A DRINKING WATER PURIFIATION SYSTEM FOR NUCLEAR REACTOR PERSONNEL

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Introduction and Summary– The chance that terrorists or state actors will strike at the water supplies of small groups of industrial, governmental or infrastructural (e.g. nuclear plant operations) is real. After recognizing the suspected plot of the microwave irradiation causing sickness of U. S. personnel in Cuba, it would not be far fetched for a state actor to consider the contamination of the drinking water of a nuclear plant. Even without intentional attempts there are several situations where nuclear plant drinking water could be unexpectedly contaminated.

Residential, public and industrial facilities that are dependent on municipal plant water are impacted by 5-6 boiling water advisories that occur each day in the U S. There are many factors that lead to such an advisory, such as loss of pressure in the distribution system, water line breaks, treatment disruptions and power outages. As an example, hurricanes that impacted Texas, the Gulf coast and Florida in 2017 and Hurricane Michael in 2018 caused multi-day shutdowns, resulting in bacterial contamination. They caused many illnesses and some deaths owing to Leptosporosis infections. Upsets and pressure changes in the piping of the distribution system leading to residences in Flint, Michigan are believed to cause shedding of Legionella bacillus from the biofilm, and a notable increase in Legionella disease.

In addition, there may be periodic, generally seasonal, microbiological or chemical contamination beyond the nominal operating performance of a municipal treatment plant, that would allow contamination beyond acceptable levels, and without detection. For instance, EPA requires coliform bacteria testing by municipal plants only on a monthly basis but real time bacterial testing is rarely done. And there is no required downstream testing for virus. Insofar as chemical contaminants, municipal plants provide monthly chemical assays. Assays on emerging contaminants of concern such as PFAS chemicals are not required. Yet recent studies show adverse animal health effects for PFAS. These long-chain perfluorocarbons, that are no longer in production are still found widespread in municipal water There is growing concern that GenX, its shorter-chain fluorinated carbon replacements, might also have adverse health effects. There is also concern about the ability of municipal treatment to effectively filter toxins from algae blooms.

The market for residential water treatment systems to complement the purity delivered by municipal plants continues to grow. After many deaths and hundreds of thousands sickened from Cryptosporidium in Milwaukee in 1993, EPA established tighter regulations for municipal water treatment plants but also established a test protocol and Guide Standard for home point of use microbiological purification devices. The Guide Standard was later modified to the NSF (National Sanitation Foundation) P231 microbiological standard that also includes larger point of entry

devices. It is generally recognized that safety from microbiological disease is best afforded when purifiers are used that meet this standard.

A point of entry system, (POE) called "CoolBlue-POE" developed by Argonide is first described at the 11th Annual CBRNe World Congress, Nov 2018, Orlando, Fl. The 8 gallons per minute device was first certified as an NSF P231 microbiological POE system in October 2018. To date there has been no other device that has passed this difficult specification as a POE. A smaller point of use system (CoolBlue®) was certified to P231 in Nov. 2015. We propose that the P231 protocol vets CoolBlue-POE for removal of biological warfare agents (BW) in the case of fresh water.

This white paper describes the technology and construction behind CoolBlue-POE. Briefly, we invented an electro adsorptive media that attracts and retains nanoparticles including bacteria, virus, many biological molecules, RNA and protein, without the adverse high pressure of membranes. When combined with ultrafine activated carbon, it can adsorb chlorine, lead and trace organics such as antibiotics, PCBs, PFOS, and PFOA. While not yet tested for chemical warfare agents, we believe it would be capable of filtering them.

One of the cartridges of the POE houses our sorbent called DEAL® that was tested separately for adsorption of radioisotopes from high level nuclear waste. In a single test, a 30 cm DEAL column removed 99% of Cobalt-60, and 92% of total gamma radiation (see data below).

Electropositive non-woven filters – In 2000 we invented a water purification filter based on aluminum oxide/hydroxide (γ-AlOOH) nanofibers, 2 nm in diameter and 250 nm long.[1] Electropositively charged γ-AlOOH filters are manufactured from non-woven media in two forms. The first non-woven form is where the γ-AlOOH is a nanosize fiber attached to a microglass fiber (Figure 1a). Polymeric fibers, primarily polyester plus cellulose are added for formability and pleatability. The nano alumina fiber content is optimized at 35 weight percent, so that the nanosize alumina fibers completely occupy the available surface of the 0.6 μm microglass fiber scaffolding, thus increasing the density of exposed electropositive charges that would collect electronegative particles in the pores of the media. The non-woven is finally covered in a layer of polymeric laminates to allow welding into pleats.

Powdered activated carbon (Figure 1b) is a second version of the non-woven media that provides a chemisorption function to the sub-micron particulate filter. [2] Although the pore size of the filter media can be varied from approximately 1 μm to 30 μm [2] a pore size in the range from 1 to 2 μm was selected for purifying drinking water from sub-micron particles. The filter media is about 0.8 mm thick for a drinking water filter, resulting in approximately 400-800 pores, a tortuous path that a particle must transit before exiting as filtrate. The media has a rapid dynamic response for adsorbing bacteria, virus and nucleic acids from biological solutions. Typically, 7 LRV (99.99999%) of bacteria (logarithm reduction value: $LRV=\log_{10}(C_{initial}/C_{final})$ where $C_{initial}$ and C_{final} are the initial and final concentrations of particles) and 5 LRV (99.999%) of viruses are retained by a pleated layer at a flow velocity of 1GPM/ft^2 at a ΔP of 2 psi.

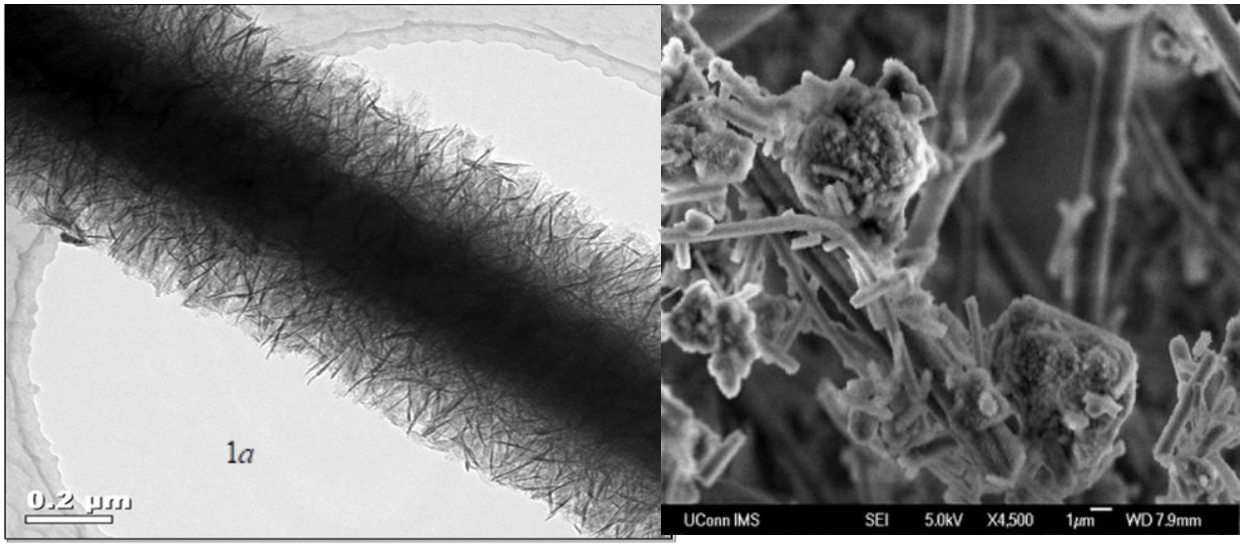

Photo courtesy of R. Ristau, IMS, Univ. of Conn.

Figure 1 a) Transmission electron microscopy (TEM) image of γ-AlOOH nanosize fiber attached to a microglass fiber; b) Scanning electron microscopy (SEM) image of powder activated carbon (PAC) with average particle size of 8 μm loaded into the NanoCeram media.

