

Filtration of Soluble Metals and Organic Contaminants by Nanoalumina Fiber Filters

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ABSTRACT

This paper demonstrates how the strong inherent electropositive charge properties of nano alumina (AlOOH) fiber that is 2 nm in diameter is incorporated into media and can be used for purification of water containing many metal ions, endocrine disruptors and PCB's. Purification of contaminants embodies three different mechanisms: electroadsorption and chemisorption by the nanoalumina. This study also correlates change in zeta potential with adsorption of Cu^{2+} ions as a function of pH of the solution.

INTRODUCTION

In IWC-2010, we described a filter media (NanoCeram/Disruptor) whose primary filtration mechanism for removing suspended solids is by electroadsorption. The active component in the filter is AlOOH nanofibers, only 2 nanometers in diameter and about 300 nm long. The nanoalumina (or NC) is also known in the literature as boehmite whiskers. In the NC filter the boehmite whiskers are bonded to a microglass non-woven scaffold. The media's pore size is 2 microns, yet it can filter suspended solids as small as a virus and do so at high flowrates. A single layer can retain 6 LRV (log retention value) of E coli bacteria and 4 LRV of MS2 virus. A dual layer increases bacteria and virus retention to greater than 7 LRV and 6 LRV respectively.

An alternative media, containing ultrafine (8 microns) activated carbon particles (PAC) was also characterized for particle retention and flowrate. Its retention of colloidal and suspended solids, including bacteria and virus, were found to be at least as good as NC. Both are superior than ultraporous membrane filters for removing colloidal solids.

Electrodesorption is a mechanism that is less dependent upon pore size than is the case with mechanical filtration by either membranes or with typical depth filters. A non-woven filter format is best suited for separation via electroadsorption.

Electroadsorption utilizes the difference in charge that may exist between a membrane surface (or fiber) and a particle in an aqueous solution, where a distribution of charges has traditionally been called EDL (electrical double layer), although it is often more complex than just two layers (Delgado, 2005). The zeta potential is a measure of the driving force between the particle and the fixed surface, acting to attract or repel the two. Most bacteria and most other particulate contaminants encountered in nature are electronegatively charged in water (Jornitz, 1998). The presence of salts and/or a moderate alkalinity can adversely affect the electroadsorption function of some commercially available electropositive media.

A novel water purification filter has been in development over the past ten years (Tepper, 2005; Kaledin, 2010). The filter's active component is a nano alumina monohydrate fiber (AlOOH). The isoelectric point of raw fibers is approximately 11.1 (Al-Shakhshir, 1994). Particles with an electronegative charge are attracted and retained by the nano alumina. Filtration efficiency is high even in the presence of salts or moderate alkalinity (Kaledin, 2010).

The purpose of this study is to evaluate the ability of the NC filter to retain soluble contaminants, specifically trace metals and several classes of organic contaminants.

This study also correlates the zeta potential (ζ) of NC filter discs with adsorption of metal ions.

EXPERIMENTAL

MEDIA CHARACTERISTICS - The media consists of nano alumina fibers that are electroadsorptively grafted to a 0.6 μm diameter microglass fiber (Figure 1). X-ray diffraction patterns have identified the monohydrated nano alumina as predominantly pseudoboehmite (AlOOH). Larger cellulose or polymer fibers are added to produce a flexible media that is capable of being pleated. The surface area of the nano alumina, computed from the external surface of the 2 nm fiber is about 600 m^2/g , and its BET surface area ranges between 200 and 550 m^2/g . This suggests that most of the surface area is external and accessible to particles and macromolecules, as compared to granular sorbents, where most of the surface area is within internal pores and unavailable to particles and large macromolecules.

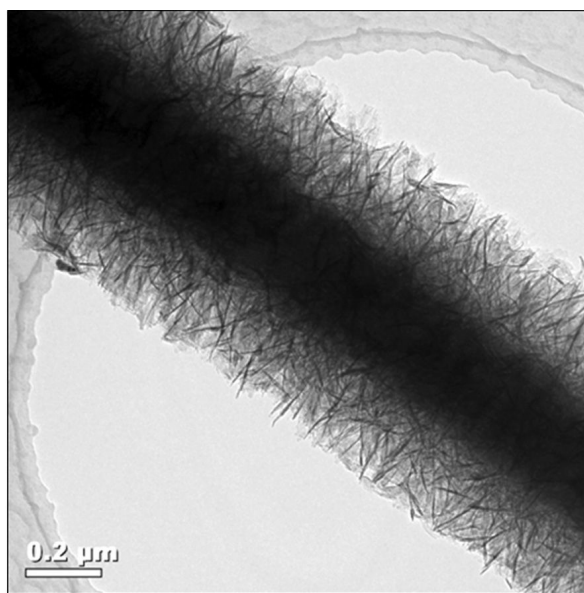


Photo courtesy of R. Ristau, IMS, Univ. of Conn.

Figure 1 TEM image of nanoalumina bonded to microglass fibers

The pore size of the NC media can be varied from about 1 to 30 μm , although a 2 μm pore size was selected as optimum for water purification filters. Each layer of media (0.8 mm thick) has an average of 400 vertical pores. Each pore has greater than 550,000 nano alumina fibers. The number of positive charges in each pore, owing to the Al^{3+} has been calculated to be $2 \cdot 10^{12}$ proton charges.

The media can be modified by addition of ultra-fine or nano size particles to the formulation (Kaledin, 2010). NC-PAC media (PAC with average particle size of 8 microns) has high dynamic adsorption efficiency as compared to GAC (granular carbon media). PAC filters have been commercialized and has been certified under NSF/ANSI (Standard 53, 2007) as being safe for use in purifying drinking water (Oulman, 1964). In this study, 25 mm filter discs with either NC or NC-PAC were prepared as described in Refs. (Tepper, 2005; Kaledin, 2010).

