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**ULTRAFILTRATION OF MUNITION WASTES
(HMX, RDX AND TNT)**

by
Curtis R. Blodgett

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Ultrafiltration experiments were performed on both synthetic and actual munition plant waste streams containing various soluble concentrations of TNT, RDX, and HMX at pH 3.0, 7.0 and 11.0 using membranes and equipment from three manufacturers. Up to 50% of the TNT was removed, but most of this was adsorbed on the membranes and not found in the concentrate stream.		

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PREFACE

During the manufacture of certain munitions, suspended particles less than 200 microns in size, as well as soluble quantities of TNT, RDX, and HMX are found in waste streams. The use of multi-media filters prior to carbon adsorption columns has proven ineffective due to plugging of the filters.

Because of recent developments and improvements in ultrafiltration membranes, it was felt that this process might alleviate some of these problems.

This report describes the investigation of ultrafiltration as a means of cleaning up munition plant waste streams. The customer order number for this work was Al-0-R0001-A1-48.

The analytical work was performed by John T. Walsh and Rosalinda Bagalawis, while Richard Erickson helped immeasurably with running the equipment and gathering data.



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ULTRAFILTRATION OF MUNITION WASTES (HMX, RDX, and TNT)

INTRODUCTION

Waste streams from certain Army ammunition plants contain suspended and dissolved quantities of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). TNT in waste streams presents a particularly acute problem because exposure to sunlight or alkali turns the water a deep rusty orange-like color. While the color bodies have not been totally identified, it has been postulated that azo-compounds, Meisenheimer complexes, and many other nitro-aromatic compounds are formed as a result of the reactions of TNT.^{1,2,3}

The purpose of this study was to explore ultrafiltration (UF) as a technique for removing suspended and dissolved organic compounds from pink water and to determine whether ultrafiltration can be used as a single step process or in combination with other processes.

In ultrafiltration, water passes through a semi-permeable polymeric membrane under a driving force of hydrostatic pressure, usually less than 7.0 kgf/cm² (100 psig). The process fluid flows across the membrane which has pore diameters in a range of 0.002 to 0.015 microns. Suspended solids and the larger colloids are rejected at the membrane barrier while water will permeate the membrane and emerge as ultrafiltrate. To best understand

¹N. E. Burlinson, M. E. Sitzmann, D. J. Glover, and L. A. Kaplan. 1979. Photochemistry of TNT and Related Nitroaromatics: Part III. Technical Report NSWC/WOL TR 78-198, Naval Surface Weapons Center, Silver Spring, MD.

²R. K. Andren, J. M. Nystrom and R. J. Erickson. 1975. Treatment of TNT Munitions Wastewaters Using Polymeric Adsorption Resins. Food Sciences Laboratory, US Army Natick Research and Development Command, Natick, MA.

³M. R. Crampton. 1973. Meisenheimer Complexes, Dept. of Chemistry, The University of Durham, England. Technical paper.

where ultrafiltration can be used, it is important to understand where it fits in with other filtration and separation processes.

The process of reverse osmosis utilizes membranes with such small pore sizes (approximately 0.0005 to 0.0150 microns) that species of atomic dimensions are retained at the barrier. Thick boundary layers cause high solution concentrations at the membrane surface resulting in high osmotic pressures. Thus, extremely high pressure gradients across the membrane [21 to 105 kgf/cm² (300 to 1500 psig)] are needed to overcome the osmotic pressure and cause solvent to permeate the barrier. This process is very effective for the removal of ionic impurities.

In microporous and other gross filtration methods, the process stream flows into the filter surface which usually consists of finite open pores of well controlled size (approximately 1 micron). Species will enter the pore and, if of the right size, will become trapped. With very small solute molecules the filter quickly becomes loaded or plugged and must be cleaned often or replaced.

With ultrafiltration, there are looser, more open membranes which reject molecules in solution or suspended material. Working pressures are also much lower ranging from 0.7 to 7.0 kgf/cm² (10 to 100 psig). The retention of molecular species, the recovery of solutes in either the concentrate or the permeate, and the flux rate depend on complex interactions between the membrane, the solution, and the fluid control techniques. The limitation on solvent flux through the membrane is the phenomenon of concentration polarization. On older ultrafiltration equipment a colloidal gel layer would build up on the membrane until the convective transport of solute to the membrane surface equaled the diffusive back transport rate of the solute from the surface. The thickness of the gel layer thus increased and reduced the solvent (water)

permeate flux rate. Modern ultrafiltration equipment is designed to be operated under flow conditions which result in high shear at the membrane surface to minimize the build-up of the gel layer.⁴

UF membranes are available in tubular, spiral wound, or flat disc design (See Figures 1 and 2). The tubular design is comprised of a bundle of straw-like tubes packed tightly inside a large diameter cylinder sealed at both ends. The relatively large tube opening (1.1 mm) requires little or no prefiltering and can be cleaned quite easily. The feed solution is pumped through the openings in the ends of the tubes and permeate is forced out the sides of the tubes by adjusting the back pressure. The velocity of the solution going through the tubes creates a shear that removes build-up of material from the membrane surface and thus permits running for long periods of time before cleaning is necessary.