Both PAC and non-PAC media are manufactured under Argonide license by Ahlstrom LLC. AgIon, a silver zeolite is added to some grades and serves as a bacteriastat, improving bacterial performance. Argonide pleats the media and sells individual cartridges under the NanoCeram® trademark, while Ahlstrom sells the non-woven media under the Disruptor trademark. In water, the γ-AlOOH has high electropositive forces, with zeta potential ranging up to +50 mV between pH 3 and 8. The two-micron pore size allows a flow rate two orders of magnitude greater than an ultra porous membrane, consuming very little power. Due to the strong electropositive forces, the AlOOH filter could retain greater than 7 LRV of bacteria and 5 LRV of MS2 virus, as much or greater than ultraporous membranes.

In 2008, we reported [2] on the addition of powdered activated carbon (PAC) to the γ-AlOOH structure. The study showed that the PAC actually enhanced the retention of virus and other particulates without disaffecting other properties. The new PAC media has a dynamic adsorption rate of at least two orders of magnitude greater than that of granular carbon beds. Our conclusion was that γ-AlOOH-PAC had promise as a chem-bio filter for purifying water. From a commercial standpoint, we have found that 80% of our residential market prefers PAC filters rather than the single function γ-AlOOH microbiological purifier.

PAC as a Chemical adsorbent –

Halogens Nanoalumina can adsorb ultrafine and nanosize sorbent particles resulting in high dynamic efficiency. This can be seen with PAC vs granular carbon (GAC) and adsorption of elemental iodine. Figure 2 shows a breakthrough curve for the adsorption of 20 ppm of iodine

by a 25 mm diameter disc of filter media at a flow rate of 20 mL/min. At 0.5 ppm, iodine becomes unpalatable and also exceeds regulatory limits. A breakthrough curve is shown for the PAC media where approximately 0.85 liter of water was retained by the PAC disc to below the 0.5 ppm level. (Detection level ~ 0.1 ppm iodine). The data was also presented for 25 mm discs sectioned from the media of three different commercially available activated carbon filter cartridges. Their base weights are somewhat comparable to the PAC.

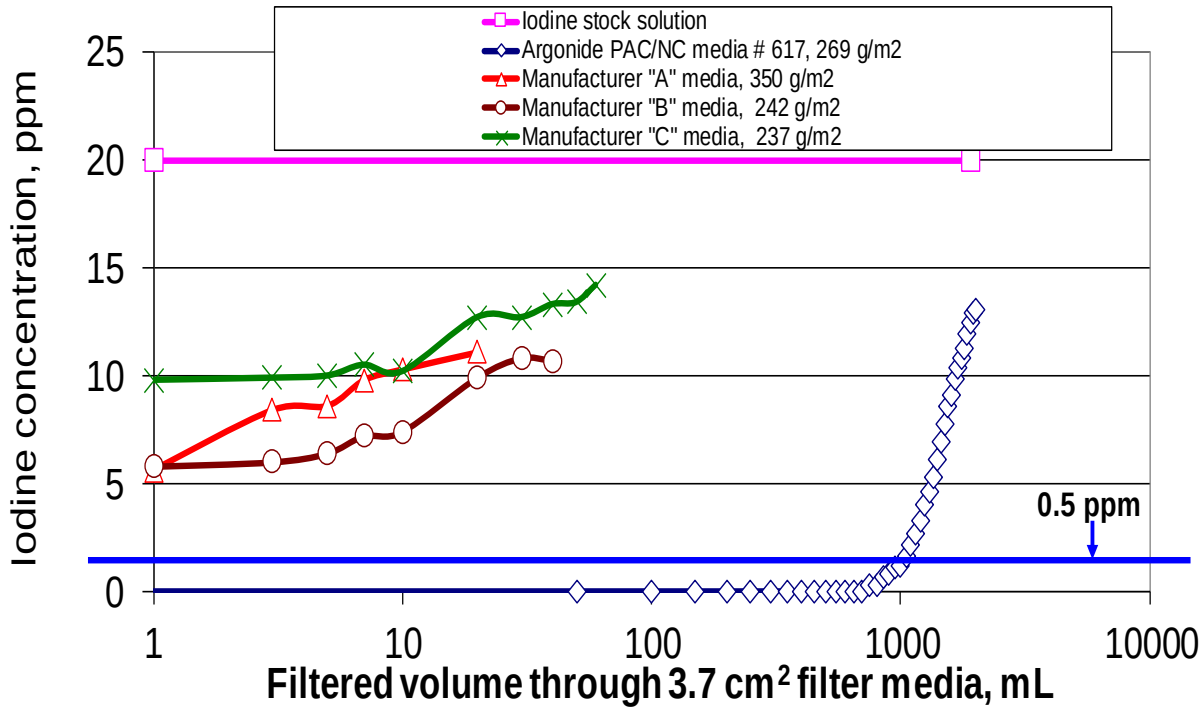

Figure 2 - Adsorption of 20 ppm iodine by a 25 mm diameter disc

A stack of three layers of the respective medias was tested under the same conditions (see Figure 3). In this case the PAC media retained approximately 3,800 mL to the 0.5 ppm level while the other medias retained no more than about 8 mL.

A similar test series compared GAC versus γ-AlOOH/PAC vs a chlorine hypochlorite challenge, which showed similar results. In this case, we used sodium hypochlorite to produce a 2 ppm solution of free chlorine. The flowrate was 16 mL/min through a PAC media (32% PAC) that was 25 mm in diameter. Chlorine input and output concentrations were measured by a Tracer (LaMotte, Inc) with a detection limit of 0.01 ppm. The test results with PAC were compared to three different manufacturers that were tested with iodine and presented in Figures 2 and 3. The results showed superior retention of chlorine by PAC media as compared to the other samples (see Figure 4). The adsorption capacity for the PAC was calculated as 350 mg Cl_2/g PAC to full saturation at input concentration of 2 ppm and flow velocity 10 cm/min.

