Development & Testing of the Decontamination Effluent Treatment System

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Engineer Research and Development Center (ERDC)

Problem

The Army has no capability to treat and/or recycle the effluent from its aqueous based chemical, biological, radiological and nuclear (CBRN) decontamination operations. This effluent is still very hazardous and a major handling, logistical, and potentially a political burden.

ERDC

Simulant Selection

ERDC/EL SR-16-2

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Composition of CBRN Decontamination Effluent and Development of Surrogate Mixtures for Testing Effluent Treatment Technologies

Jonathon A. Brame, Victor F. Medina, Imee Smith, and Lawrence Procell

July 2016

Environmental Laboratory

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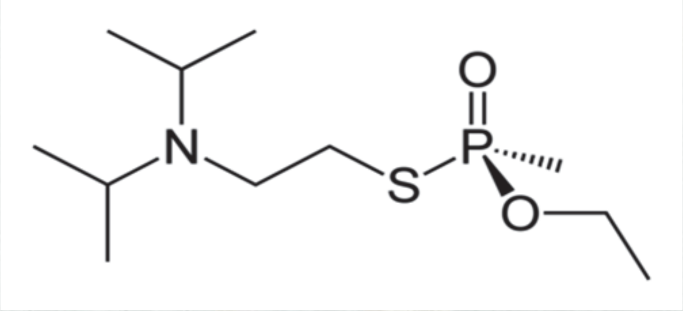
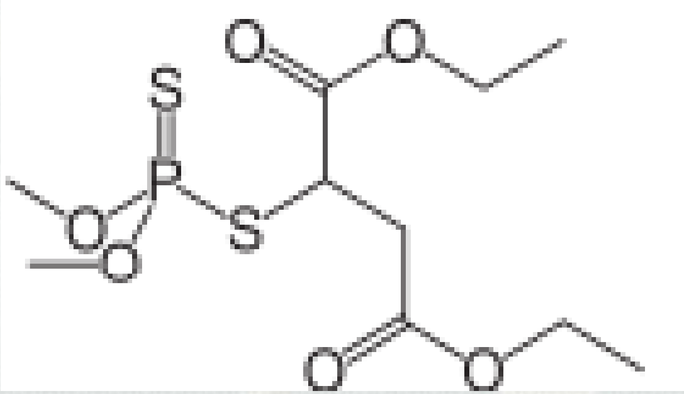


VX

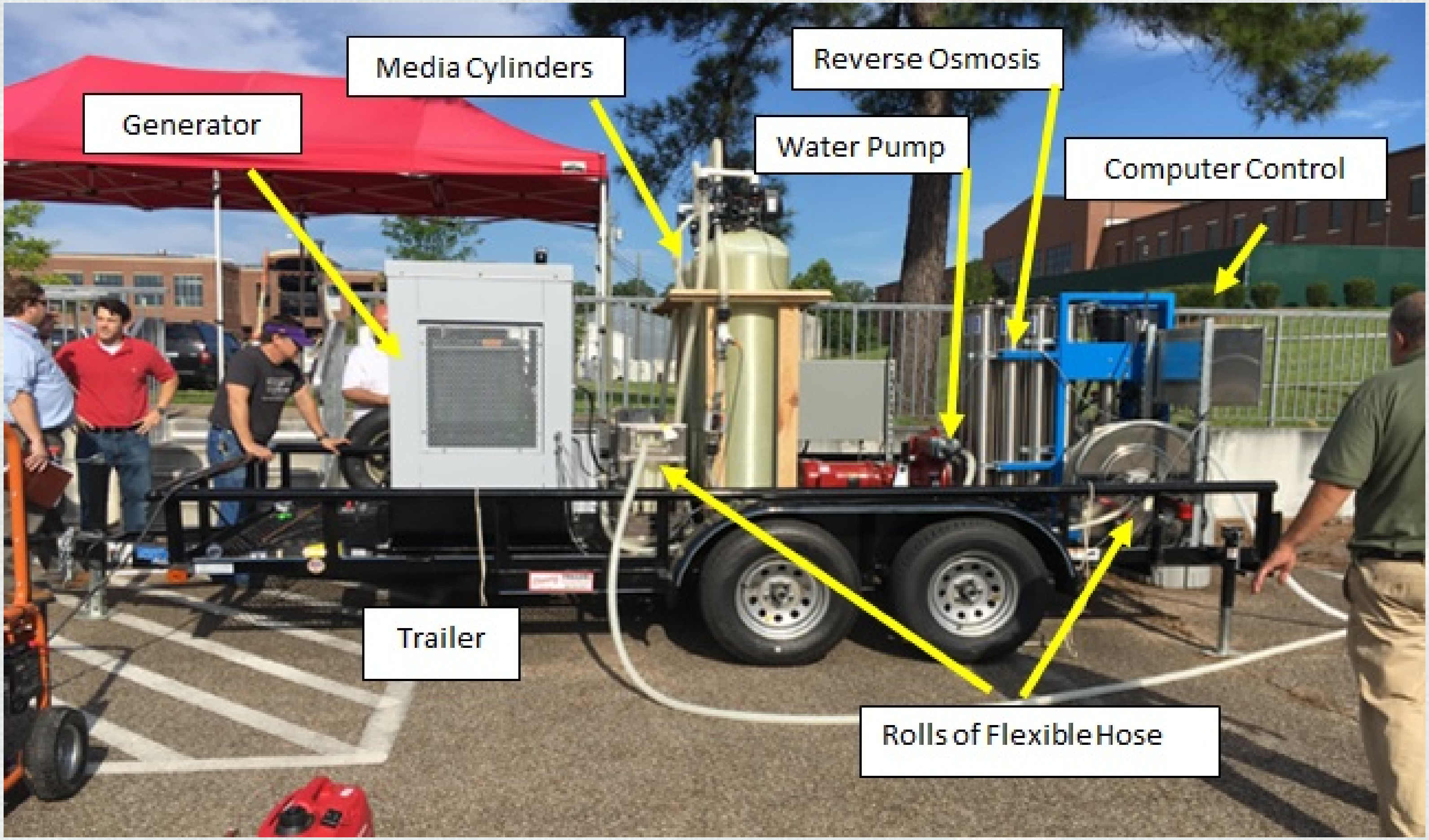


Malathion

Cs-133 as surrogate for Cs-137

https://www.researchgate.net/publication/306307888_Composition_of_CBRN_Decontamination_Effluent_and_Development_of_Surrogate_Mixtures_for_Testing_Effluent_Treatment_Technologies

The Decontamination Effluent Treatment System (DETS)



Treatment Strategy

- Sediment – Settling (tank or blivet) & sand filter
- Surfactant – Granular Activated Carbon (GAC)
- Bleach –GAC
- Oils/Greases/Misc. Organic Compounds – Incidental removal, GAC, Reverse Osmosis (RO)
- Chemicals – Incidental removal, GAC, RO
- Radioisotopes – Incidental removal, Sand, RO (especially Cesium [Cs])