The spiral wound membrane is composed of a scroll-like configuration consisting of alternating sheets of membrane and permeate carrier layers which are attached to a perforated permeate tube (See Figure 2). The spacer sheet between the two membranes serves to increase turbulence thus promoting a higher mass transfer rate, to give strength to the membrane and to create passages for flow. The spiral wound module has an exceptionally high membrane area to volume ratio and is especially good for viscous solutions. One drawback of the spiral wound module is that a 140 micron prefilter is required.⁵

⁴C. R. Blodgett. 1975. Evaluation of Ultrafiltration as a Method for Removing Nitrocellulose Fines from Munition Plant Wastewater. Report EPA-IAG-DS-0753, Food Sciences Laboratory, US Army Natick Research and Development Command, Natick, MA.

⁵T. S. Shen, C. R. Hoffman. 1980. A Comparison of Ultrafiltration of Latex Emulsions and Macromolecular Solutions. Presentation, 5th Membrane Seminar, May 12, 1980, Clemson University, South Carolina.



FIGURE 1. TUBULAR DESIGN

SPIRAL WOUND MEMBRANE MODULE

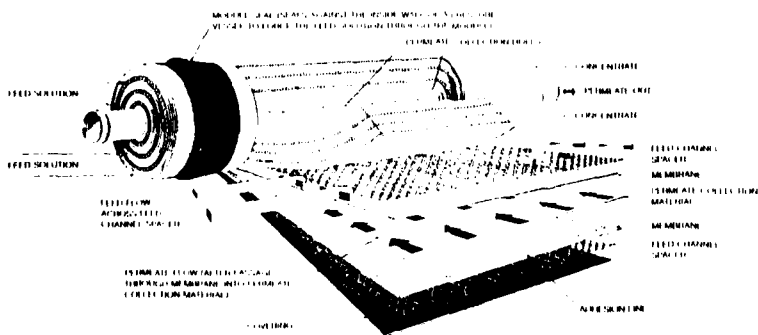


FIGURE 2. SPIRAL WOUND MEMBRANE MODULE

The disc type membranes look very much like filter paper circles, but are made of a non-cellulosic anisotropic polymer. They consist of a very thin (0.1 to 1.5 μm), dense skin with extremely fine, controlled pore texture on a thicker (50 to 250 μm), open-celled spongy layer of the same polymer. Stirring of the solution controls concentration polarization. Generally, disc type membranes are used only for small sample sizes (2 liters or less).

The scope of work required testing both synthetic and actual munition plant waste waters at three different pH levels. The synthetic stream was tested at four different concentrations in both the UV light exposed and unexposed state. Tubular, spiral wound and disc type UF membranes from three different manufacturers were tested.

APPROACH

Letters were sent to fifty manufacturers of membrane type systems requesting their comments on the ultrafiltration of TNT, RDX and HMX waste streams (See Appendix A). They were further asked to furnish literature as well as the purchase or rental costs of their bench scale equipment. Of the fourteen companies that replied, only four made bench scale equipment small enough for our sample size. Three companies stated that Reverse Osmosis (RO) would work while others thought that UF might work, but RO would probably be the better choice for compounds with such low molecular weights. Romicon Corporation of Woburn, MA, was selected to furnish the tubular UF membranes and equipment; Abcor Corporation of Wilmington, MA, was chosen to supply the spiral wound UF membranes and Amicon Corporation of Danvers, MA, was selected to furnish the disc type membranes.

A literature search to determine what previous work was done in this area was made using the Defense Technical Information Center computer system and S.D.C.'s Orbit IV International Search Service. Only seven references were uncovered which are listed in Appendix B. The work by Bhattacharyya and Garrison⁶ on membrane ultrafiltration of TNT waste was the only reference relevant to this study.

⁶Dibakar Bhattacharyya, Kenneth A. Garrison, and Robert B. Grieves. 1977. Membrane Ultrafiltration for Treatment and Water Reuse of TNT-Manufacturing Wastes. Water Pollution Control Federation Journal, 49(5): 800-808.

MATERIALS AND METHODS

Chemicals

Practical grade 2,4,6-trinitrotoluene (TNT) containing 10% added water was purchased from the Eastman Kodak Company, Rochester, NY. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in 50:50 ethanol: H₂O solutions (lot number 21-35) was obtained from Holston Army Ammunition Plant. Desensitized octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (lot number SR-655-61) was also obtained from Holston Army Ammunition Plant. All three chemicals were washed with distilled H₂O, oven-dried at 65°C for 24 hours, and placed in a desiccator for several days before use.

The synthetic samples of TNT, RDX, and HMX were prepared by adding the appropriate amount of each chemical to water at 95°C and vigorously stirring (1720 rpm) for 30 minutes. Not all of the chemicals would dissolve even using this intense method. To overcome this problem 1/2 to 2% of acetone was added to the water and the solubility was improved remarkably. The addition of acetone had little or no effect on the UF results.

Munition Waste Streams

Samples from munition waste streams were obtained by Mr. Charles Denzler of the US Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland. These waste streams were taken from the Iowa Army Ammunition Plant, the Milan Army Ammunition Plant, the Kansas Army Ammunition Plant and the Lonestar Army Ammunition Plant.

