

PETROLEUM SEPARATION FROM WATER USING POLYMERIC SURFACTANT INFUSED MEDIA

Presented at the 13th Annual Produced
Water Conference
Houston, Texas
January 15, 2003

Author: Kirk Abbott
Director of Engineering
MYCELX® Technologies Corporation

Petroleum Separation from Water Using Polymeric Surfactant Infused Media

by
Kirk W. Abbott

**13th Annual Produced Water Conference
Houston, Texas
January 15, 2003**

Abstract:

The application and potential of MYCELX™ Technology, referred to as “polymeric surfactant infused media”, is outlined for separating and removing petroleum compounds from water. Loading and subsequent fouling on membrane and deionization systems are discussed. Benefits and additional data are presented on MYCELX hydrocarbon removal capabilities in various water treatment applications.

MYCELX: A Definition...

MYCELX is a polymer compound formed as a synthesis product of natural drying, semi-drying, and non-drying oils with a synthetic polymer [Composition Patents: 5,437,793 and 5,746,925 / Chemical Abstract Service (CAS) #173967-80-1 and #173967-81-2]. The MYCELX polymer is infused and cured into a variety of substrates (i.e. filter cartridges and absorbent materials) so that it is homogeneously dispersed throughout the base material(s). As hydrocarbon compounds come in contact with MYCELX, they are dissolved and bonded to, and will not re-disperse or emulsify into water.

MYCELX infused five-micron cartridges are engineered to remove petroleum-type hydrocarbons ranging from oil to gasoline, including “BTEX” compounds – Benzene, Toluene, Ethylbenzene and Xylene(s), at over 99% in a single-pass without significant pressure drop or clogging (roughly 0.5 psi to saturation).⁽¹⁾ MYCELX cartridges can separate oil-water mixed emulsions and remove semi-soluble compounds. MYCELX infused cartridges are proven effective in removing Alkanes, Alkenes, Cycloalkanes, Aromatic Hydrocarbons (BTEX), Crude Oils, Vegetable Oils, Complex Monomers, Polymers, Organo-metallics, PCBs, MTBE and Chlorinated Organic compounds.

MYCELX infused materials are extremely hydrophobic and will not absorb water. Typically, oil sorbents and filters absorb many times their weight in water. MYCELX materials only absorb hydrocarbon based pollutants, so when saturated, only the MYCELX material and the pollutant are left (i.e. no residual water).

MYCELX is a non-hazardous / non-toxic material, and declared compliant to section 300.915 of the NCP by the EPA. MYCELX infused cartridges and media are easily disposed of by incineration. They have an extremely light water drag-out and low ash content, resulting in a clean burning waste with a BTU value comparable to alternative fuels. The hazardous nature of the MYCELX cartridges are dictated by the absorbed/adsorbed contaminates. In many cases, petroleum saturated MYCELX materials can be land filled with other petroleum saturated materials (i.e. oily rags, sorbents and oil filters).

MYCELX Hydrocarbon Removal Applications:

Pretreatment for Membrane Systems

Membrane systems, such as Reverse Osmosis (RO), Nano-filtration (NF) and Ultrafiltration (UF), are used in a variety of water treatment applications. Membrane technologies work as molecular sieves and through size exclusion, remove organic and inorganic contaminants larger than a given pore size.

Membrane systems are often on-line for long periods of time processing large volumes of water. Even trace amounts of organics retained by the membrane can accumulate over time and reduce permeate flow, increase differential pressure and cause contaminant slippage into the permeate. Petroleum-type organic foulants rapidly clog membranes because the organic foulant and the membrane materials are similar. Like attracts like.