ZETA POTENTIAL AND ADSORPTION OF SOLUBLE METAL IONS

Streaming and zeta potentials - The streaming potential apparatus is described in Refs. (Tepper, 2010 and Oulman, 1964). Briefly, the streaming potential is measured by means of a pair of Ag/AgCl electrodes located on both sides of the filter inside the channel. The solution of a known conductivity is placed in a pressurized vessel and pressure is applied to the vessel and therefore to the filter. The zeta potential is an important and reliable indicator of the surface charge of filters. Zeta potential cannot be measured directly in the case of charged depth media but must be deduced from experimental data, e.g., from measuring streaming potential. It has been long recognized (Mossman, 1959) that in the capillary flow situation the apparent zeta potential (ζ_{apparent}) is a function of bulk conductivity of filtered liquid (λ_b) while the true zeta potential (ζ_{true}) is a function of bulk conductivity of filtered liquid (λ_b) as well as surface conductance (λ_s). NC and NC-PAC are shown to have high values (greater than +50 mV, (Tepper, 2010)) of ζ_{true} for pH in the range from 5.6 to 10.

Composition of metal ion solutions - Table 1 defines the sources of metal ions Pb, Hg, Au, Ag, As (III), As (V), Cu, Ni, Fe, Cr III, Cr VI, and Al stock solutions, their amounts and target concentrations. The hexahydrated form of aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, Fluka Cat #06232) was used to avoid potential explosion of anhydrous AlCl_3 upon dissolving in water. Analyses of stock solutions and filtrates were done via ICP/MS method (accuracy ~ 15%) at ELAB, Inc., (now Pace) Labs. All stock solutions were prepared using reverse osmosis water with a conductivity of 5 mS/m.

Table 1 - Preparation of challenge solutions

Metal	MW, g/mole	Source salt	Amount of salt, mg/L
Pb	207	PbCl_2	6.7
Hg	201	HgCl_2	6.8
Au	197	$\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$	13.3
Sn	119	SnCl_2	3.8
As III	74.9	As_2O_3	2.6
As V	74.9	As_2O_5	3.1
Cu	63.6	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	3.6
Ni	58.7	NiCl_2	3.3
Fe	55.9	FeCl_3	7.3
Cr III	52.0	$\text{Cr}_2(\text{SO}_4)_3$	5.6
Cr VI	52.0	CrO_3	2.9
Al	27.0	$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	6.3

Table 1 (continued) - Preparation of challenge solutions

Me	Ion	Counter ion	Metal ion input concentration ^a	
			ppm	$\mu\text{mole/L}$
Pb	Pb^{2+}	Cl^-	3.6±0.5	17±2
Hg	$[\text{HgCl}_4]^{2-}$	H^+	4.9±0.5	24±2
Au	$[\text{Au}(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}]^-$	Na^+	5.0±0.8	25±4
Sn	Sn^{2+}	Cl^-	1.4±0.2	12±2
As III	$[\text{AsO}_2]_n$ or AsO_3^{3-}	H^+	1.9±0.3	25±4
As V	$[\text{AsO}_4]^{3-}$	H^+	2.4±0.4	32±5
Cu	Cu^{2+}	Cl^-	1.3±0.2	20±3
Ni	Ni^{2+}	Cl^-	1.4±0.2	24±3
Fe	Fe^{2+}	Cl^-	1.7±0.3	30±5
Cr III	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	SO_4^{2-}	1.3±0.2	25±4
Cr VI	$[\text{CrO}_4]^{2-}$	H^+	1.8±0.3	35±6
Al	Al^{3+}	Cl^-	0.8±0.1	29±4

Note: a) Measured by the ICP/MS method.

Results of Table 1 indicate that measured molar metal concentrations are within the 2σ accuracy (i.e., $25 \pm 13 \mu\text{mole/L}$) for all 12 samples. It should be noted that Hg, Au, As(III), As(V), and Cr(VI) exist in aqueous solutions as negatively charged ions.

EPA concentration limits for metals – Table 2 shows the EPA concentration limits for metals in water.

Table 2 – EPA concentration limits for metals

Metal	Maximum permissible limit, ppb	Metal	Maximum permissible limit, ppb
Pb	15	Sb	6
Hg inorganic	2	Cr total	100
Al ^a	50 to 200	Be	4
Fe ^a	300	Cd	5
Mn ^a	50	Cu	1300
Ag ^a	100	Se	50
Zn ^a	5000	U	30
Tl	2	Ba	2000
Ra-226 & Ra-228	5 pCi/L	As	10

Note: a) List of national secondary drinking water regulations

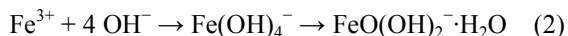
Sample collection and analytical results - A 47 mm disc (0.8 mm thickness, basis weight 200 g/m^2) of NC media was punched out and placed in a filter holder with an effective filtration area 8.2 cm^2 . A 250 mL aliquot of the effluent was collected at a flow rate 60 mL/min. Table 2 shows the initial and final pressure drop during the filtration process. Filtration was terminated in the case of Fe and Al solutions because of a high pressure drop (~42 psi). Aqueous solutions of AlCl_3 are ionic and such solutions are found to

be acidic, indicative of partial hydrolysis of the Al^{3+} ion. The reaction can be described (simplified) as:



Reaction (1) would lead to formation of aluminum oxide hydroxide precipitates that could clog the NC filter.

Similarly, when dissolved in water, iron (III) chloride undergoes hydrolysis. $FeCl_3$ in slightly basic water reacts with the hydroxide ion to form a floc of iron (III) hydroxide. The reaction can be described as:



It is likely that for aluminum and iron the flocculated particles are removed by electroadhesion forces rather than by chemisorption of soluble ions (see below).

Figure 2 and Table 3 show the output concentration for each of the metal ions.