Costs & Flow Rate

Unit	Cost	Comments
Reverse osmosis unit with pump & Prefilter Cleaning units for scale and organics Sand Filter Media Unit Carbon Filter Media Unit Water Softener Media Unit UV sterilization unit (not used in these studies)	$13,621.44	Price is for all the units described
Kubota Generator	$9922.45	
Bredel Pumps with mounting equipment and Hoses	$13,283.09	We purchased 2, but only 1 was used. Cost is for 1 unit.
Flanges	$1,066.00	
Hose Reels	8,939.92	
Trailer Trailer Upgrades	$5000.00 $1500.00	We determined upgrades were need after the initial demonstration
EZ Touch Control Unit with associated software	$1800.00	
Pressure gauges	$1000.00	Estimated
Wiring	$500.00	Estimated
Total	$56,632.90	

Flow Rate

- Battalion Sized Event involving people and vehicles to give volume
- Assume treatment time per day of 12 hours
- Adapted from planning factors of operational DECON (Army G3/5/7 Decontamination Planning factors)
- 10 gpm

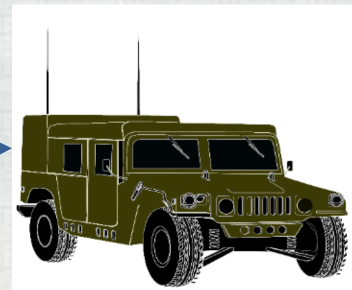
Costs

- Table to the left summarizes costs of elements of the system.
- The equipment costs were less than $60,000.
- Keeping costs low allows for a unit to be disposed of in its entirety if it gets highly contaminated during treatment.
- Enhancement of monitoring equipment is the greatest estimated additional cost.

Vehicle Decontamination Exercise

Wash Water

Pressure Wash
Sponge Wash
Rinse



Decon Effluent

DETS Pilot System (Trailer Mounted)

Clean Water

Discharge

and/or

Reuse

Details

- 27 June 2017
- 6 hours of total activity
- DETS operation 2 hours
- 10 large military vehicles & 20 cars, trucks, minivans were washed w/ soapy water & rinsed.
- 1200 gallons collected and spiked with Malathion, cesium, and bleach. Target concentrations were 10 mg/L.
- Contaminated water treated with the DETS
- Observers from JPM-P, Army MSCoE, JPdM A&RS, ECBC, DTRA, & USEPA

27 June 2017 DETS demonstration

Results

Constituent	Analytical Method	Influent Concentration	Effluent Concentration	%Removal
Turbidity	USEPA Method 180.1	>4200 NTU	1.825 ± 1.145 mg/L	100.0%
Hardness	Summation of Ca^{2+} and Mg^{2+} concentrations as measured by ion chromatography	82.36 ± 40.79 mg/L	0 mg/L	100.0%
Total Chlorine	Standard Method 4500-Cl G	0.26 ± 0.07 mg/L	0 mg/L	100.0%
Surfactants	Spectrophoto-metric method as given in Kloos (2015)	1.422 ± 0.359 mg/L	0.019 ± 0.017 mg/L	98.7%
Total Organic Carbon	USEPA 5310B	58.23 ± 29.7 mg/L	1.18 ± 0.84 mg/L	98.0%
Malathion	Phosphorus balance	26.71 ± 12.16 mg/L	0.08 ± 0.05 mg/L	99.7%
Malathion	USEPA 8141A	24.7 mg/L	0.000097 mg/L	100.0%
Cesium	USEPA 6020A	2.97 ± 4.21 mg/L	0 mg/L	100.0%

All measurements indicate that the DETS is highly effective treating constituents found in decontamination wash water.

Concentrate & Reuse

Constituent	Average Initial Concentration	Concentration in Concentrate at midpoint of evaluation	Concentration in Concentrate at end of the evaluation
Turbidity	>4,200 NTU	827 NTU	859 NTU
Total Suspended Solids (TSS)	3,088 ± 1,532 mg/L	1,192 mg/L	756 mg/L
Total Organic Carbon (TOC)	58.2 ± 29.7 mg/L	35.9 mg/L	41.4 mg/L
Conductivity	218 ± 134 mS/cm	592 mS/com	689 mS/cm
Hardness	82.4 ± 40.8 mg/L	40.7 mg/L	32.1 mg/L
Surfactant	1.42 ± 0.36 mg/L LAS	0.80 mg/L LAS	0.82 mg/L LAS
Free Chlorine	0.26 ± 0.07 mg/L	0.20 mg/L	0.20 mg/L
Malathion	26.71 ± 12.16 mg/L	19.08 mg/L	19.85 mg/L
Cesium	2.96 ± 4.2 mg/L	0.06 mg/L	0.08 mg/L

Take home message: The concentrate is not much different than the initial concentration.

So, it can also be returned to the reactor & treated

Approach Zero Discharge

Recycling analysis assuming 600 gal reused after treatment:

- Without concentrate treatment: 4000 gal
- With single concentrate treatment: 7000 gal

Documentation

Videos

Vehicle exercise

https://youtu.be/d9TZvYzUMn0

Marketing video

https://youtu.be/9aNgCDKj_fU

Control system

https://youtu.be/S2JQ6ZWqKCw

Publications

Military Engineer Article

https://www.researchgate.net/publication/322552627_Treating_Contaminated_Effluent

Army Chemical Review – In Press

Technical Report – In editing

ERDC/EL-TR-17-XX

EL

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Environmental Quality/Installations

SIMULATED VEHICLE DECONTAMINATION AND FIELD EVALUATION OF THE DECONTAMINATION EFFLUENT TREATMENT SYSTEM (DETS), 27 JUNE 2017, AND ASSOCIATED BACKGROUND STUDIES

Victor F. Medina, Scott A. Waisner, Edith Martinez-Guerra, Jared Johnson, Jonathan Brame, Elizabeth Gao, and Martin Page

January 2018

Approved for public release; distribution is unlimited.

Mass Personnel Decontamination (MPD) study

- 24 May study on at Vicksburg station
- prepare a simulant of MPD in a 3000 gal blivet based on grey water simulant formulations (1800 gal of solution)
- spike with CBRN simulants (malathion & cesium)
- Contact me if interested in observing

MPD Simulant Formulation (1800 gal)