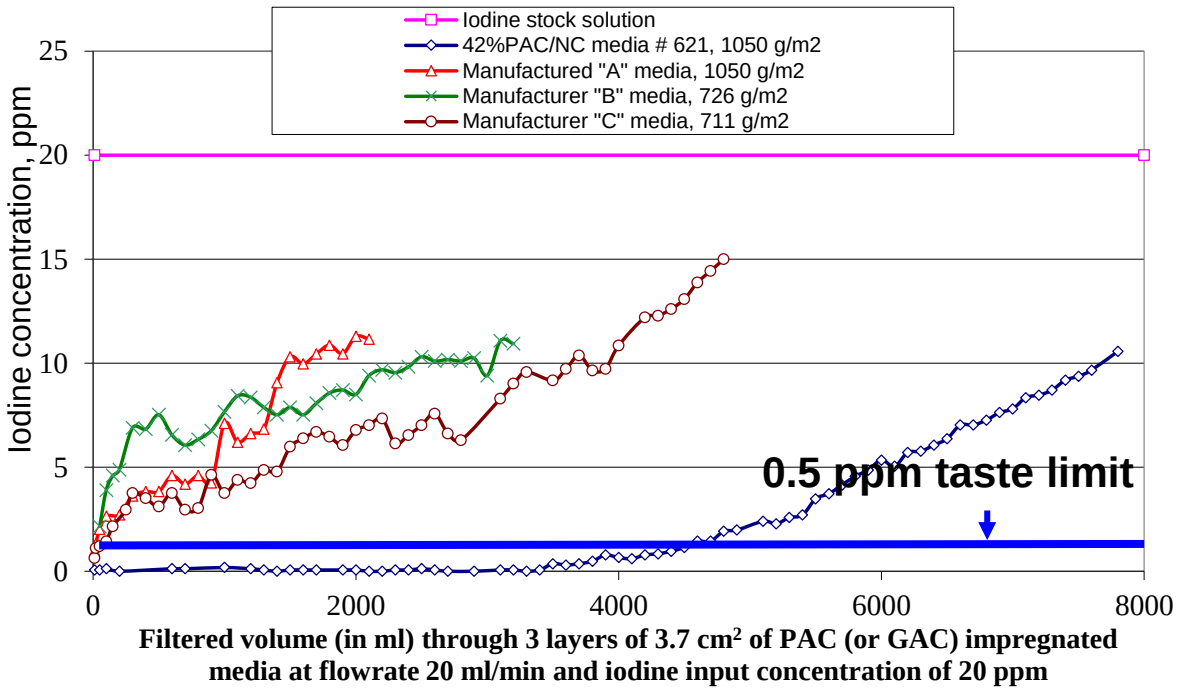

Figure 3 – Iodine adsorption by 3 layers of media

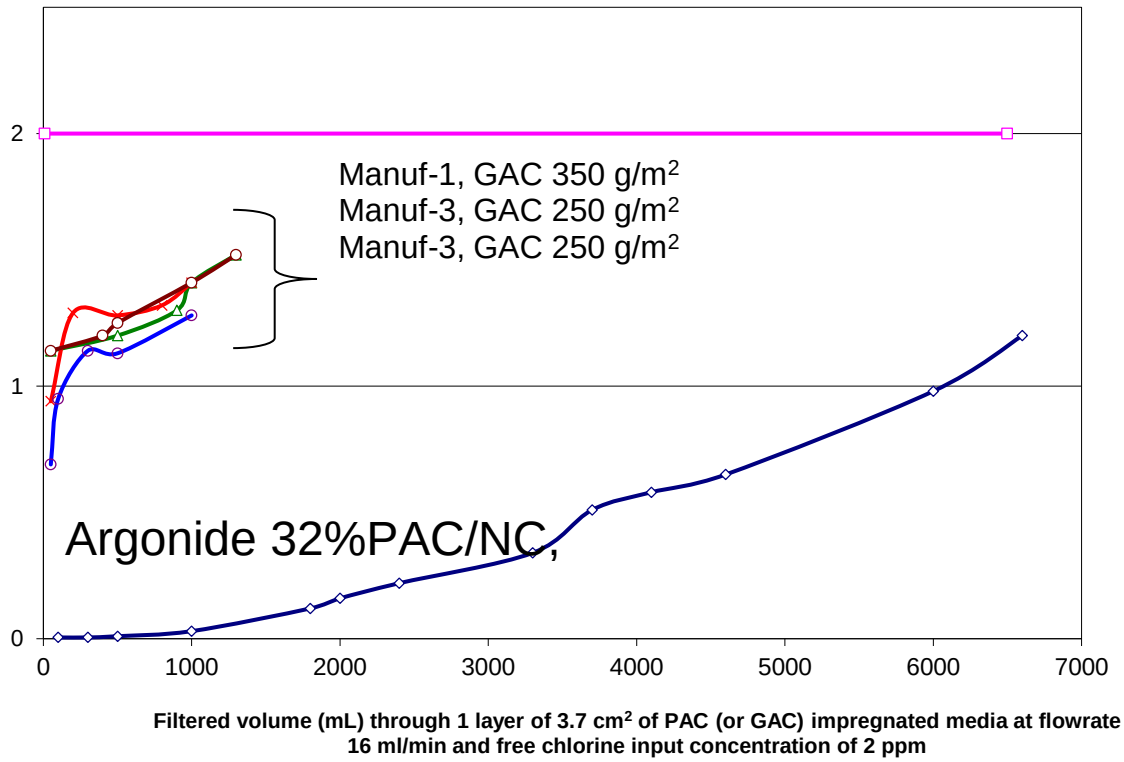

Figure 4 – Chlorine adsorption by various carbon media

Antimicrobials.

Endocrine Disruptors - A study on the adsorption of Penicillin G, BPA and Flumequine by PAC filter discs (47 mm diameter) was undertaken by the University of California.[3] It is attached as an appendix. The challenge concentrations were in the ppm range because the researchers were not equipped to assay the antibiotics in the ppb range. When challenged with a concentration of 2 ppm of Penicillin G at a flowrate of 1 GPM/ft^2, the entire antibiotic was removed up to 13 L of water. This equates to 281 gallons of water processed per ft^2 of media. Note that the flowrate and filter thickness were commensurate with a single layer of filter media operating at nominal flowrate. There are six layers of γ-AlOOH/PAC in the POE plus a carbon block plus carbon in the DEAL/carbon filter, ALL OPERATING IN SERIES.

PCB- Commercial production of PCBs in the US began in 1929 and continued until they were banned in 1979 after years of toxic effects of PCB exposure had been noted. PCBs were typically synthesized by chlorinating biphenyl with chlorine gas, substituting chlorine atoms for hydrogen atoms on the biphenyl molecule. Individual chlorinated biphenyl molecules are called congeners. Individual congeners are identified by the number and position of the chlorine atoms around the biphenyl rings. Theoretically, there are 209 possible PCB congeners ranging from the mono-substituted 2-chlorobiphenyl to the fully-substituted decachlorobiphenyl. Varying the conditions of this chlorination process produced different mixtures of congeners with different physical properties.

The NSF test method involves a PCB challenge of a 10 µg/L congener mixture called Aroclor 1260. The "12" equals the number of carbon atoms and "60" equals the percent of chlorine by mass in the mixture. Aroclor 1260 contains a higher degree of chlorination of the biphenyl functional group (congeners in the penta, tetra, hexa, hepta, octa, etc.) (Harris, 2010). Arochlor 1260 contains congeners 135, 151, 147, 149, 153, 168, 174, 180-193.

Testing - A 47-mm diameter sample of PAC and non-carbon nanoalumina were tested separately at Pace Analytical for their ability to remove 209 PCB congeners from a spiked solution containing a total PCB level of 20 µg/L (0.02mg or 20,000 ng). This concentration of 0.0208 mg/L was double the NSF challenge of 0.01mg/L and included congeners that are not contained in the Arochlor 1260. The experimental plan was to test the full range of PCBs and additionally test for the removal of congeners with a lower degree of chlorination that the NSF Challenge Arochlor 1260 included.

Each disc was subjected to 1 liter of the spiked solution at a flow rate of 65 ml/min (equal to 1 GPM/ft^2). This is equivalent to 44 gallons through a 2.5"x10" cartridge (450 in^2 filter surface area). USEPA Method 1668A was used (NSF uses EPA 505) with specified reporting limits ranging from 0.250 to 3 ng/L depending on which chlorinated biphenyl congener is being tested. The challenge was continuous rather than giving the filter a chance to rest. The detection limits in this set of data corresponds to 0.25 to 0.75 ng/L. Table 1 lists the 10 congener groups, the influent

challenge concentration, and the effluent concentrations for carbon and non-carbon nanoalumina materials.

Both NC and PAC filters were able to remove the larger congener groups where the Arochlor 1260 would fall. The NSF challenge is 0.01 mg/L or 10,000 ng/L and the NSF requirement effluent is 0.0005 mg/L or 500 ng/L, while allowing the filter to rest between adsorption cycles. The samples were able to remove double the NSF concentration with very high filtration efficiency. Moreover, these tests were done with no on/off cycling, which should lead to even better removal rates. The fact that nanoalumina was capable of filtering PCBs was not expected, let alone that it outperformed the PAC. The mechanism may be related to its high zeta potential that may play an important if not exclusive role in removing PCB congeners. The data on halogens, endocrine disruptors, and PCBs are highly suggestive that PAC is a superior method for filtration of trace chemical agents from drinking water.

Table 1 - Filtration of PCB Congener Groups

Congener Group	ng/L influent	PAC/NC ng/L, effluent	NanoCeram ng/L, effluent
Total monochloro biphenyls	158	2.36	0.377
Total Dichloro Biphenyls	629	0.85	Nd
Total Trichloro Biphenyls	1260	Nd	Nd
Total Tetrachloro Biphenyls	4490	Nd	Nd
Total Pentachloro Biphenyls	4870	Nd	Nd
Total Hezachloro Biphenyls	4460	Nd	Nd
Total Heptachloro Biphenyls	2460	Nd	Nd
Total Octachloro Biphenyls	1810	Nd	Nd
Total Nonachloro Biphenyls	473	Nd	Nd
Decachloro Biphenyls	187	Nd	Nd
Total PCBs (ng/L)	20797	3.21	0.377

"nd"= non-detected

DEAL - In 2013, we began the development of a γ-AlOOH media we call DEAL®. We coated diatomaceous earth, a naturally occurring high surface area silica with γ-AlOOH.[4] High resolution transmission electron microscopy (HRTEM) showed that (Figure 5) the alumina was deposited as two-dimensional (2D) quantum-sized γ-AlOOH structures, developing high surface area. This new form of electropositive media, while a powder had a high capacity for adsorbing electronegative particles (and some electropositive ones too! (for example *fr*-virus)). We developed tubular porous plastic blocks consisting of DEAL powder and polymer binders. This gave us the option of blending the powder with other additives such as activated carbon, AgIon (a bacteriastat), a lead adsorbent, or iron oxide/hydroxide, a sorbent for arsenic, etc.