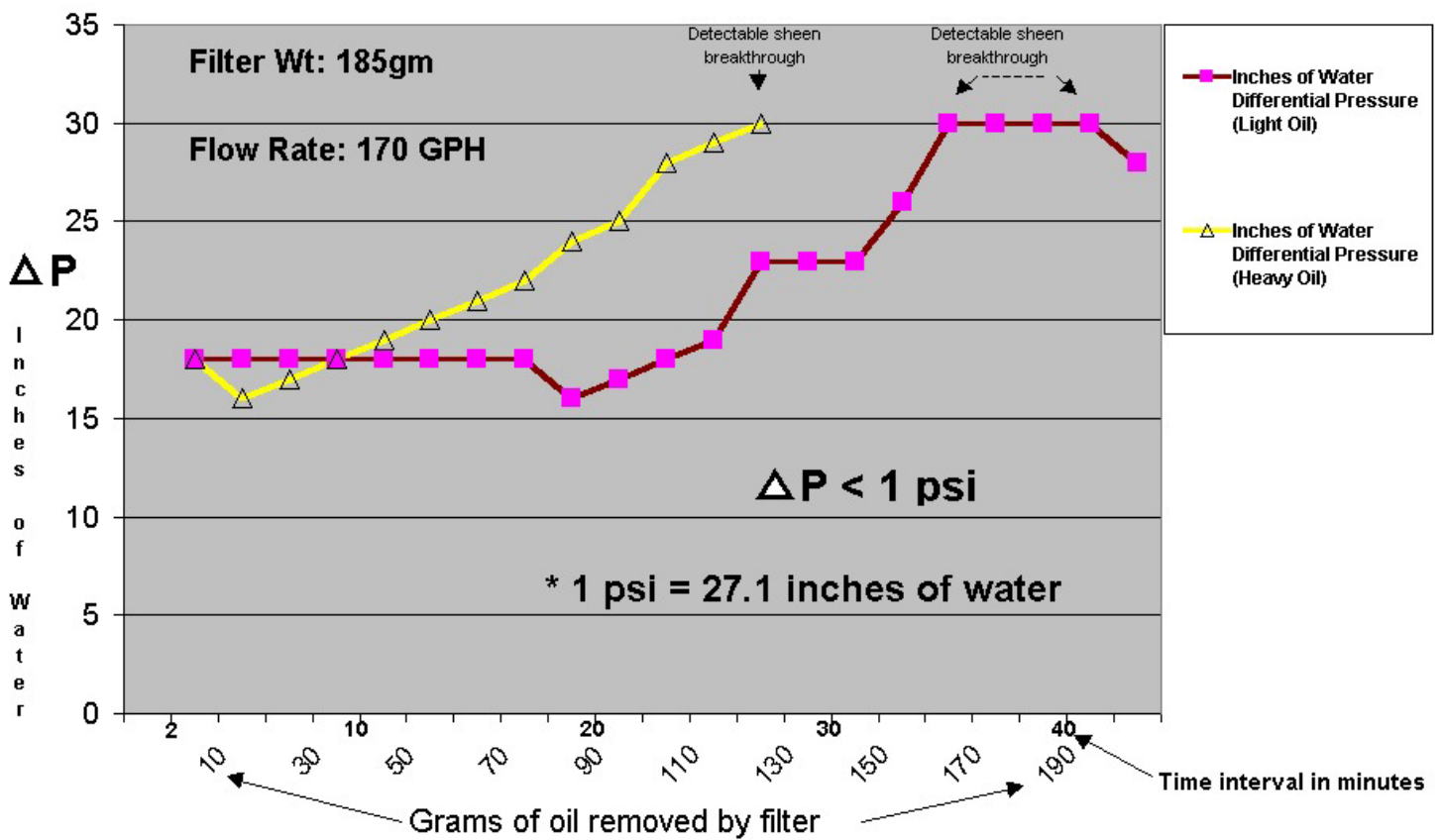
As a result of incipient and chronic organic fouling of membrane systems, large pressure drops occur, and membranes must be periodically cleaned. Cleaning petroleum-type organic fouling is more problematic because chemicals that are effective in removing the organic fouling agents tend to denature and damage the membranes. Again, this is because the membranes are chemically similar to the foulants themselves. ⁽²⁾ The control of organic fouling in membrane systems really depends on reducing organic contaminants prior to the membrane system rather than periodic membrane cleaning.