Total Organic Carbon Analyzer

Total Organic Carbon (TOC) was determined by injecting a 40 µL sample into a Beckman Total Organic Carbon Analyzer with a Beckman I.R. Detector, Model 915.

The combustion chamber was set at 950°C, the flow rate at 150 cc/min and a pressure of 0.35 kgf/cm² (5.0 psig).

High Performance Liquid Chromatography

Concentrations of TNT, HMX, and RDX were determined on a Waters Associates Model 201/402 liquid chromatograph (LC) using a U.V. detector and a C-18 reverse phase column. The mobile phase was 30% methanol and 70% water using a flow rate of 1 cc/min and sample size of 50 µL. Peak areas were determined by a Hewlett-Packard Integrator, Model 3380A, programmed to give parts per million (ppm) directly.

Total and Suspended Solids

Total solids were performed by placing a well-mixed 25 mL aliquot of the test sample in a pre-weighed evaporating dish and evaporating to dryness at 95°C. The dried sample was cooled for 1 or more hours in a desiccator and weighed. This cycle was repeated until a constant weight was obtained.

Suspended solids analysis was performed by passing a well-mixed 50 to 75 mL sample through a 0.45 µm type HA filter obtained from Millipore Corporation. The pre-weighed filter was washed with distilled water and then dried to a constant weight at 95°C. Samples were weighed on a Mettler, Gram-Atic, balance which was accurate to 0.05 mg.

Ultrafiltration Equipment

The ultrafiltration runs were carried out using the Romicon HFXSMK11 and HF2SSS ultrafiltration systems. The HFXSMK11 system has a maximum flow rate of 22.7 L/min (6 gal/min) while the HF2SSS has a maximum flow rate of 94.6 L/min (25 gal/min). The inlet pressure for the smaller system was maintained at 1.75 kgf/cm² (25 psig) while the outlet pressure was kept at 1.40 kgf/cm²

(20 psig). The larger system was run at an inlet pressure of 1.12 kgf/cm² (16 psig) while the outlet pressure was 1.19 kgf/cm² (17 psig). The smaller ultrafiltration system was operated between 26° and 46°C while the large unit was run at 26° to 35°C. Due to friction from the pump on the small ultrafilter the temperature gradually rose as the run progressed. In the case of the larger unit, which has an air pump, the temperature slowly fell as the run progressed.

Ultrafiltration Membranes

The following three different Romicon hollow fiber membranes were tested: PM1, PM2, and PM10. These membranes are constructed from a vinyl copolymer having a membrane area of 0.1 m² (1.1 ft²) and an operating pH range of 1.5 to 13.0. A PM1 membrane was also used in the large ultrafiltration unit and its membrane area was 1.4 m² (15 ft²).

Also tested were 2 spiral wound membranes having an area of 0.5 m² (5 ft²) which were purchased from the Abcor Corporation. These were the S2HFK 130 VPO and the S2HFM 100 VPO membranes. The small Romicon ultrafiltration system was adapted by an Abcor Corporation technician to accept these membranes. This was necessary because Abcor Corporation does not manufacture bench scale ultrafilters. The Abcor membranes can be safely used in a pH range of 2 to 12, at temperatures up to 90°C and pressures up to 5.6 kgf/cm² (80 psig). The material of construction is proprietary and Abcor Corporation would not disclose this information.

The final membrane tested was the UM05 membrane from Amicon Corporation. This was a disc type (flat sheet) membrane with an anionic charge and was used with a stirred cell, model 402. The molecular weight (MW) cut-off for this membrane was 500.

DISCUSSION

Twelve 19-liter (5 gallon) containers of munition waste were received from each of the following Army Ammunition Plants: Iowa, Kansas, Lonestar, and Milan. The individual containers were coarse filtered and blended together to obtain a uniform sample from each plant. The average analysis of the waste water from these plants is found in Table 1, below.

Table 1. Analysis of Waste Water from Four Army Ammunition Plants

Plant	Concentration (ppm)			Total Organic Carbon (ppm)	
	HMX	RDX	TNT	Analyzer	Theoretical
Iowa	2.1	13.9	94.4	66.4	37.5
Kansas	2.1	11.5	<0.3	188.0	2.3
Lonestar	3.4	27.0	26.4	51.2	14.69
Milan	7.7	70.2	98.5	75.7	49.07

Despite the care taken in blending samples, there were some discrepancies in LC values for the HMX, RDX, and TNT from run to run. This may have been caused by quantities of each ingredient precipitating out of solution during storage at 5°C even though the samples were heated to at least 26°C and shaken prior to analysis. The RDX value in Table 1 for the Milan Army Ammunition Plant exceeds its water solubility. This is probably due to the presence of organic solvent used in the manufacture of RDX. When comparing the total organic carbon (TOC) values obtained from the Beckman Analyzer with the values obtained by a carbon balance from the Waters LC, we see a very large difference, especially for the Kansas Army Ammunition Plant. This shows that these waste

waters contained large amounts of other organic compounds. This is verified by the chromatogram which shows 11 peaks for the Milan waste stream and 8 peaks for the waste streams from the other 3 plants.

