WASTEWATER RECOVERY FROM A TEXTILE BLEACH AND DYE OPERATION, BENCH SCALE EVALUATION

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Harlingen's WWTP #2 treats approximately 3 MGD using a combination of primary settling, trickling filters, biotowers, secondary clarification, and sand filtration. Beginning in 1990, a facility for recovering treated wastewater effluent using RO was brought on line. This 2 MGD facility produces high quality product water from filtered wastewater, which is used by a local textile bleach and dye plant. The textile plant requires water with low TDS and organic carbon concentrations. The bleach and dye operations at the textile plant increase the concentrations of color and TDS. Originally the textile plant used only reactive dyes, however, recently indigo dyes have also been included in some of the textile processes. The resulting industrial wastewater is returned to the WWTP and contains high concentrations of a mixture of dyes and a TDS concentration of approximately 2500. This water is treated by extended aeration, clarification, and chlorination before being dechlorinated and discharged into a tidal zone. The treated industrial wastewater is blended with the RO concentrate and the treated domestic wastewater effluent before discharge. A greater demand for process water is anticipated and it has been proposed that this demand be met by re-using the industrial wastewater which is currently being discharged after treatment. This report determines characterization of wastewater from the textile plant and bench-scale evaluations of treatment options and makes recommendations for candidate processes to be evaluated during pilot scale.

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1. Introduction and Background

The City of Harlingen's Wastewater Treatment Plant #2 treats a flow of approximately 3 MGD using a combination of primary settling, trickling filters, biotowers, secondary clarification, and sand filtration. Beginning in 1990, a facility for recovering treated wastewater effluent using reverse osmosis (RO) was brought on line. This 2 MGD facility produces high quality product water from filtered wastewater, which is used by a local textile bleach and dye plant. The textile plant requires water with low total dissolved solids (TDS) and organic carbon concentrations. The bleach and dye operations at the textile plant increase the concentrations of color and TDS. Originally the textile plant used only reactive dyes, however, recently indigo dyes have also been included in some of the textile processes. The resulting industrial wastewater is returned to the wastewater plant and contains high concentrations of a mixture of dyes and a TDS concentration of approximately 2500. This water is treated by extended aeration, clarification, and chlorination before being dechlorinated and discharged into a tidal zone via the Arroyo Colorado. The treated industrial wastewater is blended with the RO concentrate and the treated domestic wastewater effluent before discharge to the Arroyo Colorado.

A greater demand for process water is anticipated and it has been proposed that this demand be met by re-using the industrial wastewater which is currently being discharged after treatment. The following issues must be evaluated before such an expansion of water reclamation activities at Harlingen's Wastewater Treatment Plant #2 can be undertaken:

- potential impact of recycling the industrial wastewater on reclamation operations;
- nature and quantities of waste streams generated after expansion;
- treatment strategies, determination of feasibility, and preliminary cost estimates for the recovery and re-use of the textile wastewater effluent;
- treatment or disposal strategies for residual streams; and
- the long-term performance anticipated through each unit process after reclamation of textile process water is implemented.

A three-phase effort was initiated to provide the information needed to proceed towards facility design for expanded reclamation activities:

A. Characterization of wastewater from the textile plant and bench-scale evaluations of treatment options.

B. Identification of the most promising treatment options for on-site evaluation using small continuous flow units operated over a period of several weeks. Examples of such continuous flow tests include single or multi-stage stand tests of RO, nanofiltration (NF), or ultrafiltration (UF) membranes and chemical pretreatment in conjunction with small filtration pilots.

C. Long-term (4 to 9 months) pilot evaluation of no more than two process trains selected based on results from phases 1 and 2. The exact duration of phase 3 should

reflect a balance between the desirability of a pilot trial which is as long as possible while meeting requirements for delivering build-out on reclamation capacity. In the case of membrane processes, one purpose of these longer pilot runs is to optimize operating conditions including cleaning type and frequency, feed water pressure, and flow rates. Data on potential for long-term membrane fouling, water quality, and characteristics of the concentrate(s) should also be collected.

This document presents the results from phase 1, and makes recommendations for candidate processes to be evaluated at pilot scale during phase 2.

2. Review of Treatment Options for Textile Industry Wastewaters

Based on reviewed published literature, several treatment options were identified early in the study as candidates for further evaluation. Figure 2.1 shows the existing treatment process with four suggested options for the additional treatment needed for the dye wastewater. Three out of the four options were explored in phase 1 bench scale evaluations including:

A. Coagulation/Flocculation as pretreatment to membrane filtration
B. Membrane Separations, and
C. Carbon Adsorption as either pretreatment prior to micro/ultra- filtration or alone.

A fourth option, chemical oxidation using ozonation, peroxide, or an advanced oxidative process, was initially ruled out based on cost and effectiveness.

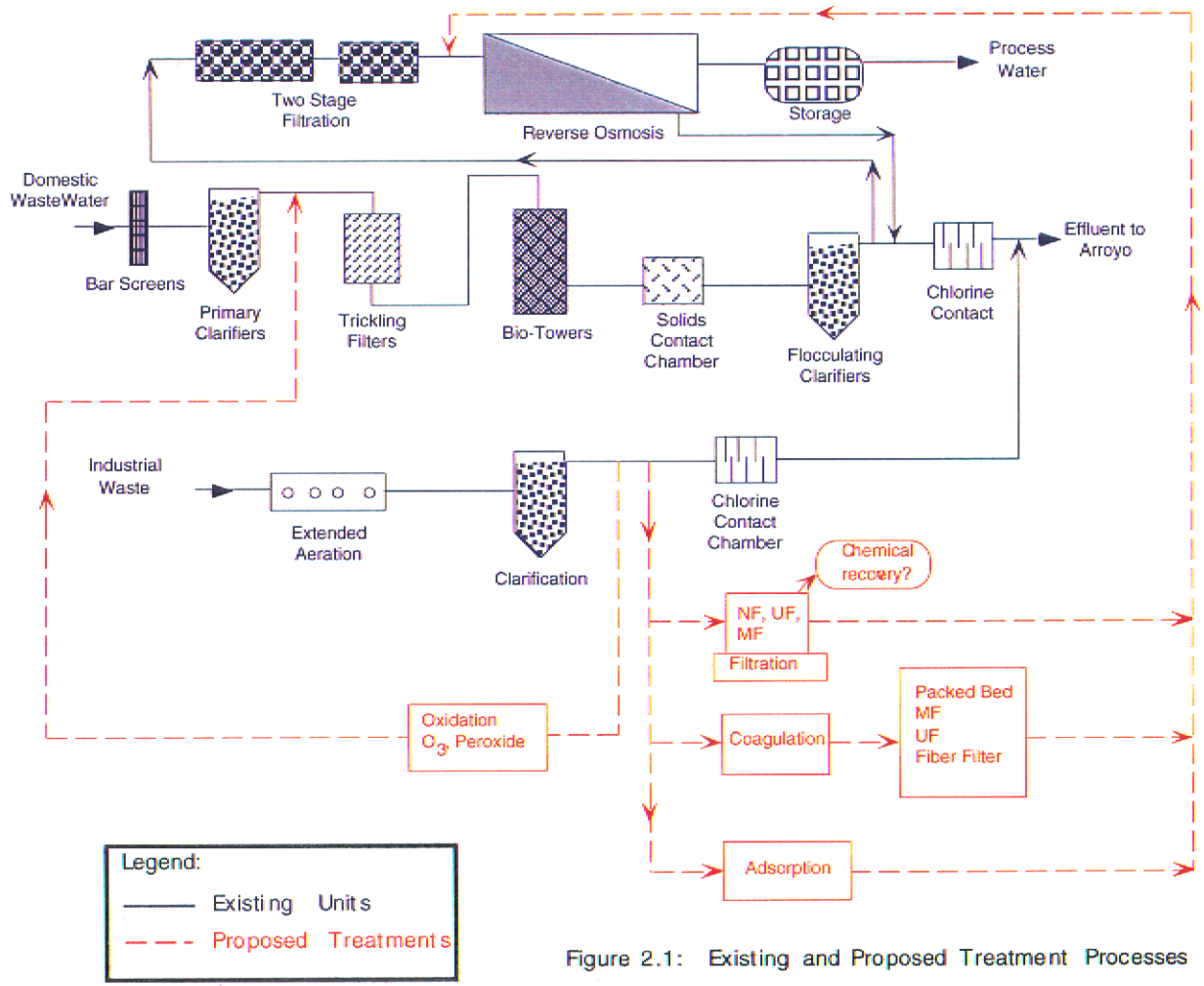

Figure 2.1: Existing and Proposed Treatment Processes

3. Characterization of the Industrial Waste Stream

Three dye wastewater samples and one treated domestic wastewater sample were analyzed as showing in Tables 1 and 2. The dye wastewater samples were taken on 6/26/96 (Dye WW#1), 9/18/96 (Dye WW#2) and 1/22/97, (Dye WW#3). All the samples were refrigerated until used. The domestic wastewater was sampled on 1/22/97.

The pH of the dye wastewater samples is approximately neutral (Table 1). They have very low turbidities, and have conductivities typical of dye waste streams. The total organic carbon (TOC) varied for the three samples indicating the variability of wastewater stream over time. Most of the TOC was found to be dissolved (passing through a 0.45 μm membrane). The TSS (total suspended solids) was measured and found to be rather low, which is expected since the wastewater was sampled after clarification.

The domestic wastewater also has low turbidity and low TSS. The TOC in this water is significantly lower than that of dye wastewaters, due to the fact that this water passed through a secondary treatment process. The DOC accounted for 77% for TOC. The conductivity of this water is also low compared to the dye wastewaters.

An electronic particle counter (Coulter Multisizer) was used to determine the particle size distribution in the wastewater. Particle size distributions of the three dye wastewater samples and the domestic wastewater sample are shown in Figure 3.1. Overall, the particle counts are low in all the samples as is consistent with the low turbidity measured. Most of the particles are less than 1 μm in size.

Dialysis experiments were performed with membranes ranging from 100 to 50,000 Daltons (0.0001 - 0.005 μm). Figure 3.2 shows the UV absorbance results for 100, 500, 1000, 5000, 10000, and 50000 Dalton membranes. From these results, it is evident that roughly 50% of the particles (or colloidal material) in the wastewater is between 0.005 and 0.45 μm, and almost none is below 0.001 μm.

Fouling Indices: SDI and MFI and MPFI

Filtration experiments using the Millipore SDI test apparatus (Catalog Number ZWRQ 032 75; 0.45 μm pore size membrane, 47 mm diameter) were performed at 30 psi on Dye WW #2 and Domestic WW to determine the silt density index (SDI), modified fouling index (MFI), and mini plugging factor index (MPFI).

Silt Density Index: SDI is a commonly used fouling index to determine whether pretreatment is required before application of RO. Although commonly used, the method is open to considerable criticism, as the index is not linearly related to the quality of water (e.g. colloidal content), nor does it correlate with downstream RO performance when the SDI values are low (<2). SDI is determined by measuring the time it takes to filter 500 ml of sample through a 0.45 μm filter at 30 psi, over a 15 minutes time interval. SDI is then estimated from the following equation:

Table 1: Wastewater Characterization

Parameter	Dye WW #1 (6/26/96)	Dye WW #2 (9/18/96)	Dye WW #3 (1/22/97)	Domestic WW (1/22/97)
pH	7 - 8 (Varies with time)	7-8	7-8	7-8
Temperature (as measured in the laboratory) (°C)	22 - 24	22 - 24	22 - 24	22 - 24
Turbidity (raw WW/0.45μm filtered)	1.7 /0.3			
Conductivity (mMho/cm)	5.74	4.6	3.52	2.04
Color (Platinum-Cobalt Units)	1092	1046	254	72
TOC (Total Organic Carbon) (mg/l)	32.6	48.1	41.8	18.2
DOC (Dissolved Organic Carbon) (mg/l)	30	36	31	14.4
TSS (total suspended solids) (ml/L)	0.0029	0.0345	0.002	0.0228
Total Metals (Al, Cr, Cu, Fe, Mg, Mn, Ni, Zn)	31.5 mg/l			
UV absorbance at 254nm (0.45μm filtered)	1.12	1.33	0.61	0.191
Alkalinity	Recommend measurement at site			
COD (mg/l)	840 (2/97), 855 (1/97), 801 (12/96), 813 (11/96)			
CBOD	299 (2/97), 304 (1/97), 346 (12/96), 352 (11/96)			
MW dist. of organics	Not provided			
MFI (modified fouling index)	(See text)			
SDI (silt density index)	(See text)			

Table 2: Metal Analysis

Element	Dye WW#1 Conc. (mg/l)	Dye WW #2	Dye WW#3	Domestic WW
Al	0.45	0.42	0.44	0.44
Ca	66.75	79.6	91.03	98.41
Cl	1060.00	a	a	a
Cr	0.03	a	a	a
Cu	0.03	a	a	a
Fe	0.04	0.04	0.05	0.04
Mg	27.52	26.98	29.91	33.22
Mn	0.01	a	a	a
Na	1097.30	a	a	a
Ni	3.35	0.72	0.45	0.2
Si	32.09	37.96	19.95	10.3
Zn	0.03	a	a	a

a: Not measured due to breakdown of ICP spectrophotometer.