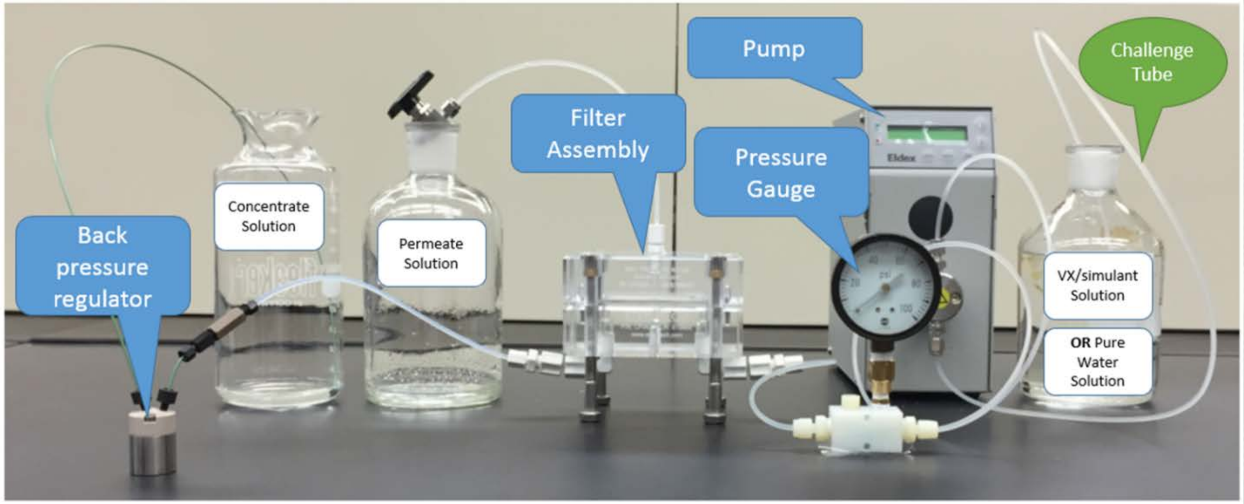
Malathion			
0.064	3.5mL/55gall	for 10 ppm	
For 1800 gallons			
114.54545	mL for 10 ppm		
57.3	mL for5 ppm		
Cs			
6.33 mg/L CsCl for 5 ppm of Cs			
43126.29	mg of CsCl		
43.1	g CsCl		
Surfactants			
0.3785455	g/gall		
681.4	g of Dawn	for 10 ppm	
Approx 731 mL			
Sediment			
34065	mg of soil		
34.065	g of soil for 5ppm		

3000 gal blivet

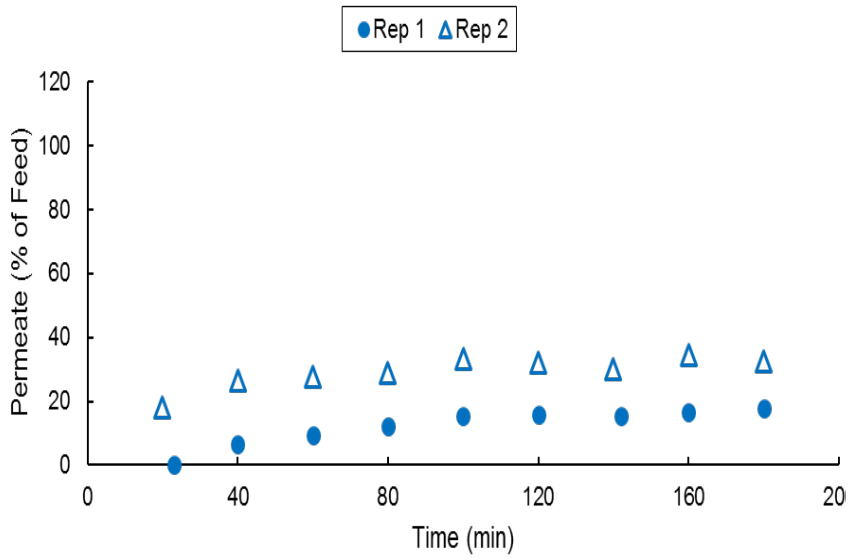
Allied Studies at Edgewood Chemical & Biological Center

- Purposes:
  - To test DETS treatment processes on actual agent (VX)
  - Provide comparison with Malathion simulant
- Studies Tested interactions with:
  - Sand
  - Granular activated carbon
  - *Membrane Removal.
- Funding by ERDC and DTRA
- Presented with approval by Larry Procell

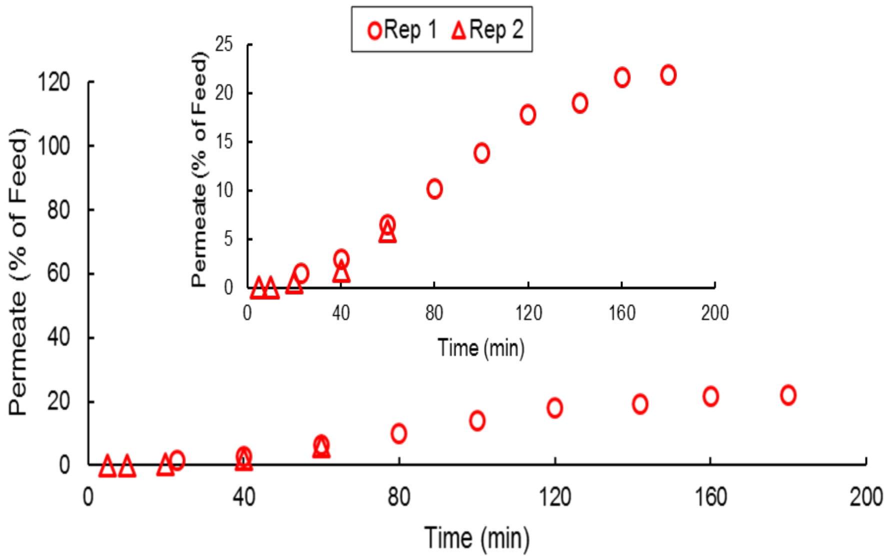
Removal by Membrane



Results suggest that although not identical, Malathion and VX perform similarly in our most important unit process.



VX Results



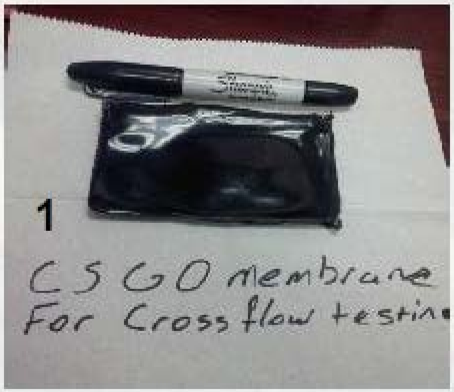
Malathion Results

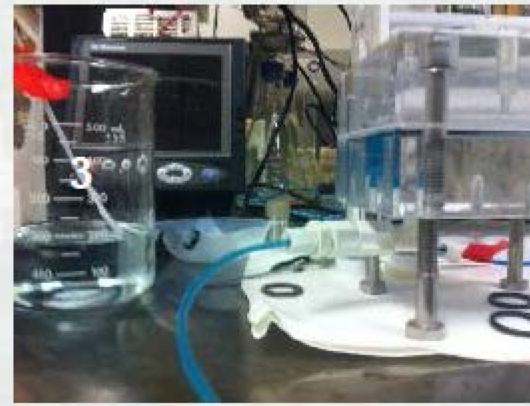
Engineer Research and Development Center