Most of the experimental work was performed in the batch mode, for example, the permeate was continuously removed and the remaining stream was recycled to the feed tank where it became increasingly concentrated. See Figure 3 below.

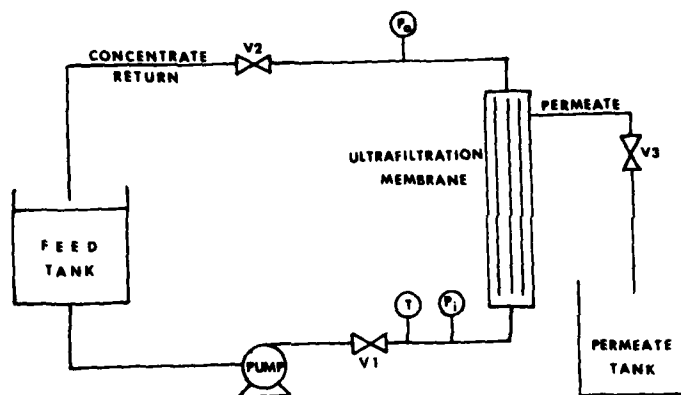


FIGURE 3. FLOW DIAGRAM OF THE ULTRAFILTRATION SYSTEM USED FOR REMOVAL OF HMX, RDX, AND TNT

In this mode, valves 1 and 3 (V1 and V3) are fully open and valve 2 (V2) is partially open to bring the system to the appropriate pressure. In most cases the inlet pressure (P_1) was 1.75 kgf/cm^2 (25 psig) and the outlet pressure (P_0) was 1.40 kgf/cm^2 (20 psig).

The initial work was performed on the small Romicon ultrafilter using the PM10, 2 and 1 membranes and the Iowa waste stream.

Table 2. Summary of Results Using 3 Ultrafiltration Membranes at 3 pH Levels on the Iowa Ammunition Plant Waste Stream

Membrane	pH	FLUX (L/m ² -h)	PERCENT REMOVED					
			HMX	RDX	TNT	TOC	Dissolved Solids (ppm)	Suspended Solids (ppm)
PM10	3.0	182.5	0	1.7	17.3	20.8	68.0	76.3
	7.0	203.7	9.2	2.0	14.4	18.5	0	92.7
	11.0	260.9	44.1	1.9	--	10.0	3.3	96.2
PM2	3.0	53.8	0	0	15.6	16.0	10.7	97.1
	7.0	75.7	0	0	9.5	7.7	0	89.1
	11.0	41.9	0	0	--	10.5	40.1	98.4
PM1	3.0	17.5	0	1.6	34.2	34.6	0	92.0
	7.0	23.5	0	0	25.4	20.7	0	98.1
	11.0	37.7	36.4	49.9	--	18.9	19.8	99.1

Table 2 shows that the PM1 membrane was superior to the other two membranes because it permitted more TNT and TOC removal. The figures were calculated by comparing the permeate LC values to the feed LC values. Best TNT removal was obtained at pH 3.0. The flux at pH 3.0 was generally not as high as at pH 7.0. It can also be seen that most of the suspended solids were removed by the PM1 and PM2 membranes. Because the best results in the above experiments were obtained on the PM1 membrane, it was selected for further testing with both the synthetic and the additional munition plant waste streams.

Additional experiments were performed with the PM1 membrane using 70 ppm TNT, 30 ppm RDX and 10 ppm HMX as our full strength base. We then made up

additional concentrations of 2x, 1/2x and 1/4x. Because of solubility problems, especially at the higher levels (2x) one to two percent acetone was added for some of the runs. Even when using acetone we were only able to solubilize 115.8 ppm TNT, 46.1 ppm RDX, and a surprisingly low 9.7 ppm HMX. Unfortunately, the addition of acetone prevented accurate TOC measurements for 7 of 16 acid runs, 9 of 20 neutral runs, and 2 of 7 base runs because of evaporation while passing through the ultrafilter. A summary of the results using the small PM1 membrane is found in Table 3.

Table 3 shows that the highest flux rates occurred at pH 7.0 and that generally pH 3.0 was better than pH 7.0 for TNT removal (an average of 29.5% vs. 19.8%). It is interesting to note that the percent TNT removal was higher for the munition plant waste streams than it was for the synthetic waste streams. The results for the UV-exposed waste vs. the unexposed waste indicated no appreciable difference at full strength and half strength, but at 1/4 strength considerably more UV-exposed TNT is removed. The results for HMX and RDX were quite erratic with many runs showing no removal while others showed up to 40% removal. Also, in some cases pH 3.0 was best while in others pH 7.0 is best.

To obtain good scale-up data, 9 experiments were run using the large PM1 membrane on the large Romicon ultrafilter. There was no significant difference in TNT removal at either pH 3.0 or pH 7.0 for the actual munition waste streams, but pH 7.0 was better for the synthetic stream (See Table 4). Comparing these values with those in Table 3 we find that in most cases the larger column was superior. Once again, pH 7.0 generally gave higher flux rates than pH 3.0 and the large PM1 membrane gave lower flux rates than the small PM1 membrane.