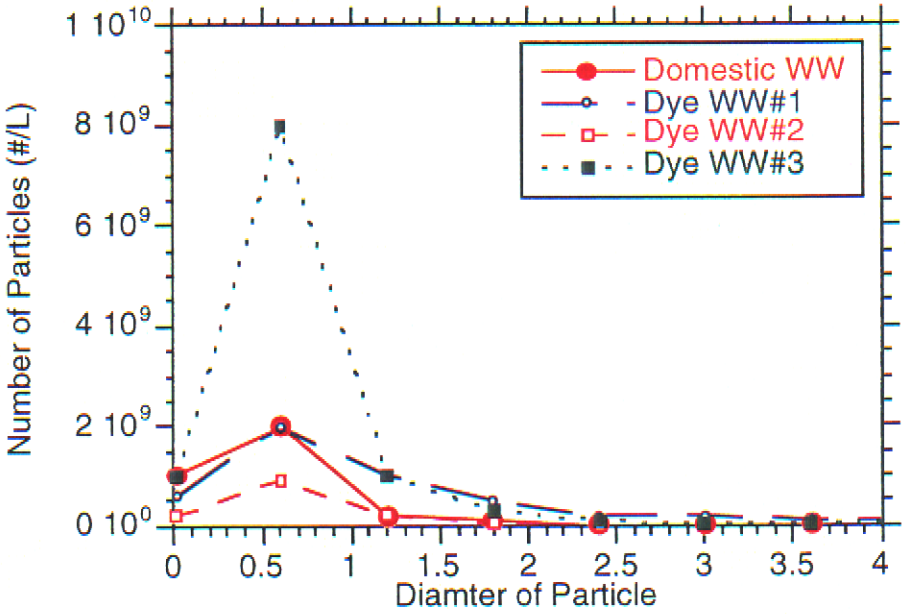

Figure 3.1: Particle Size Distribution for the wastewater samples

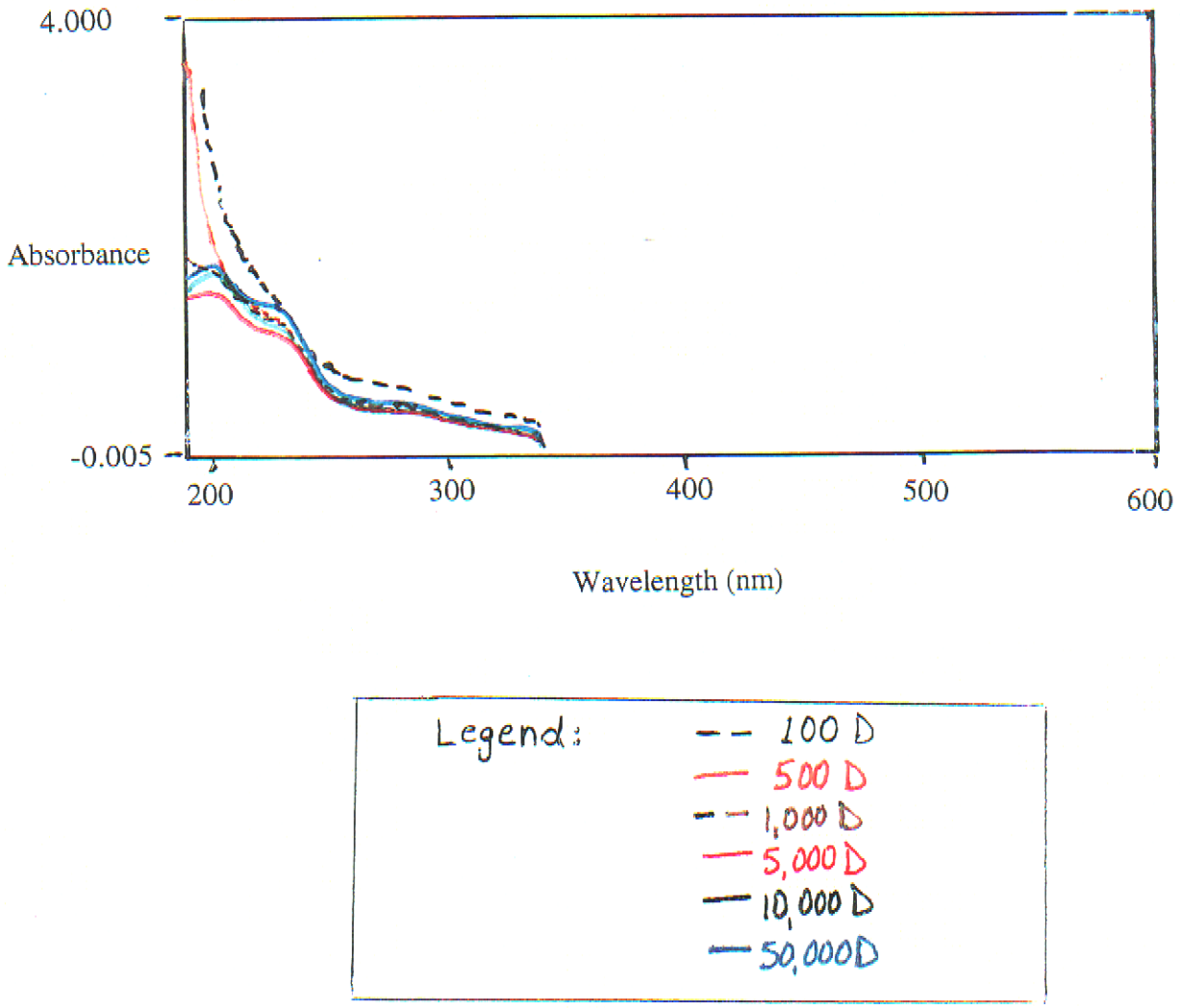

Figure 3.2: UV Absorbance of Dye waste water retained by membranes with different molecular weight cut offs. Note that most colloidal matter is larger than 50,000 D (0.005µm) and none is below 100 D (0.001m).

$$SDI = 100 * \frac{(1 - t_i/t_f)}{t}$$

where

t_i = time it takes to collect 500 ml of sample at the beginning of test (minutes)

t_f = time it takes to collect 500 ml of sample at the end of test (minutes)

t = duration of the test (usually 15 minutes)

Waters with SDI values in the range of 0-3 are expected to cause little or no fouling in RO systems, while moderate fouling is expected when SDI values are in the range of 3-5. Waters with SDI values greater than 5 cause severe fouling and pretreatment is imperative.

SDI tests on Dye WW#2 and domestic WW could not be completed due to the severe fouling of the membrane by the high concentrations of colloidal matter in these waters. In Figure 3.3, the total volume of water filtered through a 0.45 μm membrane (@ 30 psi) is plotted as a function of time. It took about 150 seconds to filter first 0.1 L of Dye WW #2 and 1150 seconds to filter the next 0.06 L. Domestic WW took longer (250 s for the first 0.08 L and 1050 s for the next 0.03 L). Based on these results, the SDI values are expected to be considerably higher than the suggested upper limit for RO of 5. It should be noted that the SDI value for domestic WW is expected to be higher than that of Dye WW #2, as is evident from the low volumes of permeate collected for this water.

Modified Fouling Index: MFI is determined using the same procedure as that of SDI, except that the volume of permeate collected is recorded every 30 s for a 15 minute filtration period. The ratio (t/V_{tot}) is plotted as a function of V_{tot}. Three regions corresponding to blocking filtration, cake filtration and cake compression are usually evident in the relation between t/V_{tot} and V_{tot}. The slope of the linear portion of the curve (cake filtration region) gives MFI. Pretreatment is recommended for waters with MFI values higher than 10 s/L^2.

The MFI curves for domestic WW and Dye WW #2 are shown in Figure 3.4. The steep slopes of these MFI curves suggest that considerable cake compression occurs relatively rapidly. Both waters have high MFI values, suggesting the need for pretreatment. As with SDI tests, the domestic WW appears to be more fouling in nature than Dye WW #2.

Mini Plugging Factor Index: MPFI curve is obtained by plotting the flow rate (L/s) as a function of time. MPFI is the slope of the linear part of the curve which corresponds to the cake filtration region. Like MFI, MPFI curve illustrates the regions of blocking filtration, cake filtration and cake compression. Waters with MPFI values greater than 2e-4 L/s^2 need pretreatment before application to RO.

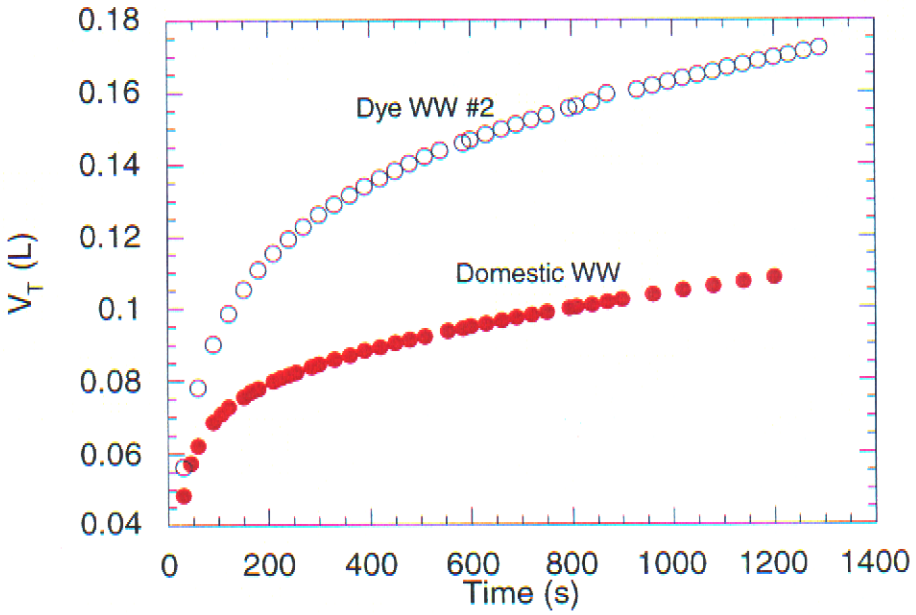

Figure 3.3: Total volume of water filtered through a 0.45 µm filter (@ 30 psi) over time. The lower curve indicates greater fouling.

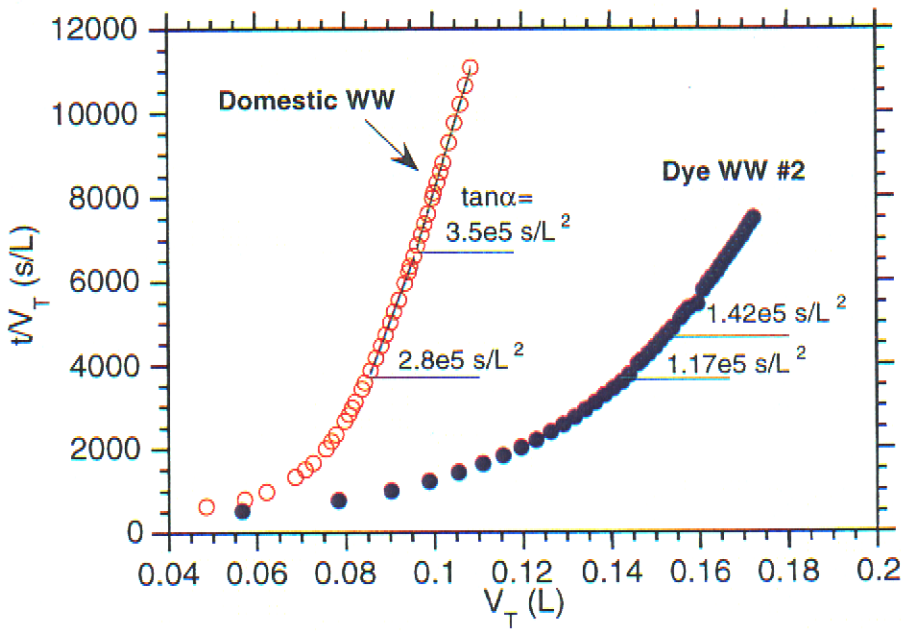

Figure 3.4: Ratio of filtration time and filtrate volume (t/V_{tot}) as a function of total filtrate volume V_{tot}. The upper curve indicates greater fouling.

