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Dye Removal from Effluents of Textile Industries by ISO9888 Method and Membrane Technology

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ABSTRACT

Dye removal from effluents of textile industries of Iran was investigated through biodegradabilitymethod and membrane technology . Basic, reactive, disperse and acidic dyes were selected, based onusage rate in Iran. The Zahen - Welenze method (ISO 9888) was applied to study the biodegradabilityof dyes. Results showed the final COD and dye removal (%R) as (%61,% 57), (%73, %76), (%25, %14),and (%32, %8) for acidic, basic, reactive and disperse dyes, respectively. Also, the ADMI value ininfluent and effluent wastewater were (4063, 1768), (271, 111), (2359, 2211) and (2073, 966), respectivelyfor 4 types of dyes. Four types of selected membranes were: (PPT) NF (MWCO= 300Da), (PWB) NF(MWCO= 600Da), (TFC) RO (MWCO= 50Da) and UF (MWCO= 20KDa). Results with membranesfor maximum %R were %93, %76 and > %95, with NF300, NF600 and RO (for all types of dyes), respectively, demonstrating the high removal potential of reverse osmosis membrane.

INTRODUCTION

Effluents from textile industries contain different types of dyes, which because of high molecular weight and complex chemical structures, show low level of biodegradability. Hence, direct deposition of these effluents into sewage networks, produce disturbancesin biological treatment processes.

On theother hand, these types of effluents produce high concentrations of inorganic salts, acidsand bases in biological reactors leading to the increase of treatment costs (2).

Dyes are mostly stable in light and heat. Also,application of technologies which give them more stability in the environment against sunlight, bleaches and oxidants, should be considered.

The classic and conventional treatment methods for these types of effluents are based on chemical precipitation, activated sludge, chlorination and adsorption on activated carbon (2, 11). In 1979, a study was done on the adsorption of dyes on waste textile fibers. Results were not satisfactory forall types of dyes; besides, separation of fibers from the effluent was not economically feasible (5). In another study which was conducted in 1994, dye removal efficiency using the method of activated sludge was not sufficiently high, for all types of dyes. Also,the system was not economically efficient because of relatively high costs of carbonre generation (9). So, regarding the stringent regulations for industrial effluent deposition into water bodies, selection of a treatment method with high removal efficiencies for dyes and showing less operational problems, seems to be important. In this regard and based on a few numbers of studies,membrane filtration may be considered as an appropriate treatment system (6, 8, 13).

The major objective of this research was planned to study the efficiency of membrane filters for dye removing from textile effluent sand comparing the results with biological process through ISO 9888 method. The control method was the comparison between flux of distilled water initially and after dye washing process, with the flux of dye passing through the membrane, in different operational conditions.

The specific objectives were as follows:

1. Determine the degradability of dyes with ISO 9888 method;
2. Study the performance of Nanofilters [NF with MWCO (Molecular Weight CutOff) =300 and 600 Daltons],(Daltons: The unit that state the relationship between pore size and molecular weight cutoff) and Reverse Osmosis (RO with MWCO = 50 daltons membranes);
3. Determine dye removal efficiencies byADMI method;
4. Determine dye removal percentage (%R), COD (Chemical Oxygen Demand) and TDS.

MATERIALS AND METHODS

I. Four types of dyes with the highest usage rates in Iran (Reactive, Disperse, Acidic and Basic) were selected for the treatment investigation. Characteristics of these dyes are presented in Table (1).

II. The biodegradability of synthetic solutions of dyes (with concentrations in the range of industrial effluents (0.01%) was studied (1,4,6,10,14). Also, the Zahen-Wellens (ISO 9888) standard method was applied (ISO 9888 1999). The biodegradation or elimination of water-soluble organic compounds or wastewater ingredients by aerobic microorganisms is determined using a static aqueous test system (ISO 9888). The test mixture contains an inorganic medium, activated sludge as a mixed inoculum and an organic test compound as the sole source of carbon and energy other than the sludge. The amount of test compound added is chosen to result in an initial concentration of chemical oxygen demand (COD) between 100 mg/l and 1000 mg/l, depending on its water solubility and on its toxicity to the bacteria in the inoculum.