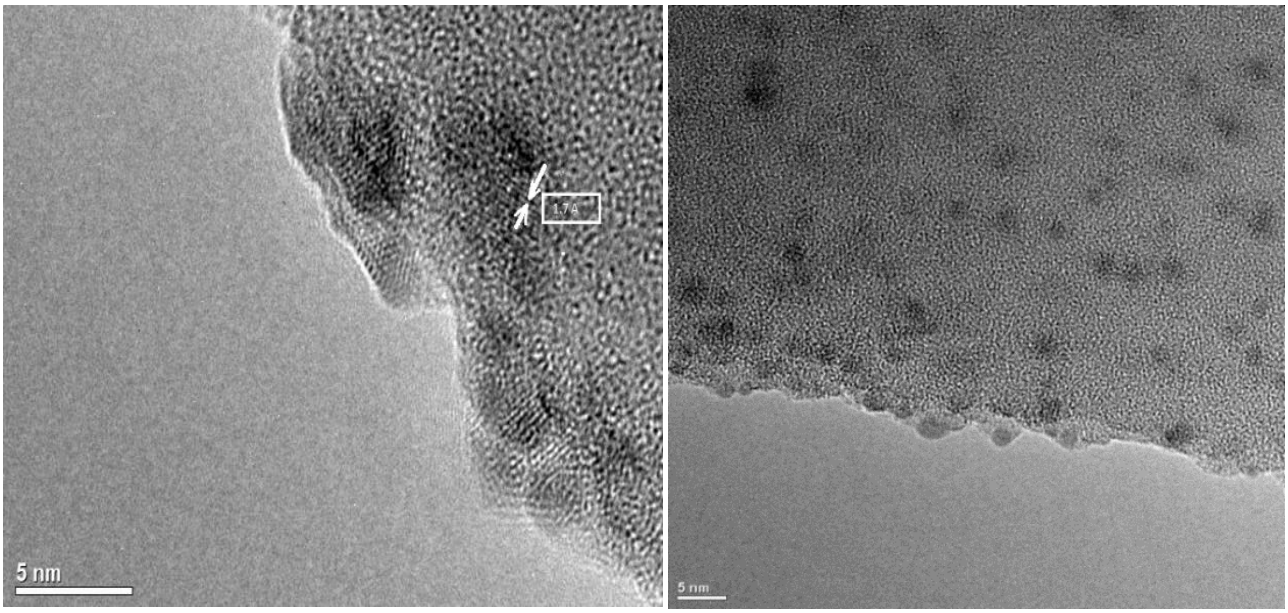

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Figure 5 –TEM characterization of 2D γ-AlOOH coating: *a*) HRTEM image of the 2D γ-AlOOH crystallites with atomic resolution; *b*) HRTEM image of the edge and surface coverage of the diatomaceous earth particle by the 2D γ-AlOOH crystallites

DEAL as a Radioisotopic adsorbent -The growing volumes of liquid nuclear waste poses a significant cost to the nuclear industry. A recent announcement by the DOE is that Nuclear power plants will be retaining their wastes for the foreseeable future and the Yucca Flats site is no longer being considered for consolidating wastes, increasing the number of domestic targets for terrorists for decades. The Savannah River site (SRS) has an inventory of approximately 37.1 million gallons of high-level waste (HLW). Many of the tanks at Hanford and SRS are leaking into the groundwater. The current Department of Energy's estimated cost for retrieval, treatment and disposal of DOE generated waste exceeds $50 billion, to be spent over several decades. Several of radwaste metal ions, such as cesium and strontium can be adsorbed by ion exchange resins. However, removing or concentrating soluble transition metals such as Manganese-54, Cobalt-58 and Cobalt-60 or their colloidal oxides and hydroxides is very difficult.

A test of DEAL with radioisotopes was done at the Brunswick Nuclear Plant in North Carolina. The test was performed on off-standard water that could not be reprocessed by plant systems and needed to meet specific guidelines for discharge. Analysis noted that there were traces of cesium and cobalt in the water (Table 2). In a multiple test series, several ion exchange resins, along with DEAL were tested in order to evaluate methods for cleaning the water. The DEAL experiment involved adding sodium hydroxide to raise the pH to 7.8, thereby favoring the conversion of soluble radioactive metals to form colloidal oxides and hydroxides. The neutralized solution was passed through a column containing 50 mL of packed DEAL60 (coated 60-micron DE). The glass

column was approximately 300 mm long and 15 mm in diameter. The flow rate was approximately 10 mL/min and the detection time duration was 15 minutes.

Table 3 shows analytical and radiochemistry measurements of the effluent. The results of radiochemistry measurements were converted to a dimensionless quantity (that is, to the dilution factors) of part-per-trillion (ppt) level for input concentrations and part-per-quadrillion (ppq, $1{:}10^{15}$) for filtered water. For example, Table 2 shows the activity of Co-60 as 4.591 nCi/mL that converts to $4.054 \cdot 10^{-15}$ g/mL or 4.054 ppq.

During the course of the tube test it was noted that a greenish color band, approximately 4 mm high formed at the influent (note- cobalt oxides and hydroxides are colored green or greenish-blue) and this color advanced through the first 40 mm of the column as the test proceeded, suggesting that the colloidal radioisotopes were concentrated in that 40 mm of sorbent.

Table 2- Raw Water Chemistry at the Brunswick Nuclear Plant in North Carolina

Nuclide	Activity (nCi/mL)	Mass of 1 Ci,[a] mg	Mass fraction, ppt[b]
Mn-54	0.1171	0.129	0.015
Co-58	0.03508	0.0314	0.0011
Co-60	4.591	0.884	4.06
Zn-65	0.1599	0.121	0.0193
Cs-134	0.03513	0.773	0.0276
Cs-137	1.030	11.565	11.91
Total Gamma Activity	5.968		16.033

Notes: a) 1 Ci=$3.7 \cdot 10^{10}$ Bq/ln(2)$N_A \cdot t_{1/2}$ (s) where N_A is Avogadro constant and $t_{1/2}$ is half-life in seconds; b) part-per-trillion (ppt, $1{:}10^{12}$)

Table 3 – Removal efficiency of radionuclides from raw water

Nuclide	Activity (nCi/mL)	DEAL60, pH7.8 Activity (nCi/mL)	Removal efficiency, %
Mn-54	0.1171	0.00703	94%
Co-58	0.03508	Not done	
Co-60	4.591	0.04994	98.9%
Zn-65	0.1599	Not done	
Cs-134	0.03513	0.01451	59.4%
Cs-137	1.030	0.03774	63.4%
Total Gamma Activity	5.968	0.4489	92%

The results showed that DEAL adsorbed 92% of the total gamma activity. A significant cause of the reduction was 98.9% removal of Cobalt-60, plus removal of Cs-137. This suggests that DEAL's presence in a water purifier can act as an adsorbent of certain radioisotopes, such as those

that form metal oxides and hydroxides in neutral solution (transition metals, rare earths, trans uranium elements).

Natural Organic Matter and P231 Testing - In addition to removing toxic chemical, microbiological and radio isotopic agents from drinking water sources, the water purifier must remove background materials that would interfere with the ability of the purifier to perform its mission. A major example is NOM (Natural Organic Matter). Membranes (UP, NP, RO) are notorious for being easily clogged by NOM. NOM are also problematic in that many of them are hydrocarbons that are readily converted to carcinogenic halogenated hydrocarbons when subsequently sanitized with chlorine. Another interferent is insoluble particulate. The NSF P231 protocol and USEPA Guide Standard [5] addresses the test requirements for a microbiological filter system for a POU or POE, where the filter must remove respectfully 6 LRV (or ≥99.9999%) of bacteria, 4 LRV of MS2 virus and 3 LRV of cysts. The mechanical filter unit has to be tested for a duration of 10.5 days. There are few systems that have been P231 certified for POU, and only one (Argonide's) for POE.