The MPFI curves for domestic WW and Dye WW#2 are plotted in Figure 3.5. The cake filtration region is not discernable, suggesting significant cake compression during initial stages of filtration. This is indicative of the high fouling nature of both waters.

4. Coagulation/Flocculation

For DOC removal, several jar tests were performed to compare three flocculants: Aluminum sulfate (alum), ferric chloride (Catfloc 8964) and poly aluminum chloride (Catfloc 2973). Aluminum sulfate was obtained from Rhone-Pouleng Basic Chemical Company, Shelton, CT. Ferric chloride and poly aluminum chloride were obtained from Calgon Corporation, Pittsburg, PA. Figures 4.1 to 4.3 illustrate the DOC removal by these flocculants at various concentrations and pH values.

Removals of DOC as a function of alum dosage and pH are shown in Figure 4.1. Removals in the range of 22 to 33% were obtained at doses in the range of 50 to 200 mg/l and at pH values between 4 to 5. Slightly less removals (13 to 33%)were observed in the pH range of 5.5 to 6.5 for the same dosages. The highest DOC removal of 41% was observed at 200 mg/l alum, at a pH of 5.7.

DOC removals as a function of ferric chloride (Catfloc 8964) concentration and pH are shown in Figure 4.2. The highest DOC removals (around 60%) were obtained at pH values between 4 and 5 and with doses above 100 mg/l. Removals in the range of 40 to 45% were observed at lower pH values (3 to 4.5). Low DOC removals between 30 to 40% were observed at pH values of 6 to 8.

Removals of UV absorbance (@254 nm) when poly aluminum chloride (Catfloc 2973) was used are shown in Figure 4.3. Significant reductions (60 to 70%) in UV absorbance were obtained at pH values of 5.7 to 6.7 and dosages greater than 90. For PACl dosages between 10 to 70 mg/l, UV absorbance reductions increase almost linearly from 3 to 43 %, at near neutral pH values (7 to 7.5).

5. PAC Adsorption

Simple batch experiments were performed to estimate the TOC (dye) removal in Dye WW #2 with powdered activated carbon (PAC). The PAC used was Calgon Carbon Corporation; Product number: WPL Powd 50BG of 325 mesh size, a density of 46 lb/ft^3 (736 g/l) and an Iodine number close to 600. Figure 5.1 shows results fitted to a Freundlich adsorption isotherm. A good fit is observed for Freundlich isotherm constants of values K= 3.822 g/mg and 1/n= 0.71465. Using these values, the carbon usage rates (mass of PAC/Vol of Dye WW #2) are plotted as a function of TOC removal rates in Figure 5.2. Very high doses of PAC are needed for even low removals of TOC. Similarly it is reasonable to conclude that carbon usage rates for GAC contactors would also be prohibitively high (Figure 5.2).

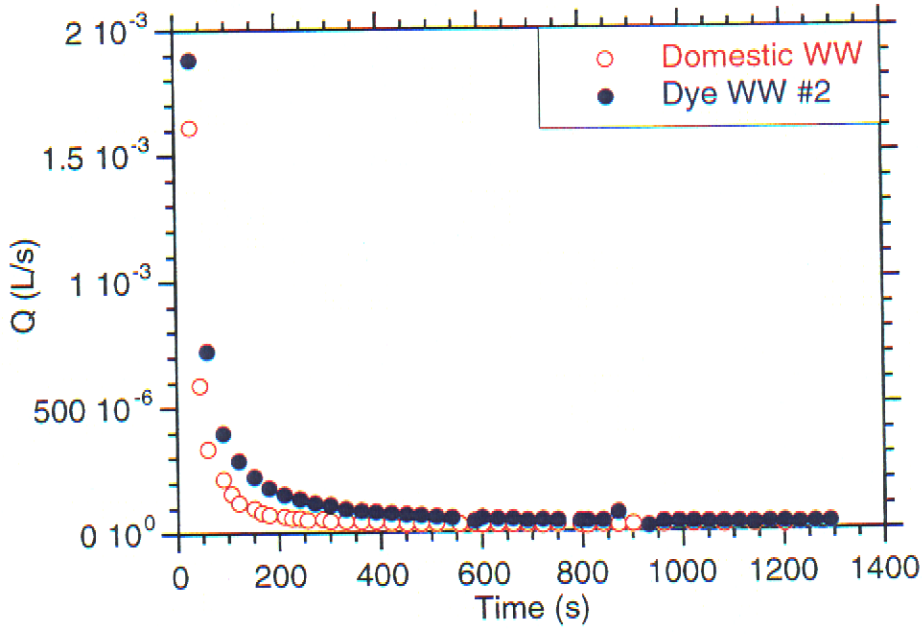

Figure 3.5: Filtrate flow as a function of time.

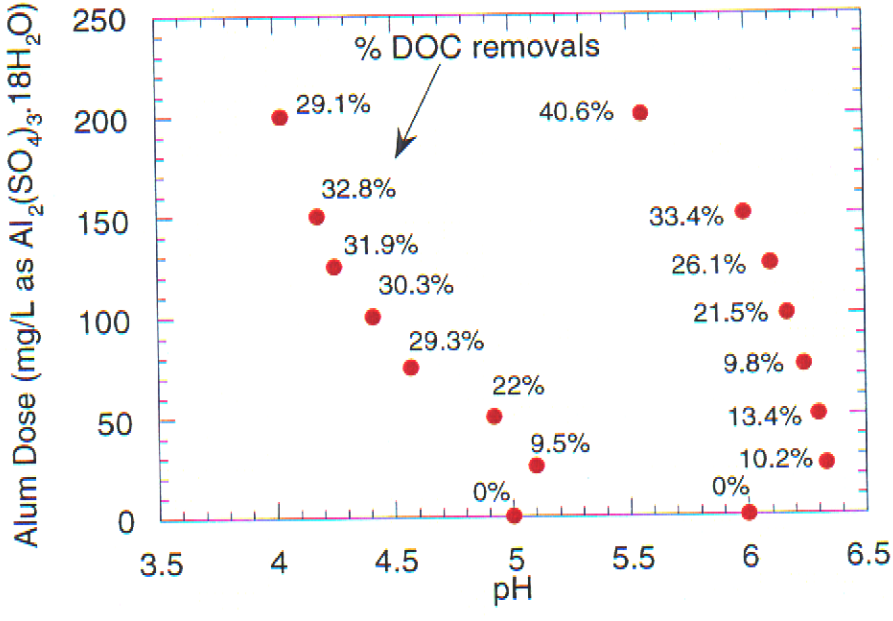

Figure 4.1: DOC removals as a function of alum dosage and pH

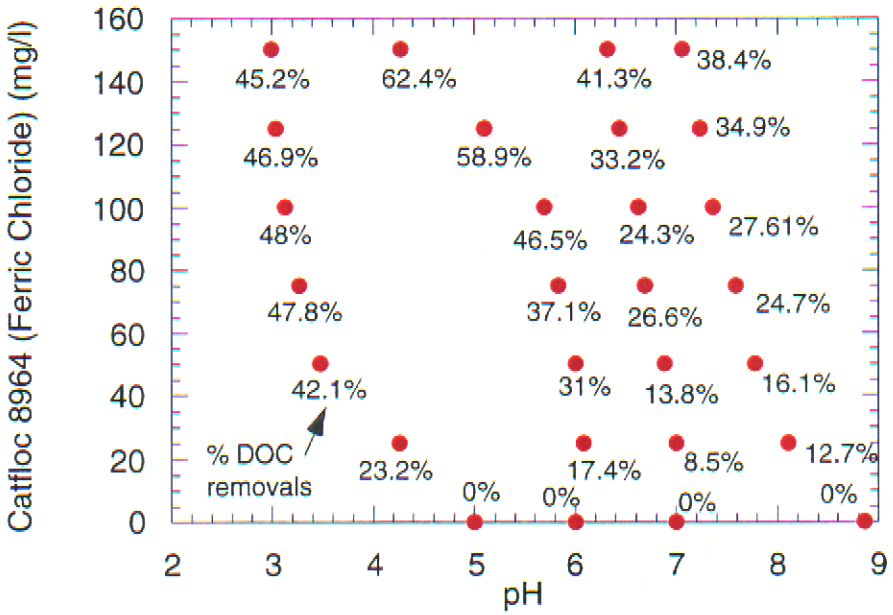

Figure 4.2: DOC removals as a function of ferric chloride dosage and pH

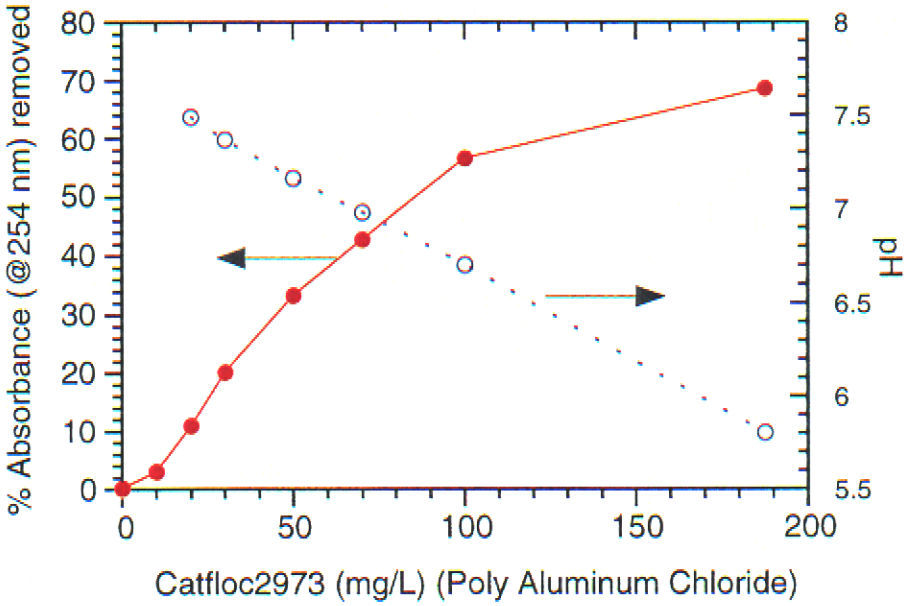

Figure 4.3: DOC removals as a function of poly aluminum chloride dosage and pH

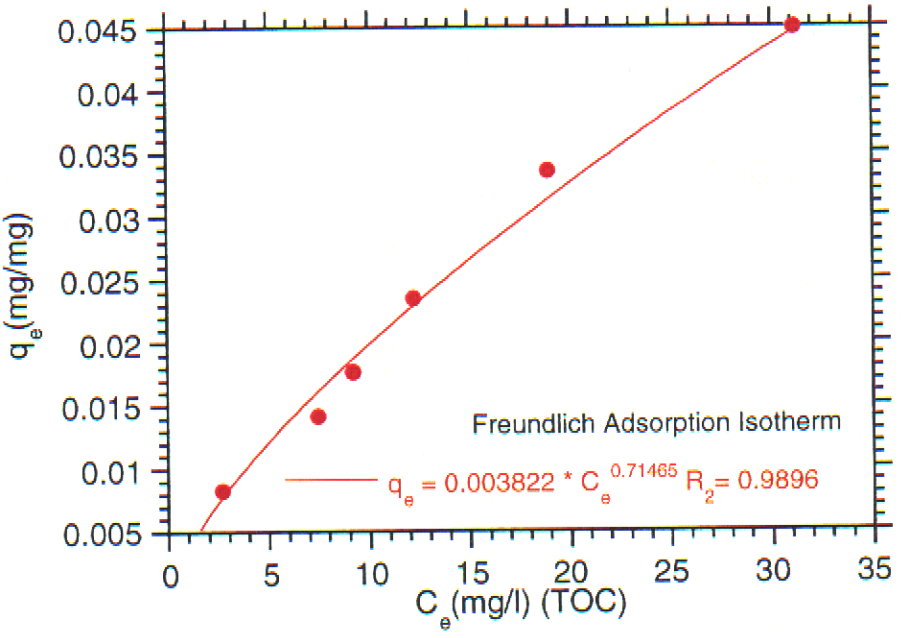

Figure 5.1: Freundlich adsorption isotherm for powdered activated carbon and Dye WW #2.