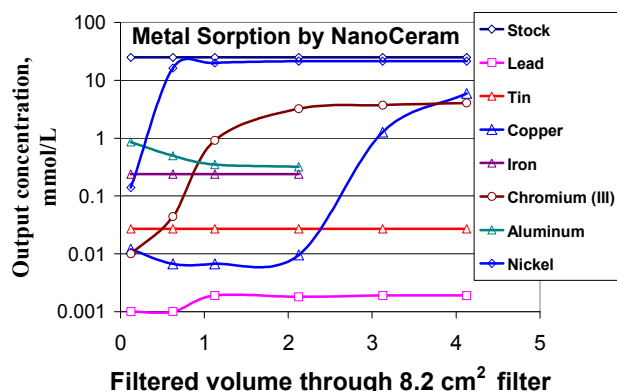


Figure 2 - Output concentration for each of the metal ions

Table 3 - Sample collection and analytical results

Metal	Input ppm	pressure drop, psi	
		Initial	Final
Pb	3.6	3	4
Hg	4.9	4	4
Au	5.0	4	4
Sn	1.4	4	7
As III	1.9	4	8
As V	2.4	4	4
Cu	1.3	4	4
Ni	1.4	4	4
Fe	1.7 ^a	5	42
Cr III	1.3	4	8
Cr VI	1.8	4	
Al	0.78 ^a	4	42

Table 3 (continued) - Sample collection and analytical results

Metal	Output concentration in a given aliquot ^a , ppb					
	0-250 mL	0.5-0.75L	1.0-1.25 L	2.0-2.25 L	3.0-3.25L	4.0-4.25 L
Pb	0.18	0.20	0.38	0.36	0.38	0.38
Hg	3200	4600	4700	4700	4800	4700
Au	4200	4900	4800	4900	4900	4900
Sn	2.7	2.7	2.7	2.7	2.7	2.7
As III	1800	1800	1800	1800	1800	1800
As V	1300	2100	2200	2200	2300	2300
Cu	0.67	0.37	0.37	0.53	71	330
Ni	8.6	980	1200	1300	1300	1300
Fe	14	14	14	14 ^b		
Cr III	0.59	2.6	54	19	220	240
Cr VI	1000	1800	1800	1800	1800	1800
Al	24	14	9.8	8.9 ^b		

Notes: a) a 250 ml aliquot was collected at flow rate 7.3 mL/cm²/min through 47 mm NC disc with surface area 8.2 cm²; b) filtration process terminated because of high pressure drop.

Table 3 shows that NC media has very good initial removal efficiency for Pb, Sn, Cu, Ni, Cr (III) and much higher capacity removal for Pb, Sn, and Cu.

Development of a sorption model and estimating projected capacity of metal ions by pleated cartridges in clean (RO) water background - A model was developed (Kaledin, 2009) that describes the adsorption of viruses and other charged particulates (including ions) by the electropositively (or electronegatively) charged depth filter media that was applied to the case of the NC filter media (Kaledin, 2009).

The surface area derived via BET adsorption for the nano alumina closely matched the calculated surface area assuming a 2 nm diameter. Helium adsorption showed less than 10% porosity. This indicates that the large surface area of the nano alumina fibers (up to ~500 m²/g) is on the surface and available for adsorption, like flagella, as seen in Figure 1.

Extremely high surface area and resulting almost instant adsorption permitted us to reduce the complexity of the diffusion solutions as compared to one for a porous solid, where there is complexity owing to particle migration below the surface, through micro- and macropores. Although the expressions for the breakthrough curves derived from different models are algebraically different, the numerical difference is quite small and it became a common practice to use the simpler linear driving force models to further simplify the algebraic solutions. The analytical solution for a breakthrough curve is given by the following asymptotic equation (see, e.g., (Ruthven, 1987)):

$$c_b^+ = \frac{1}{2} (1 - \text{erf}(\sqrt{z^+} - \sqrt{\theta^+})) \quad \text{for } z^+ \geq \theta^+ \quad (3)$$

$$\text{for } z^+ \gg 1$$

where $c_b^+ = c_b/c_0$ is dimensionless concentration
 c_0 is challenge concentration
 c_b is bulk concentration
 θ^+ is a dimensionless value of corrected time θ defined as $t-z:\varepsilon/v$
 z^+ is a dimensionless value of z
 z is depth of the media
 ε is porosity of the media
 v is flow velocity
 erf is the error function

Equation (3) therefore allows prediction of a breakthrough curve for large values of z^+ from constants derived from experimental measurements of the dynamic adsorption isotherms (see Figure 2).

Table 4 shows metal sorption capacities and values of z^+ by NC filter media derived from the breakthrough curves of Figure 2.

Table 4 - Metal sorption from RO water by NC filter media

Me	Input concentration, ppm	Sorption capacity (mg/g media)	z^+
Pb	3.6	180	3
Hg	3.0	~5	n.d.
Au	5.0	~5	n.d.
Sn	1.4	>29	n.d.
As III	1.9	<1	n.d.
As V	2.4	4	n.d.
Cu	1.3	32	30
Ni	1.4	3	5
Fe II	1.7	>90	n.d.
Cr III	1.3	33	8
Cr VI	1.8	~0.2	n.d.
Al	0.78	>8	n.d.

Note: n.d. - not determined

Table 4 shows NC media has very good removal efficiency and very likely good long term removal efficiency for Pb, Sn, Fe II, Cr III and Al. Furthermore, Ref. (Wilson, 2002) reported good initial removal efficiency for Co II, In III, Zn II, and Sc from distilled water by 3 mm thick NC media. From these results we can project 3 mm thick NC media has very good initial removal efficiency and very likely good long term removal efficiency for all rare earth elements (i.e., Sc, Y, La and lanthanides) (Jørgensen, 1988) and actinides (Seaborg, 1994) in their +2 and +3 oxidation states.

With parameters presented in Table 4 and with the use of Eq. (3) it becomes possible to project

performance of a single layer pleated cartridge (with no PAC) at different input concentrations. Table 5 presents projections metal ions in a background of clean RO water, to a 10 ppb cut-off and EPA advisory (Table 2) limits.

