



# Evaluating GEG-2000 Organoclay Media PFAS Removal Feasibility in Process Water Centrate

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## **Abstract:**

Environmental occurrence of perfluoroalkyl and polyfluoroalkyl substances (PFASs) are widely detected in process water centrate and containment ponds due to the massive uses of PFAS in everyday consumer products, water/oil repellents, fire-fighting foam, and many others since the 1950s. However, the environmental pollution by them still exists today. PFAS in centrate and process water ponds can contaminate the neighboring soil and groundwater and pose serious health concerns to humans and ecosystems.

Water treatment techniques such as ferric or alum coagulation, granular/micro-/ultra-filtration, aeration, oxidation, and disinfection are primarily ineffective in removing PFASs. However, adsorption media treatment, such as organoclays and granular activated carbon, preferably removed longer-chain PFASs and the perfluorosulfonic acids than the perfluorocarboxylic acids, initial testing of the small chain PFASs also show significant removal rates.

Column testing of clarified centrate contaminated with 2.1 µg/L [ppb] of total PFASs through GEG-2000 organoclay (14-40 mesh) shows ~97% removal with a contact time of 12 minutes (n=1). Subsequently, the organoclay filtered through granular activated carbon (12-40) with the same contact time returned an additional 75% removal of PFASs for a combined removal rate of >99%.

## **1. Introduction**

Poly- and perfluoroalkyl substances (PFASs) are a group of chemicals that have been used directly in or as part of the manufacturing of a wide variety of industrial and consumer products. These include, but are not limited to, fire-fighting foams, paper and cardboard coating materials employed in food packaging, ScotchGard™, and Teflon™. One class of PFASs is perfluoroalkyl acids (PFAAs), which are stable chemicals made of a carbon backbone surrounded by fluorine atoms and a terminal acid

group carboxylic or sulfonic acid. These PFAAs are incredibly resistant to degradation and thus stable in both water and soil and highly persistent in the environment (Buck RC, 2011).

PFAAs are water-soluble, unlike most other bioaccumulative organic and persistent pollutants. Several PFAAs have been detected in U.S. surface waters, including lakes, rivers, and tributaries, in the ng/L range or lower (Wattigney WA, 2009), and found in groundwaters at similar concentrations

(Megan H. Plumlee, 2008). A survey of U.S. landfills of varying climates and waste ages measured the concentrations of 70 PFASs in 95 samples of leachate. The national release of PFASs was estimated by coupling measured concentrations for the 19 PFASs where more than 50% of samples had quantifiable concentrations, with climate-specific estimates of annual leachate volumes (Johnsie R. Lang, 2017). Some of these chemicals are detected in the blood of animals in remote regions of the world (Magali Houde, 2006). Due to concerns about the widespread occurrence and potential health effects, major U.S. manufacturers of PFOS and PFHxS stopped production in 2002 (John L. Butenhoff, v2009), while the worldwide use of PFOA and longer chain PFCA homologs is currently being phased out by their significant manufacturers (Andrew B. Lindstrom, 2011). Replacements for these phased-out compounds include less extensively studied shorter chain PFASs, such as PFHxA and other fluorinated compounds, which generally are more rapidly excreted in humans and animals than the long chain-length compounds (Gordon, 2011). However, these shorter-chain PFASs are still highly persistent in the environment.

Some of these chemicals have also been detected in the U.S. finished/tap waters in the low ng/L range (Oscar Quiñones, 2009). Higher levels (hundreds of ng/L to several µg/L) of some PFASs are found in finished drinking water, particularly near sites of industrial use (Emmett, Frances, & Hong Zhang, 2006). Other potential routes of human exposure include ingestion from food, food packaging, treated carpets, upholstery, and clothing, house dust, protective sprays, and waxes sold as consumer products (Gloria B. Post, 2012).

Human epidemiological studies have found associations with numerous health endpoints resulting from exposure, including drinking water exposure (Gloria B. Post, 2012). An independent panel of prominent environmental epidemiologists concluded that probable links exist between six adverse health conditions and PFOA exposure in a community with contaminated drinking water, including kidney cancer and testicular cancer (Verónica M. Vieira, 2013). Several associations of PFAA exposure with health effects are documented in the general population, including a study that found an association between PFOA and PFOS exposures and a “reduced humoral immune response

to routine childhood immunizations in children aged 5 and 7 years” (Philippe Grandjean, 2012).

In 2009, the U.S. Environmental Protection Agency (EPA) established Provisionary Health Advisory (PHA) values for PFOA and PFOS of 0.4 and 0.2 µg/L, respectively, in response to an emergency in Decatur, Alabama, meant to protect from short term exposure (U.S. Environmental Protection Agency (EPA) International Decontamination Research and Development Conference, 2013). Also, PFOS and PFOA have been added to the EPA’s Contaminant Candidate List 3 of chemicals under consideration for future drinking water regulation in the U.S. (USEPA, 2009). Both chemicals, as well as perfluoroheptanoic acid (PFHpA), PFNA, perfluorobutane sulfonic acid (PFBS), and PFHxS, were also added to the EPA’s Unregulated Contaminant Monitoring Rule 3 (UCMR 3), which requires nationwide monitoring by public water suppliers to provide occurrence data needed for regulatory decision making (Office of Water - U.S. Environmental Protection Agency, 2012). As some PFAAs have been shown to have the potential to harm humans, experts must examine all treatment options for their ability to remove these chemicals from contaminated water sources.