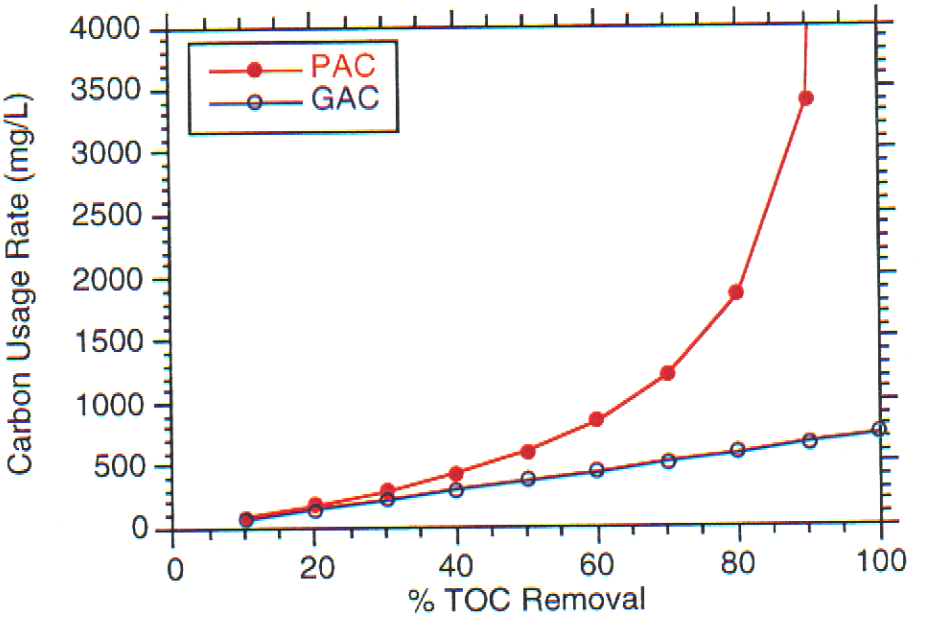

Figure 5.2: Carbon usage rates as a function of TOC removals based on Freundlich adsorption isotherm for powdered activated carbon and Dye WW #2. Estimates of CUR for GAC contactors are made assuming similar equilibrium adsorption characteristics of the GAC as observed for the PAC.

6. Membrane Filtration

Filtration experiments were performed in cross flow mode using a commercial bench scale membrane cell (Osmonics SEPA CF Membrane Cell). The SEPA CF system consists of a two-piece acrylic membrane cell and a cell holder constructed of high grade anodized aluminum. The membrane is sandwiched between the halves of the membrane cell and fits into the aluminum cell holder as shown in Figure 6.1. The cell holder is equipped with a piston clamping mechanism to seal the cell with the aid of pneumatic power. Feed water enters the bottom half of the cell and flows tangentially across the membrane surface. Permeate flows into the upper half of the cell and is collected through a central collection channel and exits through the permeate outlet. A schematic of the filtration setup is shown in Figure 6.1. A constant feed flow was provided by a progressing cavity pump (Moyno 500 Pump, Model 33160). A 5 μm prefilter was used to protect flow sensors from large particles. The feed and permeate flow rates were monitored and recorded using rotameters and flow sensors. Feed and permeate pressures were monitored using pressure gauges and pressure transducers. A data acquisition system consisting of an analog to digital converter (Biopac Systems, Goleta, CA) was used to record the signals from flow sensors and pressure transducers to a Macintosh computer. The experimental system, including the membrane cell, can be operated at a feed pressure up to 100 psi.

Experiments were conducted in two flow configurations as shown in Figure 6.1. In one mode, both concentrate and the permeate streams were recycled to the feed tank. In the other mode, only concentrate was recycled to the feed tank. In this second configuration, as filtration progresses, the feed water is concentrated and may be assumed to simulate the downstream stages of a multi-stage RO unit.

<u>Mode 1: Both concentrate as well as permeate streams recycled.</u>

In this mode, the characteristics of the feed water remained essentially constant for the entire duration of filtration. The performance of two nanofiltration membranes and two microfiltration membranes (MWCOs ranging from 150 to 8000 Daltons) in terms of water quality and specific flux are evaluated. The removals of TOC, conductivity and UV absorbance @254 nm during filtration through these membranes are shown in Figures 6.2a to 6.2d.

The nanofiltration membrane, Desalination DS-5 (MWCO of 150-300 Daltons) achieved best removals: 98% for TOC and UV absorbance and 50% for conductivity. This is expected, owing to the low MWCO of this membrane. Lower removals were obtained for the Hydranautics membrane, NTR-7450, which has slightly larger MWCO of 500-600 Daltons. Removals in the range of 95% for TOC, 80% for UV absorbance and 20% for conductivity were obtained with this membrane.

The ultrafiltration membranes, Hydranautics NTR-7410 (MWCO 1100 Daltons) and the Desalination UF-G50 (MWCO 8000 Daltons), due to their high MWCO, obtained

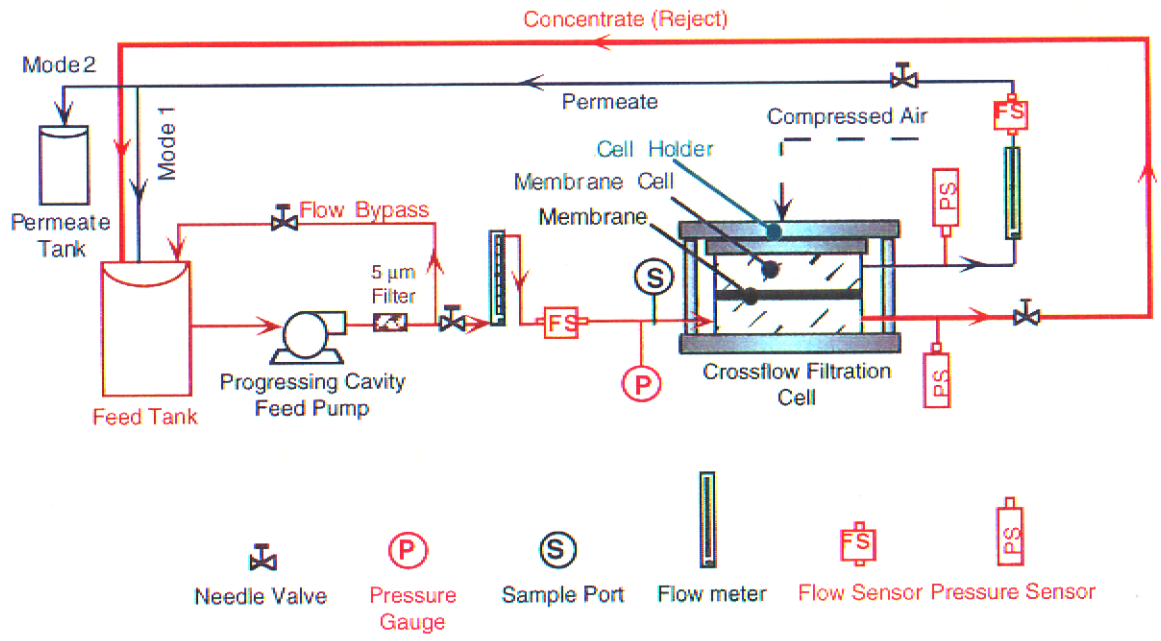

Figure 6.1: Schematic of the cross flow filtration experimental set up.

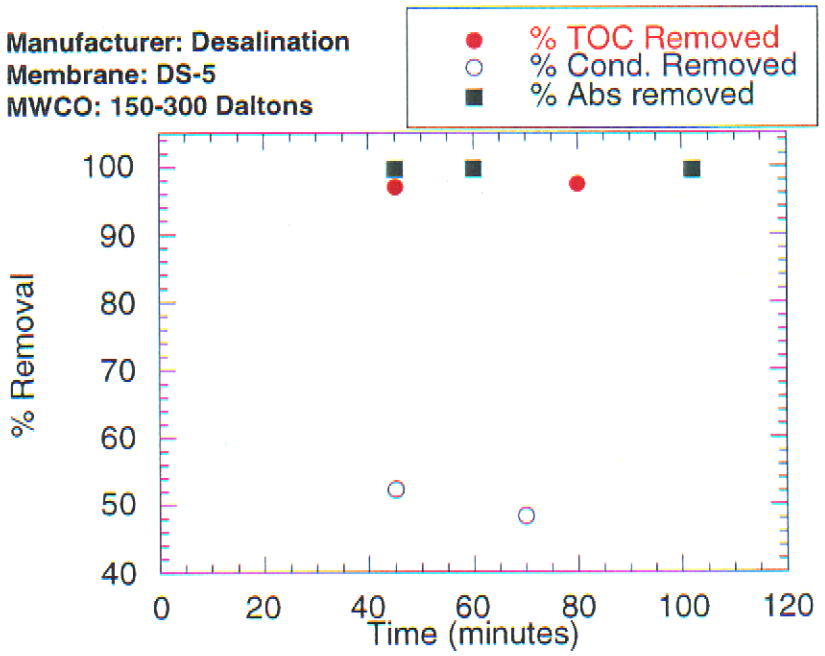

Figure 6.2a: Removals of TOC, UV absorbance @254 nm and conductivity by Desalination DS-5 (MWCO 150-300 Daltons) membrane during filtration of Dye WW#2

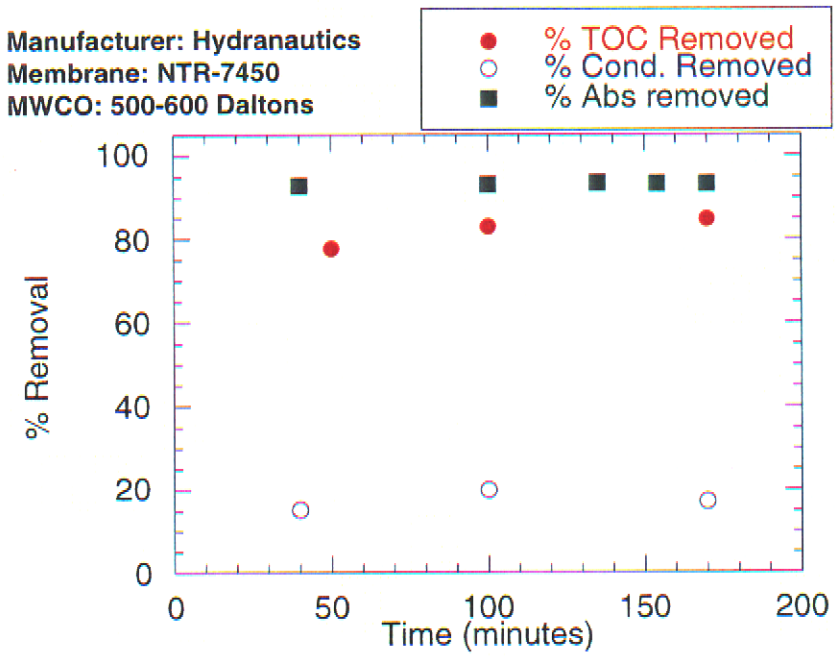

Figure 6.2b: Removals of TOC, UV absorbance @254 nm and conductivity by Hydranautics (MWCO 500-600 Daltons) membrane during filtration of Dye WW#2

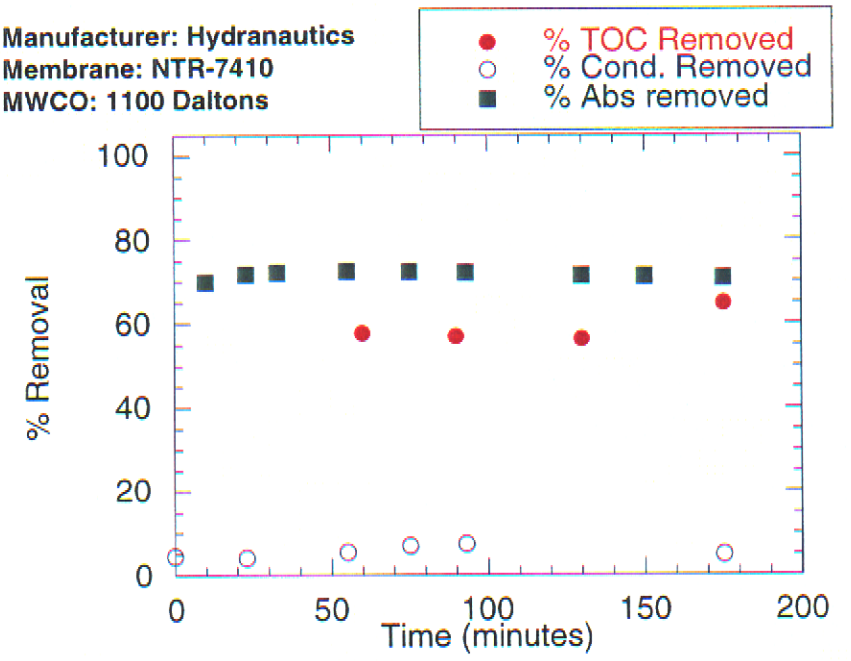

Figure 6.2c: Removals of TOC, UV absorbance @254 nm and conductivity by Hydranautics NTR-7450 (MWCO 1100 Daltons) membrane during filtration of Dye WW#2