Measurement of the concentration of COD is made at the beginning and end of the test (normally 14-28 d) and at the intermediate time intervals, as required. To allow for any significant adsorption of the test compound onto the sludge,

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samples are also taken 3 h after the beginning of the test. Values obtained at this time are used as the basis for calculating the percentage of ultimate biodegradability at each sampling time. In this international standard method, three glass vessels were provided: Vessel (F_T) (the main reactor) containing test medium (10 ml of buffer solution (KH_2PO_4, K_2HPO_4, $Na_2HPO_4.2H_2O$, NH_4Cl) and 1 ml of each of the following solutions for 1000ml test medium: $MgSO_4.7H_2O$, $CaCl_2.2H_2O$, $FeCl_3.6H_2O$), test compound (any type of dye solutions at a concentration of 100 mg/l) and inoculum (0.2 g/l of activated sludge that was obtained from a wastewater treatment plant of textile industry in Tehran), blank vessel (F_B) containing test medium and inoculum, and the third vessel (F_C) containing the reference compound (ethylene glycol) with a concentration of 3000mg/l for checking the procedure.

Table1. **Characteristic of dyes used in this research**

Types of Dyes	Commercial Name	Characteristics
Basic		
(Cationic)	Acryson	Navyblue (2RN(Wegschelder))
	Acryson	Red (GTL(Wegschelder))
	Dragonacryl	Violet16 (3RN Red-Violet)
	Dragonacryl	Yellow 13
	Maxilon	Yellow (G1 400%)
Acidic		
(Anionic)	Acid Robin	F
	Acid Yellow	FL-2G
	Acid Blue	22NA
	Acid Rodamin	B
Reactive		
	Remazol	Blue (RSP)
	Remazol	Bourdon (B)
	Remazol	Orange (JR)
	Remazol	Yellow (RG)
	Alilon	Violet (S-3RL)
	Cerylen	Black (RNFS)
Disperse	Liapters	Turguzeblue (BG)
	Polycaron	Red (B)

To start the test, the vessels were aerated and incubated, at a temperature within the range of 20-25ºC. Aeration was provided to insure homogeneity of dissolved oxygen in the reactor. The pH value was checked at regular intervals and adjusted at 7 ± 0.5. Samplings were made in all reactors at t_1 (the starting time after 3± 0.5), at the end of the test (day 27th or 28th) and at four intermediate intervals (days 3rd, 7th, 14th and 21st). Samples were then filtered and COD concentrations and removal percentage were measured, as follows:

$$\%\text{COD removal} = \left[1 - \frac{p_c\, T_t - P_C B_t}{P_C T_1 - P_C B_1}\right] \times 100 \qquad (1)$$

In which:

$P_C\,T_1$ = COD concentration, (mg/l), at time t_1 in vessel F_T

$P_C\,B_1$= COD concentration, (mg/l), at time t_1 in vessel F_B,

$P_C T_t$= COD concentration, (mg/l), at time t (day28) in vessel F_T

$P_C B_t$= COD concentration, (mg/l), at time t (day28) in vessel F_B

Based on the recommendations in the methodology, the experiment is correct only if the biodegradability percentage in Fc after 28 days exceeds 70%. Otherwise, it should be repeated with changes in operating conditions.

Determination of dye rejection coefficient (R%) and dye concentration was conducted following the procedure of ADMI, in which the dye concentration in a sample is determined by ADMI value. This procedure can be divided into six steps:

1-Measurement of sample by using single beam spectrophotometer DU650. The wavelengths at which transmittance measurements must be made depend on the method of calculation C.I.E (Commission on Illumination) tristimulus values: the weighted ordinate method, the 10 wavelength selected method and the 30 wavelength selected method. In this research, 30 wavelengths between 380-730 nm with $\Delta\lambda$=10nm were selected. The spectrophotometer was calibrated by platinum cobalt standards (1.246 gr. potassium chloroplatinate and 1gr crystallized cobaltous chloride) (APHA et al. 1995, section 2120).

2-Calculation of C.I.E. tristimulus values (X, Y, Z), by using convenient related tables (Wyszecki & Stile 1967; Nassau 1998) .The tristimulus values for colorless sample (blank sample: distilled water) were selected as the basis for calculating X, Y and Z in all samples, as: X_C=98.06, Y_C=100, Z_C=118.14 (Allen et al. 1973).

3-Conversion of six tristimulus values, X_C, Y_C, Z_C and X_S, Y_S, Z_S (colored samples) to Munsell values (V_X, V_Y, V_Z) by applying tables giving the interdependence of X and V_X, Y and V_Y, Z and V_Z (Wyszecki & Stile 1967).