Table 3. Summary of Ultrafiltration Results Using the Small PMI Membrane

Waste Stream	pH	FLUX 1/m ² -h		PERCENT REMOVED											
		EXP ¹	UNEX ²	HMX		RDX		TNT		TOC					
				EXP	UNEX	EXP	UNEX	EXP	UNEX	EXP	UNEX				
Synthetic Double Strength	3.0	--	45.2	--	0	--	0	--	23.1	--	--	2% Acet			
Synthetic Full Strength	3.0	35.5	33.3	16.3	4.4	0	3.7	10.5	25.3	7.8	0	0			
	7.0	47.2	51.9	6.1	4.1	0.3	0.3	23.5	13.2	22.1	13.4	13.4			
1/2 Synthetic Strength	3.0	--	40.1	0	0	0	0	7.8	8.9	6.9	1% Acet				
	7.0	35.0	39.2	0	0	0	0	7.4	16.1	9.4	1% Acet				
1/4 Synthetic Strength	3.0	30.7	--	32.0	33.0	15.4	15.7	70.0	22.8	1/2% Acet	1/2% Acet				
	7.0	36.2	36.3	36.0	0	34.6	0	55.3	7.7	1/2% Acet	1/2% Acet				
Kansas AAP	3.0	--	17.5	--	0	--	7.2	--	*	--	1.7				
	7.0	--	36.0	--	0	--	16.5	--	*	--	2.0				
Lonestar AAP	3.0	--	12.2	--	0	--	0	26.2	26.2	29.7	29.7				
	7.0	--	18.8	--	2.9	--	0	26.2	26.2	31.4	31.4				
Milan AAP	3.0	--	12.1	--	40.4	--	42.2	--	66.1	--	36.5				
	7.0	--	23.6	--	26.8	--	5.9	--	30.2	--	33.3				
Iowa AAP	3.0	--	17.5	--	0	--	1.6	--	34.2	--	34.6				
	7.0	--	23.5	--	0	--	0	--	25.4	--	20.7				

¹EXP = exposed to UV

²UNEX = unexposed to UV

*The Kansas Waste Stream has little or no TNT (<1 ppm)

Table 4. Ultrafiltration Results Using the Large PM1 Membrane on the Large Romicon Ultrafilter

Waste Stream	pH	FLUX (ℓ/m^2-h)	PERCENT REMOVAL			
			HMX	RDX	TNT	TOC
Synthetic Full Strength	3.0	18.2	0	1.0	23.2	1/2% Acetone
	7.0	20.0	0	3.0	37.5	1/2% Acetone
Milan	3.0	11.5	9.9	16.2	46.5	27.9
	7.0	14.3	25.3	21.1	45.9	27.7
Lonestar	3.0	12.2	6.1	13.7	39.9	35.9
	7.0	11.4	15.6	6.1	41.9	34.5
Iowa	3.0	14.6	4.2	2.8	31.4	33.3
	7.0	14.9	3.8	1.9	30.6	35.8

A UV exposed run using the large PM membrane at pH 3.0, not shown in Table 4, removed the same amount of TNT as the similar run not UV exposed.

The Abcor HFK130 and HFM100 membranes and the Amicon UM05 membrane were next examined. An attempt was made to obtain the Millipore PSAL membrane which was reported by Bhattacharyya and Garrison, to be extremely effective in removing TNT but a representative from Millipore Corporation stated that Millipore was never able to successfully reproduce that membrane and thus it is no longer available. Table 5 gives a summary of the runs made on the Abcor and Amicon membranes.

Table 5 shows that the LC results using the HFM100 membrane were very poor for both the synthetic and the actual waste streams. The results using the Abcor HFK130 membrane were considerably better. The best TNT removal was at pH 7.0 although the best TOC reduction occurred at pH 3.0. Once again

Table 5. Summary of Ultrafiltration Runs Made
Using the Abcor and Amicon Membranes

Membrane	pH	FLUX (ℓ/m^2-h)	PERCENT REMOVED				Waste Stream
			HMX	RDX	TNT	TOC	
HFM 100	3.0	121.2	1.0	2.0	6.0	26.0	Synthetic
	7.0	110.4	10.4	2.7	0	1% Acet	Synthetic
	3.0	127.2	0	3.4	14.2	23.3	Iowa AAP
	7.0	98.6	0	3.9	31.5	15.5	Lonestar AAP
	3.0	59.8	0	0	*	0	Kansas AAP
	7.0	65.7	0	0	*	7.9	Kansas AAP
HFK 130	3.0	77.9	2.0	0	15.7	21.0	Synthetic
	7.0	73.4	13.3	1.5	47.5	14.5	Synthetic
	3.0	80.5	4.5	0	11.4	10.8	Iowa AAP
	3.0	43.8	0	0	*	6.7	Kansas AAP
	7.0	53.6	9.5	0	*	1.8	Kansas AAP
	3.0	71.5	0	4.0	8.9	45.0	Lonestar AAP
	7.0	74.7	0	2.2	12.3	13.7	Lonestar AAP
	3.0	67.2	1.4	6.1	12.7	25.0	Milan AAP
	7.0	68.6	0	12.1	14.1	22.1	Milan AAP
UM05	3.0	4.8	31.3	15.7	45.6	--	Synthetic
	7.0	7.5	19.4	5.2	42.7	--	Synthetic

*The Kansas AAP Stream contains less than 1 ppm

the results for HMX and RDX removal were somewhat erratic at both pH 3.0 and pH 7.0 with neither pH showing very good removal. The flux rates were higher than those obtained with the PM1 membrane with an average of 68.2 L/m²-h at pH 3.0 and 67.6 L/m²-h at pH 7.0.