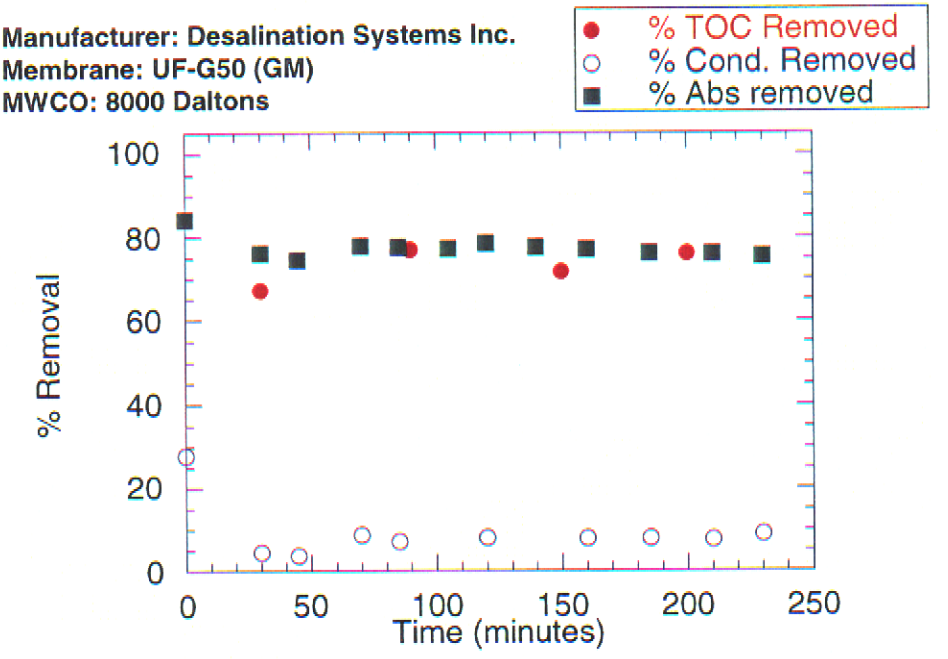

Figure 6.2d: Removals of TOC, UV absorbance @254 nm and conductivity by Desalination UF-G50 (MWCO 500-600 Daltons) membrane during filtration of Dye WW#2

less removals for TOC and UV absorbance (60 to 80%). The Hydranautics membrane with a MWCO 1100 exhibited lower removals compared to the Desalination membrane with a higher MWCO of 8000 Daltons. Reasons for this are likely linked to the chemistry of the membranes rather than their apparent MWCO. As expected, owing to their high MWCO, both membranes achieved only a 5% removal of conductivity.

Average removals of TOC are summarized in Figure 6.2e. TOC removals by microfiltration with coagulation are included for comparison. These results were obtained by filtering the supernatant of settled water, in the jar tests discussed above, through the 0.45 μm syringe filters. Based on these results, ultrafiltration appears to be a good pretreatment option.

The permeate flux, as a function of time, is plotted in Figure 6.3a for these four membranes. Fluxes through the two nanofiltration membranes (MWCO: 150-300 & 500-600 Daltons) are similar and showed no fouling during the short duration of the filtration experiment of 110 to 180 minutes. The UF membrane with MWCO of 1100 Daltons, exhibited significant fouling, with a 75% decline in permeate flux. Recall that this membrane also exhibited poor removals of TOC and UV absorbance. Two pressures (40 & 60 psi) were used with the Desalination UF-G50 membrane. No flux decline was observed at either pressure and, as expected, higher fluxes were observed at higher pressure. It should be noted that these four filtration experiments were run at different pressures as indicated in Figure 6.3a. The specific flux data (permeate flux divided by the transmembrane pressure) are shown in Figure 6.3b. The relative performance of these membranes is similar to the previous flux data shown in Figure 6.3a. The permeate fluxes reported in Figures 6.3a and b, are within the ranges usually reported for membranes with these MWCO's.

Mode 2: Concentrate stream recycled.

In this mode, the concentration of the solutes and/or colloidal matter in the feed increased over time, as the permeate stream was not recycled. Experiments were conducted with dye wastewater and domestic wastewater using membranes of 2 MWCO's (Desalination Systems Inc., UF-G80-MWCO 10,000 D and DS-5-DK-MWCO 150-300 D).

Ultrafiltration:

Two dye wastewater samples (Dye wastewaters #2 and #3) and domestic wastewater were used in ultrafiltration experiments (MWCO 10,000 D). The feed concentrations of TOC increased over time in this mode as shown in Figure 6.4a. Feed TOC concentrations increased by about 60 to 70% for Dye WW#2 and 3 and about 50% for domestic wastewater. Negligible increases in UV absorbance were observed for Dye WW #3 and domestic wastewater as shown in Figure 6.4b. In contrast, the UV absorbance of Dye WW #2 increased significantly over time indicating that a UV absorbing fraction of the TOC is concentrating over time. This also indicates the variability of dye in wastewater samples. Negligible increases in conductivity were

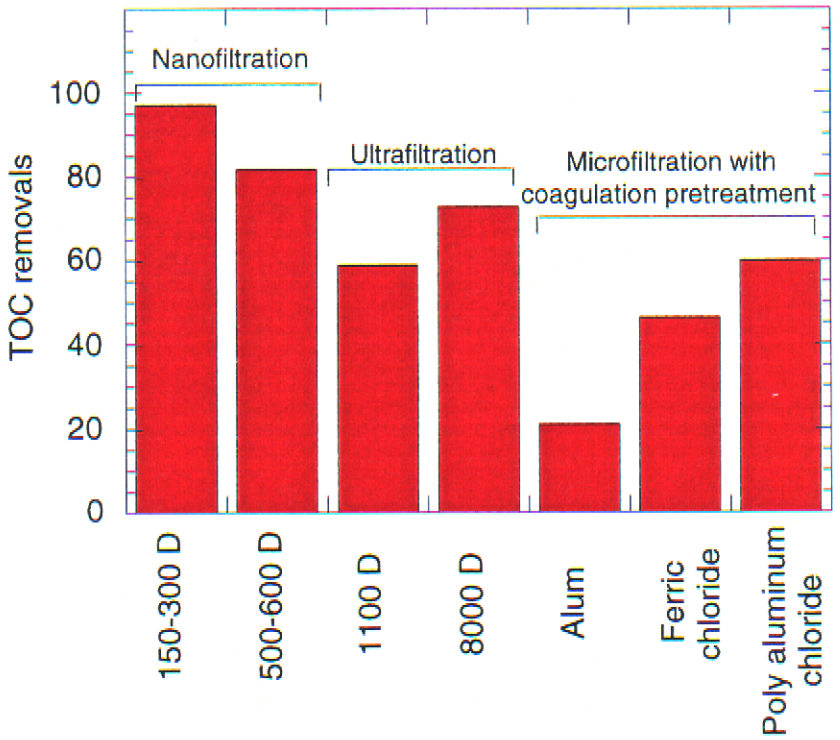

Figure 6.2e: TOC removals using different membranes and coagulants

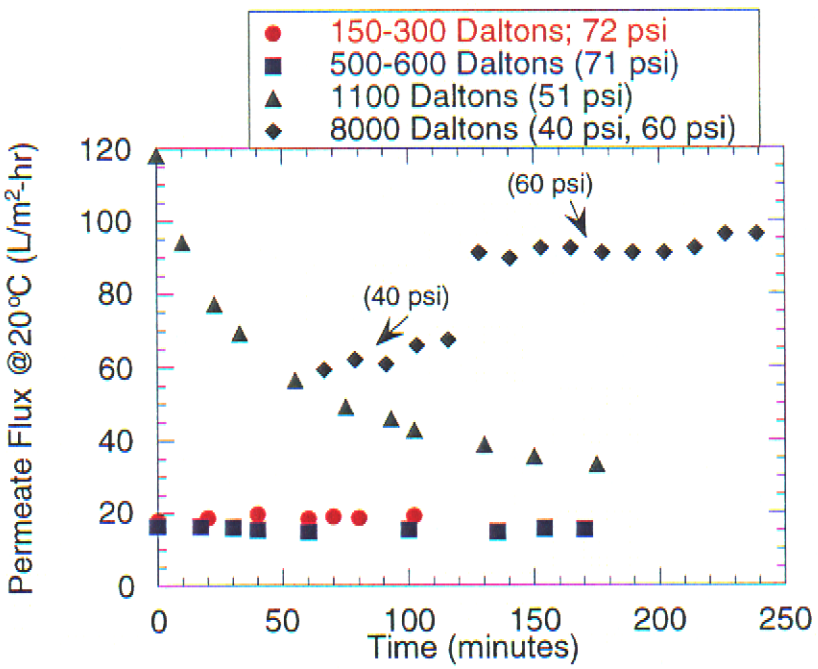

Figure 6.3a: Permeate Flux as a function of time during filtration of Dye WW #2 with 4 membranes

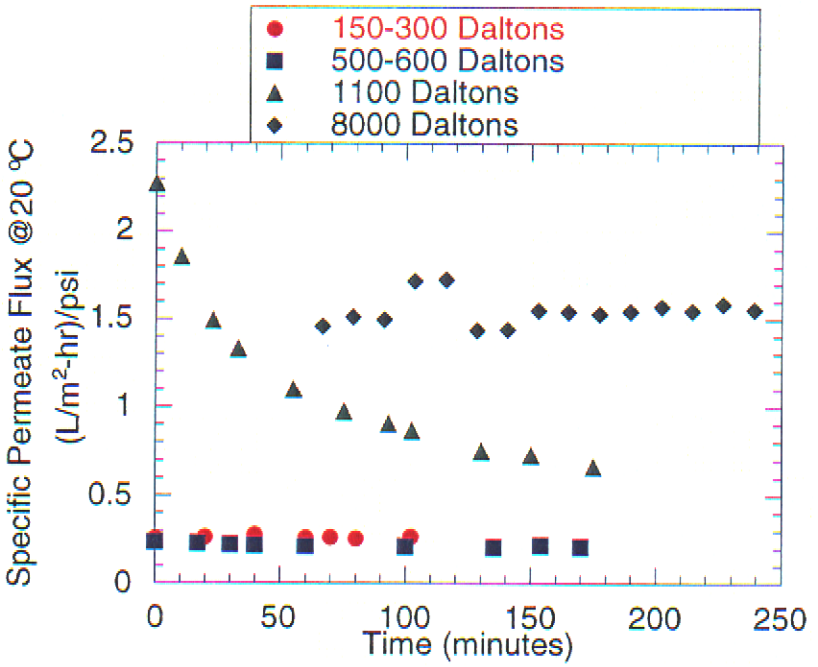

Figure 6.3b: Specific permeate Flux as a function of time during filtration of Dye WW #2 with 4 membranes

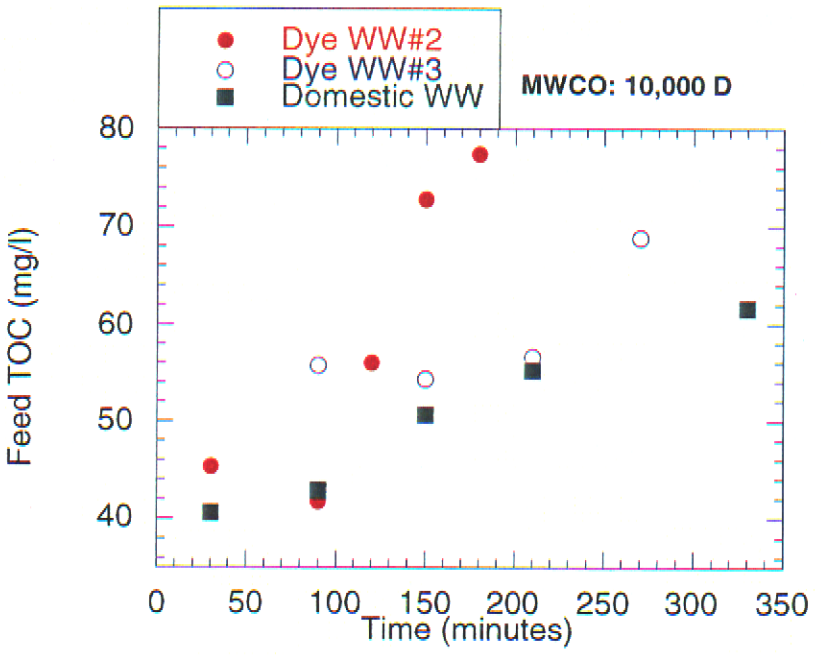

Figure 6.4a: Feed TOC concentration as a function of time during filtration of Dye WW #2, #3 and Domestic WW using ultrafiltration membrane of MWCO 10000 D

observed as this membrane can not retain salts (Figure 6.4b).