Novel Membrane Technologies

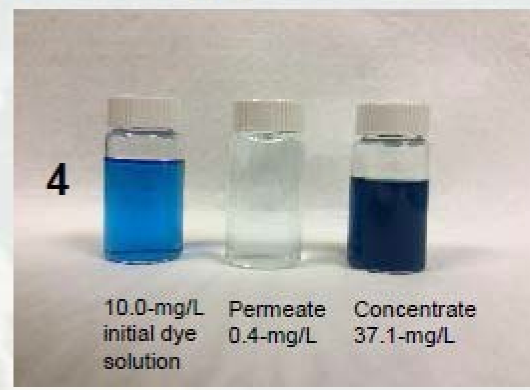
Last update (16-Mar-16)

Successful Implementation of Cross-Current Testing of GO Membranes – the most advanced system we have identified to date





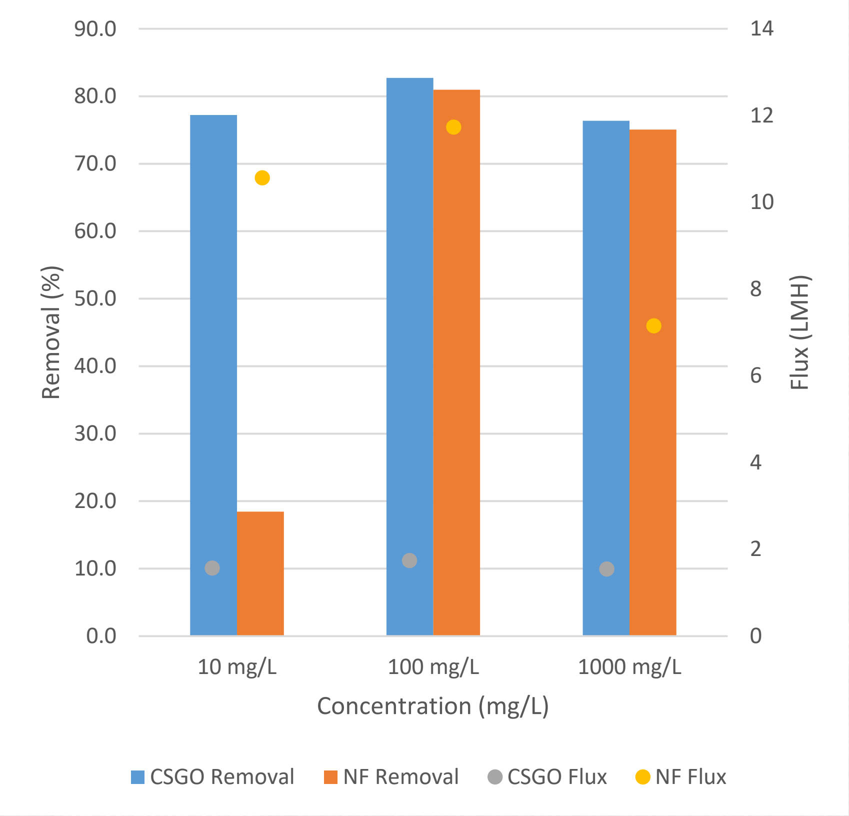
1. A chitosan/graphene oxide (CSGO) membrane was prepared. We found that these membranes can swell, but by sandwiching them between paper filters, the swelling could be controlled.
2. Our cross flow reactor. The flow was set at 10 mL/min. Pressure was 50 psi. Flux was ~1.4 gfd (2.3 LMH). We treated 1 liter of solution.
3. The beaker is the permeate.
4. The results – a 10 mg/L dye solution was treated. The permeate had a concentration of 0.4 mg/L, a 96% reduction. The concentrate was 37.1 mg/L.



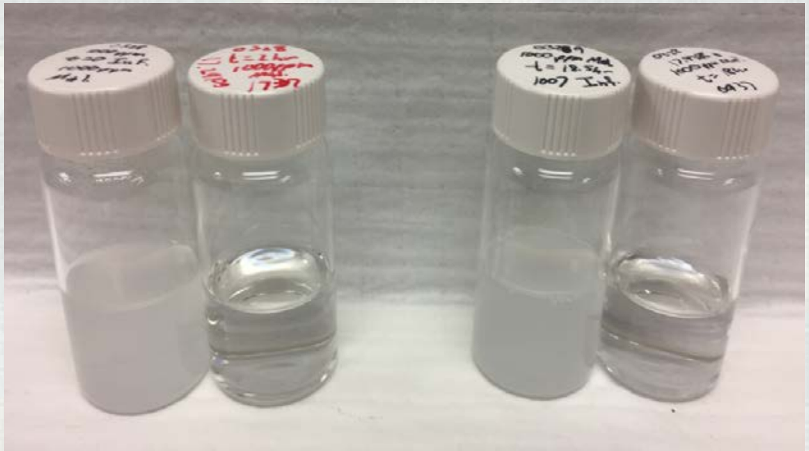
Treatment of Malathion, comparison to NF

Chitosan-graphene oxide composite membrane (CSGO)
vs.
Nanofiltration (NF)

Dow Filmtec Flat Sheet Membrane, NF, PA-TFC



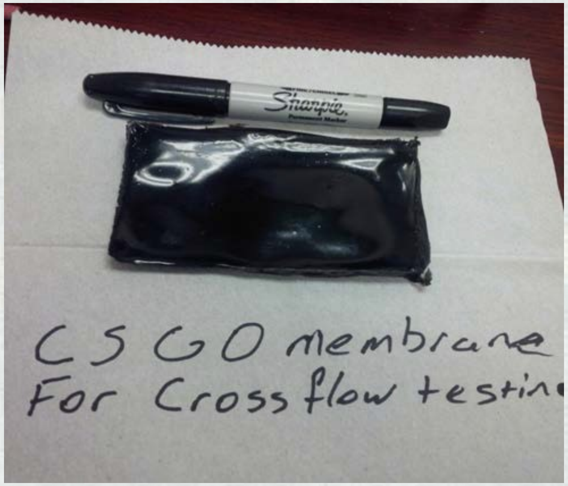
1000 mg/L Malathion before & after treatment.
Treated samples visually less turbid



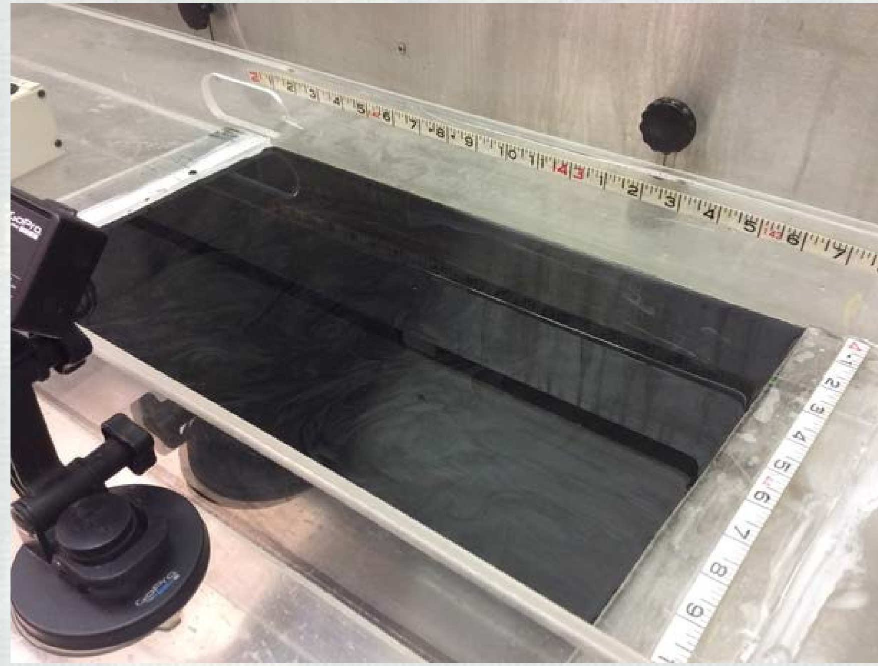
- Removal of Malathion by CSGO comparable to that of NF, even better at low concentration.
- Differenced due to different removal mechanisms
- CSGO flux rates about 3.5 to six times lower than NF, but more consistent.

