



## Project Summary

# Separation of Hazardous Organics by Low Pressure Reverse Osmosis Membranes – Phase II, Final Report

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**Extensive experimental studies showed that thin-film, composite membranes can be used effectively for the separation of selected hazardous organic compounds. This waste treatment technique offers definite advantages in terms of high solute separations at low pressures (<2 MPa) and broad pH operating range, and the use of charged membrane would allow the selective separation of some organics from feeds containing high salt concentrations. In addition, feed pre-ozonation of selected organics provided significant improvement in flux and rejection characteristics for both charged and uncharged membranes because of the formation of ionizable organic acid intermediates during the ozonation that did not interact as strongly with the membrane. The overall ozonation/membrane process effectively produced permeate water of high quality while it minimized the volume of waste that must be further treated.**

***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

Chemical manufacturers generate millions of tons of wastes containing various hazardous priority pollutants each year. The development of alternative technologies for the treatment of various hazardous wastes is becoming increasingly important as concerns grow over their dis-

posal. These and other wastes, such as leachate from unsecured disposal sites, contain a wide variety of priority pollutants such as pesticides, herbicides, PCB's, chlorinated hydrocarbons, and heavy metals. Much of this waste is relatively dilute and so must be concentrated before further treatment.

Several methods such as biological treatment, stripping, and carbon adsorption have been used to treat dilute wastewater. Ozonation has also been found to be effective in oxidizing some hazardous organics to less toxic compounds. Membrane processes can be used to purify wastewater and produce a 20- to 50-fold decrease in waste volumes that must be treated with other processes such as incineration or wet air oxidation.

### Membrane Concepts and Applications

Membrane processes are gaining considerable attention for the purification and volume reduction of dilute hazardous wastes. The development of low pressure reverse osmosis (RO) membranes (such as aromatic polyamide and sulfonated polysulfone) has resulted in membrane processes that give high water flux at low pressures (< 2 MPa). These thin-film, composite membranes can provide high solute separations and have definite advantages in terms of energy savings, capital cost, and broad pH (2 to 12) operating range. The low pressure membranes can simultaneously separate hazardous organics and inorganics. Membranes containing charged groups can also selectively separate ionizable compounds.



Membrane performance is measured in terms of membrane rejection ( $R$ ), permeate water flux ( $J_w$ ), and extent of water recovery ( $r$ ). The rejection is a measure of solute separation by the membrane and is defined as

$$R = 1 - \frac{C_p}{C_i}$$

where  $C_p$  and  $C_i$  are the solute concentrations in the permeate and feed streams, respectively.

Thin-film, composite membranes have been used to remove major pesticides, carcinogenic substances, priority organic pollutants, etc. However, although low pressure polyamide membranes have successfully separated chlorinated phenolics, there was a water flux drop due to membrane/solute interactions.

## Objectives

This work deals with the use of low pressure thin-film, composite membranes for the concentration and separation of selected chlorophenols (CP's) and chloroethanes (CE's) with and without feed pre-ozonation. Two types of membranes were used: aromatic polyamide (FilmTec FT30\*) and carboxylated (negatively-charged) polyamide (FilmTec NF40) membranes. Membrane feed pre-ozonation will result in the formation of organic acid intermediates; this should result in less flux drop and, since these compounds are ionizable, in high separations by charged as well as uncharged membranes. Separation and flux characteristics of both charged and uncharged membranes were studied with both non-ozonated and ozonated (selected CP's and CE's) solutions to evaluate the effectiveness of the ozonation/membrane process for the enhanced removal of priority organic pollutants.

## Experimental

Membrane experiments were conducted with a system (Figure 1) containing both a batch and a continuous flow cell so that the performance of two different membranes could be studied at the same time. The thin-film, composite membranes used in the experiments were the NF40 and the FT30-BW; the NF40 was placed in the batch cell and the FT30 in the flow cell. The pump shown in the system provided flow of solution through the continuous cell and mixing in the batch cell; compressed nitrogen supplied the pressure driving force for the system. The operat-

ing conditions were: system pressure ( $P_{avg}$ ) of 0.3 to 1.4 MPa, feed pH's of 3.0 to 9.4, and system temperature of 24°C.

The procedure used for experiments involving ozonation/membrane process is outlined in Figure 2. Membrane feed solutions were ozonated in a 1.8-L stirred reactor with a flow of 0.20 standard L/min (SLPM)  $O_2$  containing 2% ozone. Pre-ozonation times ranged from 0 to 60 min. After ozonation, solutions were mixed for several hours to allow decomposition of residual ozone. Membrane experiments were then carried out with the ozonated solutions.