The final membrane tested was the Amicon UM05. Table 5 shows that at either pH 3.0 or 7.0 over 42% of the TNT from a synthetic stream was removed. PH 3.0 was best for the removal of HMX and RDX with removals of 31.3 and 15.7%, respectively. However, the flux rates were extremely poor, especially at pH 3.0.

Until this time we have discussed the percent removal of HMX, RDX and TNT by UF as a comparison between the initial sample (Feed) and the permeate, assuming that the material being removed was becoming concentrated in the feed tank (See Figure 3). However, when the concentrates were analyzed, only 6 of the 77 runs showed increased levels of TNT, 38 showed increased levels of RDX, and 31 showed increased levels of HMX. Three of 31 acid runs, 2 of 36 neutral runs, and 1 of 10 alkaline runs showed some concentration of TNT. Sixteen acid runs, 17 neutral runs, and 5 base runs showed some concentration of RDX; and 9 acid runs, 14 neutral runs, and 6 base runs showed some concentration of HMX. The best run for concentrating TNT was a Milan sample at pH 7.0, which was concentrated to 9.8% on an Abcor HFK120 membrane.

The best run for concentrating RDX was also a Milan sample on the Abcor HFK130 membrane at pH 3.0. This sample showed an increase in concentration of 29%. The next best increase in concentration was 18.2% on a PM1 membrane at pH 3.0 also using the Milan stream. The Milan stream contains a very high level of RDX (70.2 ppm) which may account for the higher concentrations achieved. Most of the other runs showed less than 10% increase in concentration for RDX.

For HMX a maximum increase in concentration of 53.8% was achieved at pH 3.0 using the PM1 membrane on the Milan stream. There were several other good runs showing concentration increases of 31 to 43% at pH 3.0 using the PM1 membrane.

Material and carbon balances were performed on many of the ultrafiltration runs to determine the fate of the HMX, RDX, and TNT being removed but not found in the concentrate.

An example of these calculations is found in Appendix C. These calculations show that the material balances do not balance and therefore material must be adsorbing on the surfaces of the membranes.

To verify our theory that the material was being lost due to adsorption we flushed a membrane for 30 minutes with 1% NaOH and analyzed the resultant solution. The solution was cloudy and had an intense brownish-orange color. The LC analysis revealed no TNT, RDX, or HMX, but very large peaks were found at retention times of 1.7, 2.3, 2.9, 3.2, and 4.3 which are typical of the decomposition products of these compounds (see Figure 4).

To circumvent the problem of decomposition from NaOH we next flushed a membrane for 30 minutes with 10 liters of a 2% acetone solution immediately following another run. An analysis of this sample revealed trace levels of RDX, a slightly higher level of HMX (1.3 ppm) and a significant level of TNT (7.1 ppm). This accounted for 92.5% of the starting material. It is believed that a longer flush would have removed even more material because a sodium hydroxide flush of the membrane after the acetone flush still produced the brownish-orange color. See Figures 5 and 6 for examples of HPLC chromatograms showing the effect of NaOH on HMX, RDX, and TNT.

To determine if the membranes could become fouled if run longer than the 2 to 4 hours of a typical run, we conducted a run for 2 days with the Abcor



Figure 4. HPLC Chromatogram of HMX, RDX, and TNT Following a 1% NaOH Flush of a PM1 Ultrafiltration Membrane

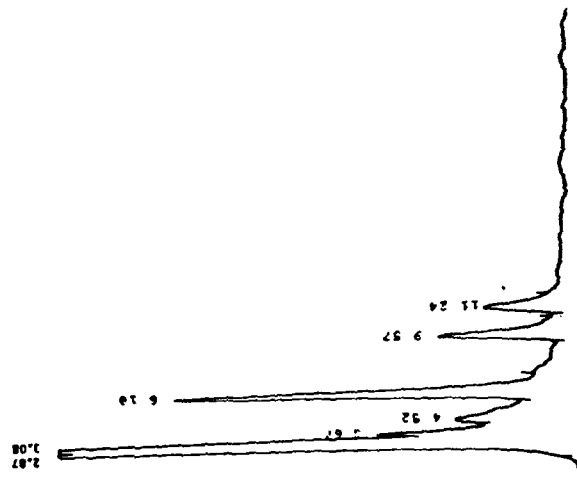


Figure 5. HPLC Chromatogram of an Unexposed, Synthetic HMX, RDX, and TNT Solution at pH 11.0 (note disappearance of TNT)