Scalable and Freestanding Membranes

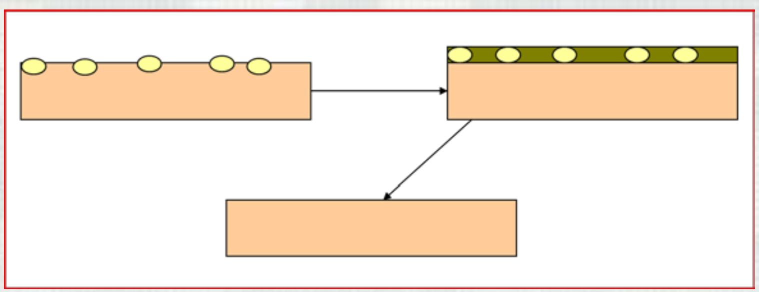
47mm



7 X 12 cm



30 X 45 cm

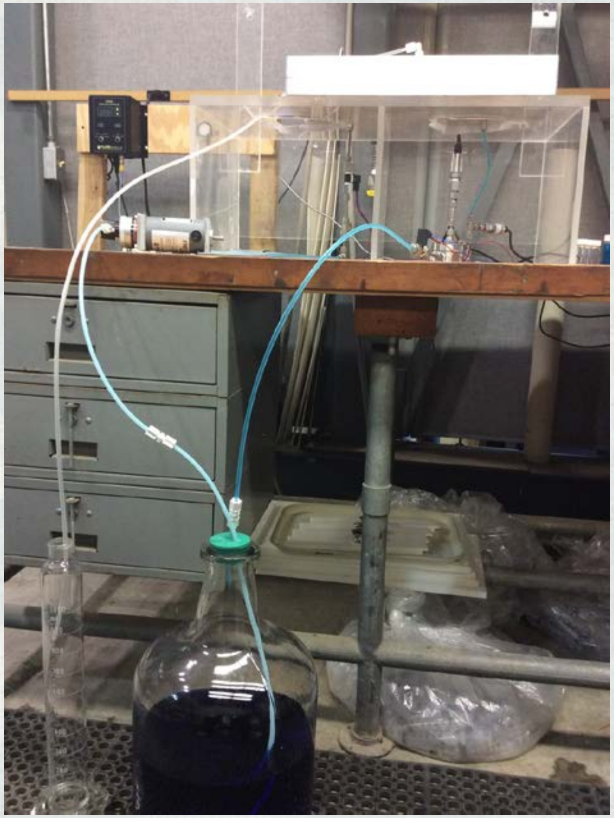


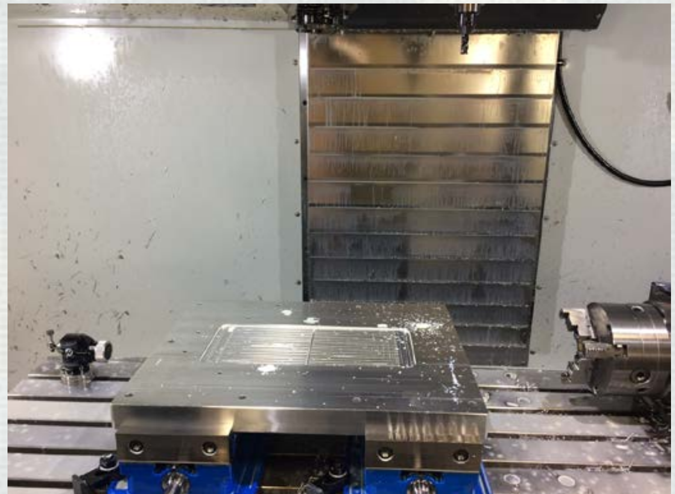
Can this process be modified for surface remediation?

Setting video: https://youtu.be/BplAGoNMz54

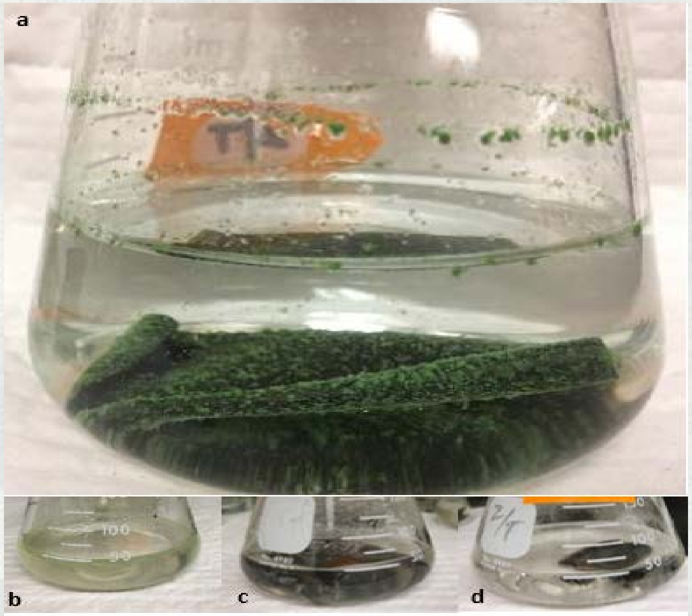
Crosslinking Graphene Oxide and Chitosan to Form Scalable Water Treatment Membranes- *Mattei Masters Thesis MSU 2017*