Membrane performance was measured in terms of flux drop from that of distilled water flux (DWF) and solute rejection. Membrane feed, concentrate, and permeate samples were analyzed by Total Organic Carbon (TOC) and High Pressure Liquid Chromatography (HPLC) direct injection. TOC was measured with the use of a Beckman Model 915-B Carbon Analyzer. HPLC analysis (phenolics) were performed with a Varian 5000 liquid chromatograph with a MCH-5 column (reverse phase octyldecylsilane on silica) and a UV-50 variable detector at 220 and 280 nm.

## Results and Discussion

Membrane separation of selected hazardous organics with and without feed pre-ozonation were investigated with the NF40 and FT30 membranes. Single component studies were conducted with trichlorophenol (TCP); multicomponent systems examined consisted of TCP/humic acid (HA) mixtures and mixtures of CP, dichlorophenol (DCP), TCP, trichloroethane (TCE), and tetrachloroethane (TTCE). A wide range of ozonation times and pressures were studied, and since many of the compounds studied were ionizable, several membrane feed pH values were investigated. Membrane performance results are presented in terms of solute rejection and flux drop. The percent of flux drop (at a particular pressure) is defined as:

$$\% \text{ Flux Drop} = \frac{\text{Distilled Water Flux} - \text{Flux with Wastewater}}{\text{Distilled Water Flux}} \times 100$$

Membrane stability was checked by standard sodium chloride (NaCl) and sodium sulfate ( $Na_2SO_4$ ) rejections and DWFs. For the NF40 (negatively charged nanofiltration membrane made of carboxylated polyamide) the DWF at 1.38 MPa was found to be  $11 \times 10^{-4} \text{ cm}^3/\text{cm}^2 \text{ s}$  (23.3 gal/ft<sup>2</sup> day). Sodium chloride and sodium sulfate rejections were 30% and 97%, re-

spectively. The DWF of the FT30 (an aromatic polyamide membrane) was also  $11 \times 10^{-4} \text{ cm}^3/\text{cm}^2 \text{ s}$  at 1.38 MPa; NaCl and  $Na_2SO_4$  rejections for this membrane were 96% and 97%. The low NaCl rejection of the NF40 illustrates the principal advantage of the charged membrane over RO membranes such as the FT30. The FT30 membrane gives high rejections of most solutes, whereas the NF40 membrane can be used to selectively separate compounds with different charges.

## Studies with Trichlorophenol

Membrane feed solutions of 50 mg/L TCP were ozonated from 0 to 60 min. The pH of the solutions decreased after ozonation; this drop in pH indicated the degradation of the TCP to intermediate organic acid compounds. HPLC analysis indicated that after 5 min of ozonation the TCP concentration was reduced to 24.7 mg/L, and after 15 min, was <0.5 mg/L. Formation of  $CO_2$  during the ozonation was indicated by reduction in TOC and the presence of  $CO_2$  in the high pH trap placed after the ozonation reactor.

Figure 3 shows flux drop as a function of ozonation time for the NF40 membrane for low (3.3 to 3.6) and high (8.8 to 9.4) pH membrane feeds. At low feed pH, TCP was not ionized and so interacted strongly with the membrane; adsorbed TCP displaces water in the membrane pores, causing significant water flux drop. Ozonation of TCP resulted in the formation of organic acids that did not interact as strongly with the membrane and so caused less flux drop. At the high feed pH the TCP was ionized; the negatively charged solute did not interact as strongly with the charged membrane and the flux drop was less than that at the lower feed pH. Since the ozonation products were also ionizable, the flux drop for ozonated solutions was also smaller under the high pH conditions.

TOC rejections for the NF40 membrane are shown in Figure 4. It can be seen that both an increase in feed pH and ozonation time increased rejections. An increase in feed pH resulted in the ionization of the TCP or the organic acid intermediates formed during ozonation. These negatively charged species were more highly rejected by the negatively charged NF40 mem-

\* Mention of trade names or commercial products does not constitute endorsements or recommendations for use.