We achieved certification of P231 for POU in a system called CoolBlue, capable of lead (1000 gallons), chlorine and microbial removal. A three cartridge POE system that uses two of the technologies described in the present work is certified to the USEPA Guide Standard [5] by the International Association of Plumbing and Mechanical Officials (IAPMO) [6]. The TOC (total organic carbon) and turbidity simulate high NOM and particulate. NOM is significantly adsorbed by AlOOH, and competes with virus for sites on the media

We achieved certification under P231 for a POU (single faucet) microbiological pure water purifier in November 2015. The system, CoolBlue®, is capable of the required microbial reduction while also reducing lead up to 1000 gallons, as well as Class 1 particulates. Most of our initial CoolBlue clients were residential distributors. However, one was a supplier to the US government, who also expressed interest in a larger, Point of Entry (POE) P231 system. We decided to develop it, not only to satisfy our customer, but also for residential whole house use, medical, hospital (with a focus on legionella) and nursing homes, school and child care centers. We hope that once certified it would be of interest for certain chemical/biological/radiological (CBR) drinking water purification defense systems. The POE system, which we have named CoolBlue-POE, has been P231 certified in October 2018.

Figure 6 is a photograph of the POE system; a schematic of the unit is in Figure 7 and a design is in Table 4.

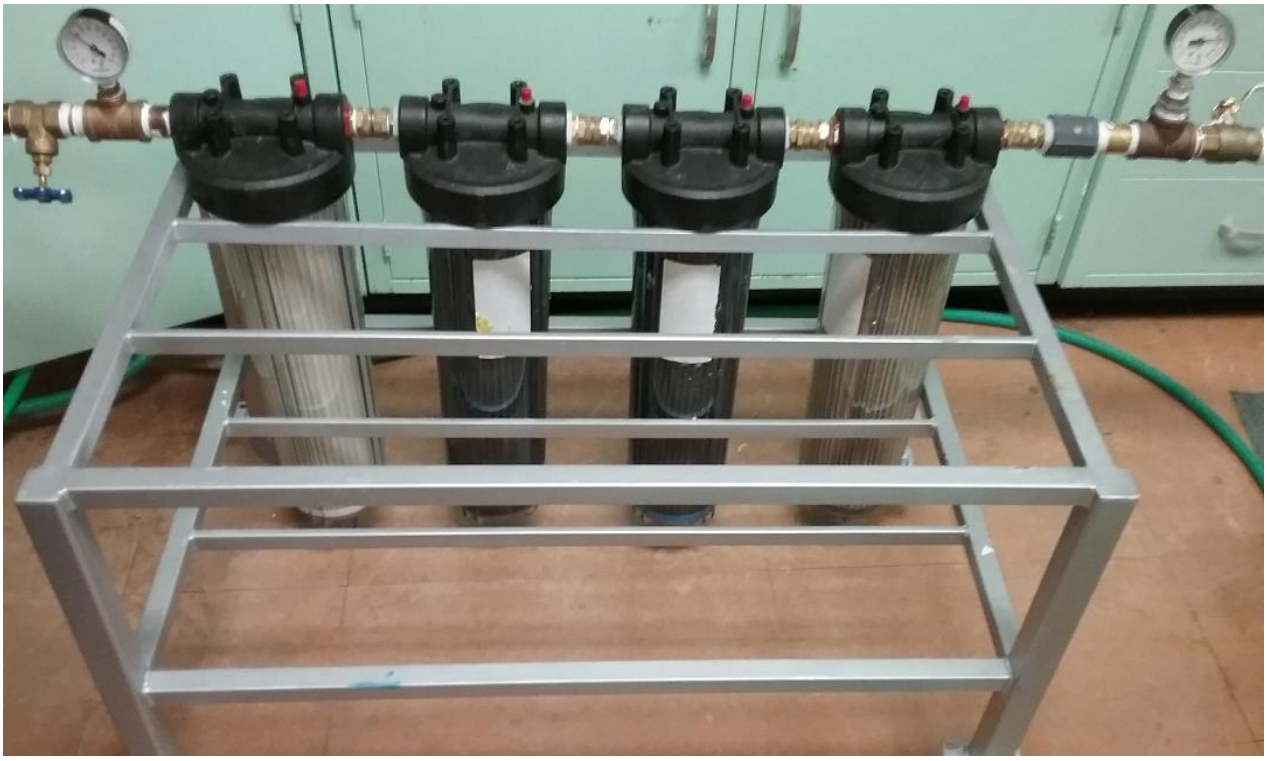

Figure 6 - A photograph of the CoolBlue-POE system

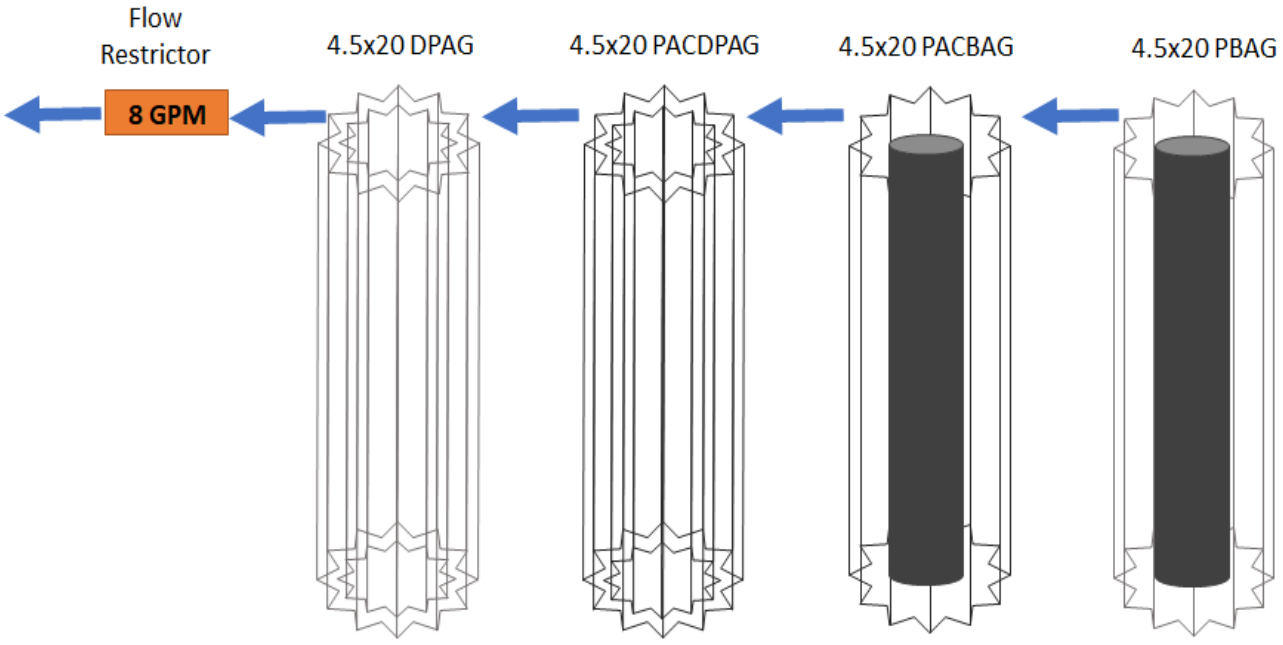

Figure 7– Schematic of CoolBlue-POE

Table 4 - Design of CoolBlue-POE CBR water purification system

Function	Part description	Outer layer part description	Inner layer part description	Characteristics
Prefilter	Pleated water filter cartridge with a core carbon block	Pleated 4.5"x20" γ-AlOOH fibrous media with Ag ion	15%DEAL/ PAC 2.5"x20"carbon block	surface area=10 ft^2
Stage 1	Pleated water filter cartridge with a core carbon block	Pleated 4.5"x20" γ-AlOOH/PAC fibrous media with Ag ion	15%DEAL-porous plastic/PAC 2.5"x20"carbon block	surface area=10 ft^2
Stage 2	Double pleated water filter cartridge	Pleated 4.5"x20" γ-AlOOH/PAC fibrous media with Ag ion	Pleated 4.5"x20" Fibrous γ-AlOOH PAC media with Ag ion	surface area=15 ft^2
Stage 3	Double pleated water filter cartridge	Pleated 4.5"x20" γ-AlOOH fibrous media with Ag ion	Pleated 4.5"x20" Fibrous γ-AlOOH media with Ag ion	surface area=15 ft^2