TOC removals were slightly different for Dye WW #2 (80%) and #3 (74%) as shown in Figure 6.4c. About 75% of the TOC was removed during filtration of domestic wastewater. Negligible removals of conductivity (10%) were observed, owing to the high MWCO of this membrane as shown in Figure 6.4d. About 50% of UV absorbing material was removed during filtration of Dye WW#3 and domestic WW. Higher removals of UV absorbance (80%) were achieved during filtration of Dye WW #2.

Permeate fluxes as a function of time during filtration of Dye WW#2, #3 and domestic WW are shown in Figure 6.5a. The rate of flux decline was different for the two Dye wastewater samples, suggesting some variability in the dye wastewater over time. Domestic WW caused more flux decline than Dye WW#2. Normalized permeate flux (defined as the permeate flux divided by the initial flux) declined at a faster rate during the filtration of domestic wastewater as shown in Figure 6.5b, suggesting higher fouling of the membrane during the filtration of this water.

Nanofiltration:

Dye wastewater #3 and domestic wastewater were used as feed waters during these experiments with Desalination DS-5-DK membranes with MWCO 150-300 D. The feed TOC concentrations increased by 50% during the filtration of domestic wastewater. The feed TOC of domestic wastewater showed no particular trend (Figure 6.6a). UV absorbance increased by about 50% for Dye WW #3 and by about 73% for domestic WW. About a 34% increase in conductivity was observed during filtration of Dye WW#3, while about a 25% increase was observed for domestic WW.

Figure 6.6b shows the TOC and conductivity removals remained constant in the range of 98% and 50% respectively during the filtration of Dye WW#3 and domestic WW despite their increases in feed concentrations.

About a 20% reduction in permeate flux and normalized permeate flux was observed during the filtration of Dye WW #3 and about a 5% reduction was observed for domestic WW, as shown in Figures 6.7a and b. This may be due to the low increases in feed TOC concentrations for domestic wastewater.

These results suggest that it is very useful to know more about the molecular weight distribution of dyes in the textile wastewater.

7. Conclusions

The following conclusions are made based on the bench scale tests conducted during this study.

1. Textile mill wastewater requires pretreatment to reduce the fouling of RO membranes. However, it also appears that the fouling potential of domestic wastewater is comparable

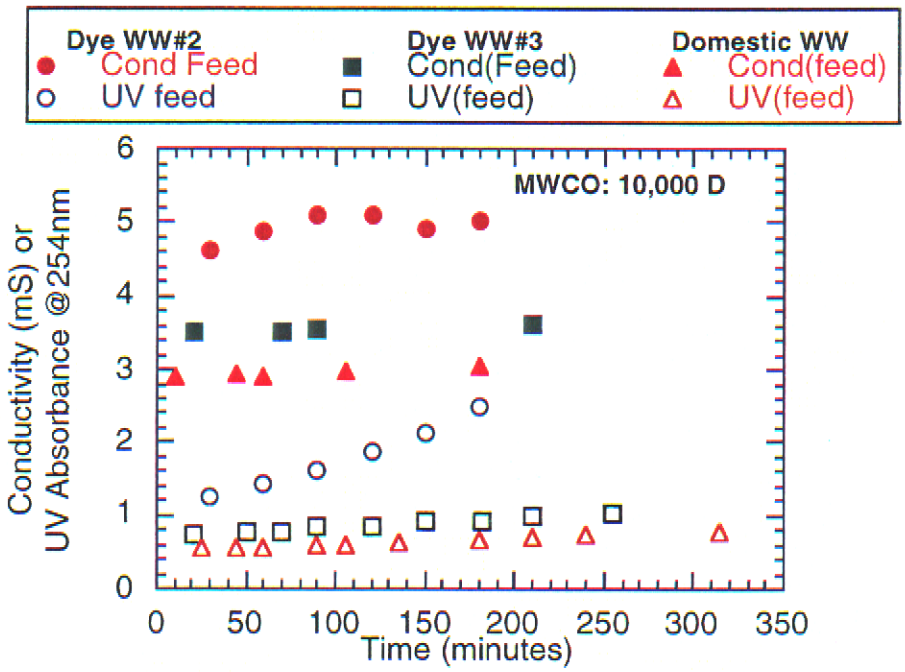

Figure 6.4b: Feed Conductivity and UV absorbance (@254 nm) as a function of time during filtration of Dye WW #2, #3 and Domestic WW using ultrafiltration membrane of MWCO 10000 D

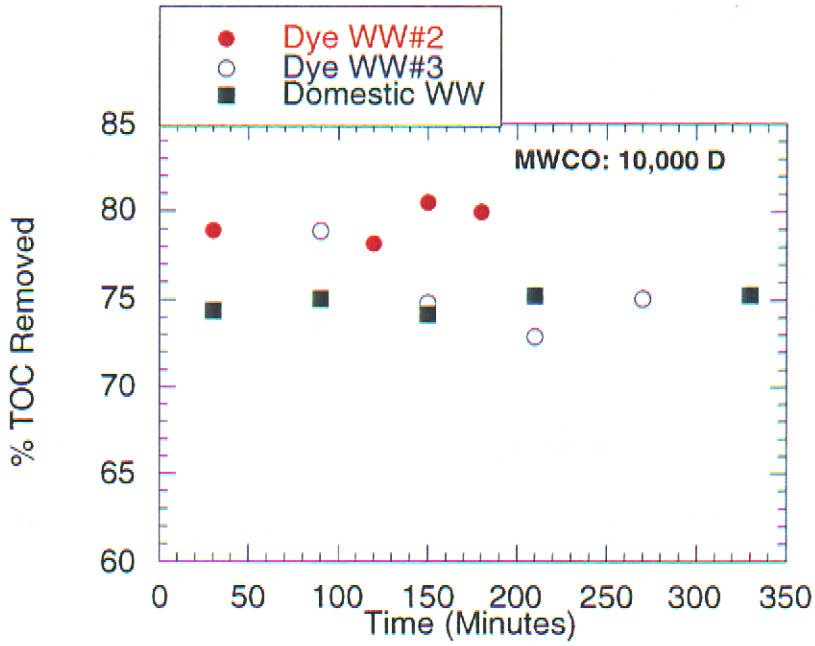

Figure 6.4c: TOC removals as a function of time during filtration of Dye WW #2, #3 and Domestic WW using ultrafiltration membrane of MWCO 10000 D

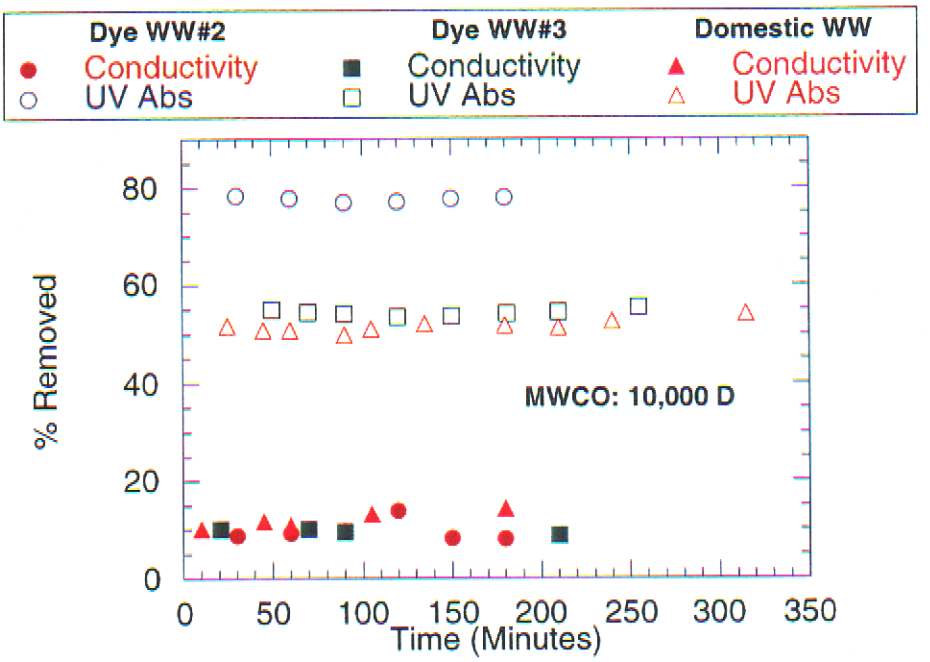

Figure 6.4d: Removals of conductivity and UV absorbance (@254 nm) as a function of time during filtration of Dye WW #2, #3 and Domestic WW using ultrafiltration membrane of MWCO 10000 D

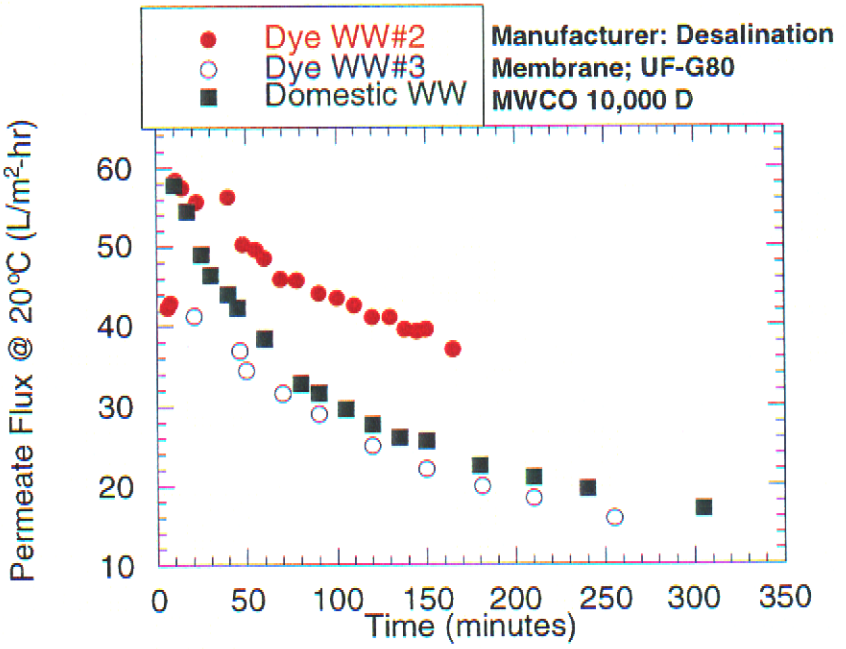

Figure 6.5a: Permeate flux as a function of time during filtration of Dye WW #2, #3 and Domestic WW using ultrafiltration membrane of MWCO 10000 D

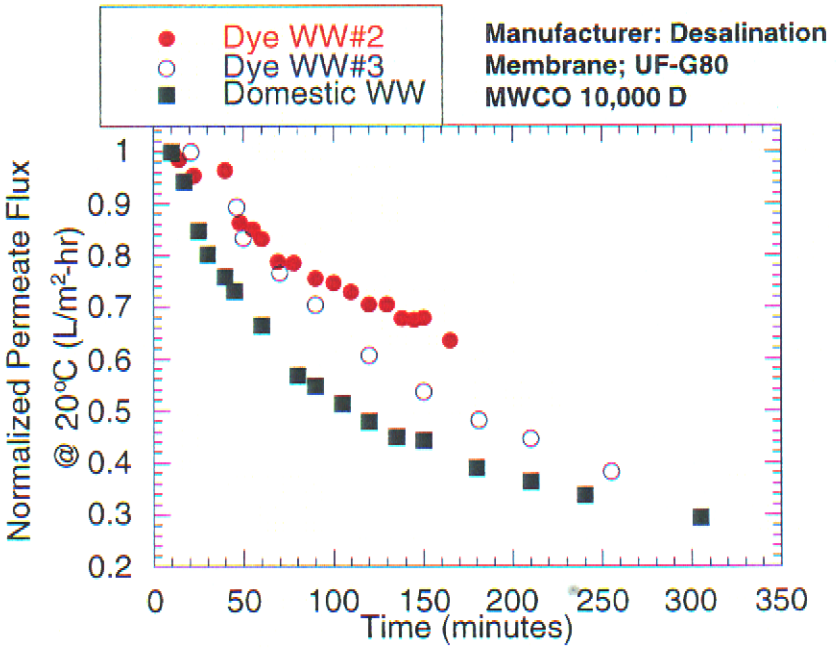

Figure 6.5b: Normalized permeate flux as a function of time during filtration of Dye WW #2, #3 and Domestic WW using ultrafiltration membrane of MWCO 10000 D