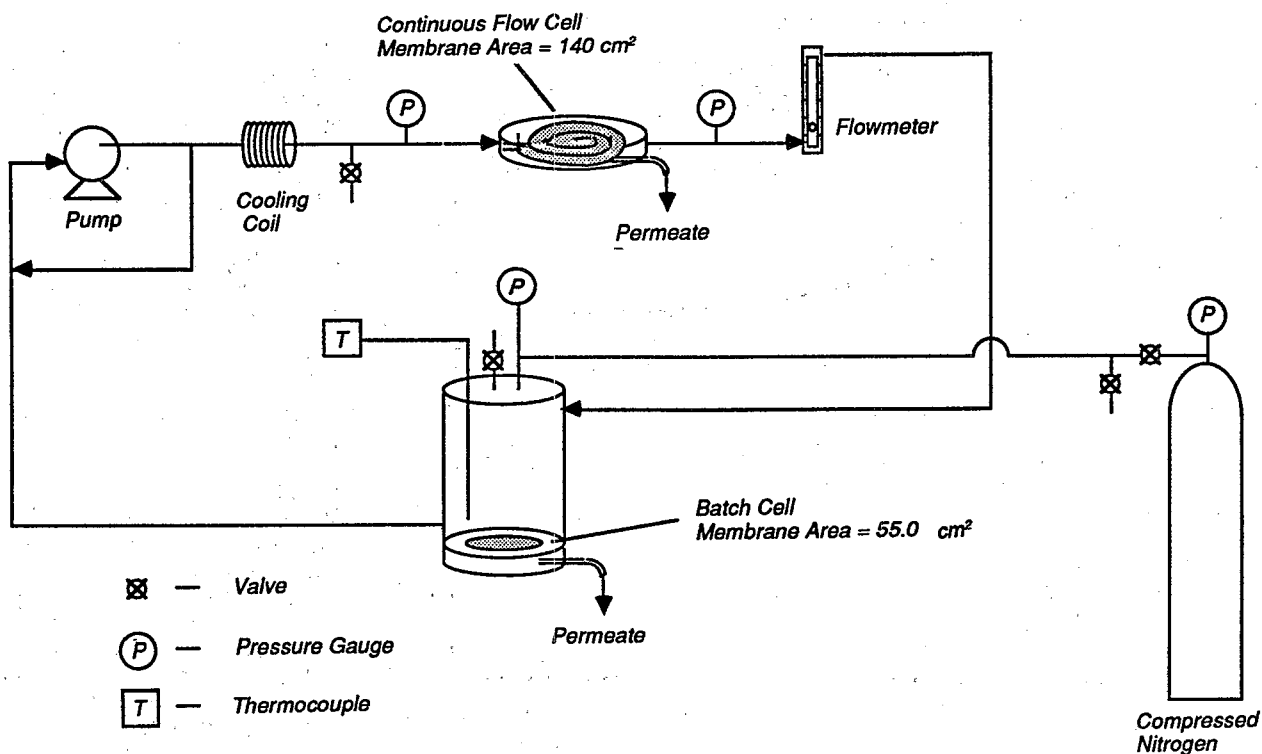


Figure 1. Schematic of system for membrane experiments.

#### Ozonation of Solution

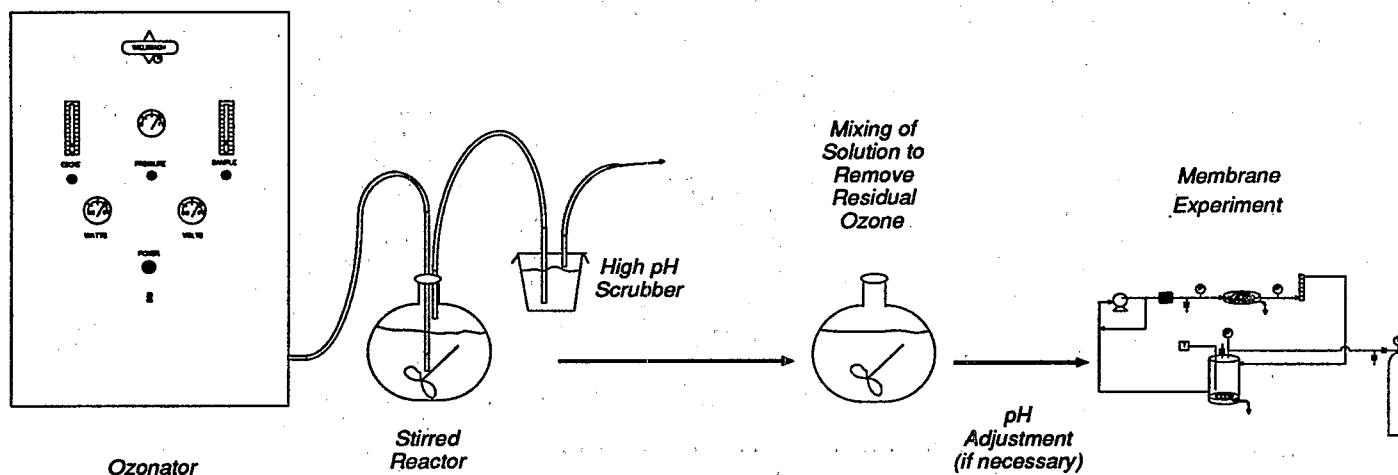


Figure 2. Schematic of ozonation process for ozonation/membrane experiments.