As mentioned above, one of the basic properties of many filtration membranes is that they are composed of hydrophobic polymers. This causes them to attract and attach hydrophobic molecules, i.e. oils, and other organic compounds. Attempts made to solve this problem using prefiltration have been largely unsuccessful due to high pressure drops and contaminant slippage across these filter materials after they have captured and clogged with hydrophobic organic compounds and oils. The prefilter pressure drop increase is mostly due to the swelling of the polymer and organic foulant coagulate. Generally, the result has been prefilter organic fouling as opposed to cross flow membrane fouling, but due to the large volume of water processed by membrane systems, membrane fouling still occurs. ⁽²⁾

To address the problem of increasing pressure drop on membrane prefilters, MYCELX Technologies Corporation, developed an oleophilic cartridge which exhibits insignificant pressure drop even as it saturates with viscous organics (Figure 1). What makes the MYCELX molecule novel, aside from its high affinity for organic compounds, is that the polymer itself and its coagulate product with petroleum is viscoelastic. ⁽³⁾ Generally, viscoelastic materials become thicker and denser with shear. The MYCELX-induced viscoelastic phase actually contracts as water shears over the cartridge. Essentially, the opposite of swelling occurs as the contaminants are absorbed. This is a very important fact because as water passes through a MYCELX infused cartridge, the coagulate contracts allowing for essentially zero pressure drop to saturation (roughly 0.5 psig @ saturation), generally with 99.9% first-pass efficiency.

Figure 1

LOW DIFFERENTIAL PRESSURE (TO SATURATION)



Case Study 1.0 – Government Contractor Installation

An industrial manufacturing plant extensively uses RO to recover process water due to its location in the desert where water is scarce. This facility initially attempted recovery of process waters utilizing membrane technology. They found that maintenance, cleaning and replacement of membranes only gave them 50 percent of their initial projected yield. The system was deemed effective but uneconomical. Consequently, polymeric surfactant (MYCELX) cartridges were deployed as RO membrane prefilters. After processing nearly a million gallons of water the facility has found that membrane service life has extended ten-fold, resulting in a 50 percent decrease in cost to treat. MYCELX technology allowed the plant to economically re-use their process water – a precious resource in this case.

Case Study 2.0 – Machining Facility Process Water Recovery

MYCELX cartridges (i.e. 4 x 30” PP five micron Septa) were installed prior to NF membranes.

System Configuration:

UF → MYCELX Unit → Holding Tank → NF → RO

System Details:

- The Ultrafiltration (UF) system consists of "Sintered Stainless Steel (0.1 Micron) Membranes". The UF system intermittently discharges between 20-80 ppm emulsified lube oil @ 40 gpm.
- The MYCELX cartridges polish this residual emulsified lube oil. The MYCELX unit captures on average 2.64 kilograms of hydrocarbon and treats between 85,000-100,000 gallons (cost-to-treat totally depends on inlet concentration of oil).
- Typical operating pressure drops across the MYCELX unit are between 2.5 psi (initial) and 3.0 psi (final). The filters are changed when visible sheen breaks through to the Hold Tank.
- The NF system consists of spiral-wound polymer membranes ("TriSep/Filmtec NF70 type") and flows 40 gpm as well.
- The NF system feeds two 20-gpm RO systems with different brands of spiral-wound membranes. The first are Filmtec BW30 type membranes & the second consists of Hydranautics' equivalents.

The MYCELX unit significantly reduced the rate of NF membrane fouling and preserved the NF system's percent recovery. Preliminary indications are that the MYCELX cartridges will extend the NF membrane service-life by a factor between 5-7 times, as well as reduce annual energy requirements, maintenance and downtime.

Oil/Chlorinated Hydrocarbon / BTEX Removal:

Case Study 3.0 – Electric Utility Application

The utility industry – like many others seeking to protect the environment while at the same time reducing their risk of fines, costly cleanup efforts and unwanted public scrutiny – is striving to prevent oil and PCB contamination of soil and water.