Table 5 - Projected performance of NC pleated cartridges

Metal	Input, ppb	Output, ppb	NC cartridge (diam X length)	Flow rate, GPM	Filtered volume, gallons
Pb	3600	15 ^a	2.5x10	3	86
			4.5x20	30	770
	150	15 ^a	2.5x10	3	5300
			4.5x20	30	48,000
Sn	1400	2.7 ^b	2.5x10	3	200
			4.5x20	30	1800
Cu	1400	1300 ^a	2.5x10	3	940
			4.5x20	30	8500
	10	10	2.5x10	3	200
			4.5x20	30	1800
Fe(II)	1700	From 14 to 300 ^a	2.5x10	3	200
			4.5x20	30	1800
Cr III	1300	100 ^a	2.5x10	3	150
			4.5x20	30	1400
	10	10	2.5x10	3	75
			4.5x20	30	675
Al	1700	From 24 to 200 ^a	2.5x10	3	200
			4.5x20	30	1800

Note: a) to EPA advisory limits (see Table 2); b) to ~2.7 ppb limit

Enhanced lead reduction by NC + PAC + ATS - ATS (Amorphous titanium silicate) powder (Average particle size ~25 μm) is highly effective as a soluble lead adsorbent. The new NSF/ANSI lead standard (Standard 53, (2007)) requires removal of soluble lead at pH 6.5 and soluble/insoluble lead removal at pH 8.5 to 10 ppb. The NC and NC-PAC media adsorb insoluble particulate lead with a very high efficiency, greater than about 99%. We prepared 45-wt%ATS/NC loaded media as described in Ref. (Kaledin, 2010). Two 47 mm diameter discs made from ATS/NC composite media with basis weight of 266 g/m² were inserted into a 47-mm filter holder and tested with soluble lead solution at a constant (no cycling) flow rate of 60 mL/min (translates into 4 GPM through ATS2.5x10 double pleated cartridge). From the breakthrough curves we calculated filter sorption capacity of an ATS pleated cartridge 2.5 X 10" long. We computed the capacity to be 33 mg[Pb]/g of media and a projected service life at 4 GPM flow rate through for approximately 6000 L (1500 gallons) of soluble lead at an input 150 ppb (pH 6.5) and end-point of 10 ppb. This

capacity is better than that of PAC2.5x10 (720 gallons) and for 21-wt%ATS/11-wt%PAC2.5x10 (1400 gallons) cartridges reported in Ref. (Tepper, 2010). This is projected at much higher flow rate (by a factor of 5.7) of 4 GPM in the former case vs 0.7 GPM for two latter cases. This confirms that ATS is highly effective as a lead adsorbent when incorporated into NC and PAC.

METAL ION CHEMISORPTION MECHANISMS

A. Complexes with adjacent oxygen atoms - Chemisorption by boehmite nanofibers with specific surface area 143 m²/g (McBride, 1982), may involve the formation of a surface complex with adjacent oxygen atoms (McBride, 1982) (Figure 3).

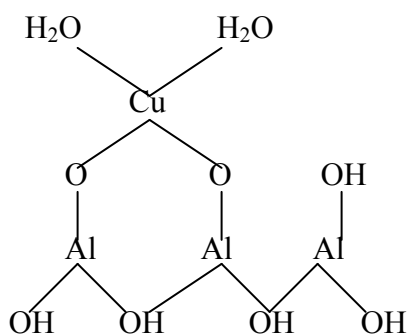


Figure 3 – Complexing with adjacent oxygen atoms

B. Complexes with single oxygen atoms - Complexes with a single oxygen atom with hydrogen bonding (Ottaviani, 1980) holding the Cu²⁺ in a rigid structure (Figure 4).

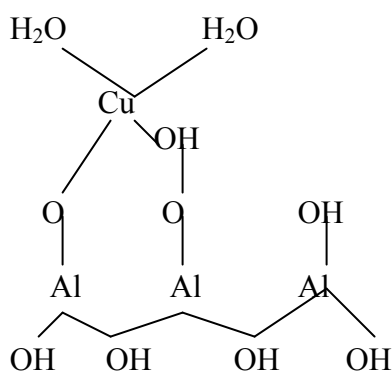


Figure 4 – Complexing with single oxygen and a hydrogen bond

Metals that were filtered to below the EPA limits included lead, tin, nickel, iron, cobalt, indium, zinc and chromium (III and VI). Figure 5 shows good correlation of zeta potential (Kaledin, 2010) and chemisorption of Cu²⁺ ions on boehmite nanofibers

with specific surface area 143 m²/g (McBride, 1982). The adsorption of Cu²⁺ increases continuously with pH 7 where complete recovery is achieved.

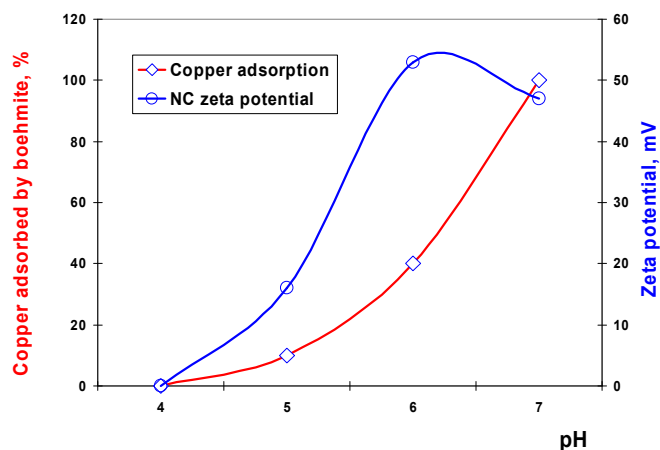


Figure 5 - Correlation of ζ_{true} and chemisorption of Cu²⁺ ions on boehmite nanofibers with specific surface area 143 m²/g (McBride, 1982)

We presume that those metals that tend to form hydroxides in alkaline solutions complex in either the A or B type of structure. Experiments showed that those metals that were filtered to below the EPA limits included lead, tin, nickel, iron, cobalt, indium, zinc and chromium (III and VI).

PHARMACEUTICAL AND ENDOCRINE DISRUPTORS

Studies (Leoning, 2008) have shown that up to 41 million Americans in 24 major cities are exposed to pharmaceuticals in drinking water, often at micrograms/L concentrations. 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 (Donn, 2008) but studies of rural water supplies appear to have received less attention.

