effect, we have a “double stick” molecule with active receptor sites on both ends with the contaminant covalently bonded in between both ligand layers.

The nano-coatings are a self-assembly of discrete supramolecular aggregates, using reversible coordinate bonding interactions to provide access to elaborate and precisely designed structures that have generated an enormous amount of interest (1).

Recent work has demonstrated that As(+3) in combination with appropriately designed bridging thiolate ligands (L) can self-assemble into a discrete dinuclear As L structure, supported by a secondary² supramolecular interaction between the lone pair of As(+3) and the aromatic ring of (L). These secondary bonding interactions (SBIs) can take many forms, as shown in the assembly of a naphthalene-imide with As(+3) where weak arsenic-oxygen interactions support a highly symmetric complex in solution. The SBIs similarly work to confer selectivity for a target analyte (1).

The research company’s proprietary adsorbent filter media for arsenic will load 0.3% (As) per layer so a filter, containing one kilogram of nano-coated TiO₂ can remove 3.0 grams of arsenic from 10 kilo-liters of water. This filter can be “regenerated” eight more times for a cumulative treatment capacity of 100 kilo-liters of water. Note that the arsenic level is lowered from 300 parts per billion (ppb) to less than 10 ppb. The filter cost, plus solution for regenerating ten times, is about \$41.00, including profit margin. The cost for treated water is \$0.41 per thousand liters, or \$1.57 per thousand gallons.

The graphic in Figure 2 shows the loading of a contaminant, in this case lead (Pb), to a substrate (TiO₂), then loading on the next layer, which is a bifunctional ligand then loading on another layer of contaminants (Pb), and another layer of nano-coating or bifunctional ligand, and so on.

Working with two heavy metals, lead (+2) and arsenic (+3, +5) at much higher concentration levels in solution (300

ppb), we have achieved a 16% loading of lead (Figure 3), and a 0.73 % loading of arsenic (Figure 4) by weight with two layers on our proprietary adsorbent filter media by layering the contaminant with the nano-coating bifunctional ligand.

The TiO₂ substrate shows 6.9 ppb of lead in the substrate. The first layer of lead reached 10 % by weight. The filter media is regenerated *in-situ* with a bifunctional ligand and loaded an additional 6% lead by weight for a cumulative loading of 16% with two layers.

The TiO₂ shows no arsenic in the substrate. The first layer loaded 3.5% arsenic (+3) by weight. The filter media is regenerated *in-situ* with a bifunctional ligand and loaded additional 3.8% arsenic (+3) by weight for a cumulative loading of 7.3% with two layers.

Arsenic (+5) adsorption is 70% by weight that of arsenic (+3) with no change of pH or conversion of one species to the other.

Since the contaminant is bound covalently from the bi-functional ligand layer underneath it as well as on top of it, the filter media more than passes a Toxicity Characteristic Leaching Procedure (TCLP) test, which will allow the spent media to be disposed of in a conventional landfill. At these high adsorption concentrations, the heavy metal loaded filter media becomes attractive for metal reclaim.

Pathogen Removal

Microbial contamination of drinking water is a serious problem with global significance. Water-borne pathogens consisting of bacteria, viruses, and protozoa are the cause of 80% of all illnesses in developing countries. Enteric viruses and bacteria, spread via a fecal-oral route are the primary pathogens responsible for water-related microbial infections in humans. Inexpensive solutions to this problem are urgently needed. Bio-terrorism and concerns about the safety of drinking water supplies only add to the urgency.

The research company has licensed this technology developed by Professor R.S. Bowman (New Mexico Tech) and Professor S.D. Pillali (Texas A&M University) using a clinoptilolite-dominated zeolite as the initial substrate to develop

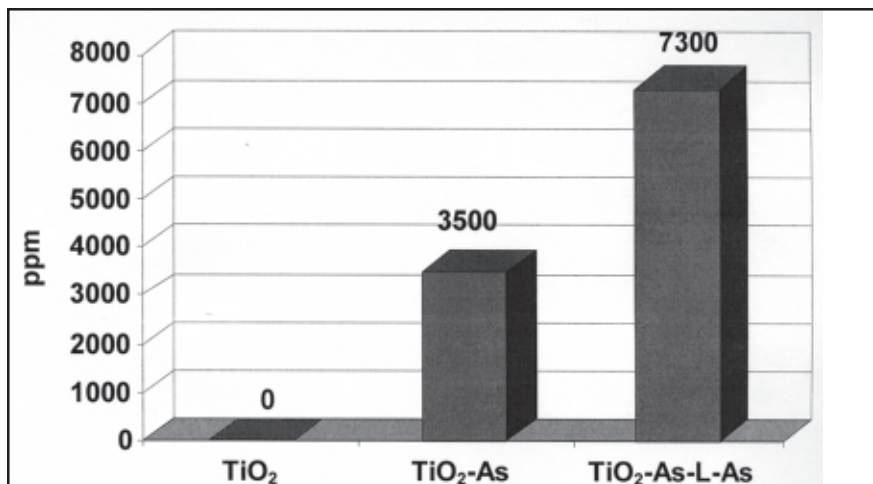


Figure 4. The TiO₂ shows no arsenic in the substrate (left). The first layer loaded 3.5% arsenic by weight (middle). The regenerated filter media had a cumulative loading of 7.3% with two layers (right).