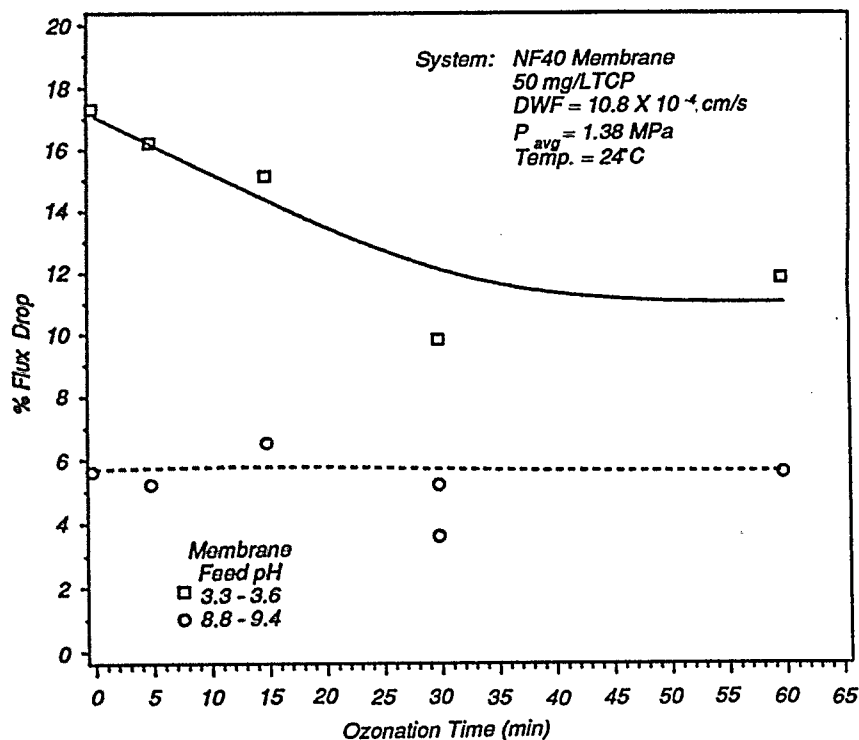


Figure 3. Effect of ozonation on flux drop for the NF40 membrane with trichlorophenol.

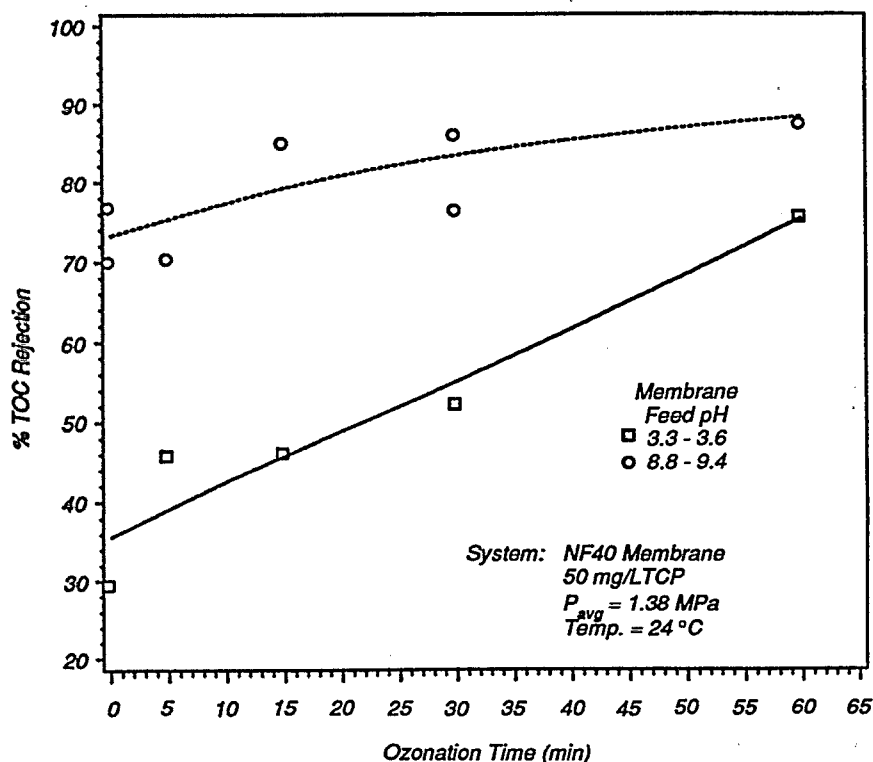


Figure 4. Effect of ozonation on TOC rejection for the NF40 membrane with trichlorophenol.

brane. Ozonation improved rejection since the organic acids that were formed ionized at lower pH's than does TCP and so these were rejected better than TCP at lower feed pH's.

Figure 5 shows the flux drop for the FT30 membrane. Under non-ionized conditions (feed pH 3.3 to 3.6), the TCP interacted strongly with the membrane, causing a large flux drop. The drop in water flux was greater than that for the NF40; the charge on the NF40 weakened the interactions between the TCP and the membrane. As with the NF40, ozonation reduced flux drop for the FT30 membrane by reducing solute interactions with the membrane. Under ionized conditions (feed pH 8.8 to 9.4), the TCP and organic acids formed during ozonation do not interact with the FT30 membrane as strongly as under non-ionized conditions and so the flux drop was smaller. TOC rejections were in the range 80% to 96%, and feed pH and ozonation did not greatly affect TOC rejection for the FT30 membrane; this membrane did not depend on charge for separation as does the NF40 membrane.