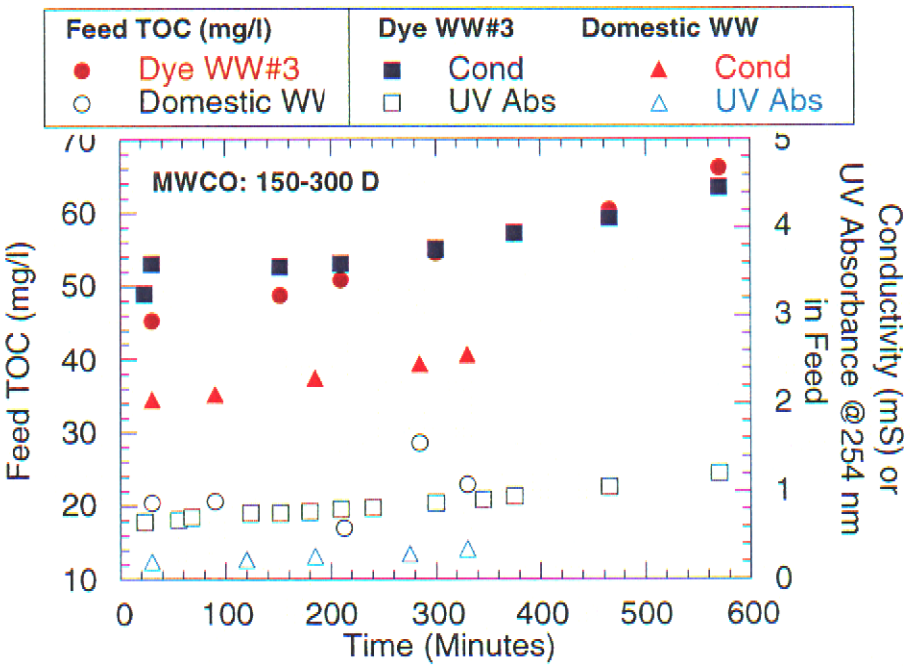

Figure 6.6a: Feed TOC, UV absorbance and conductivity as a function of time during filtration of Dye WW #3 and Domestic WW using nanofiltration membrane of MWCO 150-300 D

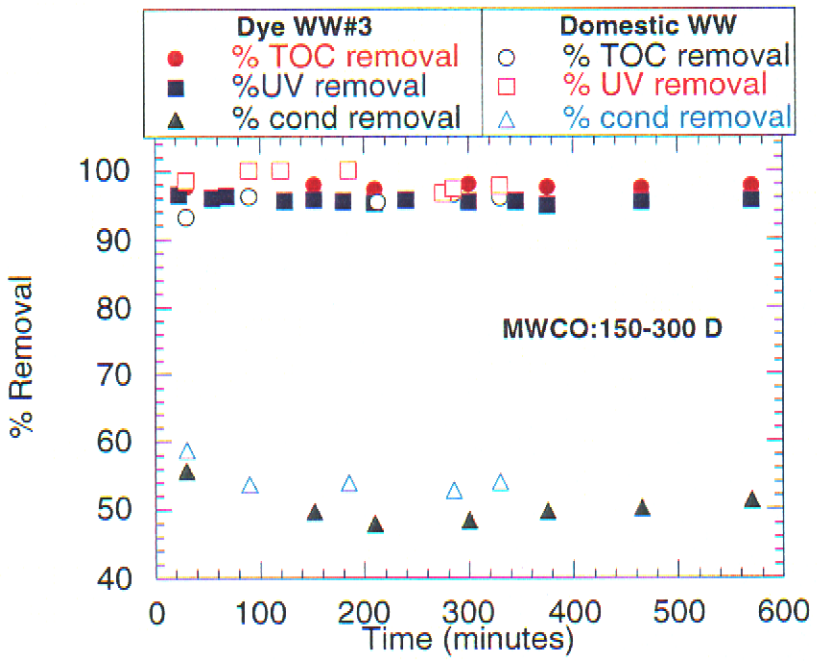

Figure 6.6b: Removals of TOC, UV absorbance and conductivity as a function of time during filtration of Dye WW #3 and Domestic WW using nanofiltration membrane of MWCO 150-300 D

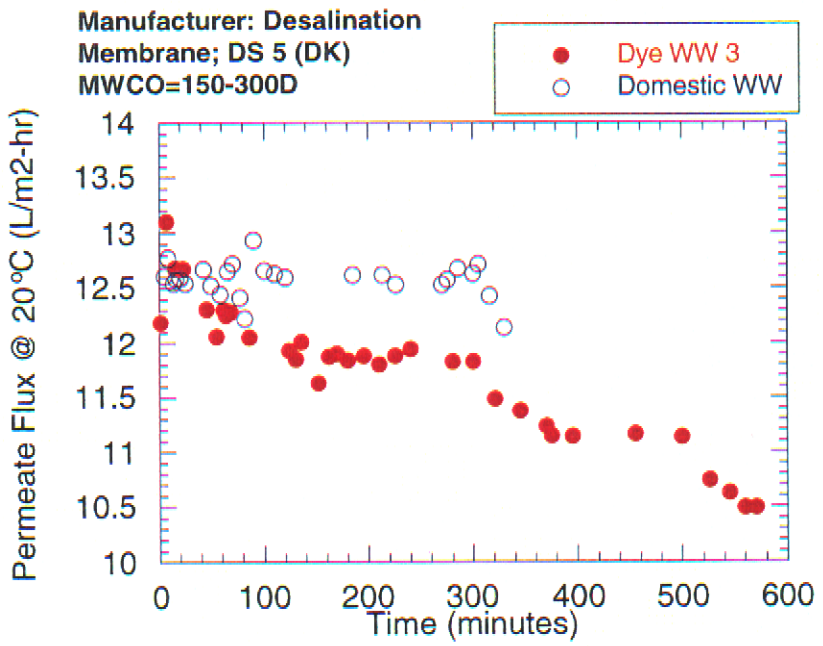

Figure 6.7a: Permeate flux as a function of time during filtration of Dye WW #3 and Domestic WW using ultrafiltration membrane of MWCO 150-300 D

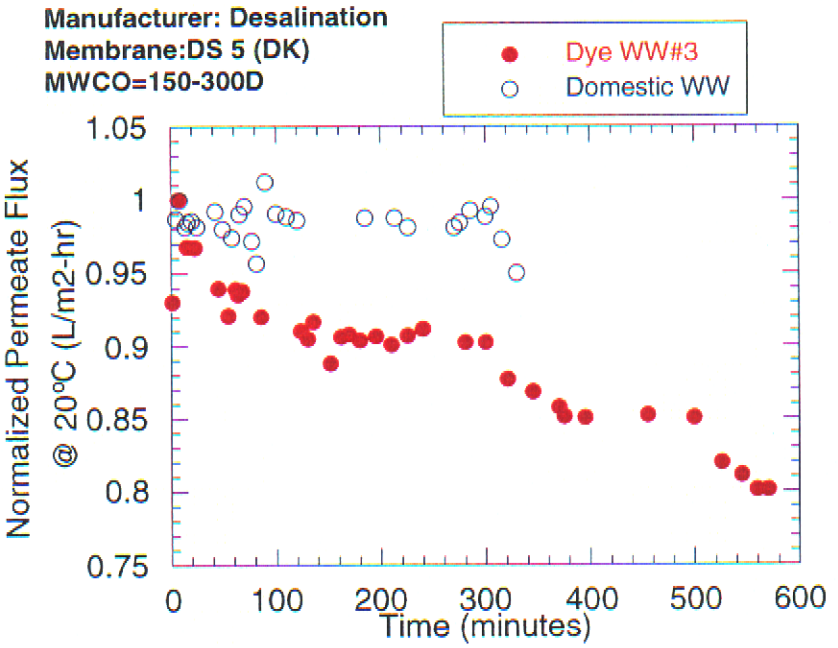

Figure 6.7b: Normalized permeate flux as a function of time during filtration of Dye WW #3 and Domestic WW using ultrafiltration membrane of MWCO 150-300 D

to or greater than that of the wastewater from the textile mill.

Analysis of the textile plant's industrial wastewater finds significant concentrations of colloidal materials and dyes which are likely to result in long-term fouling problems for a downstream RO facility. Nonetheless, even in short term fouling tests, greater fouling of membranes is produced by the domestic wastewater effluent which is currently being treated by RO. This suggests that in contrast with an upstream "pollution prevention" approach implemented within the textile bleach and dye facility, that much greater improvements in membrane operation could be realized by improving the pretreatment of the domestic wastewater. For these reasons, and to maintain simplicity of process design, the textile wastewater and the domestic wastewater could be combined before pretreatment.

2. Ultrafiltration or microfiltration pretreatment of either the textile mill wastewater alone or for the combined domestic and textile wastewaters is recommended for pilot evaluation. This study suggests that significant quantities of colloidal materials in the textile waste stream will be removed by these processes. Pilot experience with other waste streams has indicated that pretreatment using UF or MF substantially prolongs the period between chemical cleanings.

3. A chemical cleaning frequency of once every month, as is currently practiced, is relatively high. The need for frequent cleaning suggests that the treated domestic wastewater that currently feeds the RO units causes considerable fouling. This is consistent with our observation that the domestic wastewater has greater potential for fouling than does the textile plant return flow. An upgrade in pretreatment for the domestic wastewater which currently feeds the RO reclamation facility should be strongly considered along with the pretreatment needs of the recycled textile wastewater.

4. Silica concentrations in the dye wastewater and domestic wastewater are significant. Although flux reduction due to accumulation of silica on the surface of membranes and within the membrane is inconclusive, silica appears to play a significant role in fouling of membranes.

5. Coagulation pretreatment is not likely to produce adequate reductions in dissolved organic material such as residual dyes to make this process feasible. Among the coagulants tested, the polyaluminum coagulant resulted in the highest removals. Although reductions in dissolved organic carbon (DOC) in excess of 80% can be realized, very high doses (ie. 200 mg/L) are required. The resulting reduction in pH may be prohibitive. Moreover, there is a potential for reprecipitation on the RO membrane and subsequent fouling which increases as coagulant dose increases.

6. Rough estimates of carbon usage rates (CUR) required to remove DOC from the return flow indicate that carbon adsorption will not be cost effective. CURs in excess of several hundred milligrams per liter would be required to achieve DOC reductions comparable to those achieved with coagulant-pretreatment.

7. The nanofiltration membranes tested were highly effective in removing DOC (measured directly or as UV absorption at 254 nm), with removals typically ranging from 80 to over 90 percent. Removal efficiencies varied considerably from one membrane to another. Comparable DOC removals using GAC adsorption columns are estimated to require CURs in excess of 500 mg/L.

8. Tests for membrane fouling were all conducted over relatively short time periods compared with those over which adsorptive fouling of NF or RO membranes is typically observed. Nonetheless, even over the course of several minutes, substantial fouling was observed. The ultrafiltration membranes fouled to an extent that resulted in a permeate flux comparable to the NF membranes which exhibited relatively little fouling. Much of the fouling is likely to be reversible. Pilot evaluation should include an evaluation of the frequency of backwashing needed to minimize irreversible fouling.

8. Recommendations for Processes to be evaluated at Pilot Scale

Based on the bench scale results of this study, the following two candidate processes are suggested for a phase 2 evaluation at pilot scale. It is suggested that two types of feed water be used for each of the alternatives: (1) Dye wastewater and (2) 50-50 blend of domestic and dye wastewaters.

Alternative A: Reverse Osmosis with Ultrafiltration Pretreatment

Option 1: 3 stage (3-2-1) Reverse Osmosis treatment with ultrafiltration pretreatment: Under this option, a 3-2-1 train of RO modules with ultrafiltration (MWCO around 100,000 D) as a pretreatment (Figure 8.1a) may be evaluated. The filtrate from ultrafiltration unit may be collected in a break tank, which will act as the feed reservoir for the RO system. A three stage RO system is suggested to simulate the typical full scale RO unit. In a single pass configuration, as shown in Figure 8.1a, at the end of first stage, the feed water is concentrated by a factor of 1.17 (assuming 15% recovery) and by 1.27 at the end of second stage. The total recovery of the RO unit is expected to be 38% assuming 15% recovery for each element. The pilot may be operated in this configuration for a period of six weeks (Phase 1), before the recycle loop is activated to test the performance of RO at higher concentration factors. The recycle flow may be adjusted to test the performance at three other concentration factors for the 1st stage feed water (1.22, 2.5, & 6.14). A two week duration is suggested for each recovery. The following test conditions are suggested.

