High Performance Turbidity Filter

By Fred Tepper, Leonid Kaledin and Catherine Hartmann

Introduction

Turbidity in water is caused by suspended and colloidal matter such as clay, silt, finely divided natural organic matter (NOM), inorganic matter and plankton plus other microscopic organisms, according to Standard Methods 2130. Waterborne pathogens have caused significant disease outbreaks in the United States and continue to pose a significant risk. The most frequently reported waterborne disease in the United States is acute gastrointestinal illness, or gastroenteritis. The causes are usually traced to various viruses, bacteria, or protozoa. Effectively filtered turbidity can be correlated with low bacterial counts and low incidences of viral disease.

Inorganic particles provide abundant adsorption sites for bacteria, viruses, metals and other toxic substances. There

is some concern that inorganic particulate contamination has the ability to shield microorganisms from inactivation by disinfec-Organic tants. containing colloids such as humic materials consume significant chlorine, while increasing concentration of carcinogenic disinfection by-products (DBPs).

Filtration is the key unit process in surface water treat-

ment for removing particles. For conventional and direct filtration systems, the U.S. Environmental Protection Agency (EPA) requires that the turbidity level of filtered water not exceed one Nephelometric Turbidity Unit (NTU) at any time.

Electropositive filters based on nano alumina fibers

Non-woven depth filters are used for removing turbidity from drinking water as well as in a wide variety of industrial processes. Typically, wound fiber filters have a micron rating down to about one micron, with filtration efficiencies ranging up to only about 95 percent. Pleated microglass or polymeric filter media and microporous/ultraporous membranes are better suited for filtering particles smaller than about one micron. Absolute 0.2 µm membrane filters are capable of retaining all types of bacteria with very high retention (>6 log retention value: LRV) but they are transparent to much smaller particles such as viruses. Membranes and small pore fibrous filters, which function by size exclusion (as sieves), have an increasingly higher flow resistance with decreasing pore size.

A different filter mechanism is electrokinetic adsorption, where the media is charged and particles opposite to that are surface filters, they are still prone to early clogging, particularly with colloidal organics such as humic acid. An electropositive fibrous filter is desirable, particularly one that has a very small fiber diameter, maximizing the density of positively charged sites.

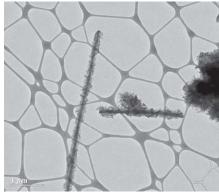
Nano alumina fibers two nanometers (µm) in diameter have been produced (Figure 1) that are tens to hundreds of nanometers long and are heavily aggregated. The surface area (via nitrogen adsorption) is 300-500 m²/g, as compared to a computed area of 500 m²/g. Since most of its area is exposed on the fibers' external surface, adsorption is very rapid as compared to granular sorbents whose adsorption kinetics are controlled by diffusion within a microcapillary network. X-ray diffraction shows the fibers are principally boehmite

(AlOOH). Boehmite is used as an analgesic in over-the-counter medical products. Loose nano fibers adsorb >99 percent of MS2 and PRD-1 bacteriaphage (virus) and bacteria, even in the presence of 0.5 percent saline. Bacteria adsorption is optimum from 20-50° C and from pH 5 to 9.

Figure 1. TEM micrograph of alumina nanofibers



Figure 2. TEM of glass/nano alumina fibers mixture



charge are attracted and adsorbed. Most colloidal particles in water are negatively charged as a result of differences in electrical potential between the water and the particle phases. Asbestos filters (which are electropositive) were used for more than a century. For the past few decades there have been many efforts to find an asbestos substitute. Membranes have been modified to provide some electropositive functionality but their flow resistance is very high and because they

Filter development

The nano alumina is distributed over a microglass fiber (0.6 µm) matrix to reduce pressure drop and provide access to particles. The fuzz attached to the microglass fibers in Figure 2 is the nano alumina. A 1.5 millimeter thick filter could sustain a flow velocity of approximately 1.5 cm/sec at 0.7 bar. Using bubble pressure, the largest pores were measured to be about seven microns with an average of two microns.

Table 1 shows zeta potential values

on this filter media as a function of nano alumina content. Zeta potential is a potential developed very close to the surface of a solid in aqueous solution caused by the charge distribution on the surface. Most particles in water tend to have a negative charge and would be attracted to electropositive surfaces. The microglass/nano alumina medium becomes highly electropositive when the nano alumina content exceeds about 15 weight percent, and is then capable of adsorbing > 6 LRV of the virus as shown in Table 1, as well as bacteria and cysts that are somewhat larger. Other data showed that artificial salt water had no measurable affect on virus or E. Coli retention. The filter was also found to re-

Table 1. Zeta potential of nano alumina filters

Nano alumina medium Wt percent on glass	True zeta potential (z _{true}), mV	MS2 retention (percent)
0	-35	8
5	-10	29
10	7	94
15	12	>99.9999
25	32	>99.9999
40	29	>99.9999
50	23	>99.9999

tain *Cryptosporidium* (>5 LRV), DNA (~99.5 percent) and endotoxins (>99.96 percent).