Environmental, Health & Safety issues-

There are significant concerns about nanofibers that the products might shed, particularly if they are fibrous. However, γ-AlOOH nanofibers also known as the mineral fibrillated boehmite, is used as a thickener in food products, as an analgesic and in the treatment of peptic ulcers. [7-10] The U.S. Army Public Health Command Water Supply Management, Aberdeen Proving Ground in their FACT SHEET 31-015-0211 opinion on *Alumina Nanofiber Filters in Drinking Water Treatment* concluded that "Boehmite (AlOOH) nanofibers can generally be considered safe. Boehmite (AlOOH) has long been used as a vaccine adjuvant (i.e., an added ingredient to improve vaccine efficacy) and it has been used in analgesics (i.e., pain relievers)". [11]

Microcrystalline boehmite is an important component of vaccines and is classified as an adjuvant for binding antigens. Alhydrogel, first described in 1926, remains the only adjuvant used in human vaccines licensed in the United States. [8] It is used in diphtheria, tetanus and pertussis vaccines as well veterinary vaccines. Alhydrogel consists of primary particles with many of the same characteristics is as the boehmite fibers in nanoalumina. Once injected with the serum into the muscle, the citrate ion in the bloodstream solvated it, it is carried to the kidney and solvated. [10] Approximately 2 billion doses have been used in humans and countless billions more in farm animals.

ADDRESSING THE CBR TERRORIST THREAT

The NSF P231 protocol addresses the test requirements for a microbiological point of use or point of entry system where the filter must remove respectively ≥99.9999% of bacteria, ≥99.99% of MS2 (electronegative) virus and ≥99.9% of cysts under diverse conditions downstream from a municipal plant. The mechanical filter has to be tested for a duration of 10.5 days. During the last 4.5 days of testing, the challenge water has a high Ph (9.0), high TOC (>10 ppm), high total dissolved solids (TDS=1500 ppm), high turbidity (>30 NTU) and low water temperature T= 4°C). The U S Army has a similar protocol (P248) that includes testing with an electropositive virus, *fr*. Since our filter media γ-AlOOH, is electropositive, one would expect that it would be ineffective in filtering *fr*. On the contrary, our γ-AlOOH, γ-AlOOH/PAC, and DEAL media filters *fr* to >99.99%.

In developing the POE and to a lesser extent the POU, powdered activated carbon beds were used in concert with other components of both systems to meet P231. In hindsight we now recognize these PAC carbon beds provide strong adsorption capability, suitable as state-of- the art-filters for retaining biological toxins and chemical warfare agents such as mustard, VX and G agents.

Characteristics of Microbiological/Biological toxin/chemical toxin/radiological toxin threats

As a barrier against BW agents- Many publications address the subject of biological warfare agents as threats to potable water. Burrows[12] lists anthrax, cholera, plague, salmonella, shigellosis and tularemia as potential bacterial waterborne threats, and only enteric virus as a viral threat. They also suggest that Cryptosporidium oocysts could be weaponized. They conclude that the practical use of any BW agent required to cause adverse health effects is of such magnitude as to be closest to the consumer. For instance, vulnerable points might include the distribution system and not large bodies of water.

Based on EPA P231 certification, we presume that the POE system provides state-of -the-art protection against waterborne microbiological warfare threat agents, presuming the system is situated downstream of a suitable municipal system.

As a barrier against biotoxins- Algal blooms such as red tides produce a number of neurotoxins such as saxitoxins, that are responsible for the illness known as paralytic shellfish poisoning (PSP). Blue-green algae (cyanobacteria) also produce freshwater toxins. Burrow and Renner list several biotoxins (Aflatoxin, Botulinum, Ricin) [12] that have been weaponized and are also waterborne threats, and several others (microcystins, Saxitoxin, Staphylococcal enterotoxins, T-2 mycotoxins and Tetrotoxin) that are threats but may not have been weaponized. Of these, Burrow and Renner list some (Botulinum, Ricin, SEB, T-2, Saxitoxin)[12] that are removed or are marginally removed by individual charcoal or point of use water purifiers. These devices offer less charcoal protection than a small fraction of a single PAC layer and would therefore be adsorbed by our POE system.

All of the biotoxins are complex organic molecules, for instance proteins such as botulinum, or polyaromatic compounds such as Aflatoxin or Anatoxin A. Saxitoxin A and Tetrodotoxin have several hydroxyl groups and would be highly electronegative and readily adsorbed by γ-AlOOH media (NanoCeram and DEAL). NanoCeram and DEAL have a high capacity for proteins. [13-15]

Trace Organics - A study on the adsorption of three endocrine disruptors by PAC filter discs (47 mm diameter) was undertaken by the University of California. [3] and is included as an Appendix. The POE system (see Table 4 and Figures 6 and 7) consists of 28 ft^2 of PAC media (3 layers) and of 28 ft^2 of nano fibrous AlOOH media (3 layers) with total surface area of 46 ft^2 of PAC media (total of 6 layers). This equates to 16,000 gallons of antibiotics laden water processed by the system. Similarly, there was quantitative removal of high concentrations (3 L to detection at a concentration of 10 mg/L) of BPA using a single PAC disc. Flumequine is an antibiotic that was also quantitatively adsorbed by a 47 mm PAC disc when challenged with 10 ppm solution up to 3 L of challenge water. The flow characteristics of the U Cal study was equivalent to that employed in the P231 testing protocol. This makes the curves in the figures of the U Cal study directly comparable to the performance data described for γ-AlOOH/ PAC media in the POE.

Note that there are the following carbon containing layers in series in the flow stream:

1- Six layers of γ-AlOOH and γ-AlOOH/PAC (Two Double Pleats cartridges)
2- Two layers of DEAL powder, blended with PAC in a porous polymeric block

The result is that the POE system offers five of highly efficient carbon in series plus three γ-AlOOH layers. We have measured the output of 2 ppm free chlorine input after 35,000 gallons of continuous challenge at 50%-on/50%-off cycle as < 0.01 ppm!

As a barrier against CW agents - The CWA's can be classified into four main classes: 1) sulfur mustard gases (H, HD) and nitrogen mustards (HN1, HN2, HN3); 2) Lewisite; 3) four nerve agents, VX, GA, GB and GD and 4) the blood agent cyanogen chloride, CK. The CW agents are found in the liquid state under ambient conditions. The vapor pressure and volatility increase in the order VX<GA<HD<GD<Lewisite <GB. Unlike GA and GB, HD, Lewisite, VX and GD are associated with low water solubility. [16] VX is the most persistent CW agent as given by its low volatility and Henry's Law constants. Moreover, it is most resistant to water hydrolysis and hence to degradation in aqueous media. Despite their low solubilities, HD and Lewisite are rapidly hydrolyzed in water. The threat from waterborne chemical agents is therefore greatest with VX.

Protection against the above-mentioned liquid agents (other than the blood agents) is usually accomplished with activated carbon, as in respirators or collective protective atmospheric filters. The multilayer PAC sorption and particulate filter layers of our POE would provide protection against these agents.

As a barrier against radioisotopes- The possible sources of radioisotope contamination include: state actors (e.g. polonium poisoning by Russian agents), theft of high-level liquid nuclear waste from a nuclear plant or extracting radioisotopes from orphan medical irradiation devices. (Cs-137, Sr-90, Co-60).

We envision that the two main mechanisms for removal of radioisotopes is the filtration of metallic radioisotopes either in metallic form as nanoparticles, as oxides or hydroxide (gels-like, sub-micron) particles. Our POE has six separate layers in series array, each capable of removing nanosized particles with high efficiency.

Data presented above show that DEAL, a component of the POE, has the capability to adsorb Cobalt-60 with high efficiency which we had anticipated, plus other metal oxides or hydroxides (Manganese) that we had anticipated. We had not anticipated the significant reduction of cesium. Its reduction could have occurred by ion exchange adsorption onto the AlOOH.