Experimental Method – The University of California tested PAC filter discs supplied by Ahlstrom Filtration, LLC. Filter discs (47 mm diameter) were placed in a filter holder and challenged with Penicillin G, a representative antibiotic, Bisphenol A and Flumequine, at 2 or 10 mg/L, concentrations several orders of magnitude greater than typically found in drinking water. High challenge concentrations were used because of the difficulty of measurement at µg/L levels. The flow was 50 mL per minute or 1 gpm/ft². Penicillin G, Bisphenol A and Flumequine breakthrough curves were determined by HPLC (Agilent 1200), equipped with a Diode Array Detector, and a Phenomenex Gemini C₁₈ column (5µm, 250 × 4.6 mm, (XU, 2010)). The isocratic mobile phase was a mixture of methanol and pH 3.0 KH₂PO₄ 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 and the detection wavelengths were 232, 227 and 224 nm respectively.

Penicillin G – When challenged at 2 mg/L, the entire antibiotic was removed from up to 13 L of water. (Figure 6) This equates to 281 gallons of 2 mg/L water processed per ft² of media. At more typical concentrations in the range of 2µg/L, the projected dynamic capacity to breakthrough would be 281,000 gallons (for more details see below), assuming that the water was free of other competing compounds.

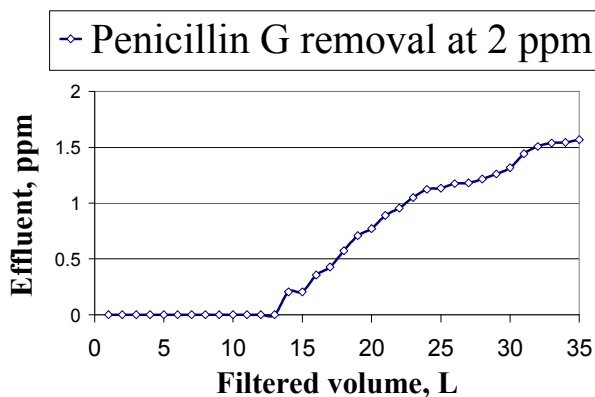


Figure 6 - Penicillin G removal at 2 mg/L

Bisphenol A – BP^A (Wikimedia, 2010) 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 and diabetes. Affects of Bisphenol A are highly controversial and have been studied in great detail in other publications. Figure 7 shows the removal of 10 mg/L of BPA from water. The capacity of the 47 mm disc was 3 L, equating to treating 322,000 gallons per ft² of media assuming a BPA concentration of 2µg/L (for more details see below).

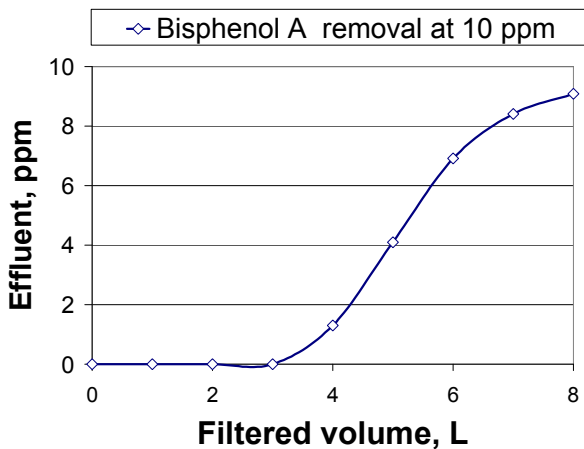


Figure 7 - Bisphenol A removal at 10 mg/L

Flumequine - Flumequine (Wikimedia, 2010) is a chemotherapeutic antibiotic that is implicated in DNA damage, ocular toxicity, liver damage, and anaphylactic shock. Figure 8 shows the removal of 10 mg/L of Flumequine using PAC. The Flumequine capacity of a single 47 mm disc at 10 mg/L was quantitative up to 3 L of challenge water. This equates to treating 322,000 gallons per ft² of media at a concentration of 2 µg/L (for more details see below).

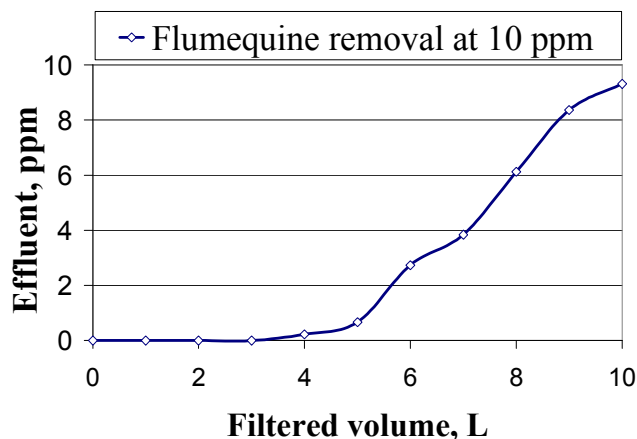


Figure 8 - Flumequine removal at 10 mg/L

Table 6 shows endocrine disruptor sorption capacities and values of z⁺ by NC filter media derived from the breakthrough curves of Figures 6-8 and Eq. 3.

Table 6 – Endocrine disruptors sorption from water by PAC-NC filter media

Endocrine disruptor	Input, ppm	Sorption capacity (mg/g media)	z ⁺
Penicillin G	2	220	25
Bisphenol A	10	265	35
Flumequine	10	380	35

Note: ECD – endocrine disruptor

Table 6 shows PAC-NC media has very good removal efficiency for trace quantities of three types of endocrine disruptors (EC)

Figures 9-11 show comparison of experimental curves with predictions based on Eq. 3 with parameters of Table 6.