Phase 1. Single pass configuration (6 weeks)

Feed Flow to the front end:	6 gpm
Permeate Flow:	15% recovery for each element
Recycle Flow	0 gpm
Wasteflow	0 gpm
Pressure	150 psi

Phase 2. With recycle (2 weeks for each recovery percentages)

Feed Flow to the front end:	6 gpm
Permeate Flow:	15% recovery for each element
Recycle Flow	1.4 gpm (50% recovery), 3 gpm (75%), and 3.4 gpm.(90%)
Wasteflow	2.3 gpm, 0.8 gpm, 0.25 gpm
Pressure	150 psi

Option 2: Single element Reverse Osmosis treatment with ultrafiltration pretreatment: Under this option, a single RO module with ultrafiltration (MWCO around 100,000 D) as a pretreatment (Figure 8.1b) may be evaluated. Though Option 1 is strongly recommended, Option 2 will provide similar data at less cost, albeit not as extensively as Option 1. The filtrate from the ultrafiltration unit may be collected in a break tank, which will act as the feed reservoir for the RO module. In a one pass configuration, as shown in Figure 8.1b, the RO unit is run at 15% recovery. The pilot unit may be operated in this configuration for a period of four weeks, before the recycle loop is activated, to test the performance of RO at higher concentration factors. The recycle flow may be adjusted to test the performance at four other concentration factors (1.21, 1.7, 3.4, and 8.5) with a two week duration for each. The following test conditions are suggested.

Phase 1: Single pass configuration (4 weeks)

Feed Flow to the front end:	2 gpm
Permeate Flow:	0.3 gpm @15% recovery
Recycle Flow	0 gpm
Wasteflow	0 gpm
Pressure	150 psi

Phase 2: With recycle (2 weeks for each recovery percentages)

Feed Flow to the front end:	2 gpm
Permeate Flow:	0.3 gpm @15% recovery
Recycle Flow	1 gpm (30% recovery) 1.4 gpm (50%), 1.6 gpm (75%), and 1.67 gpm.(90%)
Wasteflow	0.7 gpm, 0.3 gpm, 0.1 gpm, 0.033 gpm
Pressure	150 psi

Alternative B: Reverse Osmosis with Microfiltration pretreatment

In this alternative, a microfiltration unit is used for pretreatment. The rest of the process is similar to Alternative A and is shown in Figures 8.2a and b.

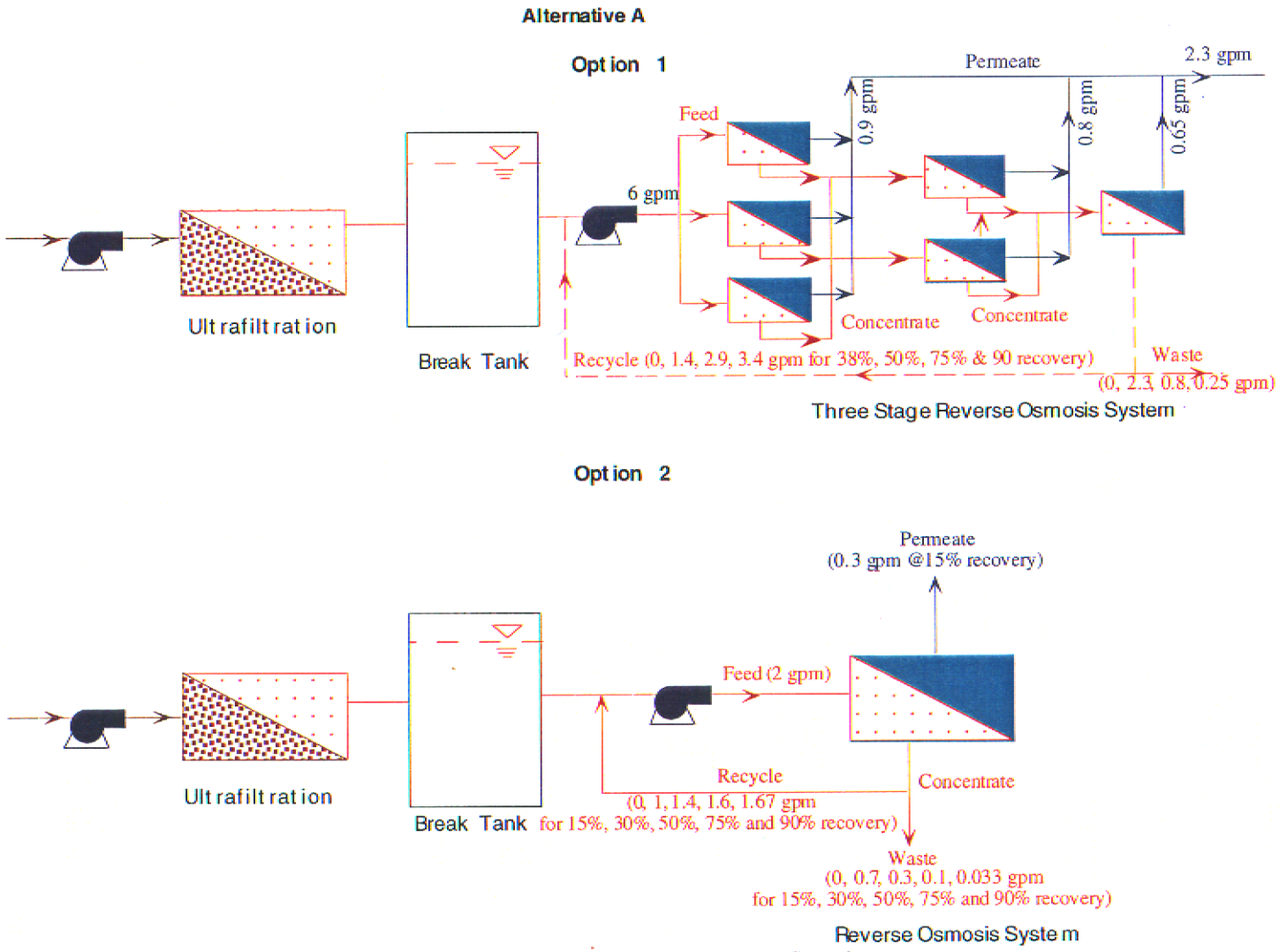

Figure 8.1a and b: Reverse osmosis with ultrafiltration pretreatment

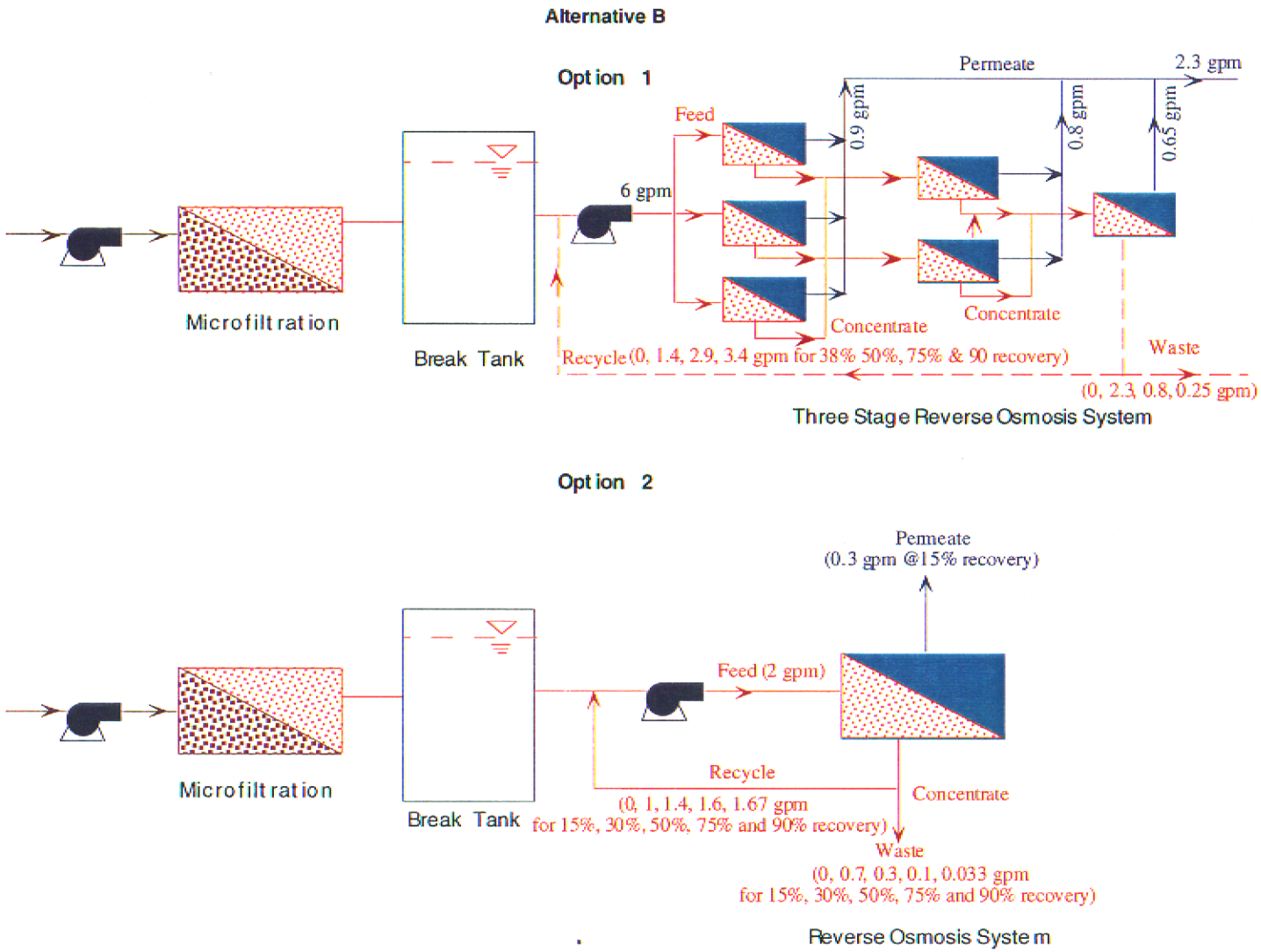

Figure 8.2a and b: Reverse osmosis with microfiltration pretreatment

Monitoring:

It is suggested that the following parameters be measured at a frequency of 4 samples a day, unless otherwise indicated.

Ultra/Microfiltration Unit:
Time
Feed and filtrate Pressures
Feed flow, filtrate Flow
Feed and filtrate turbidities
Feed water temperature
Particle size distribution in feed and filtrate (once a day)
UV absorbance @ 254 nm in feed and permeate (twice a day)
TOC in feed and filtrate (once a day for ultrafiltration and once in two days for microfiltration unit)
Silica Concentration in feed and filtrate (once a day for ultrafiltration and once in two days for microfiltration unit)

Reverse Osmosis unit:
Time
Feed and permeate pressures
Feed, waste, recycle and permeate flows
Feed water temperature
Feed turbidity
UV absorbance @ 254 nm in feed and permeate (twice a day)
TOC in feed and filtrate (once a day)
Conductivity of feed and permeate
Silica Concentration in feed and filtrate (once in two days (preferably once a day))

Further suggestions

Silica appears to cause significant fouling of the membranes. It is highly recommended that a collaborative study be undertaken with the textile plant personnel to investigate the possibility of reducing silica (and perhaps dye) concentrations at source. Chemical pretreatment of feed water may be considered to reduce the adverse effect of silica on permeate flux.

Appendix A: Abbreviations & Units

Abbreviations:

Alum	Aluminum Sulphate Hydrate
DOC	Dissolved Organic Carbon
MF	Micro Filtration
MFI	Modified Fouling Index
MGD	Million Gallons per Day
MFPI	Mini Plugging Factor Index
MWCO	Molecular Weight Cut Off
NF	Nano Filtration
PAC	Powdered Activated Carbon
PACL	Poly Aluminum Chloride
RO	Reverse Osmosis
SDI	Silt Density Index
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UF	Ultra Filtration
UV	Ultra Violet
V	Volume
WW	Wastewater

Units:

Daltons (D)	10^{-12} meters
hr	hour
L	Liters
lb/ft^3	Pounds per cubic foot
m	meter
mg/l	10^{-3} grams per liter
ml	10^{-3} liters
mm	10^{-3} meters
mS	10^{-3} Siemens
nm	10^{-9} meters
psi	pounds per square inch
s	seconds
µm	10^{-6} meters