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Textile Dye Removal by Membrane Technology and Biological Oxidation

MITRA GHOLAMI,[1]* SIMMIN NASSERI,[2] MOHAMMAD-REZA ALIZADEHFARD[3] AND ALIREZA MESDAGHINIA[2]

[1]*Iran University of Medical Sciences, Department of Environmental Health Engineering, Alvand Street, Arjantin Sq., P.O. Box 15875-4199, Tehran 15168, Iran*
[2]*Tehran University of Medical Sciences, School of Public Health, Department of Environmental Health Engineering, P.O. Box 6446, Tehran 14155, Iran*
[3]*Polymer Engineering Department, Amirkabir University of Technology, Tehran, Iran*

The objective of this research was to evaluate the effectiveness of two methods for dyestuff removal from a textile waste stream. In the first step, different types of dyes used in textile industries were studied in order to determine the types with highest usage rates. In this regard, basic, reactive, disperse and acidic dyes were selected. In the second step, dye biodegradability was studied through Zahn-Wellens method (ISO-9888 1999). Results showed final chemical oxygen demand (COD) and dye rejection coefficients (R%) of (61%, 57%), (73%, 76%), (25%, 14%), (32%, 8%) for acidic, basic, reactive and disperse dyes, respectively. In the third step, spiral-wound membrane modules nanofilter (NF) with a molecular weight cut off (MWCO) of 300 and 600 dalton (Da) and reverse osmosis (RO) of 50 Da were used. The operating conditions in phase 3 were adjusted as: temperature 30 to 35°C, pressure 4 bar for NF membranes and 7.5 bar for RO, flow rate of 10 L/min, and dye concentration of 0.01%. Results showed that COD and dye rejection coefficients for NF with 300 Da and for acidic, basic, reactive and disperse samples of dyes were (6%, 55%), (44%, 70%), (33%, 36%) and (71%, 93%), respectively. These results for NF with 600 Da were (7%, 54%), (64%, 76%), (33%, 29%), (59%, 92%) and for RO were (95%, 99%), (96%, 98%), (45%, 99.6%). Results clearly showed higher removal efficiency for the membrane treatment than for biodegradability studies.

Key words: **dye removal, biodegradability, membrane filtration, textile industries**

Introduction

Effluents from textile industries contain different types of dyes. Because of this high molecular weight and complex chemical structures, they show low levels of biodegradability. Hence, the direct disposal of these effluents into sewage networks produces disturbances in biological treatment processes. On the other hand, these types of effluents produce high concentrations of inorganic salts, acids and bases in biological reactors leading to the increase of treatment costs (Goozen and Shayya 2000).

The traditional and conventional treatment methods for these types of effluents are based on chemical precipitation, activated sludge, chlorination and adsorption on activated carbon (Goozen and Shayya 2000). In

* Corresponding author; mitra326@yahoo.com

1979, a study was done on the adsorption of dyes on waste textile fibers. Results showed that these methods were not satisfactory for all types of dyes. In addition, separation of fibers from the effluent was not economically feasible in a biological reactor (Karimi and Amirshahi 2000). In another study, which was conducted in 1994, dye removal efficiency using activated sludge was not sufficiently high, for all types of dyes (Paggaudo 1994). So, regarding the stringent regulations for industrial effluent disposal into water bodies, the selection of a treatment method with high removal efficiencies for dyes and ease of operation seem to be important. In this regard and based on a number of previous studies, membrane filtration may be considered as an appropriate treatment system (Tinghui et al. 1983; Liu et al. 1994; Ohnishi and Okhuma 1998). In 2002, research was done on the removal of dyes by polyamide-based nanofiltration membrane and the effects of concentration, pH and salt on flux and retention were studied. Results showed that the membrane showed acceptable rejection for anionic and direct dyes but for cationic dye, was not suitable for such an application (Akbari et al. 2002).

The main objective of this research was to investigate the efficiency of membrane filtration for dye removal from textile effluents and to compare the results with a biological process (ISO-9888 1999 Method). The control method was the comparison between fluxes of distilled water initially and after the dye washing process, with the flux of dye passing through the membrane, under different operational conditions.

The specific objectives were as follows:

1. Determine the degradability of dyes with ISO-9888 (1999) Method.
2. Study the performance of nanofilters (NF) with MWCO = 300 and 600 Da, and reverse osmosis (RO) with MWCO = 50 Da.
3. Determine dye removal efficiencies by ADMI (American Dye Manufacturer Institute) method (Allen et al. 1973; APHA et al. 1998).
4. Determine the dye rejection coefficient (R%) (Juang and Liang 1993; Watters and Biagtan 1991) and COD (APHA et al. 1998).

