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Project Summary

Synthetic Organic Compound Rejection by Nanofiltration

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A study was conducted to evaluate the rejection of six synthetic organic compounds (SOCs) from a potable water source by a nanofiltration membrane process. The SOCs were ethylene dibromide (EDB), dibromochloropropane (DBCP), chlordane, heptachlor, methoxychlor, and alachlor. To investigate SOC rejection, a membrane pilot plant was constructed that utilized a single, 4- by 40-inch FilmTec N 70* spiral wound, thin film composite membrane with a molecular weight cutoff of 300. The effects of different operating pressures and membrane feed stream velocities on membrane rejection of SOCs are reported. Trihalomethane formation potential (THMFP), total organic halide formation potential (TOXFP) and general water quality in and out of the membrane are also reported. Accurate organic and inorganic mass balances were conducted on solutes.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The purpose of this cooperative agreement was to determine the capability of a nanofilter membrane to reject SOCs from a potable water source.

The scope of work involved selecting a potable water site, building a membrane pilot plant, securing and preparing the SOC feed, operating the pilot plant, analyzing the data and reporting. Only one nanofilter membrane was used for this project because of economic constraints; however, the selected membrane, a FilmTec N 70 nanofilter with molecular weight cutoff (MWC) of 300, had been used at four sites on other projects because the N 70 controlled permeate THMFP to less than the THM MCL of 0.10 mg/L and was as productive as any membrane that successfully controlled THMFP.

Site Selection

The initial site selected for this project was at Flagler Beach, Florida, so that the project could be done at the same time as another project investigating the long-term cost and performance of membrane processes to control THMFP at the same site.The Flagler Beach water treatment plant had, however, no means to acceptably discharge the SOC-contaminated stream. Because complete containment of the SOCs was not feasible, the SOC project site was at the University of Central Florida (UCF) in Orlando, FL. After two attempts to use the UCF irrigation water storage tanks, the pilot plant was moved to a site adjacent to the UCF wastewater treatment plant. A 4-inch-diameter 206 foot-cased deep well was drilled into the Floridan aquifer—the same aquifer used by UCF and the majority of Florida utilities for drinking water. The SOC-contaminated membrane streams were discharged to the UCF wastewater treatment plant.

Pilot Plant Construction

A 14- by 12-foot by 3-inch concrete pad was poured adjacent to UCF

*Mention of trade names on commercial products does not constitute endorsement or recommendations for use

wastewater treatment plant and the Civil and Environmental Engineering field laboratory (CEEFL) building. A 10-foot cube, steel research building was assembled on the pad. The research building had a 110/220 amp power line, lighting, ventilation fans, a locked fence, and raw water. A flow diagram of the membrane pilot plant built for SOC removal is shown in Figure 1. Well water was pumped through one of two parallel 1 μ prefilters, a totalizer, and back flow prevention device. Following prefiltration, H_2SO_4 was added to control $CaCO_3$ scaling and the desired SOC was added. The acid and SOC-containing water then passed through a high pressure pump that pushed the water through the membrane. Chlordane, heptachlor, methoxychlor, DBCP and EDB feed stock was prepared by first dissolving the SOC in an organic solvent, acetone or methanol, and then diluting the SOC solution in permeate water. Organic solvents were necessary because the pure SOCs were insoluble in water. Alachlor was obtained as a water-soluble, formulated compound and was directly dissolved in water for SOC feed stock preparation.

Operation

The membrane was installed in a donated custom Mitco* skid, which consisted of flow and pressure gauges on feed, permeate, and concentrate lines; the pressure vessel; and the high pressure pump with concentrate and pump recycle lines, all of which were mounted on a steel frame. Flow and pressure readings were monitored daily by gauge readings and direct flow measurement of the concentrate and permeate streams. The membrane feed, permeate, and concentrate stream SOC concentration was monitored 13 times during a 31-day period that was divided into four different recovery periods and one flushing period. The membrane pilot plant was operated at approximate recoveries of 10% (10%R), 30% (30%R), 30% with recycle (30%RR) and 50% with recycle (50%RR). Samples were taken after the end of each period of operation to determine if any adsorbed SOCs could be flushed from the membrane. O solutes in the membrane feed, perm and concentrate streams were monit once during each recovery period. Th were THMFP, TOXFP, dissolved org carbon (DOC), color, total hardness (calcium hardness (CaH), alkalinity (pH, total dissolved solids (TDS), sod (Na), sulfates (SO_4) and iron (Fe).