4-Calculation of Adams-Nickerson color Difference (DE). The value of DE is calculated from the following equation (Allen et al. 1973; APHA et al. 1998):

$$DE = [(0.23\ \Delta V_Y)^2 + (\Delta\ (V_X - V_Y))^2 + (0.4\ \Delta\ (V_Y - V_Z))^2]^{1/2} \quad (2)$$

$\Delta V_Y = V_{Ys} - V_{Yc}$, $\Delta V_X = V_{Xs} - V_{Xc}$, $\Delta V_Z = V_{Zs} - V_{Zc}$

5- Calculation of calibration factor (F). At first, the transmitance was measured for each standard solution at 30 selected wavelengths, followed by calculating the tristimulus values. Then DE for each standard solution was calculated from equation (2). The calibration factor (F) for each standard solution was calculated by the following equation:

$$F = \left(\frac{(APHA)_n \times b}{(DE)_n} \right) \quad (3)$$

In which:

$(APHA)_n$=APHA color value for the nth solution standards (Concentration of platinum cobalt)

$(DE)_n$= Color Difference value

b= Cell path used in spectrophotometer, cm

6- Calculation of ADMI color value. Through the following equation (Allen et al. 1973; APHA et al. 1998), in which F is the mean value of calibration factors for different standards:

$$\text{ADMI value} = \frac{(F) \times (DE)}{b} \quad (4)$$

The Rejection Coefficient (%R) was determined for each sample at 30 different wavelengths by the following equation (Juang & Liang 1993):

$$R = \left[1 - \frac{LOG(T_p)}{LOG(T_f)} \right] \times 100 \quad (5)$$

In which:

T_f = Light transmittance for the influent solution into each reactor

T_p= Light transmittance for the effluent solution (after 28 days in biological reactors, or permeate of the membrane system).

III. At the third step, a pilot plant setup was designed and constructed to study membrane separation efficiency for the different dyes (Figure 1). Also, Table (2) shows the specifications of the membranes used for this study.

All of the experiments followed a specific similar operational pattern with a batch hydraulic regime. Experimental steps for the determination of removal efficiencies were as follows:

1-Preparation of dye samples (Table 1) with a concentration of %0.01 (100 mg/l). In order to study the effect of dye concentration on R%, different concentrations of 0.01%, 0.025%, 0.05%, 0.1% and 0.12% of reactive dye were provided.

2-Sample flow into the membrane system (NF with MWCO of 300 and 600 Daltons, and RO with MWCO of 50 Dalton) with the 10 l/min flowrate.

3-Measurement of the influent flux of distilled water at different temperatures and pressures (for NF membranes: 0.5, 1, 2, and 4 bars and for RO, 7.5 bars) and.

4-Determination of J_{ww} as the distilled water flux (J =flow rate (Q)/ membrane surface area (A)).

5–Membrane chemical washing followed by rinsing with distilled water and with the following procedure:

-Washing the membrane with 1% NaOH solution (for NF 300) and sodium triphosphate (for NF 600 and RO 50), at 4 bar pressure and 30-35 ° C temperature, for 15 minutes.

- Rinsing with distilled water.
- Determining of the distilled water flux after the first washing step (J_{wc1}).

-Washing with 1% HCl solution (for NF 300) and 1% citric acid solution (for NF 600 and RO).

- Rinsing with distilled water.
- Determining of the distilled water flux after the second washing step (J_{wc2}).