For utilities, the problem occurs primarily in manholes and in transformer yards where storm water is exposed to old transformers and capacitors that may still have/had oil or fluids that contain some PCBs. In order to perform maintenance, the storm water (containing traces of oils, lead and PCBs) must be pumped out of the manholes and retention wells, and be treated before it can be discharged to the environment or municipal sewer systems – an expensive process for any organization.

For one utility, this practice – excluding pumping and transportation of the water to a treatment facility – cost 25 cents per gallon. JoDAN Technology, LTD (JDT) was asked to develop a treatment system to address the oil/PCB/contaminant concerns. In cooperation with the electric utility, JoDAN developed the JMOR™ System consisting of particle filtration and MYCELX separation technology.

In June 2000, JDT designed, built and began testing first system. This system used particulate bag filters followed by an MX-12 (12 x 30" MYCELX -infused cartridges). After 4 months of operation the system processed 1,300,000 gallons of manhole wastewater at a cost of 2.8 cents per gallon. The system removed PCBs, oil and grease, copper, and hydrocarbons to Below Detectable Limits (BDL). As an unexpected bonus, the system also reduced the particulate lead from the effluent water. See Table 1.0.⁽⁴⁾

Table 1.0: Results from treating 1,300,000 gallons of manhole water.

	PCB1254	TPH	Oil&Grease	Lead	Copper
	ppb	ppm	ppm	Avg. ppm	ppm
MYCELX Effluent	<1.0	<5.0	<5.0	0.020	<0.01
Avg. Influent	3.74	367.9	17698	33.0	11.6
Max. Influent	40.0	21400	141000	150.0	87.0

- Values presented are from the utility's analysis of influent and effluent samples
- The lead and copper removal was due to the metals being tied up as organo-metallics
- All PCB samples were analyzed as PCB Aroclors
- PCB effluent samples were all < 1.0 ppb

Case Study 4.0: Land Fill Discharge Water

An owner of a landfill requested technical support to remove trace oil and PCBs to below 65 ppt (parts per trillion) from landfill storm water run-off. A MYCELX cartridge unit was placed down stream of a 1µm particle filter and sand filter. Results from the 1st trial are listed in Table 2.0

Case Study 5.0: Industrial Wastewater

An industrial manufacturer generates PCB contaminated water which results from decommissioning electrical equipment containing PCB contaminated capacitors and transformers. Cost to have the wastewater shipped off-site and treated was over \$1.00 per gallon. JoDAN Technologies, LTD utilized MYCELX cartridges and treated the wastewater on-site for less than \$0.05 per gallon. The results are reported in Table 2.0

Table 2.0 - Results for PCB Case Studies 4.0 and 5.0

	Land Fill (MYCELX Standard Formulation) PCB 1254 2.5 gpm	Manufacturer (MYCELX Standard Formulation) PCB 1254 5 gpm
Influent	129 ppt	174 ppb
Effluent	BDL(<65 ppt)	BDL (<1.2 ppb)

Case Studies 6.0 & 7.0: BTEX & MTBE Removal (See Appendix)

Data for Benzene & Toluene removal (case study 6.0), and BTEX & MTBE removal (case study 7.0) are presented in the attached appendix.