Many of the radioisotopes (rare earths, transuranium elements, transition metals) are likely to be found as particles in their elemental state or as their oxides or hydroxides. Their particle sizes are likely to be sub-micron, probably nanosized, and perhaps gel-like. Our POE may be suitable for collecting these kinds of contaminants. It is constructed of a series array of six highly efficient nanosized particle filters.

Summary- The CoolBlue-POE system provides several different filtration mechanisms- particle impaction, electroadsorption, van der Waals adsorption and ion exchange, and does it redundantly through a series array of filters. The result is a highly protective CBR filter capable of high flow rate (8 GPM). It has been certified as a microbiological filter.

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APPENDIX

Removal of Trace Pharmaceuticals and Endocrine Inhibitors Using Disruptor® PAC Technology

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ABSTRACT

An Associated Press investigation shows "A vast array of pharmaceuticals - including antibiotics, anticonvulsants, mood stabilizers and sex hormones - have been found in the drinking water supplies of at least 41 million Americans" (3). Contamination of our water by these compounds is of concern for the overall health and proper development of all forms of life. Finding effective methods of removing these compounds from waste and potable water is a significant challenge for existing filtration technology. Test data from The University of California, Irvine indicates that Ahlstrom's Disruptor® PAC, electroadsorptive technology containing powdered activated carbon, can remove representative trace pharmaceuticals, and phenolic monomers. This paper will present new data showing the removal efficiency and loading capacity of these compounds.

INTRODUCTION

The recent findings of pharmaceuticals in drinking water have been widely published. Studies have shown up to 41 million Americans in 24 major cities are impacted.(6) The same studies list over 30 major cities that have not tested for pharmaceuticals, have results pending, or have unspecified results.

Many of the publicized studies have been from metropolitan areas, where the source of pharmaceuticals could be from human consumption. The overuse of antibiotics of in cattle, chickens, and pigs is also a concern to the FDA (4) but studies of rural water supplies appear to have received less attention.

In previous studies, The Disruptor® technology has been shown to remove bacteria, virus, Cysts, endotoxin, and other organic and inorganic materials (2)(7). The purpose of this study was to determine if the Disruptor® PAC technology could remove representative trace pharmaceuticals, and phenolic monomers from drinking water.

METHOD

Flat samples of Disruptor® PAC grade 4604 were placed in a 47 mm diameter sample holder exposing a sample surface of 38 mm in diameter. While pharmaceuticals have been found in water sources in the range of µg/L, it is very difficult to test in this range. Samples were challenged at 2 or 10 mg/L to simplify testing and accelerate failure. The flow was 50 ml per minute or 1 gpm/ft2.

The concentrations of trace pharmaceuticals of interests, i.e. Penicillin G, Bisphenol A and Flumequine, were determined by HPLC (Agilent 1200), equipped with a Diode Array Detector, and a Phenomenex Gemini C_{18} column (5µm, 250 × 4.6 mm). The isocratic mobile phase was a mixture of methanol and pH 3.0 KH_2PO_4 buffer with a ratio of (a) 60:40 for Penicillin G; (b) 70:30 for Bisphenol A; (c) 60:40 for Flumequine. The flow rate was 1.0 mL min^{-1} and the detection wavelength was 232, 227 and 224 respectively.

RESULTS – Penicillin G

Penicillin G was used as a representative antibiotic. It was first studied using a challenge solution of 2 mg/l. Figure 1 shows that the entire antibiotic was removed from up to 13 L of water. This equates to 281 gallons of 2 mg/L water processed per ft2 of media. At more typical concentrations in the range of 2 µg/L, every square foot of media could theoretically process up to 281,000 gallons, if the water was free of other competing compounds.

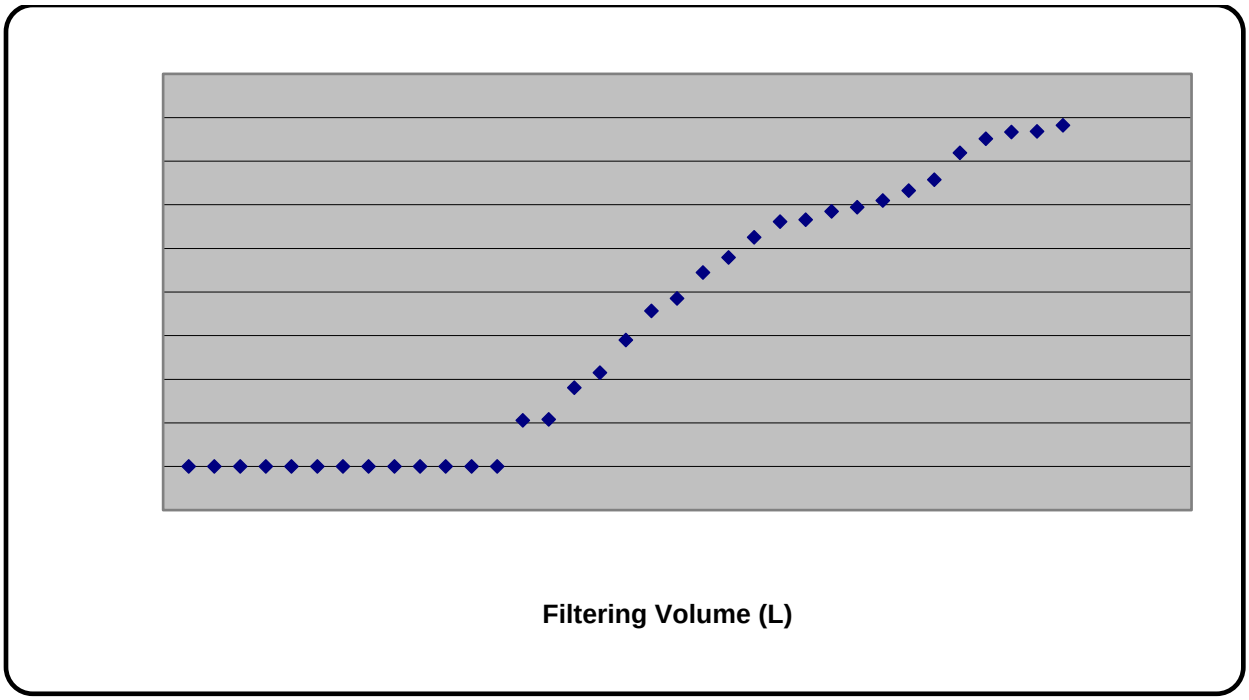

Figure 1: Penicillin G Removal from Water at a Concentration of 2 mg/L

Figure 2 shows the removal of Penicillin G from challenge water at a concentration of 10 mg/L. While this study is slightly less accurate, it required significantly less testing. At this elevated concentration, it's difficult to determine the exact point where the filter begins to fail but the 50% breakthrough point is at approximately 4 L. The 50% breakthrough point can be estimated to be 430,000 gallons for a ft2 of media when challenged with 2 µg/L. These results are consistent with results obtained at lower concentration.