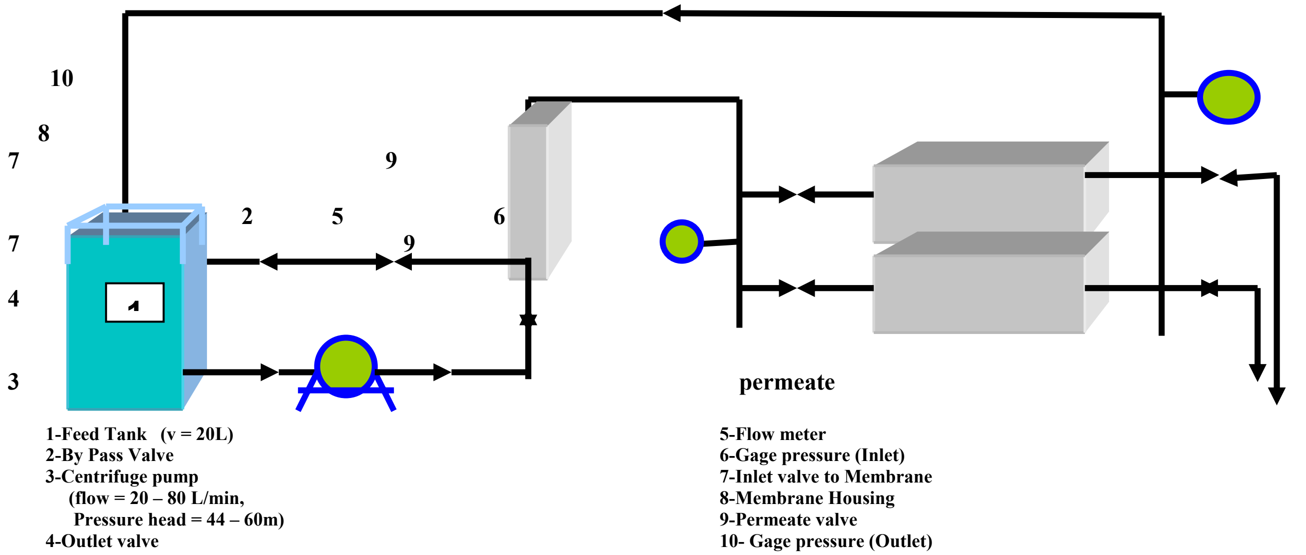
During each experiment, samples of permeate were taken and COD were measured (13). Finally, R% and ADMI values were determined.

Table 2. **Membrane types and characteristics**

Types of Membrane	Material	Module	Size (m)	Mwco(Da's)	Active Area (m^2)	T (^{O} C)	Δp(bar)	Manufacturer
NF	Poly Amid (PPT)	Spiral wound	0.051*.51 (2*20 inch)	300	0.437 ($5ft^2$)	40	0.5-3	Perma-Pure
NF	Cellulose Acetate Blend (PWB)	Spiral wound	0.051*.51 (2*20 inch)	600	0.473 ($5ft^2$)	35	0.5-3	Perma-Pure
RO	Poly Amid (TFC)*	Spiral wound	0.051*.51 (2*20 inch)	50	0.237 ($2.5ft^2$)	40	7.5	Perma-Pure

*TFC: Thin Film Composite

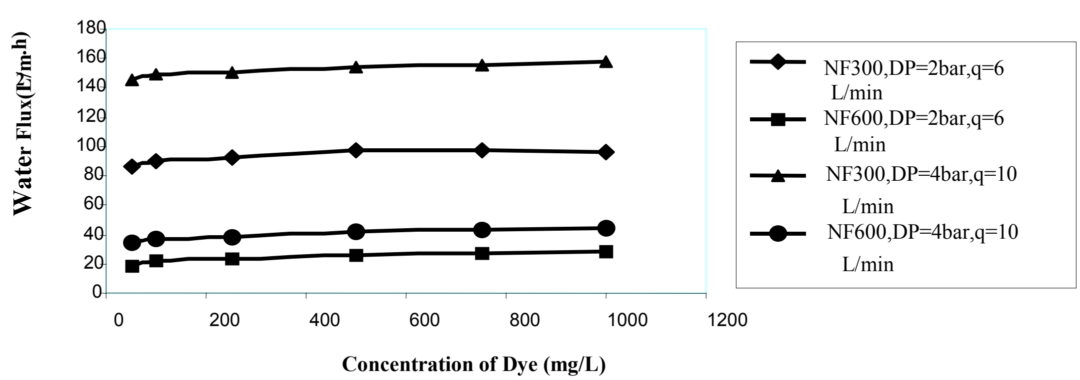
Fig.1. **Schematic of membrane pilot plant used for dye removal**



RESULT

Based on the studies at the first step, four types of dyes (Acidic, Basic, Reactive and Disperse) were selected. To investigate the effects of dye concentration, pressure, and temperature on membrane performance, the variation of flux and R% versus these parameters were studied (Figures 2,3,4). Figure (5) presents the variations of COD removal percentage with time, applying the biological method. In Table (3), results of COD, removal percentage and water fluxes (J_{wi}, J_{ww}, and Jwc1, Jwc2) before and after membrane-washing steps are presented.