Benefits of High Flow / Low Pressure Drop Cartridges

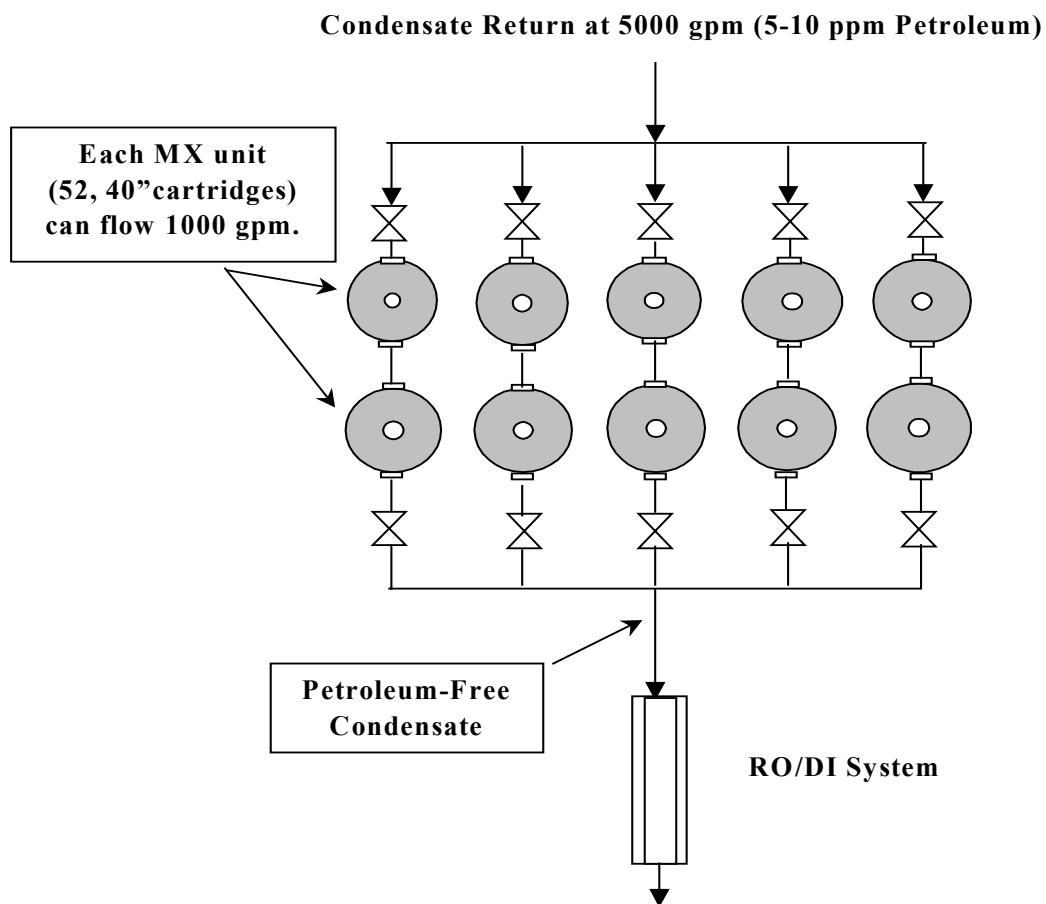
Because MYCELX cartridges operate with insignificant differential pressure ($\Delta P < 1.0$ psi), and permanently capture organic compounds that clog and/or foul existing technologies, MYCELX separation systems save money by reducing pressure drop. Field data and energy (ΔE) calculations on ultra-low pressure drop cartridges suggest a 15 to 25 percent efficiency increase for pumps (versus conventional absorbents like carbon or clay) in applications involving mixed hydrocarbons.⁽⁵⁾

For membrane systems, ion exchange and other polishing technologies, additional savings are realized from the following:

- MYCELX systems preserve capacity, flux and percent recovery while extending service life typically 5 to 10 fold.
- High flow and small footprint (1000 gallons per minute with 33-inch diameter vessel) employing standard 40-inch high, five micron PP cartridges (Figure 2).
- Contaminants are immobilized and will not desorb, re-release and pollute downstream systems.
- MYCELX systems reduce the need for chemical additives, cleaning, regeneration and replacement of raw materials and membranes.
- Hazardous waste reduction: One pound of MYCELX media separates between one and five pounds of hydrocarbons. The waste is easily and inexpensively disposed (no residual water, high BTU value). MYCELX units run in parallel for continuous operations, eliminating shutdowns; cartridges are quickly changed, saving downtime due to maintenance and start-up of downstream polishing systems.