Advanced Upscaling

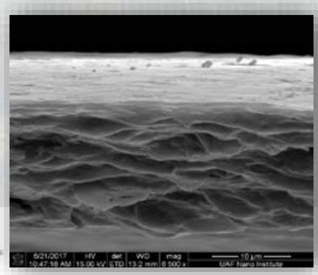


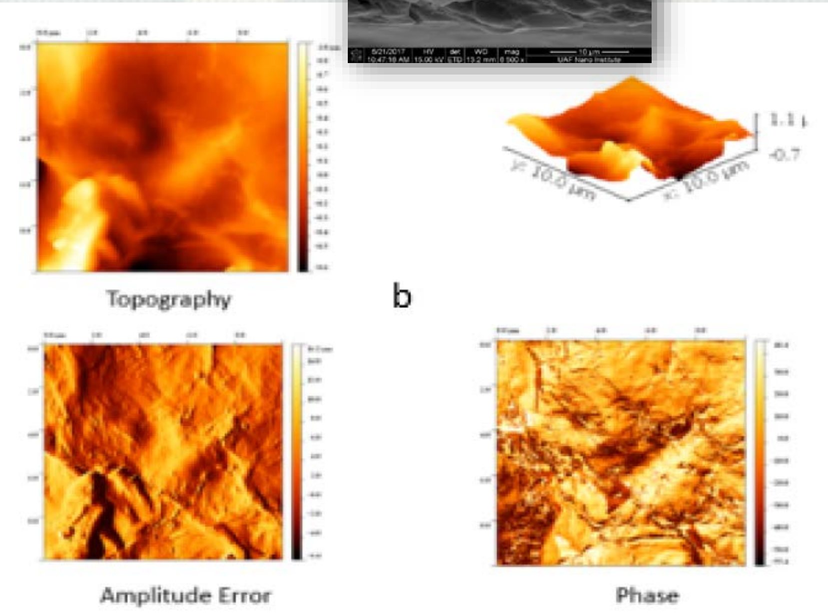


Antimicrobial properties

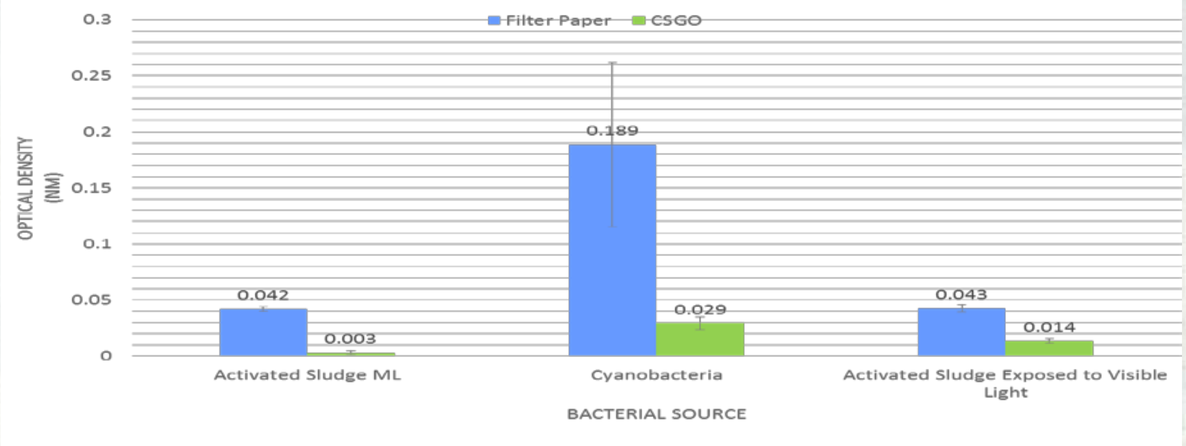


Flocculation of cyanobacteria onto a GO composite (a), control cyanobacteria (b), CSGO composite showing loss of green pigmentation (c), and AgNO3-CSGO composite showing significant loss of green pigmentation (d).



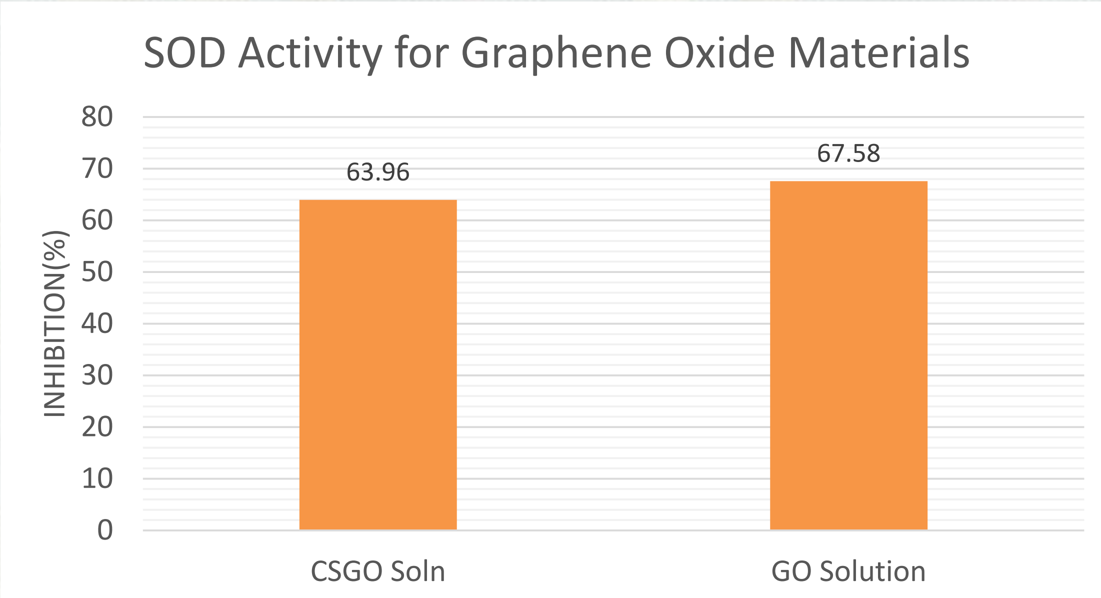


FTIR surface mapping shows wrinkled surface of CSGO associated with physical microbial deactivation.
Can we enhance this property?



Microbial density (as optical density)
Solutions with same size swatches of CSGO vs. Whatman Filter Paper

Reactive Oxygen Species



Graphene oxides have been found to create reactive oxygen species (ROS), including superoxide and hydroxyl radical.

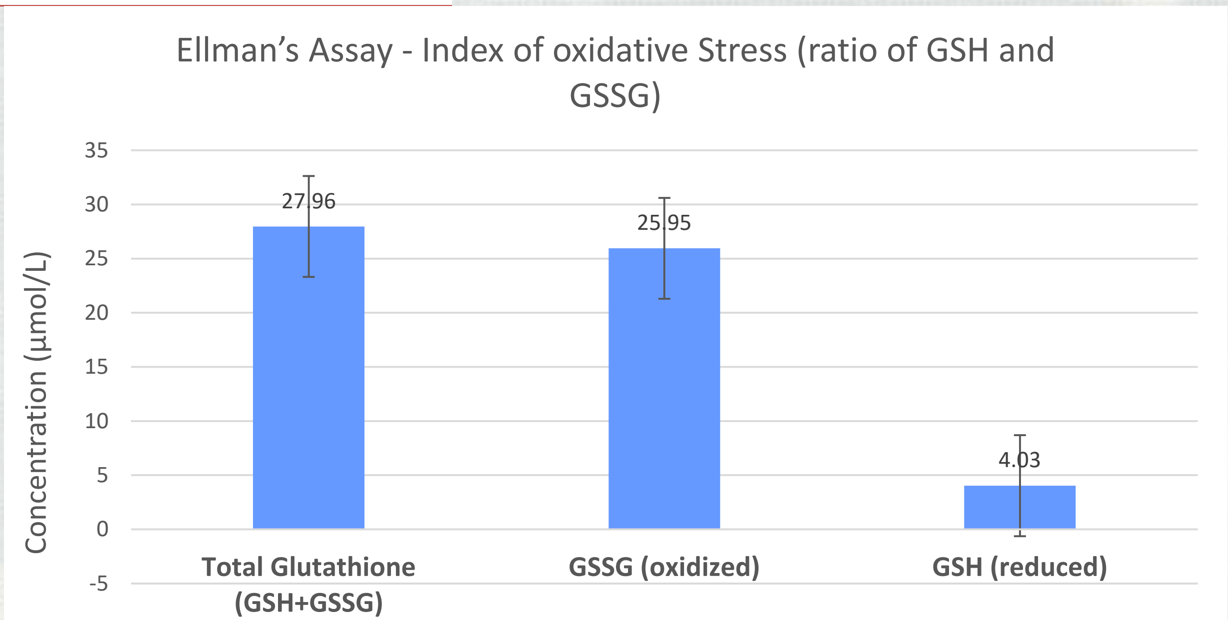
We used two assays, Superoxide dimutase (SOD) and Ellman's Assay (oxidation of glutathione) to confirm ROS activity in the CSGO composite