#### Studies with Trichlorophenol/Humic Acids

Experiments to determine the effect of water recovery on water flux and solute rejection were conducted with mixtures of 50 mg/L TCP and 10 mg/L HA. HA's are high molecular weight compounds that are present in soils and so can be found in groundwater containing hazardous organic leachates. These compounds are highly rejected by the membrane but can cause large water flux drops resulting from adsorption.

For both non-ozonated and ozonated TCP/HA, no drop in flux was observed even at high recoveries (80%); the TCP/HA and the organic acids formed during ozonation were ionized at the high feed pH (9.1 to 9.3) and so little change in water flux occurred. Rejection of the non-ozonated TCP/HA decreased from 80% at 10% recovery to 64% at a recovery of 80%; however, for the ozonated solution 84% TOC rejection was maintained even at 75% water recovery. The decrease in TOC rejection for the non-ozonated TCP/HA could have been the result of enhanced concentration of the HA at the membrane surface. Since degradation of the HA is expected during ozonation, HA concentration on the membrane surface did not increase for the ozonated solution, and TOC rejection remained high.

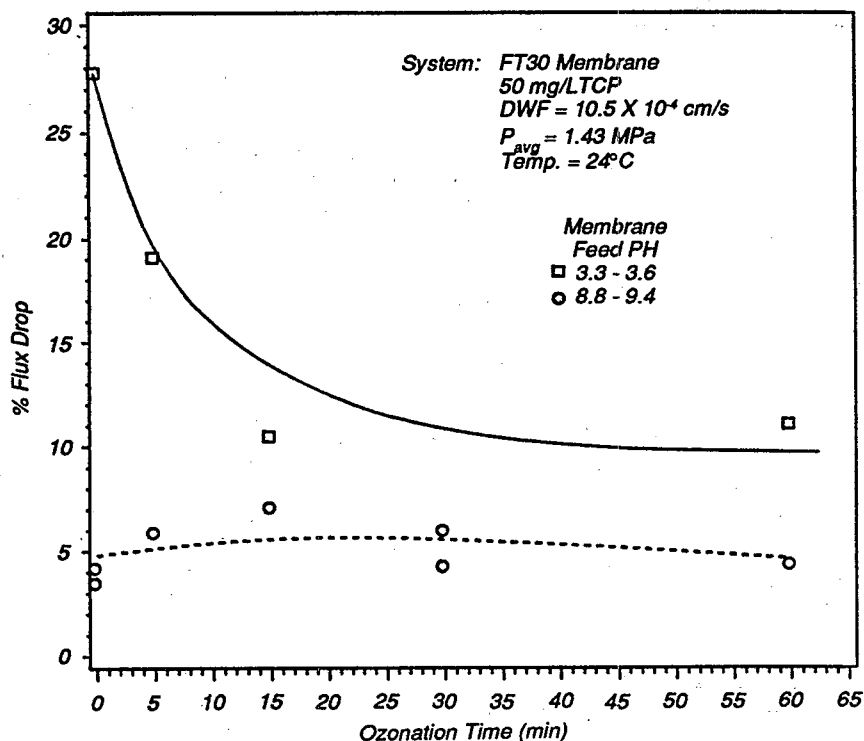


Figure 5. Effect of ozonation on flux drop for the FT30 membrane with trichlorophenol.