The media described above are modified by adding cellulose and polymeric fibers to increase strength and flexibility, while maintaining the same ratio of nano alumina to glass. Figure 3 shows the 0.8 millimeter thick medium that was used in developing cartridges.

Modeling the adsorption process

Using experimental data for adsorption of 30-nanometer diameter latex spheres, a model was developed that describes the dynamic adsorption of particles by the media. It projects breakthrough curves and filter efficiency as a function of particle concentration, flow rate, filter thickness and pH. Dynamic adsorption is rather constant over the pH range of 5 - 9. The model was tested with MS2 virus and experimental data showed excellent agreement with computed projections, even over concentrations of 103-108 PFU/ml (plaque forming units). This model has proved invaluable in projecting performance over large filter areas and for various thicknesses.

Retention of different size particles

Previous development focused on bacteria, virus and DNA and only with small disc filters. This study was extended to other size particles and to cartridge size filters.

A blue dye (Epsom) with a three nanometer particle size was diluted until it was transparent. A 25-nanometer pore size membrane was placed within a filter holder and, by using a syringe, the diluted dye was forced through the mem-

brane. The effluent was as blue as the original solution, and the membrane showed no discoloration. The experiment was repeated with a nano alumina filter,

25-millimeter diameter and 1.5 millimeters thick. In this case, the backpressure required to force the fluid was minimal. The filter caused the fluid to change from intense blue to water clear, showing that it retained the three nm particle. A separate test showed that a single thickness of

0.8 millimeter media retained >6 LRV (>99.9999 percent) of *Klebsiella terrigina* (0.5 micron).

In the EPA guide standard for certification testing of mechanical microbial filters,* natural turbidity is simulated by using AC fine test dust (1 μm) and humic acid. The test dust used in EPA Water #2 is principally silica, while the humic acid is a degradation product in the decay of natural organic matter (NOM). The humic acid consists of agglomerates that are either elongated (250 nm x 60 nm) or disklike (50-nm diam.) and have a height of 1.5 to 2 nm. The agglomerates are in the same size range as many viruses and are as difficult to filter. Humic acid is known to clog activated carbon beds.

A 25-millimeter diameter nano alumina media filter disc, 1.6 millimeters thick, was challenged by a solution of 2.5 NTU (10 mg/L) of humic acid at a flow of 40 ml/min. The filter's effluent was below 0.01 NTU for more than 200 ml at which time breakthrough occurred. At this point the filter showed no signs of clogging. In contrast, an absolute 0.2 µm membrane was challenged under the same conditions. The turbidity in the effluent immediately spiked to 1.3 NTU,

Figure 3. Nano alumina/microglass fiber/cellulose medium



demonstrating poor retention of humic acid. After clearing only 30 ml of fluid, the membrane was completely clogged. This clogging is probably the result of gel formation on the surface of the membrane, similar to the clogging that humic acid causes on sorbents such as activated carbon.

A filter cartridge, 2-inch (63 mm) diameter X 4.5-inch (114 mm) high, consisting of a single layer of filter medium 0.8 mm thick, was assembled for test. The media was pleated, resulting in an effective filter area of 800 cm². The filter was challenged starting with 15 NTU of AC fine test dust at a flow of 1 liter/min. After passing 810 liters, the turbidity was increased to 90 NTU for another 150 liters and then to about 872 NTU for the last 57 liters. The turbidimeter (sensitivity 0.01 NTU) detected breakthrough only after clearing the last 20 liters at 872 NTU (total 980 liters). At this point filter retention was >99.999 percent. During the test the cartridge retained 71 grams of dust particles or 89 mg/cm² of filter area. Figure 4 shows the spent cartridge.

A similar test was run on a pleated cartridge 2.5" (63 mm) diameter x 4" (127 mm) high. This cartridge was challenged by a continuous stream of 250 NTU test dust at 5.5 liters/min (1.5 GPM). At 90 minutes (535 liters) it had filtered out 119 g of dust while maintaining <0.01 NTU in the effluent, at which point the test was terminated without breakthrough.

The performance of the medium used in the cartridge seen in Figure 4 is compared to the data of C. Shieldst who tested submicron microglass, meltblown and membrane medium with pore size ratings in the range of 0.2 μ m, 0.5 μ m, and 1 μ m. He compared filtration efficiency, clean water flowrate and dirt holding capacity. Each media was tested for retention efficiency with latex beads of 0.4 μ m, 0.8 μ m and 3.0 μ m. Only the 0.2

Figure 4. Spent pleated cartridge filter



microglass and 0.2 membrane media achieved 100 percent retention of the smallest (0.4 µm) latex spheres. In contrast, a single layer (0.8 mm thick) of nano alumina media retained greater than 99 percent of 0.03 µm latex particles or 99.7 percent retention of MS2 virus (25 nm). Both these data justify an absolute pore size rating of 0.03 µm.