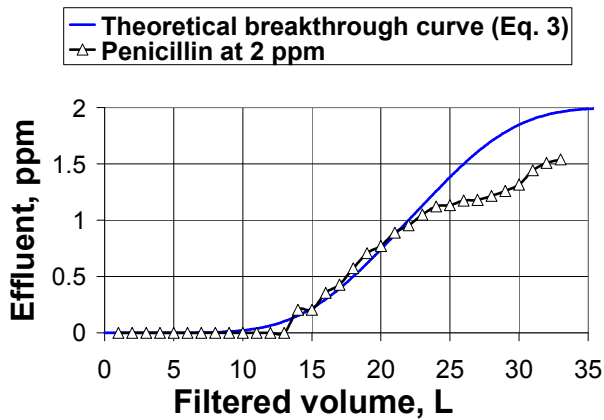


Figure 9 – Experimental Penicillin G removal efficiency at 2 ppm compared to projected performance from the model (Eq. 3)

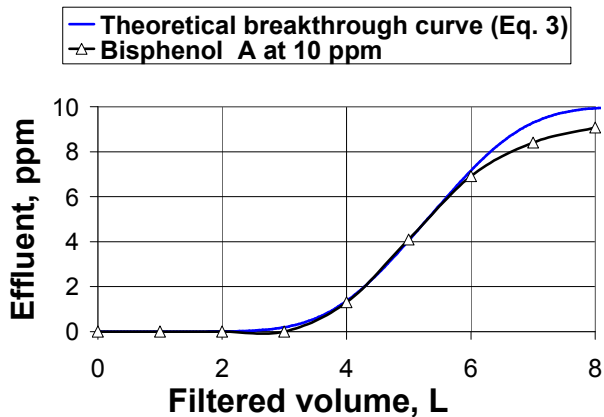


Figure 10 – Experimental Bisphenol A removal efficiency at 10 ppm compared to projected performance from the model (Eq. 3)

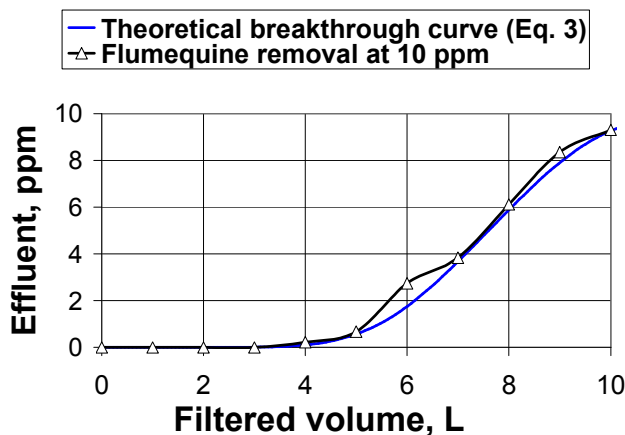


Figure 11 – Experimental Flumequine removal efficiency at 10 ppm compared to projected performance from the model (Eq. 3)

With parameters presented in Table 6 and with the use of Eq. (3) it becomes possible to project performance of a single layer pleated cartridge (with PAC) at different input concentrations. Table 7 presents projections metal ions in clean RO water .

Table 7 - Projected performance of PAC-NC pleated cartridges

Endocrine disruptor	Input, ppt	Out, ppt	PAC-NC cartridge (diam X length)	Flow rate, GPM	Filtered volume, million gallons
Penicillin G	2,000	1.0	2.5x10	3	0.96
			4.5x20	30	8.6
Bisphenol A	2,000	1.0	2.5x10	3	0.78
			4.5x20	30	7.0
Flumequine	2,000	1.0	2.5x10	3	1.35
			4.5x20	30	12

PCB's - Polychlorinated biphenyls (PCBs) belong to a group of man-made chlorinated hydrocarbons. PCBs offered chemical stability, low flammability and electrical insulating properties and were used in industrial transformers and capacitors, adhesives, and insulation materials. 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 (National Sanitation Foundation) 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). Aroclor 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 separately tested 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 20,000ng). This concentration of 0.0208 mg/L was double the NSF challenge of 0.01mg/L and included congeners that aren't contained in the Aroclor 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 than 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/ft²). This is equivalent to 44 gallons through a 2.5"x10" cartridge (450 in² 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 8 lists the 10 congener groups, the influent challenge concentration, and the effluent concentrations for carbon and non-carbon nanoalumina materials.

Table 8 - Filtration of PCB Congener Groups

Congener Group	ng/L influent	Carbon ng/L effluent	Non-Carbon 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

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 PCB's 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. Unfortunately this possibility was not recognized at the time that we were testing for endocrine disruptors.

RETENTION OF ULTRAFINE AND NANO SIZE PARTICLES IN A NANOALUMINA STRUCTURE

Non-woven fibrous filters are generally unable to retain particles in their structure if the particle size is approximately equivalent to or less than the average pore size of the filter. For instance, PAC particles, whose average size is 8 microns, have a significant distribution of particles whose size is a few microns or even sub-micron in size. The result is that these fines can be shed from conventional depth filters. They would then contaminate the fluid as well as solid downstream components such as membranes or heat transfer surfaces. We have found that electropositive forces created by the nanoalumina retain particles far smaller than the 2 µm pore size of the NC media.

The high efficiency in retaining small particles by attraction and/or chemisorption by nano alumina media is a result of a high zeta potential and a large number of charges on the nano alumina. The electrical state of a charged alumina surface is determined by the spatial distribution of ions around it.

A single layer of NC, 0.8 mm thick, and with a 2 micron pore size, has an average of 400 pores through which a particle must transit. Assuming that each nano alumina fiber is an effective adsorption site then through computation, there are greater than half a million nanofibers or adsorption sites in each pore, or greater than 200 million sites that the particle is exposed to on transit through a single layer of NC. Calculations also show that the flow path of a small particle or ion can be affected by the high zeta potential (+50 mV) as much as 1 micron away in a solution with low bulk conductivity (Kaledin, 2009) causing it to be attracted to and retained in the pore. Since the average pore size is 2 microns then the capture cross section overlaps the whole average pore at low bulk conductivity. The high tortuous path plus the ability of the surface of the pores to attract and retain small particles or ions combine to result in a high efficiency.