In addition to PFASs, organoclays have been shown to capture and store aromatic organic compounds, phenolic compounds (phenols and their derivatives), pesticides and herbicides, and other pollutants (anionic contaminants, heavy metals, and pharmaceuticals) (Yuri Park, 2011). This capacity makes them a suitable prefiltration step to other conventional treatments.

The objective of this study was to evaluate the ability of GEG-2000 organoclay and Granular activated carbon (GAC) to remove PFASs from contaminated centrate. To this end, an extensive suite of 28 PFASs [Table 1] was analyzed in clarified centrate at various steps along the process treatment train. Samples were collected during a sampling event for a representative and PFAS challenged process centrate in Michigan.

## 2. Materials and Methods

### 2.1 Sample grab and analysis

The sample collected from the centrate pond was collected in two 5-gallon sample containers by operations personnel and sent to Global Environmental Group for preparation and filtration testing.

Upon receipt of the sample, jar tests were conducted using an acrylamide-chloride salt of trimethylammonium-ethyl acrylate copolymer [AAcopolymer] in combination with aluminum sulfate and bentonite.

A test amount of the tested AAcopolymer was added into a beaker while stirring. The stirring was continued for 10 sec at 400 rpm after adding the copolymer solution. The stirring rate was then reduced to 50 rpm and continued for 10 min. The sample settled statically in the beaker for an additional 10 minutes. Visual assessments were determined in side-by-side comparisons. An optimized dose was determined to be  $3.2 \mu\text{g}/\text{cm}^3$  concentration.

The remainder of the sample volume (25 liters) was treated and clarified (through settling/decanting) to serve as the centrate source for media testing. pH was recorded at 7.15 pH units. At this stage, 1000ml of the sample was collected in a clean polyethylene sample bottle labeled "Raw."

The column used in the testing was constructed using a clear 1.25 inch [32.75 mm] inside diameter PVC pipe, an aluminum mesh screen, a rubber coupling, and a polyethylene needle valve [Figure 1].

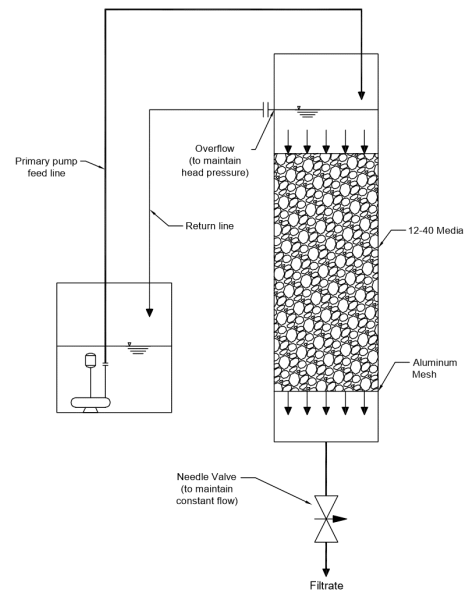


Figure 1

Pre-wetted and rinsed media was inserted into the column and then rinsed again using ambient temperature distilled water till the effluent was visually "clear."

The media height in the column was adjusted. The following parameters were used to simulate 1.0 gpm/ft<sup>2</sup> of hydraulic loading and a target contact time of 12 minutes [17.4 minutes empty bed contact time (EBCT)]:

12-40 media porosity =	0.69
Flowrate =	32 ml/min
Media column height =	70 cm [28 in]
Temperature =	ambient [21 °C]

### 2.1.1 GEG-2000 Filtration

Stage 1 test involved running the prepared "raw" centrate through the organoclay. The centrate was introduced to the top of the column and passed through the media via gravity. The flow rate was controlled by the needle valve and measured by periodic volume-time ratio grabs. The experiment commenced once at least 1000 ml has passed through the media to normalize and reach a steady state.

After commencing, 4000ml were collected. The pH was recorded at 7.11 pH units, and 1000ml of the

sample was collected in a clean polyethylene sample bottle labeled as "Post Clay." The other 3000ml were set aside for stage 2.

### 2.1.2 GAC Filtration

Stage 2 test involved running the "Post Clay" collected effluent through the GAC. Physical procedures and setpoints remained the same as stage 1. The experiment commenced once at least 1000 ml has passed through the media to normalize and reach a steady state.

The pH was recorded at 7.11 pH units, and 1000 ml were collected in a clean polyethylene sample bottle labeled as "Post Carbon."

### 2.2 Analytical Testing

The three samples, Raw, Post Organoclay, and Post GAC, were packed in ice and overnighed to a 3<sup>rd</sup> party lab that ran the samples according to EPA method 537 Modified and SW-846 Test Method 9060A: Total Organic Carbon.