Figure 2

MYCELX MX-5000S SYSTEM FOR CONDENSATE POLISHING



Conclusion

Treating and filtering feed water prior to discharge or before polishing technologies is critical to maintain operational costs. Rapidly separating dilute oily hydrocarbons and solvents in a single-pass without restricting flow is novel and creates newfound economics for oily water applications. Treatment systems employing MYCELX technology are more robust and generate savings by reducing energy, equipment, raw material, chemical, maintenance and downtime requirements.

MYCELX technology is allowing industry to more effectively address wastewater discharge, process water recovery, water re-use and zero liquid discharge (ZLD). Applications also include boilers, cooling towers, chillers, swimming pools and other close-loop water systems.

Kirk W. Abbott is Director of Engineering and Strategic Development at MYCELX Technologies in Gainesville, GA. He can be reached via e-mail at Abbott@MYCELX.com or by phone at 770.534.3118.

References:

- (1) *ULTRAPURE Water Journal*, October 2002, Volume 19, Number 8, p.16. Title "Organic Removal for Make-up and Waste Water Treatment for Membrane Systems"; D'Angelo and Abbott
- (2) *Environmental Protection**, June 2001, Volume 12, No. 6, p. 34. Title "Protection from Organic Fouling"; Alper and Abbott
- (3) *Membrane & Separation Technology News*, Article (p.1), September, 2001; Hanft
- (4) *Environmental Protection*, January 2001, p.52, Title "PCB Gone"; Alper and D'Angelo
- (5) *Environmental Protection*, January 2001, p.41, Title "No Restrictions"; Abbott

* Environmental Protection articles are available at www.eponline.com (search archives for "MYCELX")

Appendix:

Case Study 6.0 - BTEX Removal From Groundwater

Removal of Benzene & Toluene from Groundwater

Initial water test 31 May 2001 by Advanced Analytical Associates, Bozeman, Montana:

Sample #1005114 Well Head: Benzene 11 ug/L Toluene 5.3 ug/L
 Sample #0105115 Inside Sample: Benzene 27 ug/L Toluene 11 ug/L

* Both initial samples had ND as result for MTBE, Ethyl benzene, Xylenes and Naphthalene.

SAMPLE ID	LAB ID	Target Analytes	
		Benzene	Toluene
		ug/L	ug/L
WELL HEAD	105114	11	5.3
INSIDE	105115	27	11
BLANK	BW0530	ND	ND

Single-Pass MYCELX™ Filter Results

PETROLEUM SCREEN FOR FILTERED WELL SAMPLES ¹		EPA 524/525
Volatile Organic Compounds ²	None Detected	EPA 524/525
Synthetic Organic Compounds	Negative	EPA 524/525
Total Polyaromatic Hydrocarbons	Negative	EPA 524/525
Total Diesel Range Organics	Negative	EPA 524/525
Total Motor Oil Range Organics	Negative	EPA 524/525

1 PQL = Practical Quantitation Limit = 0.5 ug/l

2 Volatile Organic Compounds determined non-detect by USEPA Method 8021

Appendix:

Case Study 7.0 - BTEX & MTBE Removal From Surface Water

Removal of BTEX and MTBE from Contaminated Surface Water (ppm)

<u>Sample ID</u>	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Ethyl benzene</u>	<u>Xylene*</u>
Inlet #1 **	87	2.0	12	3.8	24
Discharge #1	0.18	0.004	0.016	0.002	0.012
Knockdown #1	99.8%	99.8%	99.9%	99.9%	99.9%

<u>Sample ID</u>	<u>MTBE</u>	<u>Benzene</u>	<u>Toluene</u>	<u>Ethyl benzene</u>	<u>Xylene*</u>
Inlet #2	17	0.92	3.2	0.48	2.6
Discharge #2	0.21	0.034	0.14	0.030	0.14
Knockdown #2	98.7%	96.3%	95.6%	94%	95%

•*Average of all Isomers

•**USEPA Method 8020 – Volatile Aromatic Hydrocarbons