Materials and Methods

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.

The biodegradability of synthetic solutions of dyes (with concentrations in the range of industrial effluents (0.01%) was studied (Liu et al. 1994; Paul et al. 1996; Buckley 1992; Juang and Liang 1993; Watters and Biagtan 1991). Also, the Zahn-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 1999). The test mixture contains an inorganic medium, activated

Table 1. Characteristic of dyes used in this research

Types of dyes	Commercial name	Characteristics Basic	
Basic (Cationic)	Acryson	Navy blue	(2RN[Wegschelder])
	Acryson	Red	(GTL[Wegschelder])
	Dragonacryl	Violet 16	(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)
Disperse	Alilon	Violet	(S-3RL)
	Cerylen	Black	(RNFS)
	Liapters	Turguzeblue	(BG)
	Polycaron	Red	(B)

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 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, 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, Na2HPO$_4$.2H$_2$O, NH_4Cl] and 1 mL of each of the following solutions for 1000 mL test medium: $MgSO_4.7H_2O$, $CaCl_2.2H_2O$, $FeCl_3.6H_2O$), test compound (any type of dye solution 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 3000 mg/L for checking the procedure.

To start the test, the vessels were aerated and incubated, at a temperature within the range of 20 to 25°C. Aeration was provided to ensure 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 27 or 28) and at four intermediate intervals (days 3, 7, 14 and 21). Samples were then filtered and COD concentrations and removal percentage were measured, as follows:

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

Where $P_C T_1$ = 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 (day 28) in vessel F_T; and $P_C B_t$ = COD concentration, (mg/L), at time t (day 28) 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 CIE (Commission on Illumination) tristimulus values: the weighted ordinate method, the 10-nm wavelength selected method and the 30-nm wavelength selected method. In this research, 30 wavelengths between 380 to 730 nm with $\Delta\lambda$ = 10 nm were selected. The spectrophotometer was calibrated by platinum cobalt standards (1.246 g potassium chloroplatinate and 1 g crystallized cobalt[II] chloride) (APHA et al. 1998, section 2120).
2. Calculation of CIE tristimulus values (X, Y, Z), by using convenient related tables (Wyszecki and Stile 1967; Nassau 1998). The tristimulus values for colourless samples (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, and 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 (coloured 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 and Stile 1967).
4. Calculation of Adams-Nickerson Colour Difference (DE). The value of DE is calculated from the following equation (Allen et al. 1973; APHA et al. 1998):

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

Where $\Delta V_Y = V_{Ys} - V_{yc}$, $\Delta V_X = V_{Xs} - V_{Xc}$, and $\Delta V_Z = V_{Zs} - V_{Zc}$.

5. Calculation of the calibration factor (F). At first, the transmittance 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:

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

Where $(APHA)_n$ = APHA colour value for the solution standards (concentration of platinum or cobalt), $(DE)_n$ = colour difference value, and b = cell path used in spectrophotometer (cm).

6. Calculation of ADMI colour 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:

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

The rejection coefficient (R%) was determined for each sample at 30 different wavelengths by the following equation (Juang and Liang 1993):

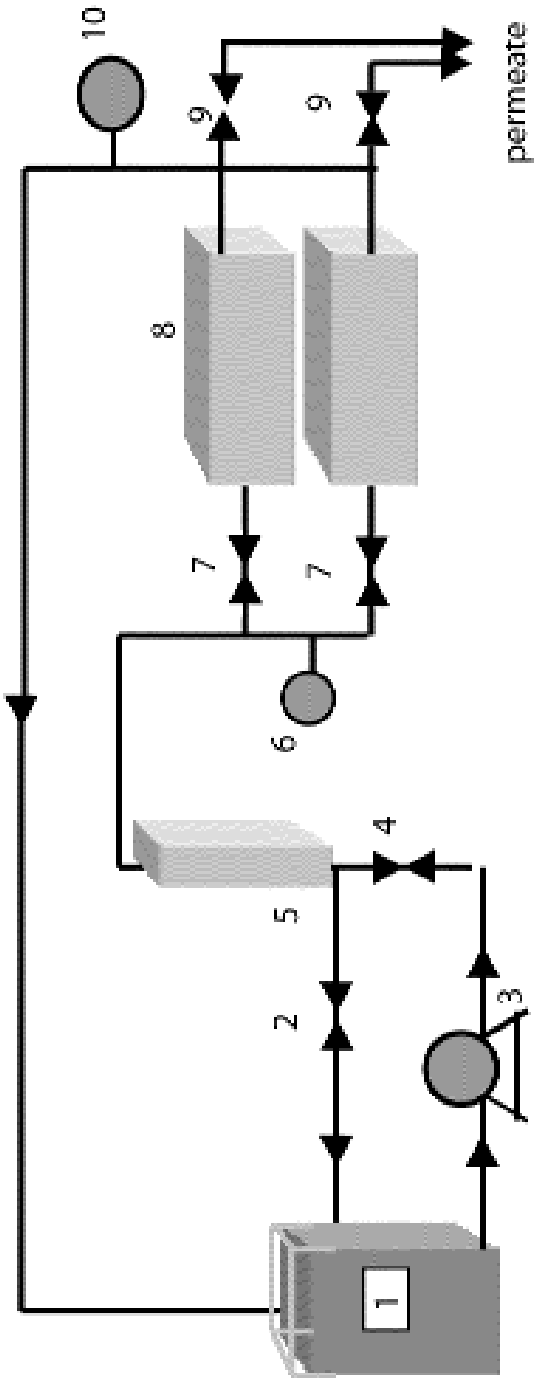
$$R = \left[1 - \frac{LOG(T_p)}{LOG(T_f)}\right] * 100 \quad (5)$$