The feed permeate and concentr stream flows were typically 4.8, 4.3, 0.5 gpm for 10%R; 3.3, 2.3, and 1.0 g for 30%R; 3.6, 2.3, and 1.3 gpm 30%RR; and 2.8, 1.4, and 1.4 gpm 50%RR. The approximate pressure dr and membrane feed stream velocities each recovery were 62 psi and 1 f/sec 10%R, 93 psi and 0.6 f/sec for 30% 107 psi and 1.1 f/sec for 30%RR, 150 psi and 1.0 f/sec for 50%RR. membrane flux ranged from 10 g/sfd 30 g/sfd, increasing with recovery. water mass transfer coefficient (M averaged 0.21 g/sfd-psi (0.021 day The water production was very const from the membrane, which operat 5137.7 hr out of a total 5202.5 availa hr during the SOC project. Only 14.0

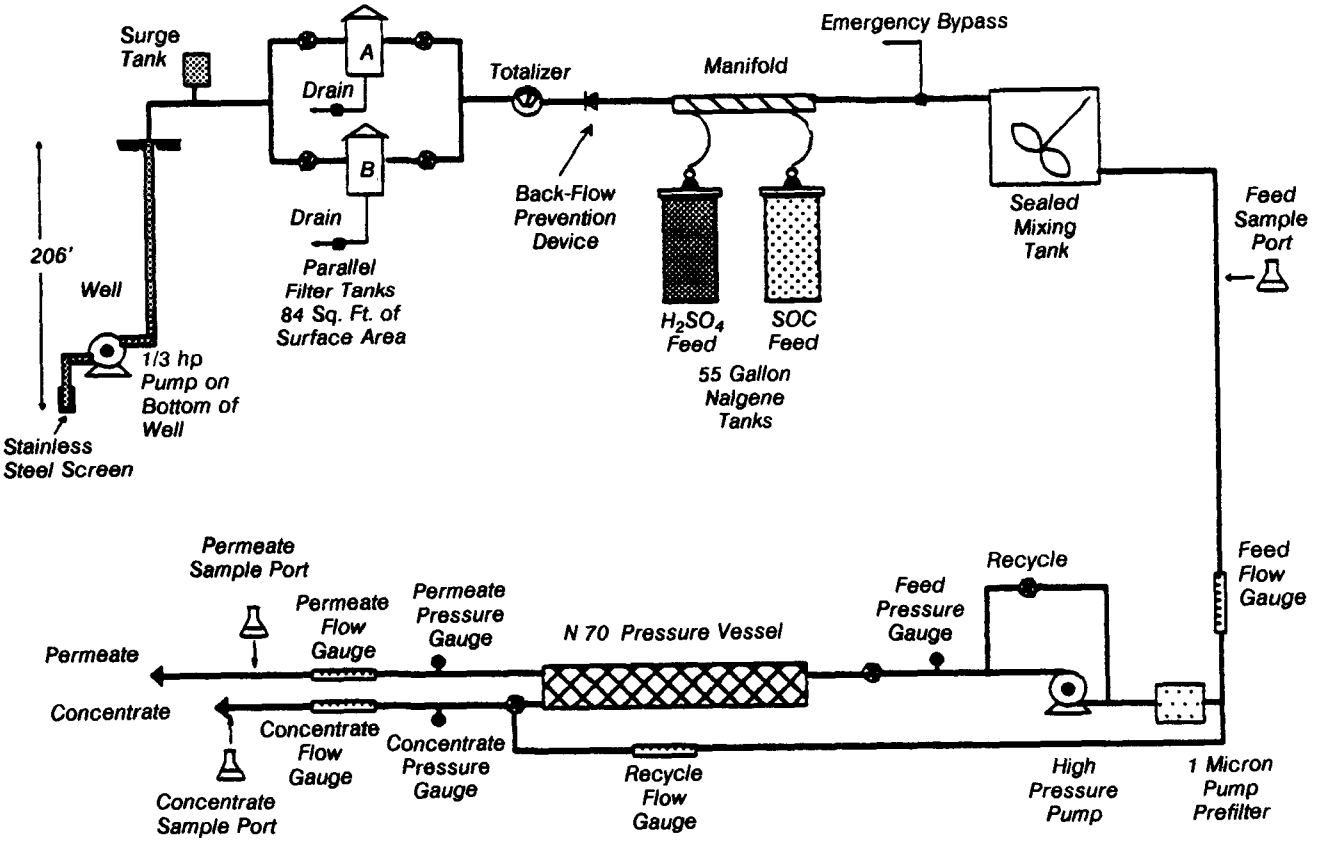

Figure 1. *Flow diagram of FilmTec N 70 Mitco Membrane Pilot Plant used for investigation of SOC rejection by Nanofiltration.*

of maintenance were needed for prefilter replacement and small repairs. The remainng 50.8 hr were spent waiting on lighting installation which was not attributable to the mechanical operation of the membrane pilot plant.

Following NaCl injection, the transient response of the membrane was determined to be accurately modeled by a first order system with a time constant of 2 min. Although initial sampling for each new SOC was done at least 4.0 hr after operation had begun, 99.9% of any permeate or concentrate concentration change would be complete in 13.8 min following initiation of the change.

The smallest molecular weight (MW) SOC was EDB (187.9). EDB feed stream concentration ranged from 260 to 22.4 µg/L during 785.1 hours of operation and from 88.4 to 22.4 µg/L in the final 443.5 hr, after the operation was stabilized. Some EDB rejection was observed for the first four samples collected; however, the membrane had been permanently fouled at the initial UCF location and was replaced after the second sample had been collected. Only 66% of the EDB had been accounted for when the fouled membrane was used. Routine operation of the membrane pilot plant was not achieved until after the fourth sample was collected. Some EDB may have adsorbed onto the fouled membrane during a period that was not representative of normal operation. No EDB rejection was observed for the final seven samples taken over the last 443.5 hr of EDB operation. Ninety four % of all the EDB input to the membrane was recovered in the concentrate and permeate streams for the entire EDB operation.