Fig. 2. **Effect of concentration on membrane performance for Reactive Dyes**



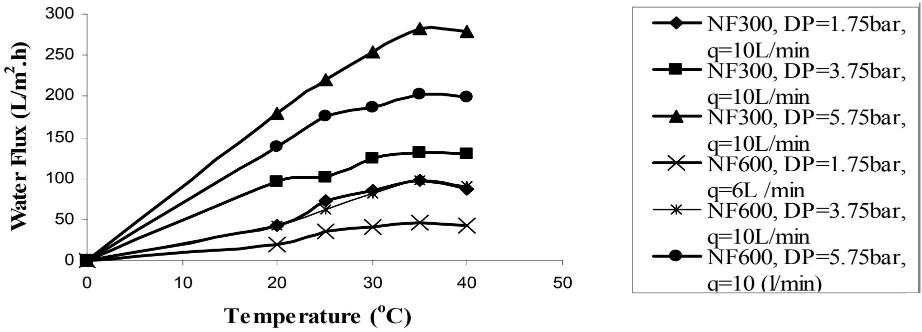


Fig. 4. **Effect of pressure on membrane performance for reactive dyes**

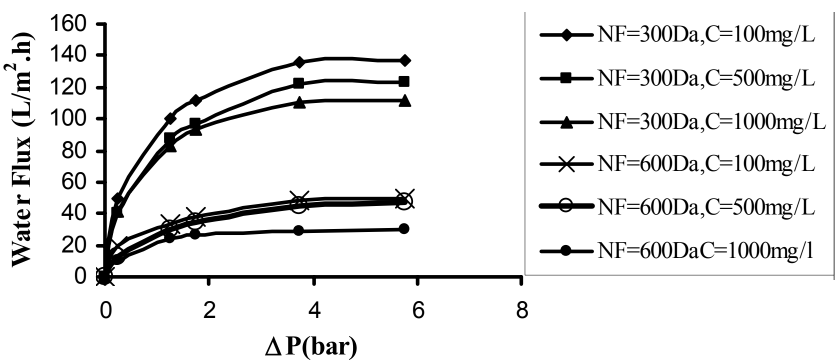


Fig. 5. **COD removal percentage versus time for different types of dyes by biological degradation**

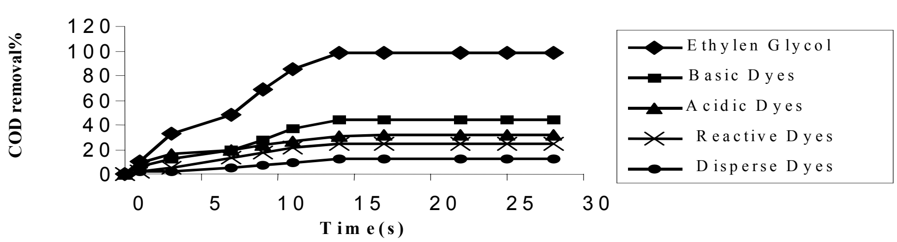


Table 3. **permeate Fluxes and COD removal percentage at different pressures, constant temperature (30-35 °C) and dye concentration=100mg/l**

(MWCO), (Da's)	Types of Dye	Types of Membrane						%COD Removal
		ΔP (bar)	J_{wi} l/m^2.h	J_{MF}* l/m^2.h	J_{ww}** l/m^2.h	J_{wc1} l/m^2.h	J_{wc2} l/m^2.h	
NF=300	Acidic	3.75	592	426	477	505	520	6
		1.75	420	387	333	375	375	5
		1.25	264	240	248	248	250	5
		0.25	116	87	75	96	100	4
NF=300	Basic	3.75	590	420	455	462	541	44
		1.75	387	387	387	387	387	42
		1.25	260	258	191	200	260	42
		0.25	120	93.5	88	110	115	42
NF=300	Reactive	3.75	310	110	150	164	192	35
		1.75	109	93	95	98	100	33
		1.25	100	85	92	94	94	33
		0.25	82	60	68	75	77	32
NF=300	Disperse	3.75	520	387	501	501	501	70.5
		1.75	387	310	359	375	375	60
		1.25	250	221	240	250	250	57
		0.25	100	96	100	100	100	54
NF=600	Acidic	3.75	383	309	310	341	341	7
		1.75	270	221	229	230	230	7
		1.25	180	154	160	160	160	6
		0.25	68	46	61	68	68	6
NF=600	Basic	3.75	382	310	347	377	377	23.5
		1.75	232	221	170	180	180	23
		1.25	185	155	157	170	170	22.5
		0.25	68	48	49.6	52	52	22
NF=600	Reactive	3.75	136	27	50	98	101	33
		1.75	50	24	30	32	37	28
		1.25	42	24	30	32	37	29
		0.25	40	26	30	32	37	27
NF=600	Disperse	3.75	341	258	292	292	294	58.5
		1.75	230	202	166	166	167	54
		1.25	160	155	93.5	93.5	94	52
		0.25	98	51.6	60.5	60.5	61	52
RO=50	Acidic	7.5	-	-	-	-	-	95
RO=50	Basic	7.5	-	-	-	-	-	96
RO=50	Reactive	7.5	-	-	-	-	-	85