The clean water flux was respectively 17, 21 and 25 ml/min/cm² for the 0.2 μ m, 0.5 μ m and 1.0 μ m microglass media.† (The author did not provide the head pressure). The liquid permeability of these microglass media was significantly higher than meltblown or membranes for each of the pore size ratings tested. Measurements show that the 0.8 mm thick nano alumina has a clean water flux of 60 and 120 ml/min/cm² respectively at a pressure of 0.5 and 1 bar.

Figure 5 shows Shield's data for the dirt holding capacity (DHC) of AC fine test dust by the different media. The DHC of the cartridge shown in Figure 4 is compared to the Shields data. The data are shown on semi-log coordinates since the relative DHC of nano alumina medium is so great that the data for meltblown and membrane media would not be discernable. It's DHC of 574 mg/in² is almost twenty times greater than the microglass media if compared at a pore size rating of 1 μm and far greater than that if compared to smaller pore size ratings of the microglass.

The data demonstrate that the nano alumina medium is capable of extraordinary capacity for adsorbing particles while achieving high retention efficiency. The filter achieves such performance at a water flux equivalent to or greater than other filter media intended for filtering sub-micron particles.

Cost benefit of the new filter cartridges

Commercialization of filter cartridges based on the new media is in its infancy. The cost of filter media at its current state of development is about \$1/ft². The projected cost at full manufacture is projected to be about \$0.30/ft. This compares to a price of \$1/ft² for membranes, \$0.30/ft² for microglass and \$0.20/ft² for meltblown media. Assem-

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bly methods for the pleated version of the new media are typical of other pleated cartridges.

Even at an early stage however, the filters offer significant payback. A major cost benefit is a projected life more than ten times greater than other cartridges. In addition, there is a benefit in reducing the inconvenience and labor cost associated with far more frequent filter changeout in the case of conventional cartridges.

A single layer of media is not sufficient to produce potable water principally because of its inability to retain >4 LRV of virus. Multilayer nano alumina depth filters are being designed for that purpose.

Conclusions

A non-woven electropositive filter medium has been developed whose active component is an alumina (AlOOH) fiber two nanometers in diameter. The nano fibers are dispersed throughout a cellulose/polymeric/ microglass fiber matrix resulting in a medium with 2 micron average pore size. A single layer, 0.8 mm thick, retains greater than 99 percent of 0.03 µm latex spheres or 0.025 µm size MS2 virus, justifying an absolute rating of 0.03 microns. It can be pleated to produce a high surface area cartridge suitable for higher flows or formed into a multilayer depth filter capable of filtering virus size particles to greater than 6 LRV. Its filtration efficiency for AC fine road dust exceeds that of literature values for microglass, meltblown and membrane filters with pore size ratings between 1 and 0.2 µm. Its dirt holding capacity for such dust is about twenty and sixty times greater respectively as compared to microglass and meltblown media. Its clean water flux (3.6 L/cm²/hr @ 0.5 bar) is typical of a 2 µm pore size and substantially greater than that of any of the abovementioned media.

The nano alumina filter is suitable for retention of all types of particles so far tested including humic acid, latex spheres, inorganic test dust, bacteria, virus, protozoa, endotoxins, DNA and RNA. The applicable particle size range is very wide, from a few microns down to several nanometers. High filtration efficiency as well as a high particle capacity can be expected even at moderate to heavy flow rates. This capability addresses a large number of applications, including turbidity and cyst

filtration from drinking water, prefilters for reverse osmosis purifiers, clarification of beverages, chemical and pharmaceutical processing, industrial waste treatment, swimming pools and clean-up of water base coolants.

References

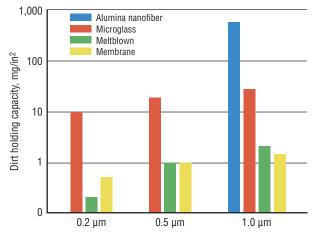
- * Guide Standard and Protocol for Testing Microbiological Water Purifiers, EPA, Report of Task Force, revised April 1987.
- † C. Shields, High Performance Microfiltration Media, Presented at American Filtration Meeting, Marriott, Baltimore/Washington Airport, Nov. 16-17, 2004.

About the authors

- ♦ Fred Tepper (corresponding author) is president of Argonide Corporation, Prior to founding Argonide, he spent a 40-year career at the Mine Safety Appliance Co., starting as a research scientist in air filtration and retiring as vice president of MSA and general manager of its Instrument Division. He is coinventor of the patent related to NanoCeram,® the filter medium discussed in this paper.
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Figure 5. Dirt holding capacity of media as a function of pore size ratings



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