DBCP (MW 236.4) was fed to the membrane in concentrations varying from 41.5 to 83.5 µg/L over 667.1 hr of operation. Partial rejection of DBCP by the membrane varied from 19.6 to 60 µg/L in the permeate stream or 19% to 52%. DBCP permeate concentrations varied inversely with the water flux and could be described by a diffusion process. The DBCP MTC varied from 2.79 to 7.43 f/day and averaged 4.27 f/day.

The membrane, under all operating conditions, completely rejected the four remaining SOCs: chlordane (MW 409.8), heptachlor (MW 373.3), methoxychlor (MW 345.7), and alachlor (MW 269.8). The detection limit for each of these SOCs was 0.6 µg/L. The absence of any SOC concentration in the permeate indicates they were sieved from permeate and were too large to pass through the pore of the membrane.

The cumulative recovery of SOC in the membrane output was, in order of their MW, 94% for EDB (MW 187.9), 96% for DBCP (MW 236.4), 100% for alachlor (MW 269.8), 91% for methoxychlor (MW 345.7), 92% for heptachlor (MW 373.3), and 90% for chlordane (MW 409.8). Only EDB was found in any flushing samples; this amounted to less than 0.01% of the total EDB and was only 0.2 µg/L in the flushing sample taken 46 hr after EDB feed was discontinued. No previously fed SOCs were ever found in any succeeding SOC analysis. The SOC mass balance indicated the higher MW SOCs were adsorbed onto the membrane and did not release during operation. If adsorption is a SOC removal mechanism, however, then SOC breakthrough could occur following longer periods of operation.

The summary of the SOC-rejection membrane project is shown in Table 1. The average MTC for 30R and 30RR is shown because recycling the concentrate had little effect on the MTCs. The membrane rejection of TOXFP, THMFP, and DOC was greater than 90% when acetone or methanol was not used to prepare SOC feed stock. Permeate TOXFP, THMFP, and DOC concentrations averaged 35 µg/L, 6 µg/L, and 0.1 µg/L; this represented 93%, 95%, and 95% rejection, respectively. The recovery of all DOC in the membrane output was 102%.