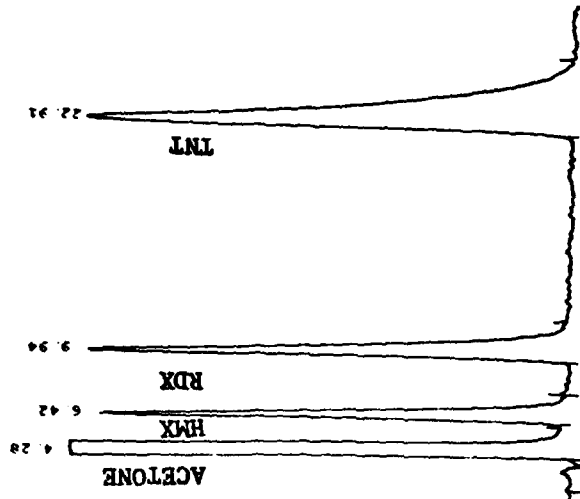


Figure 6. HPLC Chromatogram of an Unexposed, Synthetic HMX, RDX, and TNT Solution at pH 7.0

130 membrane using total recycle (valves 1 and 2 open and valve 3 closed). (See Figure 3). There was no change in the flux rates after this period indicating that the membrane was not becoming plugged. This was probably due to the low concentration of HMX, RDX, and TNT in the full-strength synthetic stream.

A similar run was made on the Iowa waste stream using the PM1 membrane and a 20% reduction in flux was found over 2 days.

Another run of interest was performed using the large PM1 membrane and a large volume of synthetic waste at pH 7.0. The run lasted 5 hours and there was a 21.5% reduction in flux rate. Part of this drop could be due to a temperature drop from 40° to 35°C as the run progressed. In this run, samples of the concentrate and feed were taken every 30 minutes and analyzed on the HPLC. The highest rate of TNT removal occurred in the first hour with a decreasing rate of removal over the next 4 hours. This is typical of adsorption where molecules quickly adsorb on a surface and the rate declines rapidly because of fewer available sites.

Although no ultrafiltration membrane was very effective for concentrating TNT, it was interesting to note that nearly all the permeate streams were free of color bodies and in most cases the concentrates were considerably darker than the feed solutions.

CONCLUSIONS

Ultrafiltration using the membranes currently available is not effective for the removal of soluble quantities of HMX, RDX, and TNT from munition plant waste waters. However, suspended solids are removed and generally there is a concentrating of other organic compounds in the actual waste streams.

Because ultrafiltration is not effective, it was not possible to determine plant costs using ultrafiltration.

This document reports research undertaken at the US Army Natick Research and Development Command and has been assigned No. NATICK/TR-82105 in the series of reports approved for publication.

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6. Bhattacharyya, Dibakar, K. A. Garrison. 1977. Membrane Ultrafiltration for Treatment and Water Reuse of TNT Manufacturing Wastes. Water Pollution Control Federation Journal, 49(5): 800-808.

APPENDIX A

Manufacturers of Membrane Equipment That Were Contacted

*Abcor Inc.
850 Main Street
Wilmington, MA 01887

Ajax International Corp.
P.O. Box 26607
San Diego, CA 92126

Aqua-Chem Inc.
Water Technologies Division
P.O. Box 421
Milwaukee, WI 53201

*Amicon Corp.
182 Conant Street
Danvers, MA 01923

*Barnstead Co.
225 Rivermoor Street
Boston, MA 02132

*Basic Technologies Inc.
1744 Donna Road
W. Palm Beach, FL 33409

CPAC Inc.
2364 Leicester Road
Leicester, NY 14481

Chemtronic Systems Inc.
3540 Lightner Blvd.
P.O. Box 85
Vandalia, OH 45377

Cochrane Environmental Systems
Crane Co.
P.O. Box 191
King of Prussia, PA 19406

*Continental Water Systems Corp.
P.O. Box 20018
El Paso, Texas 19998

Culligan USA
One Culligan Parkway
Northbrook, IL 60062

*Damrow Co.
Fond Du Lac, WI 54935

De Salination Systems, Inc.
1107 W. Mission Ave.
Escondido, CA 92025

Dorr Oliver
274 Riverside Ave.
Westport, CT 06880

Dow Chemical Co.
2020 Dow Center
Midland, MI 48640

DuPont, E. I. De Nemours & Co.
Wilmington, DE 19898

Ecodyne Corp. Craver Water Div.
2720 US Highway 22
Union, NJ 07083

El Paso Environmental Systems Inc.
123 N. Concepcion Street
P.O. Box 10751
El Paso, TX 79997

Envirex Inc.
1901 S. Praire Ave.
Waukesha, WI 53186

*Envirogenics Systems Co.
9255 Telstar Ave.
El Monte, CA 91731

*Flotronics Div Selas Corp. of America
1957 Pioneer Road
Huntingdon Valley, PA 19006

*Gaston County Fabrication
P.O. Box 308
Stanley, NC 28164

Gelman Sciences Inc.
600 S. Wanger Rd.
Ann Arbor, MI 48106

*Replied to Letter

APPENDIX A (continued)

Go-Ten Manufacturing
P.O. Box 8237
Trenton, NJ 08650

Griffolyn Co.
10020 Mykawa
Box 33248
Houston, TX 77033

Hex Industries Inc.
15001 S. Figueroa Street
Gardena, CA 90248

Illinois Water Treatment Co.
4669 Shepherd Trail
Rockford, IL 61105

Infilco Degremont Inc.
Box K-7
Richmond, VA 23288

Ion Exchange Products Inc.
4500 N. Clark Street
Chicago, IL 60640

Ionics Inc.
65 Grove Street
Watertown, MA 02172

LA Water Treatment Div. Chromalox
American Corp.
Box 1467
City of Industry, CA 91749