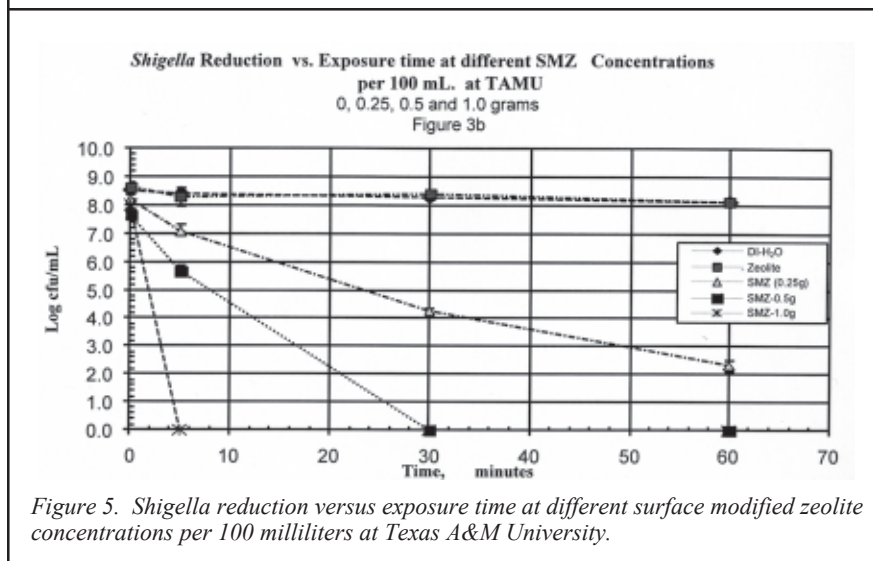


Figure 5. *Shigella* reduction versus exposure time at different surface modified zeolite concentrations per 100 milliliters at Texas A&M University.

low cost adsorptive filter media for the deactivation of bacteria and viruses. About 70% clinoptilolite by weight, the zeolite has a specific surface area of 15 square meters per gram (m²/g). Zeolite deposits are readily available globally and are very inexpensive. Surface modified zeolites (SMZ) costs less than \$0.50/kilogram (kg).

Zeolites being a clay mineral are modified by certain organic surfactants; the surface charge becomes positive and their hydrophobicity increases. Zeolites possess a net negative charge, which limits their capacity for adsorbing viruses. By applying a long chain cationic surfactant, hexadecyltrimethylammonium chloride (HDTMA-Cl), the surface charge is reversed. Once the surface charge is reversed, their ability to adsorb

many non-polar and anionic contaminants in water is greatly increased. A 30% aqueous solution yields 140 mmole/kg of HDTMA content (2).

The surfactant HDTMA acts as a biocide by forming a stable surfactant bilayer, which reverses the zeolite surface charge from negative to positive and creates a hydrophobic environment. The anionic and organic partitioning properties of SMZ promote virus adsorption. Virus removal and deactivation by SMZ can be attributed to sorption (2).

SMZ removed 100% of *E. coli* bacteria present. Enteric viruses and certain bacterial pathogens such as *Shigella spp.* have relatively low infectious doses and *Shigella* is one of the more resistant bacterial strains. To test the efficacy of SMZ against *Shigella*, a 100-cc chal-

lence solution of 1×10^{10} colony forming units per milliliter (cfu/mL) was used with four different concentrations of SMZ, mixed in a beaker and allowed to sit over four different exposure times. It took 60 minutes to achieve a 6-log reduction of *Shigella* with 0.25 g of SMZ but with 1.0 g of SMZ, it only took 5 minutes to achieve a 9-log reduction, passively.

In our tests shown in Figure 5, SMZ was very effective for removing 100% of both *E. coli* and *Shigella* in a very timely manner. With the surfactant bound to the zeolite and toxic to organisms, there is 100% deactivation of *E. coli* and *Shigella*. Additionally, SMZ remains potent for removal of bacteria over a long period of time as shown in Figures 1 and 2. The lifetime of the SMZ for viruses (MS2 & phix174) was much shorter and required a longer retention time to achieve a 2-log to 4-log reduction.

Research found that SMZ rapidly inactivates *E. coli* even after a few seconds of contact (that is why the "0" hour time point is already ~5 log below the control). As can be seen from the data, there is more than an 8-log decline in numbers as compared to the control by the end of

Day 2.

Research showed an 11-log reduction in *Salmonella* after 2 days, and it is still deactivating 100% of the *Salmonella* after day 12.

Conclusion

The research company has successfully developed nano-coating technology that is effective against all three classes of chemical contaminants: water-borne pathogens, organics, and inorganics. By using low cost, high surface area mineral substrates or sand, and functionalizing the surface chemistry with nano-coatings, we have dramatically increased both the selectivity and adsorption capacity of these substrates. The proprietary adsorption media is very low cost, can be manufactured globally, and through our multiple layer *in-situ* regeneration process has solved the problem of generating a hazardous waste as a result of removing chemical contaminants from water and recovered the metal as a resource, not landfilled it as a waste product. □

References

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2. Schulze-Makuch, D.; Pillali, S.D.; Guan, H.; Bowman, R.; Coroux, E.; Hielscher, F.; Totten, J.; Espinosa, I.Y.; Kretzschmar, T. "Surfactant-Modified Zeolite Can Protect Drinking Water Wells from Viruses and Bacteria", *EOS Transactions*, vol. 83, pp. 193, 200-201 (April 2002).

Endnotes

^a Crystal Clear Technologies Inc., of Portland, Ore., is the licensor and developer of this technology and is referred to in the text as the research company.

^bThe proprietary nanocoated filter media is trademarked under the name NMXTM.

Author Lisa Farmen has worked in the field of water, wastewater treatment, and chemical recovery as an OEM with her own manufacturing firm for 10 years. She has extensive experience in technology development through commercialization and management experience from start-up through initial public offering. Her last position was senior engineer for Texas Instruments prior to incorporating Crystal Clear Technologies.

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