As shown in Table 1, the rejection of the inorganic solutes increased by species charge and molecular weight. The rejection of the highest charged and largest MW species (SO_4^{-2}) was 100%. Rejection of the lowest MW and lowest charged species (Na^+) was 64%, the least of any inorganic species monitored. Recovery of inorganic species mass was 102% for all species except Fe and Alk which were 104% and 98%.

The percent rejection versus MW for inorganic solutes and organic SOCs is shown in Figure 2. Membrane rejection of SOCs is controlled by species MW. All SOCs with MW greater than 269.8 were completely rejected. The SOC with MW 187.8 was not rejected, and the SOC with MW 236.4 was partially rejected. More highly charged inorganic species with MWs less than 187.8 (EDB) were rejected by the same membrane. The permeate stream concentration of all partially rejected species tended to decrease as water flux increased and to increase as feed stream concentration increased, as would be expected in a diffusion controlled process. Velocity of the membrane feed streams corresponded to Reynolds numbers of less than 113. Flow velocity within the membrane varied from 0.6 to 1.1 f/sec and had no effect on permeate concentration.

Solute passage through the membrane involved convection, sieving and diffusion. The mass transport of a small uncharged SOC that passed completely through the membrane could be described by convection. The mass transport of any partially rejected organic or inorganic species could be described by diffusion. The mass transport of SOCs too large to pass through the membrane could be described by sieving. The FilmTec N 70 nanofiltration membrane had sieving properties of an ultrafilter and diffusion properties of a reverse osmosis membrane.

Conclusions

1. The membrane rejected certain SOCs for a one month period from a potable water source which indicates SOC rejection by membranes is a feasible potable water treatment process.
2. The rejection of SOCs by the membrane was dependent on SOC MW and increased as SOC MW increased.
3. SOCs with MWs of 269.8 or more were completely rejected by the membrane for all operating conditions by sieving.
4. The rejection of DBCP, molecular weight 236.4, increased as water flux increased and recovery decreased, and could be described by diffusion.
5. EDB, the smallest molecular weight SOC (187.9), was not rejected by the membrane, which indicated the mass transport of EDB through the membrane pores was by convection.
6. The SOC MW determined whether diffusion could be used to describe mass transport through the membrane pores.
7. Charged inorganic solutes were rejected by the membrane at much lower molecular weights than were the uncharged SOCs, possibly because of the electrostatic repulsion between the ion and membrane.
8. SOC mass balances showed that SOCs with MWs of more than 345.7 were not completely recovered and were indicated to have adsorbed onto the membrane.
9. Solute rejection by the membrane increased as solute MW or charge increased.

Table 1. *Summary of SOC Membrane Operation*

Parameter	Pressure psi	Recovery %	Flux g/sfd
	Solvent		
H_2O	62	10	11
	93	30	19
	107	30 Recycle	22
	144	50 Recycle	28

Species	Rejection %	CP* mg/L	MTC** f/day	Recovery %
	Solute			
EDB	0	–	–	94
DBCP	35	0.0372	4.27	96
Chlordane	100	<0.0006	–	90
Heptachlor	100	<0.0006	–	92
Methoxychlor	100	<0.0006	–	91
Alachlor	100	<0.0006	–	100
THMFP	95	0.006	–	–
TOXFP	93	0.035 +	–	–
DOC	95	0.1	0.095	102
Color	91	2 + +	–	–
TDS	85	36	0.363	102
Alk	78	20	0.647	98
TH	88	20	0.239	102
CaH	89	15	0.226	102
SO_4	100	<1	–	102
Fe	87	0.06	0.265	104
Na	64	3	1.053	102

* *permeate concentration*
** *mass transfer coefficient*
\+ *as Cl*
\+ + *as cpu*
as $CaCO_3$

10. Over 90% of the THM and TOX precursors were rejected by the membrane except when acetone was used to solublize the hydrophobic SOCs into feed stock.
11. Water flux was directly proportional to feed pressure.
12. The membrane system was consistly productive, operating 5138 hr with only 65 hr of downtime.
13. The transient response of the N 70 membrane was accurately described by a first order system with a time constant of 2.0 min.
14. The partial rejection of any solute could be described by diffusion.