The ability of electrolytes to flocculate various aqueous dispersions was first rationalized after establishment of the electric double layer (EDL) theory (Derjaguin, 1941; Verwey, 1948). Because of the different distance dependence of the van der Waals (power law) and electrical (exponential) energies, the former is always greater than the latter at sufficiently large separations. This gives a secondary minimum in the potential energy curve at ~ 10-20 nm. The interaction energy is directly proportional to particle size. The secondary minimum effects are more significant with larger particles (greater than about 1 µm in diameter (Verwey, 1948; Elimelech, 1995; Torkzaban, 2007)). The

attractive potential between two dipoles (nano-alumina fiber and PAC particle each considered here as separate dipoles) proportional to r^{-3} ; the corresponding attractive forces decrease according to r^{-4} (Verwey, 1948)

In the case of nano-alumina/microglass composite's the attraction is the cumulative effect of forces generated by the *assembly of nano alumina fibers on the second fibers in a highly organized structure*. The assembly can be viewed as infinitely long straight cylinder that has high linear charge density of 20 $\mu\text{C}/\text{m}$ and high surface charge density of 20 C/m^2 . This creates a significant electric field in the region far from the surface of the composite that penetrates farther (as far as 100 μm) and generate much stronger force than that generated by a single nano alumina fiber at $\sim 10\text{-}20$ nm. The interaction of the assembly with a particle in a solution can be modeled as an interaction between an infinitely long straight cylinder with high surface charge density of 20 C/m^2 and particle's dipole moment that induced by a strong electric field created by the assembly. This strengthened force is then able to attract and retain larger particles such as PAC. These forces attract and retain much smaller particles such as fumed silica nanoparticles (a chain of the primary spherical particles about 10-15 nm in diameter. See Figure 12). Similarly, the nano alumina fibers//microglass composite's attract and retain titania nano particles (about 10 nm), nanocarbon particles (about 30 nm), and bio-engineered nanostructures (Tepper, 2009), as well as the ATS lead sorbent described above.

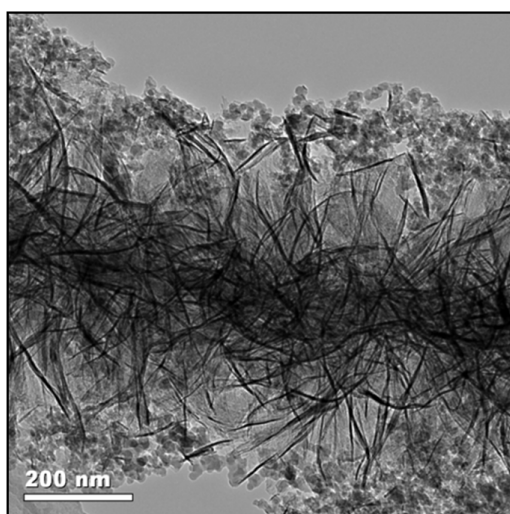


Figure 12- Nanosilica on nanoalumina/microglass fiber – Note accumulations of nanosize silica spheres on surfaces

Experiments on Shedding of PAC - The shedding of PAC particles from filter discs (25-mm diameter) was compared to filter discs without nanoalumina. The latter are labeled with “0” in Table 9. These discs were placed into a filter holders and were flushed with 1 Liter of RO water at a flow rate of 80 mL/min through the discs 3.7 cm^2 surface area. Both filter orientations with respect to the incoming water flow were tested that showed similar values of shedding for each composition, irrespective of orientation. Collected effluent aliquots were then poured into a 20 L carboy and filtered through a 0.45 micron rated membrane. Counting of PAC particles on the membrane surface was performed with the use of an optical microscope and converted into percent of shedding with respect to all PAC particles in the 25 mm diameter disc. Visual examination of membrane surfaces indicates that there was very little or no PAC shedded from NC-based samples while the control samples without nanoalumina showed considerable shedding.

These data also show that for a given composition with nano alumina fibers the shedding of PAC is much less by a factor of 10 to 50 than in a composition without the nanoalumina. Moreover PAC shedding decreases with increases in nano alumina in the composition.

Table 9 - Shedding of PAC from filters

Sample #	PAC		NA ^b , wt%	Basis weight, g/m^2	Shedding, %
	wt %	Mean particle size, μm			
AF74	28	8	6	240	0.03 ^c
F74-0 ^a	19	8	0	215	0.7 ^c
AF75	26	8	14	239	0.006 ^c
AF75-0 ^a	25	8	0	234	0.3 ^c
AF76	27	8	18	241	0.01 ^c
AF76-0 ^a	23	8	0	229	0.5 ^c
AF77	24	5	6	230	0.02 ^c
AF77-0 ^a	16	5	0	211	0.5 ^c
AF78	24	5	14	239	0.007 ^c
AF78-0 ^a	14	5	0	234	0.4 ^c
AF79	25	5	18	241	0.004 ^c
AF79-0 ^a	15	5	0	229	0.2 ^c

Notes: a) contains no nano alumina b) NA-nanoalumina; c) Calgon grade 3164-325-XF

SAFETY & ENVIRONMENTAL

Nanoalumina fibers, also known as boehmite whiskers have been used in antacid analgesics for many years. Boehmite nano whiskers have also been used extensively in vaccines and have been approved as adjuvants

by FDA for 64 years. The nanofibers are a primary component of baby shots and flu vaccines. More than 2 billion doses have been used in humans and countless more in veterinary vaccines.

Numerous studies of occupational exposures of all aluminas, including boehmite, used in industry are essentially inert in the lungs (Dinman, 1990). Aluminum in all forms, shed or dissolved from NC filters has been shown to be <20 ppb (via ICP/MS).

In our IWC-2010 paper (Tepper, 2010) reviewers referenced a website “Just the Facts” published by USPHSC (U S Army Public Health Command) citing other publications about the use of nano alumina’s in filtration and concluding that nano alumina filters were a potential hazard in drinking water. They did not differentiate AIOOH from the more persistent alumina’s such as alpha alumina.

After a number of discussions with USPHSC plus providing substantiating references, USPHSC rescinded their “Just the Facts” and replaced it with a new one (U S Army Public Health Command, 2011). Their current conclusion is that boehmite (nanoalumina) fibers can be considered safe for drinking water.

CONCLUSIONS

This study focused on the filtration of soluble contaminants that are pathogenic at low concentrations in water. Breakthrough curves were presented for filtration of several metals by nanoalumina at concentrations of concern. Metals that were filtered to below the EPA limits included lead, tin, nickel, iron, zinc and chromium (III and VI). A chemisorption mechanism is proposed. Soluble lead adsorption can be enhanced by embodying a lead specific absorbent, while the nano alumina also retains colloidal lead oxides.