ROS are highly effective oxidants.

They may contribute to antimicrobial properties.

They directly react with chemical contaminants.

Is this property "tunable"?



Graphene Publications

Abolhassani, M., C.S. Griggs, L.A. Gurtowski, J. Mattei-Sosa, M. Nevins, V.F. Medina, T.A. Morgan, L.F. Greenlee. 2018. Scalable Chitosan-Graphene Oxide Membranes: The Effect of GO Size on Properties and Cross-Flow Filtration Performance. ACS Omega. DOI 10.1021/acsomega.7b01266

Medina, V.F., C.S. Griggs, B. Petery, J. Mattei-Sosa, L. Gurtowski, S.A. Waisner, J. Blodget, and R. Moser. Fabrication, characterization, and testing of Graphene Oxide, and Hydrophilic Polymer Graphene Oxide Composite Membranes in a Dead End Flow System. *Journal of Environmental Engineering*. 143(11): DOI: 10.1061/(ASCE)EE.1943-7870.0001268

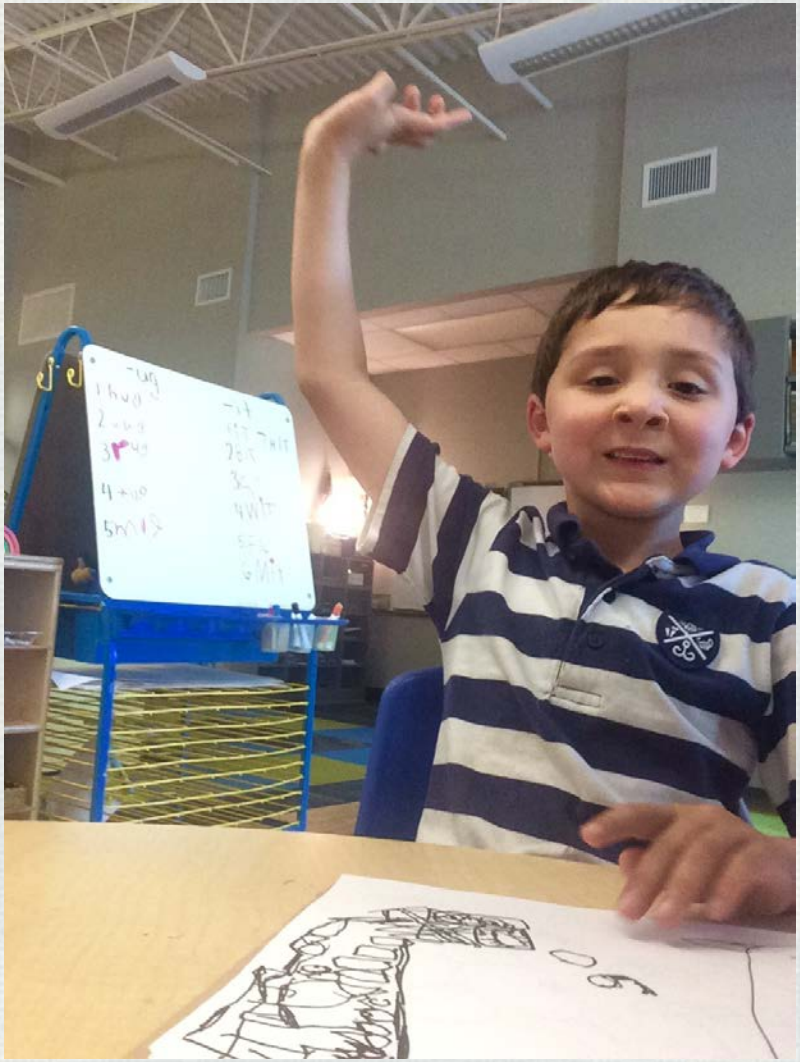
Griggs, C.S., and V.F. Medina. 2016. Graphene and graphene oxide membranes for water treatment. *McGraw Hill Yearbook of Science and Technology*. McGraw Hill Publishers. DOI: 10:1036/1097-8542.YB150695.

Download at: https://www.researchgate.net/profile/Victor_Medina9

Conclusions

- The DETS addresses a key gap in aqueous CBRN decontamination
- 10 gpm is a suitable target for a battalion sized event
- The capital costs for such a system are reasonable
- Laboratory testing showed effective treatment.
- A field evaluation focusing on vehicular decontamination showed that the wash water could be easily captured.
- The field evaluation showed effective treatment for environmental contaminants, decontamination agents, and simulants.
- Testing with live VX agent by ECBC shows that our assumptions of similarity with malathion are reasonable.
- Allied experimental work with Graphene Oxide composite membranes show promising results.

Questions?!



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Treatment Goals

- OCONUS
  - ► Discharge – Meet OEBGD requirements for discharge
  - ► Reuse – No requirements, but APHC indicated reuse is acceptable.
- CONUS
  - ► There are no documents for discharge
  - ► Sanitary Sewer – Agreement with POTW
  - ► Stormwater – Meet NPDES
  - ► Reuse – No requirements to date.
  - ► Potable

Process control and instrumentation

Control architecture: EZAutomation EZ-Touch HMI/PLC

- Customizable and programmable interface with ladder logic control
- Data recording
- Modular I/O
- Pressure sensitive touch screen – compatible with heavy gloves

Power Supply

- Kubota Diesel 9875 Watt Generator
- 240 V, 40 amp
- 60 gallon subbase fuel tank and a two-wire auto start control.
- Sound enclosure keeps noise at 68 dB(A) at 7 m (23 ft), which is helpful for communications.
- The system is also designed to be suitable for operation of sensitive electronic equipment.
- Fuel consumption varies from 0.41 to 0.84 gal/hr
- The system can also simply be plugged into a 240 V, 40 amp source.