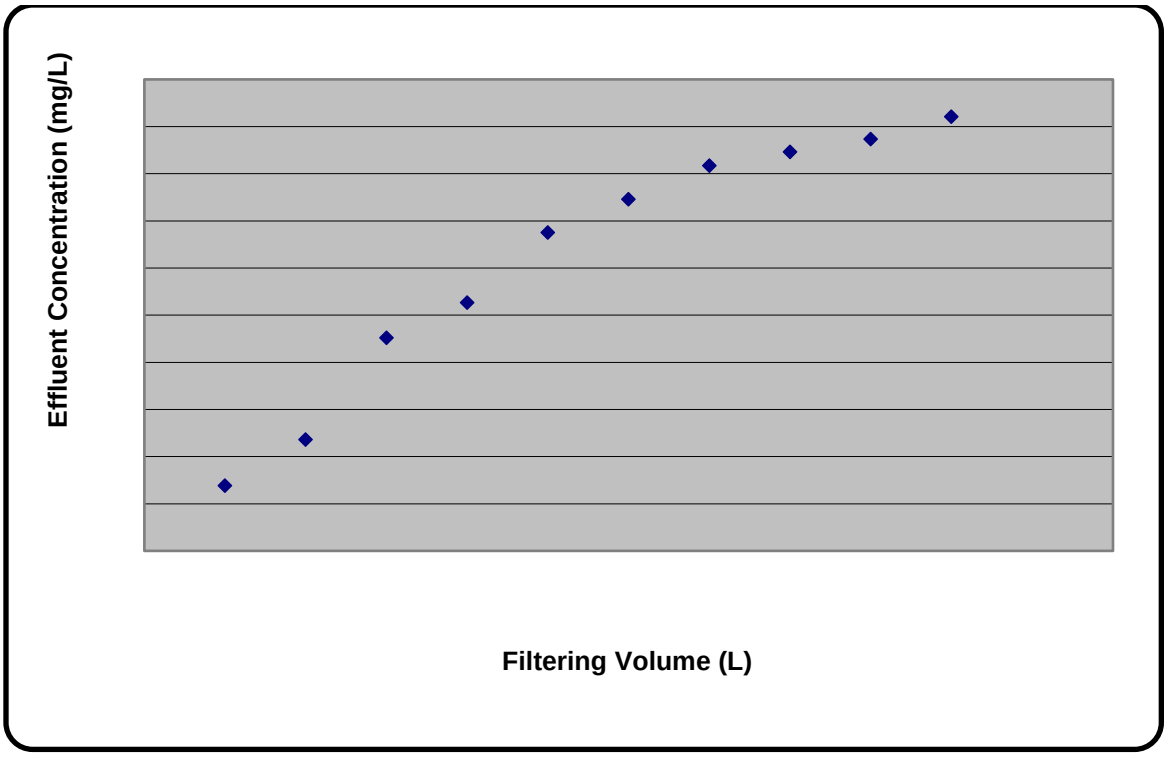

Figure 2: Penicillin G Removal from Water at a Concentration of 10 mg/L

RESULTS – Bisphenol A

Bisphenol A is a monomer used in the manufacture of polycarbonate and epoxy resins. It is known to be estrogenic and it is a concern in relationship to reproduction, heart disease, diabetes, and in other areas. The effects of Bisphenol A are a highly controversial and have been studied in great detail in other publications.

Figure 3 shows the removal of Bisphenol A from water using the Disruptor® PAC technology. Laboratory testing demonstrated complete removal of Bisphenol A from 3 L of challenge water at a concentration of 10 mg/L. This equates to treating 322,000 gallons per ft2 of media with a challenge solution concentration of 2 µg/L.

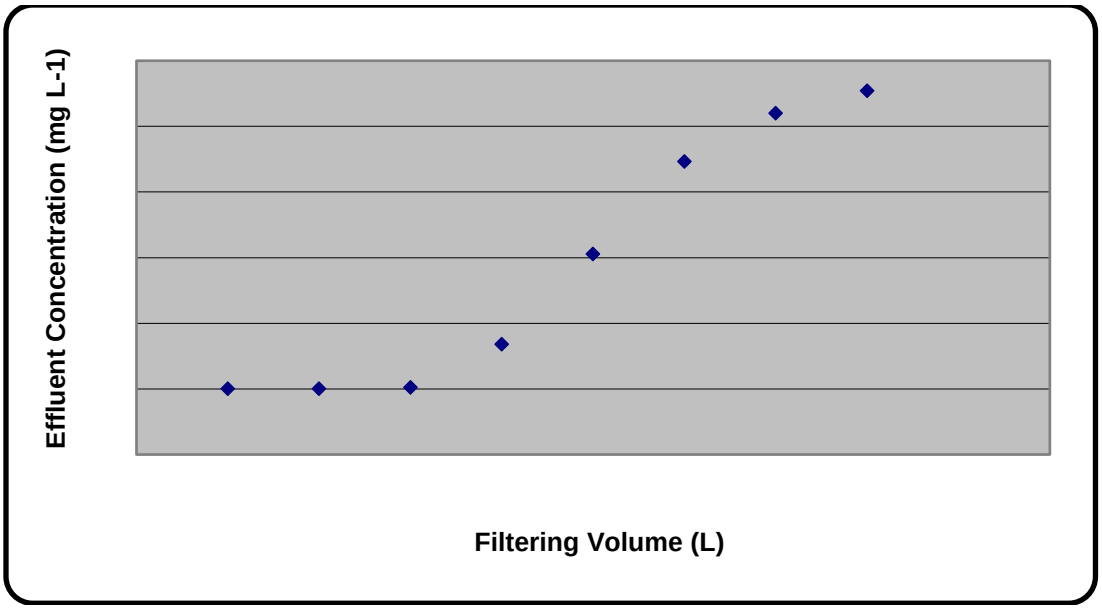

Figure 3: Bisphenol A Removal from Water at a Concentration of 10 mg/L

RESULTS – Flumequine

Flumequine is a chemotherapeutic antibiotic. It was originally a concern regarding musculoskeletal disorders such as tendon rupture. More recently, it was implicated in DNA damage, ocular toxicity, liver damage, and anaphylactic shock. It has been taken off the market but was tested as being representative of the floroquinolone drug class. Figure 4 shows the removal of Flumequine from water. Disruptor® PAC technology completely removed Flumequine from 3 L of challenge water at a concentration of 10 mg/L. This equates to treating 322,000 gallons per ft2 of media at a concentration of 2 µg/L.

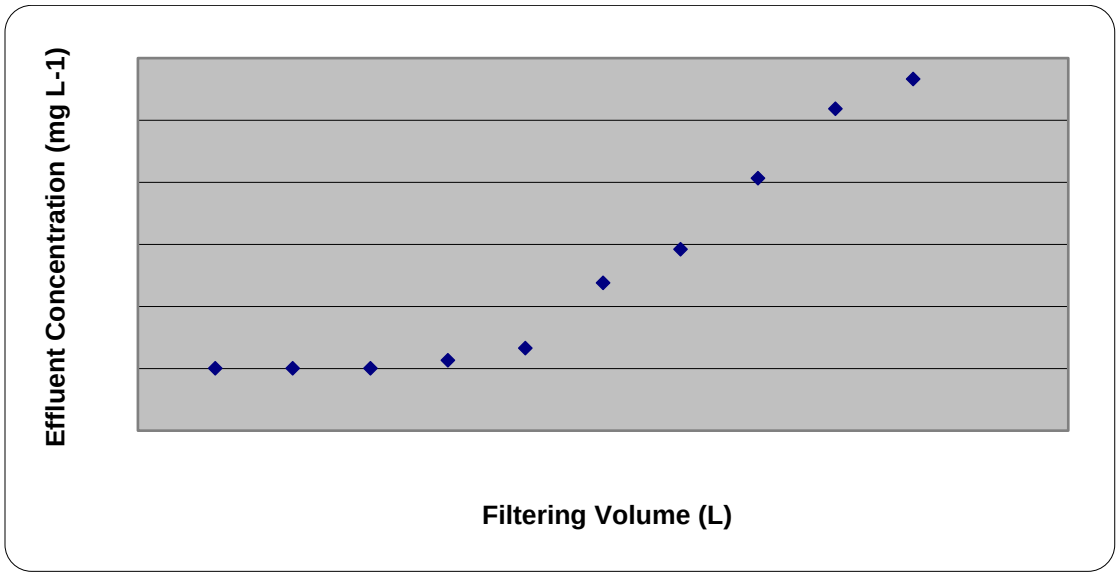

Figure 4: Flumequine Removal from Water at a Concentration of 10 mg/L

CONCLUSIONS AND RECOMENDATIONS:

The presence of trace pharmaceuticals in drinking water is an area of growing concern, with serious implications. Disruptor® PAC technology has demonstrated the ability to remove several representative pharmaceuticals from water.

Work in this area is just beginning. There does not appear to be a standardized list of concerns. Municipalities may not test for these compounds and those who do may not publish testing due to concerns over the public's ability to interpret results. Most factual studies appear to focus on analysis of what is present and not the effects of what is present. Industry organizations are attempting to minimize fears while watch dog groups are extrapolating information beyond its practical limits. Independent third parties need to establish priority pollutants and appropriate limitations. When the problem of trace pharmaceuticals is properly quantified, Disruptor® technology could be part of the solution.

FUTURE WORK:

Disruptor® and PAC technologies have both shown potential to remove organic compounds individually. Disruptor® products that do not contain PAC will be tested to help explain the mechanism for removing trace pharmaceuticals.

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