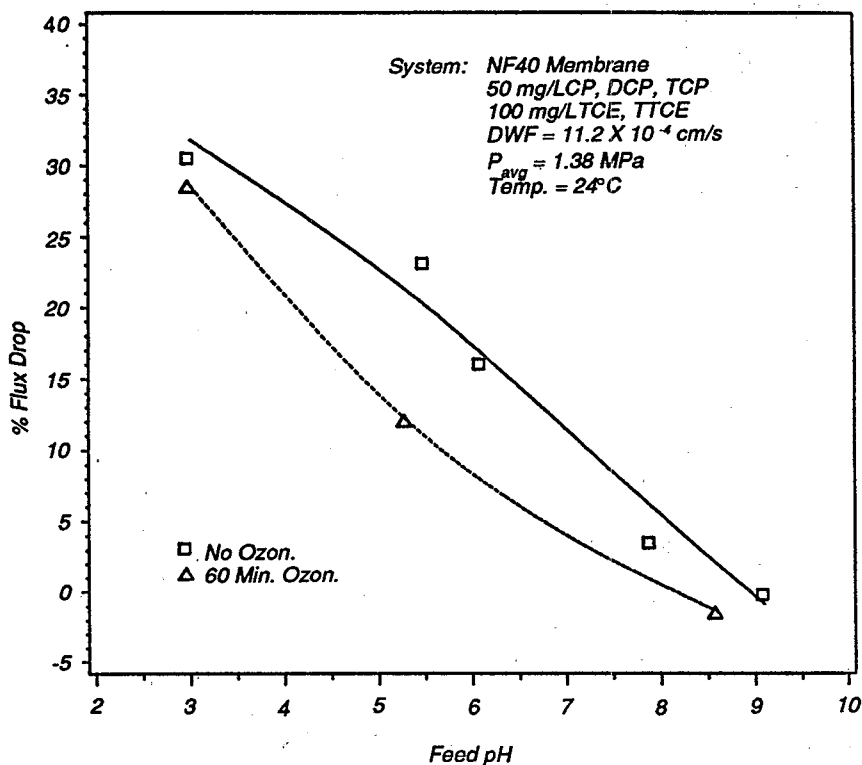


Figure 6. Effect of feed pH and ozonation on flux drop for the NF40 membrane with hazardous organic mixtures.

## Studies with Mixtures

Studies were performed with mixtures of 50 mg/L CP, DCP, and TCP with 100 mg/L TCE and TTCE to determine the effect of multicomponent systems on flux and TOC rejections for ozonated and non-ozonated solutions. The flux behavior of the mixture with the NF40 was found to be linear over the pressure range 0.34 to 1.38 MPa (50 to 200 psi), indicating the absence of surface polarization phenomena. Flux drops as a function of pH for the NF40 membrane at 1.38 MPa are shown in Figure 6. Flux improved substantially for increase in feed pH for both the ozonated and non-ozonated mixtures; ozonation did not greatly improve flux drops found for the mixture at a fixed feed pH. However, Figure 7 shows that TOC rejection was enhanced significantly for the mixture after ozonation for 60 min. While the non-ozonated mixture rejection was almost constant for the different feed pH's, it was increased to as high as 80% for the ozonated mixture. The increase was because of the formation of organic acids that ionized and were rejected by the membrane. Although the phenolics in the mixture were ionizable, the pKa of these compounds are much higher than those of the intermediates, and also, the CE's present were not ionizable. As a result, the rejection of the non-ozonated mixture did not increase over the pH range studied. The organic acids formed after ozonation, however, had much lower pKa's and so are rejected by the charged membrane.

The flux behavior of the mixture with the FT30 membrane was also found to be linear over the pressure range studied. FT30 membrane flux drops are shown in Figure 8 for an operating pressure of 1.43 MPa. Flux drop was also a strong function of feed pH for this membrane, and feed pre-ozonation did improve flux drop over the range of feed pH's studied. As with the single component TCP system, ozonation produced intermediates that did not interact with the membrane to the same extent as the mixture and so flux was enhanced. TOC rejection slightly increased with ozonation and feed pH, ranging from 81% to 95%.

## Overall Removal of Trichlorophenol

Figure 9 illustrates an example calculation of an ozonation/membrane process for the separation of hazardous organics; TCP was used as the model compound. After ozonation for 30 min the TCP concentration would be reduced to <0.2 mg/L; the TOC of the feed solution would be 66 mg/L due to the formation of CO<sub>2</sub> dur-

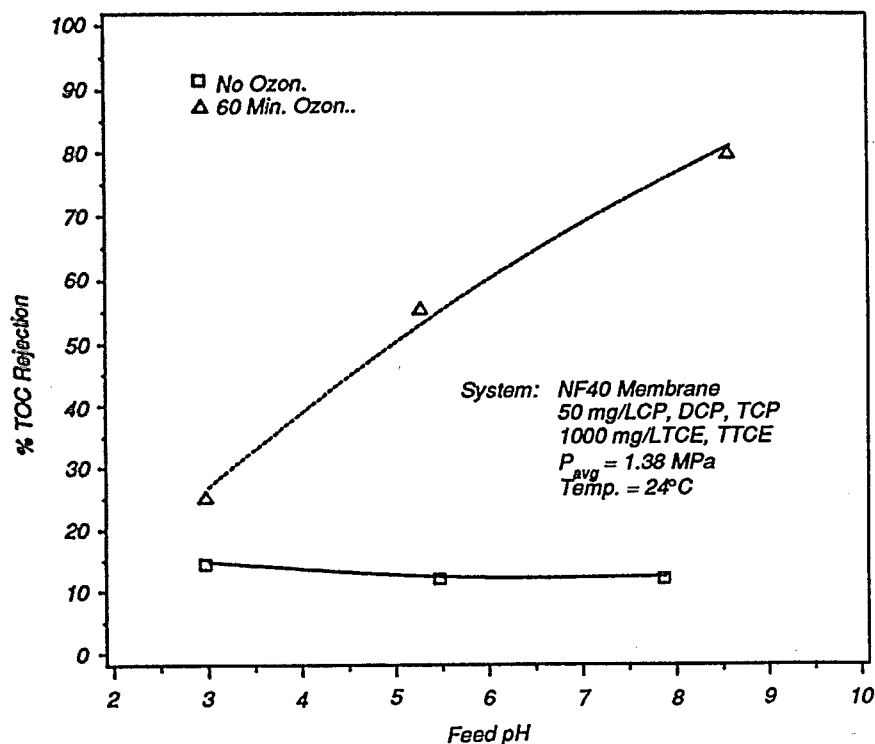


Figure 7. Effect of feed pH and ozonation on TOC rejection for the NF40 membrane with hazardous organic mixtures.