* Dye permeate flux after 20 minutes

**Distilled water flux before washing steps

DISCUSSION

Studying Figure 2 shows that concentration variations had not significant effect on water fluxes. On the other hand, flux increased with temperature up to 35ºC and then remained constant (Fig.3). Also, pressure had an increasing effect on flux up to 4 bars, followed by a stationary phase for flux with higher pressures. Based on these results, t=35ºC and ΔP=4 bars were selected as operating conditions.

A comparison is made in Table 4 between the results of R% in biological and membrane methods, which shows that the minimum and maximum biodegradability efficiencies were 8% (for disperse) and 70% (for basic) dyes, respectively. For disperse dyes, The highest R% with NF membranes was obtained with NF300 (92.5%), for disperse dyes. COD removal efficiency with this type of membrane was $\geq 50\%$. Comparing with the other study, nonofiltration membrane was a very tight membrane with an excellent rejection coefficient (Liu et al. 1994).

For acidic dyes, R% were 60%, 55% and 99.5% for biological method, NF 300, NF600 and Ro respectively. On the other hand, COD removal percentage was significant only with RO (85%).

For basic dyes, application of ISO9888 method and NF=300 and 600 showed acceptable results for R%; but the best result was obtained with RO (98.2%). Furthermore, results for COD removal percentage were not significant with NF=300 and 600 and ISO9888 method. The RO membrane showed the highest percentage of COD removal (96%) for this type of dye.

For Reactive dyes, the best results for R% and COD removal percent were achieved with RO membrane (99.6% and 85%).

Review of the unmentioned results shows clearly the high potential of RO membranes for simultaneously removing dyes and COD from textile effluents.

Based on experimental results, the following conclusions can be drawn. The highest possible dye rejection coefficient with NF membranes were obtained as 92.5% (for disperse dyes) and the least dye rejection coefficient of 36%(for reactive dyes). The best removal efficiencies (for both COD and dye) were obtained with RO membranes; hence, regarding high removal potential and decreasing price of membrane modules, this method may be recommended for finishing treatment of textile effluents.

Table 4. **Comparison between ADMI values, R% and COD Removal percentage with Biological and Membrane filtration with Biological and Membrane filtration Methods (Dye concentration = 100 mg/lit) ***

Types of Dyes	*Methods*											
	Biological Method			**Membrane Filtration**								
	ADMI VALUE	*R%*	*%COD Removal*	*NF=300Da*			*NF=600Da*			*RO=50Da*		
				ADMI	*R%*	*%COD*	*ADMI*	*R%*	*%COD*	*ADMI*	*R%*	*%COD*
Acidic												
Feed	2147	--	--	2709	--	--	2709	--	--	2631	--	--
Permeate	882	60	32	2695	55	6	1991	54	7	79	99.6	85
Basic												
Feed	1271	--	--	1650	--	--	1650	--	--	1765	--	--
Permeate	1111	70	44	292	70	44	239	76	23.5	68	98.2	96
Reactive												
Feed	2354	--	--	1251	--	--	1251	--	--	1625	--	--
Permeate	2211	12.5	25	1220	36	35	502	29	33	103	99.6	85
Disperse												
Feed	3720	--	--	3651	--	--	3651	--	--	---	---	---
Permeate	3555	8	12	127	92.5	70.5	152	92	58.5			

*Operation Conditions: temperature: 30-35°C and ΔP=4bar for NF and ΔP=7.5 bar for RO

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