Liquitech Div of Thermotic Inc.
P.O. Box 13030
Houston, TX 77019

National Tank and Pipe Co.
P.O. Box 7
10037 SE Mather Road
Clackamas, OR 97015

*Osmonics Inc.
15404 Industrial Road
Hopkins, MN 55343

*Penfield Inc.
980 Old Colony Road
Meriden, CT 06450

Permutit, NJ
Box 355
Paramus, NJ 07670

Polymer Research Corp. of America
2186 Mill Ave.
Brooklyn, NY 11234

Polymetrics Inc.
1005 Timothy Drive
San Jose, CA 95133

Rexnord Inc.
P.O. Box 2022
Milwaukee, WI 52314

*Romicon Inc.
100 Cummings Park
Woburn, MA 01801

Saltech Inc.
P.O. Box 26872
El Paso, TX 79926

Scott Environmental Div. Environmental
Tectonics Corp.
James Way
Southampton, PA 18966

*Sethco Div. Met Pro Corp.
39 Bennington Ave.
Freeport, NY

*UOP, Fluid System Div.
2980 N. Harbor Drive
San Diego, CA 92101

Vaponics, Vaponics Ltd.
Cordage Park
Plymouth, MA 02360

*Replied to Letter

APPENDIX A (continued)

Water Purification Systems, Inc.
3451E 26th Street
Los Angeles, CA 90023

Water Services of America Inc.
P.O. Box 23421
8165 W. Tower Ave.
Milwaukee, WI 53223

Western Dynetics Inc.
1152 Tourmaline Drive
Newbury Park, CA 91320

Westinghouse Electric Corp.
Gateway Center
Pittsburg, PA 15222

Xonics Inc.
6849 Hayvenhurst Ave.
Van Nuys, CA 91406

APPENDIX B

Literature Search Finds

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APPENDIX C

MATERIAL BALANCE CALCULATIONS

Run 36 Milan pH 7.0 PM1 Membrane

Compound	CONCENTRATION (mg/L)		
	Initial	Permeate	Concentrate
HMX	9.7	7.1	8.3
RDX	70.6	66.4	79.2
TNT	93.7	65.4	79.6
TOTAL	174.0	138.9	167.1

Weights

Starting material (initial) 18.11 kg
 Permeate 10.00 kg
 Concentrate 8.00 kg

Initial (I) - 174.0 mg/L

174.0 (18.11) = 3,151.1 mg

Permeate (P) - 138.9 mg/L

138.9 (10.00) = 1,389.0 mg

Concentrate (C) - 167.1 mg/L

167.1 (8.00) = 1,336.8 mg

$I = P + C + A$ (material adsorbed on membrane)

$3,151 = 1,389.0 + 1,336.8 + A$

$A = 425.3$ mg of material adsorbed on membrane

APPENDIX C (CONT'D)

CARBON BALANCE CALCULATIONS

Run 36 Milan pH 7.0 PM1 Membrane

Total Organic Carbon (From TOC Analyzer)

Initial (Feed)..... 84 mg/L
Permeate 56 mg/L
Concentrate 98 mg/L

Initial (I): 84 (18.11) = 1,521.2

Permeate (P): 56 (10.00) = 560.0

Concentrate (C): 98 (8.00) = 784.0

$I = P + C + A$

$1,521.2 = 560.0 + 784.0 + A$

$A = 177.2$ mg of C adsorbed on membrane

CARBON BALANCE FROM LC VALUES

HMX: $C_4H_8N_8O_8$ MW: 296.3

C: $4 \times 12 = 48$
 $\frac{48}{296.3} = 0.162$ or 16.2% Carbon

RDX: $C_3H_6N_6O_6$ MW: 222.3

C: $3 \times 12 = 36$
 $\frac{36}{222.3} = 0.162$ or 16.2% Carbon

TNT: $C_7H_5N_3O_6$ MW: 227.1

C: $7 \times 12 = 84$
 $\frac{84}{227.1} = 0.370$ or 37.0% Carbon

APPENDIX C (CONT'D)

Compound	CONCENTRATION OF CARBON (PPM)		
	Initial	Permeate	Concentrate
HMX	9.7(0.162) = 1.6	7.1(0.162) = 1.2	8.3(0.162) = 1.4
RDX	70.6(0.162) = 11.4	66.4(0.162) = 10.8	79.2(0.162) = 12.8
TNT	93.7(0.370) = 34.7	65.4(0.370) = 24.2	79.6(0.370) = 29.5
TOTAL	47.7	36.2	43.7

$$I = P + C + A$$

$$47.7(18.11) = 36.2(10.00) + 43.7(8.00) + A$$

$$863.9 = 362.0 + 349.6 + A$$

$$A = 152.3 \text{ mg C Adsorbed on membrane}$$

The difference in carbon levels between the Total Organic Carbon Analyzer and the LC values can be attributed to the fact that the LC values do not account for organic solvents or all other organic compounds that are found in the munition plant wastestreams.