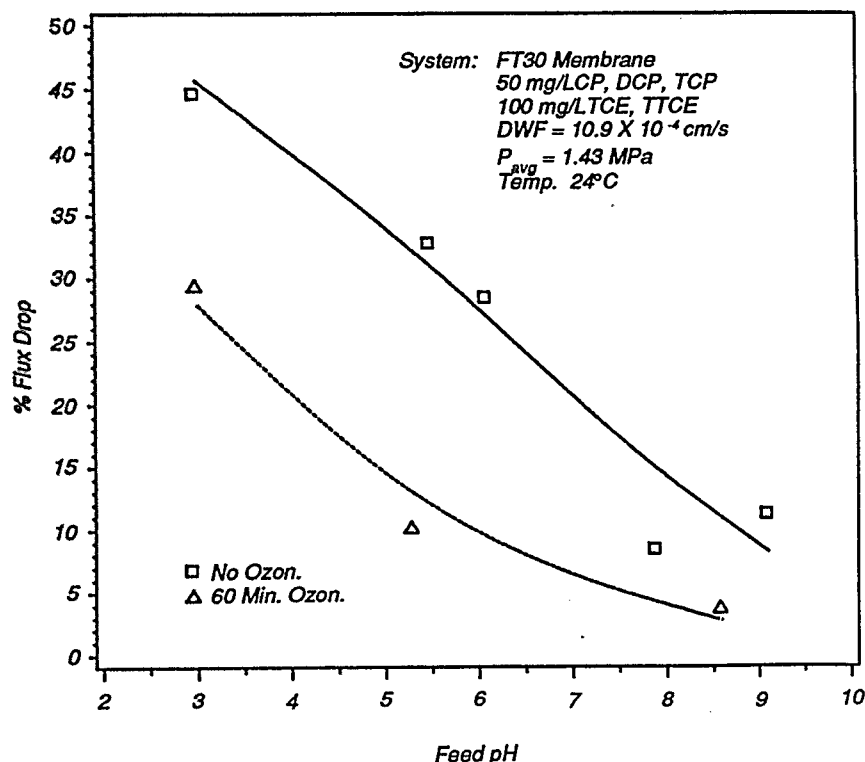


Figure 8. Effect of feed pH and ozonation on flux drop for the FT30 membrane with hazardous organic mixtures.