## 3. Results and Discussion

The certified lab showed a clear and significant removal rate for all detected PFAS compounds and TOC, as shown in Table 2.

Due to the limited number of sample sources (n = 1), statistical examination and regression analysis were ignored. However, the experiment overwhelmingly supported the theoretical hypothesis that GEG-2000 is a viable treatment process for centrate removing PFAS constituents for both high and low molecular weights, collectively removing >97% of total tested PFASs. The test also a significant reduction in TOC with >75% removal. These results indicate GEG-2000 as a promising PFAS treatment for centrate and other high-strength wastewaters. Also, the removal of TOC corresponds to the known potentials of organoclays. It presumes that GEG-2000 filtration is a viable pre-process step to polishing treatment processes such as GAC and ion exchange filters which may foul quickly due to indiscriminate fouling non-targeted constituents.

Furthermore, the experiment also shows the potential of synergetic process application. The effluent from the GAC enhanced the effective removal rate to greater than 99.7% of all tested PFASs, most of which were below the detection limit (BDL).

## 4. Conclusions

Based on the findings, the efficacy of the bench test experiment paired with industry uses and documented successful water treatment applications, GEG-2000 merits further testing to determine:

- The ultimate retention capacity of PFASs and other constituents
- Hydraulic flux (including Reynolds number and loading/mixing effects)
- Matrix interferences (specifically pH and temperature kinetics)
- Microbial effects
- Economies of scale and value.

An appropriate next phase to further investigation would be to conduct a field pilot at an active PFAS challenged wastewater holding facility that could treat uninterrupted amounts of process wastewater or leachate up to 25,000 empty vessel volumes and test various setpoints. Additional consideration of TOC removal, both total removal and type, may also strengthen application guidelines.

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Table 1: Analytical Results

Constituent	Raw ng/L	Post Clay ng/L	% Removal	Post Carbon ng/L	% Removal <sup>2</sup>	% Total Removal
<b>Fluorotelomer Sulphonic Acid 6:2 (FtS 6:2)</b>	48	0	<b>100%</b>	0		<b>100%</b>
NMethylperfluorooctanesulfonamidoacetic Acid	8.3	0	<b>100%</b>	0		<b>100%</b>
Perfluorobutanesulfonic Acid (PFBS)	13	0	<b>100%</b>	0		<b>100%</b>
Perfluorodecanoic Acid (PFDA)	6.1	0	<b>100%</b>	0		<b>100%</b>
Perfluoroheptanesulfonic Acid (PFHpS)	5.2	0	<b>100%</b>	0		<b>100%</b>
Perfluorohexanoic Acid (PFHxA)	130	0	<b>100%</b>	0		<b>100%</b>
Perfluorononanoic Acid (PFNA)	18	0	<b>100%</b>	0		<b>100%</b>
Perfluorooctanesulfonamide (PFOSA)	44	0	<b>100%</b>	0		<b>100%</b>
<b>Perfluorooctanesulfonic Acid (PFOS)</b>	610	4	<b>99%</b>	1.6	60%	<b>100%</b>
Perfluoroheptanoic Acid (PFHpA)	60	0.59	<b>99%</b>	0	100%	<b>100%</b>
<b>Perfluorooctanoic Acid (PFOA)</b>	170	1.7	<b>99%</b>	0.69	59%	<b>100%</b>
NEthylperfluorooctanesulfonamidoacetic Acid	720	22	<b>97%</b>	13	41%	<b>98%</b>
Perfluoropentanoic Acid (PFPeA)	63	2.6	<b>96%</b>	2.1	19%	<b>97%</b>
Perfluorohexanesulfonic Acid (PFHxS)	8.1	0.62	<b>92%</b>	0.41	34%	<b>95%</b>
Heptafluorobutyric acid	160	39	<b>76%</b>	0	100%	<b>100%</b>
11Cl-Pf3OUdS						
4,8-Dioxa-3H-perfluorononanoic Acid (DONA)						
9Cl-PF3ONS						
Fluorotelomer Sulphonic Acid 4:2 (FtS 4:2)						
Fluorotelomer Sulphonic Acid 8:2 (FtS 8:2)						
Hexafluoropropylene oxide dimer acid (HFPO-DA)						
Perfluorodecanesulfonic Acid (PFDS)						
Perfluorododecanoic Acid (PFDoA)						
Perfluorononanesulfonic Acid (PFNS)				0		
Perfluoropentanesulfonic Acid (PFPeS)		1.7		0	100%	
Perfluorotetradecanoic Acid (PFTeA)						
Perfluorotridecanoic Acid (PFTriA)						
Perfluoroundecanoic Acid (PFUnA)						
TOF (Total Tested PFASs)	2063.7	72.21	<b>97%</b>	17.8	75%	<b>99.14%</b>
TOC (Total Organic Carbon) <sup>3</sup>	96	42	56%	13	69%	<b>86.46%</b>

<sup>2</sup> Removal percentage by GAC from post GEG-2000 effluent

<sup>3</sup> TOC results measured in mg/L (ppm)