Alpha Version of Mobile Treatment System

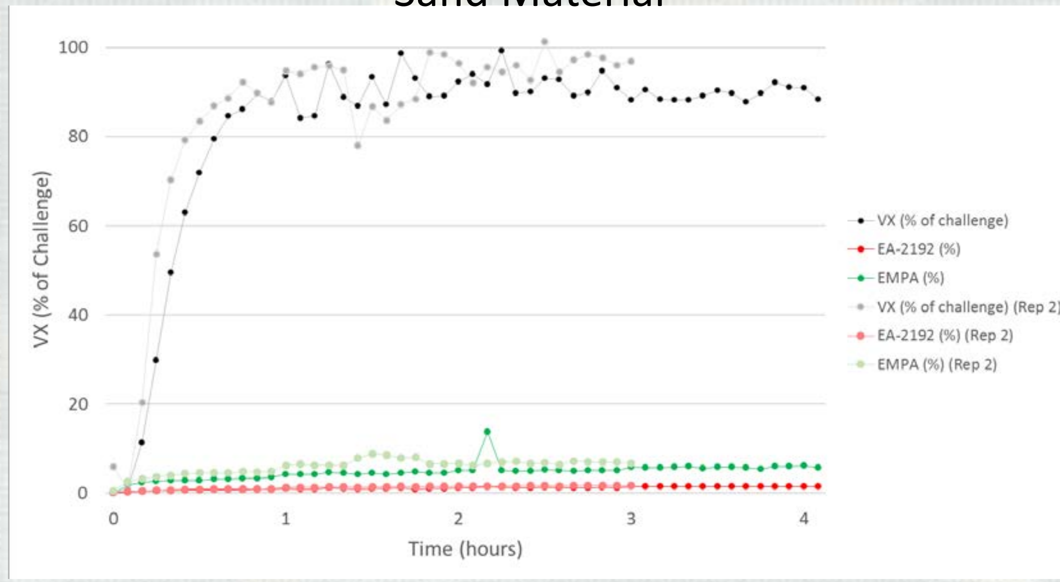
Our pilot reactor capable of treating aqueous effluent from decontamination of 200 people and 10 large vehicles per day for 3 to 5 days.

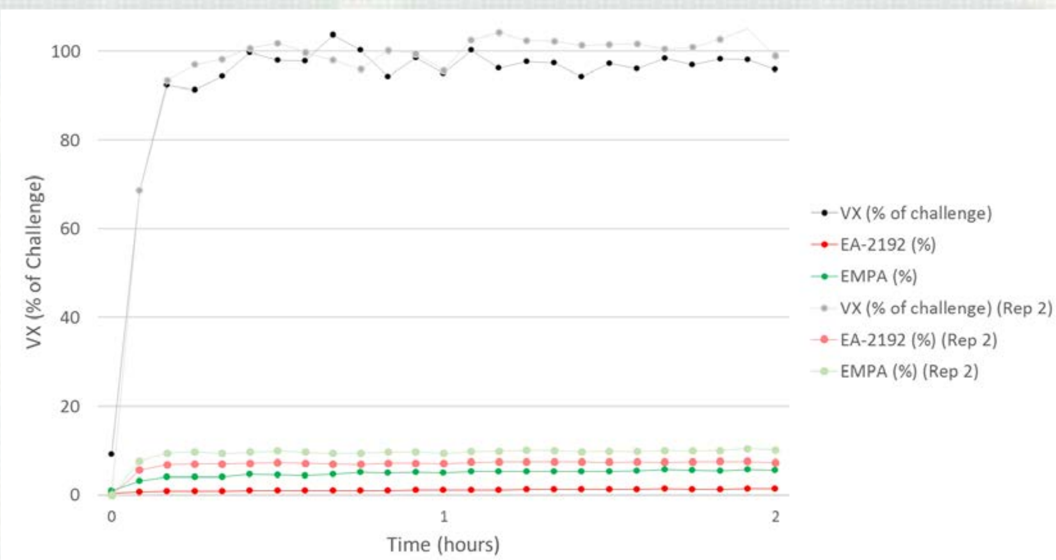
Our system treated a simulated effluent with soap, bleach, clay and cesium. The removal was >99 percent of each constituent.

VX in Sand & Anthracite

- Immediate breakthrough on both materials
- Small generation of breakdown products (assume to be hydrolysis)
- Breakdown product generation also found in untreated feed solution samples.

Sand Material



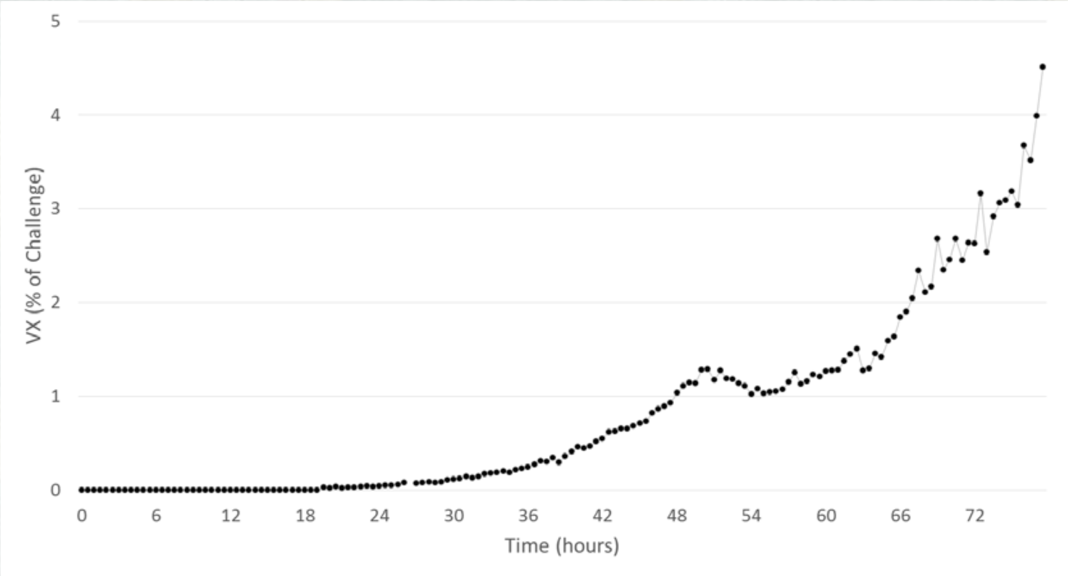


Anthracite Material

Feed Solution before and after Experiment (24 hours)

	Concentration, ng/mL			Percent Composition		
	VX	EMPA	EA 2192	VX	EMPA	EA 2192
initial	11,950 ± 226	171 ± 73	101 ± 57	97.72	1.43	0.85
final	12,026 ± 113	462 ± 6	1051 ± 95	87.40	3.87	8.73

VX in Granular Activated Carbon Column



- Adsorption effect evident.
- Complete removal for 18 hours.
- Line steepens at 72 hours
- Percent breakthrough was less than 5% at end of experiment 37.5 gal or 142L treated)
- Transformation products not detected.