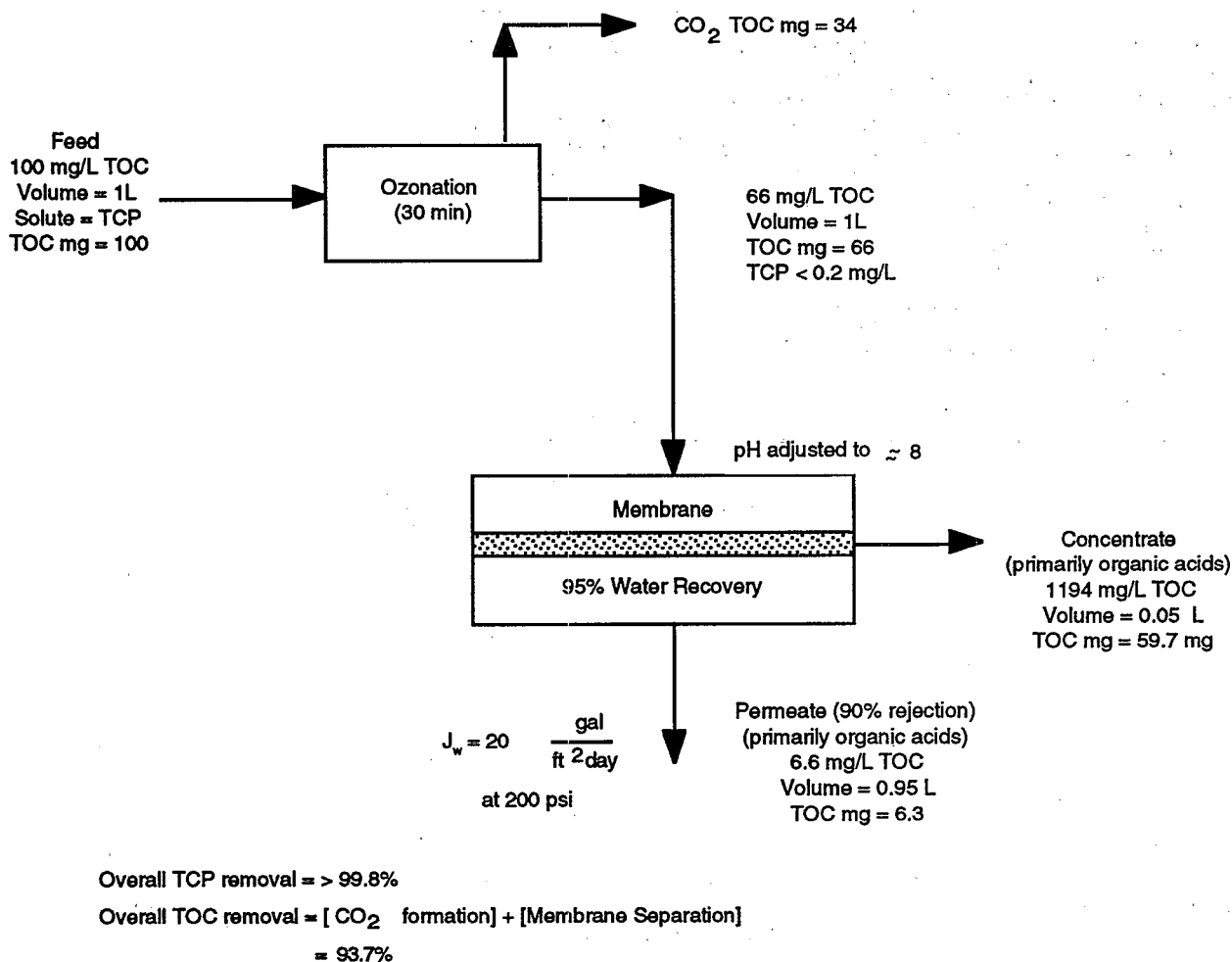
ing the ozonation. For a membrane that rejects 90% (either the NF40 or FT30), the permeate contains only 6.6 mg/L TOC (due primarily to organic acids); the TCP concentration in the permeate would be less than 0.2 mg/L. For 90% water recovery, the concentrate TOC, also mostly due to organic acids formed during ozonation, would be 1194 mg/L. This greatly reduced volume could be disposed of by incineration. The overall ozonation/membrane process would produce permeate water of high quality (overall TCP removal of >99.8%) and greatly reduce the volume and risk of waste that must be further treated. Also, since the process has been shown to be effective when using charged membranes, selective separation of hazardous organics from feeds containing high salt concentrations would be possible and allow high fluxes at low operating pressures even for feeds with high osmotic pressures.

### Conclusions

Dilute hazardous organics were effectively separated by two types of thin-film, composite polyamide membranes. Also, the separation characteristics of the organics by the membranes were improved by feed pre-ozonation. The two membranes studied, a charged nanofiltration membrane (NF40) and a low pressure (RO) membrane (FT30), had water fluxes of 10 to 13  $\times 10^{-4}$  cm/s at 1.4 MPa; NaCl and Na<sub>2</sub>SO<sub>4</sub> rejections were 30% and 97%, respectively, for the NF40 membrane and 96% and 97%, respectively, for the FT30 membrane.

For the ionizable compounds (CP's) studied, flux drops were highly dependent upon feed pH. The NF40 membrane flux drop was 17.4% at feed pH 3 but <6% at pH 9 for TCP and over 30% at pH 3 but only 3.7% at pH 7.9 for a CP-CE mixture. The FT30 membrane flux drop with TCP decreased from 27.9% at pH 3 to 4.3% at pH 9.4 and from 44.8% at pH 3.0 to <12% at pH >7.9 for the CP-CE mixture. Feed pre-ozonation reduced flux drop of both membranes for TCP and the CP-CE mixture below feed pH 6.

Rejections of the NF40 membrane increased from 29.8% to over 70% for TCP as feed pH was increased from 3.4 to >9; TOC rejections of the CP-CE mixture by the NF40 membrane were <15%. For the same mixture, the FT30 membrane TOC rejections were in the range 80% to 96%. Ozonation improved the NF40 membrane rejection to as high as 87.6% for TCP and to over 80% TOC rejection for the CP-CE mixture. HA's present in TCP solutions did not affect separation characteristics of



**Figure 9.** Example calculation for ozonation/membrane process.

the two membranes. It was shown that the ozonation/membrane process could remove >99.8% of the hazardous organic TCP and 93.7% of the TOC.

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*Richard P. Lauch is the EPA Project Officer (see below).*

*The complete report, entitled "Separation of Hazardous Organics by Low Pressure Reverse Osmosis Membranes -Phase II, Final Report," (Order No. PB91-234 625/AS; Cost: \$26.00; subject to change) will be available only from:*

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