Recommendations

1. The disposal of membrane concentrates containing SOCs should be investigated.
2. Longer operating periods with higher SOC feed stream concentrations should be used to determine if sustained rejection of higher MW SOCs can be attained and to determine if SOC adsorption is significant for different membrane types and materials.
3. Membranes differing in surface materials and pore size should be investigated for SOC rejection at higher operating pressures.
4. Rejection of SOCs by membrane processes should be investigated in water supplies of varying quality that are actually and artificially contaminated by SOCs so that the effect of solvent characteristics and SOC competition can be determined.
5. An accurate model for permeate solute concentration including membrane pore size and distribution, membrane material, solute and s vent mass transfer, recovery, pre sure, solute size, solute charge a temperature should be developed that the mechanism of solu rejection can be explained a permeate water quality predicted.
6. An assessment of SOC adsorpti onto different membrane materia should be conducted and necessa SOC adsorption isotherms should b developed for different membra materials in order that a comple evaluation of SOC membrane adsor tion can be made.
7. The effect of turbulence within t membrane should be investigated reduce membrane fouling and perm ate solute concentration.
8. SOC rejection should be investigate with a membrane array at recoveri

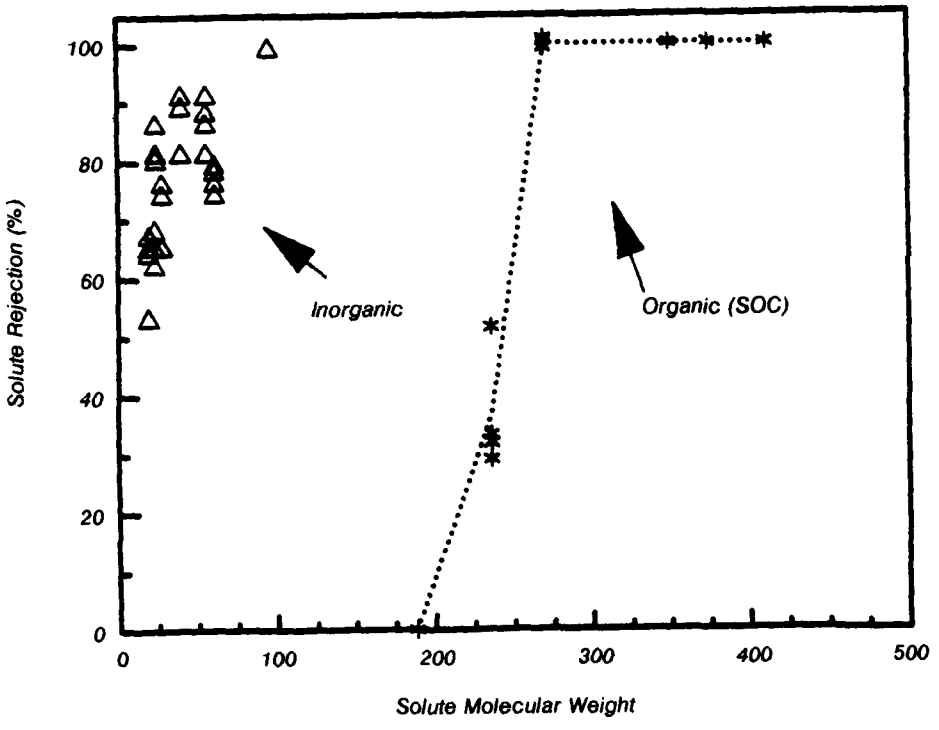

Figure 2. *Inorganic (Δ) and organic (*) percent solute rejection versus solute molecular weight from the SOC investigation using the FilmTec N 70 membrane.*

normally experienced by actual membrane plants.

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***J. Keith Carswell** is the EPA Project Officer (see below).*
The complete report, entitled Synthetic Organic Compound Rejection by Nanofiltration" (Order No. PB 89-194 245/AS; Cost: $21.95, subject to change) will be available only from:
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