The high degree of correlation of zeta potential and chemisorption of Cu^{2+} ions on pseudoboehmite nanofibers from aqueous solutions vs pH suggests further enhancements of the model that had been reported earlier (Kaledin, 2009).

The media has a high dynamic response for adsorption, allowing purification within a very shallow bed with media depth less than 1 mm (e.g., by a single layer pleated cartridge) and doing so at flow rates an order of magnitude or greater than can be achieved with an ultraporous membrane.

NC-PAC is very efficient for adsorbing trace quantities of three types of endocrine disruptors (EC). The first three tested (Penicillin G, Bisphenol A and Flumequine) were efficiently adsorbed by a single layer of PAC media (Xu, 2010). It had been presumed

that the PAC removed these organics. The experimental breakthrough curves fit a model that had been developed earlier for electrostatic adsorption by NC and PAC.

A further study was done on the filtration of PCB’s by nanoalumina and PAC, showing very high efficiency with a single layer of either NC or PAC. The nanoalumina was found to be as effective or even more effective as the PAC in retaining PCB’s to very low effluent concentrations.

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REFERENCES

- Al-Shakhshir, R., F. Regnier, F., White, J., & Hem, S. (1994), Effect of protein adsorption on the surface charge characteristics of aluminium-containing adjuvants. *Vaccine.*, 12 (5), 472-474.
- Delgado, A., Gonzalez-Caballero, F., Hunter, R., Koopal, L. & Lyklema, J. (2005). Measurement and interpretation of electrokinetic phenomena. *Pure Appl. Chem.*, 77 1753-1805.
- Derjaguin, B. & Landau, L. (1941). Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Acta Physicochim. USSR*, 14, 733-762.
- Dinman, B. (1990). The Aluminas and Health. In L.D. Hart, ed., *Alumina Chemicals Science and Technology Handbook, The American Ceramic Society, Inc., Westerville, OH*, 533-543
- Donn, J., Mendoza, M., Pritchard, J. (2008). AP: Drugs show up in Americans' water. *USA Today*, March 10.
- Elimelech, M., Gregory, J, Jia, X., & Williams, R. (2006) Particle deposition & aggregation, *Butterworth-Heinemann*
- Frank, H. (2008). Another twist in filtration for high-purity and other systems. *Water technology*, 31(9), 32-36
- Harris, G. (2010) Antibiotics in animals need limits, F.D.A. says. *The New York Times*, June 28.
- Jørgensen, Ch. (1988). Influence of Rare Earths on Chemical Understanding and Classification. In *Handbook on the Physics and chemistry of Rare Earths. Chapter 75, vol. 11. Eds. K. A. Gschneider, Jr., and L. Eyring,, Elsevier Science*
- Jornitz, M. & Meltzer, Th. (1998). Filtration and purification in the biopharmaceutical industry, 2nd ed., *Volume 174, Informa Healthcare USA, New York*, 24
- Kaledin, L., Tepper, F. & Kaledin, T. (2009). Non-woven electrostatic media for chromatographic separation of biological particles. *J. Liq. Chromat. & Related Technologies*, 32, 607-27.
- Kaledin, L., Tepper, F., Vargas, O., & Kaledin, T., (2010). Solid phase extraction of nanosize particles by nanoalumina depth media. *ENT magazine*, Issue 1, March-April
- Leoning, C. (2008). Area Tap Water has Traces of Medicines. *The Washington Post*, March 10.
- McBride, M. (1982). Cu²⁺-adsorption characteristics of aluminum hydroxide and oxyhydroxides. *Clays and Clay Minerals*, 30 (1) 20-28
- Mossman, C. & Mason, S. (1959). Surface electrical conductance and electro- kinetic potentials in networks of fibrous materials *Can. J. Chem.*, 37, 1153-64.
- Ottaviani, M. & Martini, G. (1980) Adsorption of the Cu(OH)₄²⁻ complex on aluminas studied by electron spin resonance. *J. Phys. Chem.* 84, 2310-2315
- Oulman, C., & Baumann, E. (1964). Streaming potentials in diatomite filtration of water. *J. AWWA*, 915-930.
- Ruthven, D. (1984). Principles of adsorption and adsorption processes, *Wiley-Interscience, New York*
- Seaborg, G. (1994). Origin of the actinide concept. In *Handbook on the Physics and chemistry of Rare Earths. Chapter 118, vol. 18. Eds. K. A. Gschneider, Jr., L. Eyring, G. R. Choppin and G. H. Lander, Elsevier Science.*
- Standard 53, (2007) Drinking water treatment units – Aesthetic effects, NSF/ANSI
- Tepper, F. (2005) US Patent 6,838,005
- Tepper, F. (2010) Wide particle size spectrum, high efficiency pleated filters, *IWC-10-47*
- Tepper, F. (2008). US Patent Application 2008/0026041
- Tepper, F. (2009). Nanostructured Chem.-Bio Non-woven Filter. In *Nanoscience and Nanotechnology for Chemical and Biological Defense*, Eds., Nagarajjan, R., Zukas, W., Hatton, T. A., and Lee, S., ACS Symposium Series 1016.
- Torkzaban S. (2007). Resolving the coupled effects of hydrodynamics and DLVO forces on colloid attachment to collector surfaces. *Langmuir*, 23(19); 9652-9660, 2007.
- U S Army Public Health Command, (2011).
<http://phc.amedd.army.mil/PHC%20Resource%20Library/Alumina%20Nanofiber%20filters%20FS%20Feb%202011.pdf>
- Verwey, E. & Overbeek, J. (1948) Theory of the stability of lyophobic colloids, *Elsevier, N. Y.*
- [Wikimedia](#), September 7, 2010, “Bisphenol A”
- [Wikimedia](#), September 7, 2010, “Flumequine”
- Wilson, S. (2002). Heavy metal filtration with boehmite based filters. *Sierra Community College, summer scholar at Community College Institute (CCI)*, unpublished
- Xu, H., Cooper, W., Song, W., Cousart, F., & Komlenic, R. (2010). Removal of trace pharmaceuticals and endocrine inhibitors using Disruptor[®] PAC technology. *AFS*.