Where T_f = light transmittance for the influent solution into each reactor, and T_p = light transmittance for the effluent solution (after 28 days in biological reactors, or permeate of the membrane system).

At the third step, a pilot plant setup was designed and constructed to study membrane separation efficiency for the different dyes (Fig. 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%,



1 Feed Tank (v = 20L)
2 By Pass Valve
3 Centrifuge pump (flow = 20–80 L/min, Pressure head = 44–60m)
4 Outlet valve
5 Flow meter
6 Gage pressure (Inlet)
7 Inlet valve to Membrane
8 Membrane Housing
9 Permeate valve
10 Gage pressure (Outlet)

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

Table 2. Membrane types and characteristics

Type of membrane	Material	Module	Size (m)	MWCO (Da)	Active area (m^2)	T (°C)	Δp (bar)	Manufacturer
NF	Poly amid (PPT)	Spiral wound	0.051[a] x 0.51 (2*20 inch)	300	0.437 (5 ft^2)	40	0.5–3	Perma-Pure
NF	Cellulose acetate blend (PWB)	Spiral wound	0.051[a] x 0.51 (2*20 inch)	600	0.473 (5 ft^2)	35	0.5–3	Perma-Pure
RO	Poly amid (TFC)*	Spiral wound	0.051[a] x 0.51 (2*20 inch)	50	0.237 (2.5 ft^2)	40	7.5	Perma-Pure

[a] TFC; Thin film composite.

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 Da, and RO with MWCO of 50 Da) with the 10 L/min flow rate.
3. Measurement of the influent flux of distilled water at different temperatures and pressures (for NF membranes: 0.5, 1, 2, and 4 bar and for RO, 7.5 bar).
4. Determination of J_{ww} as the distilled water flux where 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 to 35°C temperature, for 15 minutes.
    - Rinsing with distilled water.
    - Determination 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.
    - Determination of the distilled water flux after the second washing step (J_{wc2}).

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

Results

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 (Fig. 2, 3, 4). Figure 5 presents the variations of COD removal with time, applying the biological method. In Table 3, results of COD removal and water fluxes (J_{wi}, J_{ww}, and J_{wc1}, J_{wc2}) before and after membrane-washing steps are presented.

Discussion

Studying Fig. 2 shows that concentration variations had no significant effect on water fluxes. On the other hand, flux increased with temperature up to 35°C and then remained constant (Fig. 3). Also, pressure had an increasing effect on flux up to 4 bar, followed by a stationary phase for flux with higher pressures. Based on these results, t = 35°C and $\Delta P = 4$ bar 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

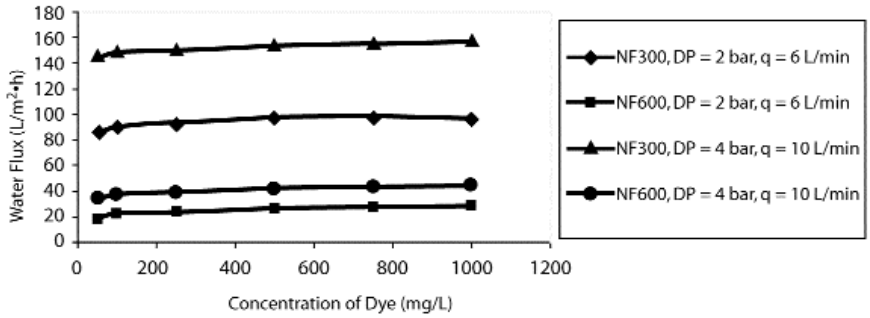


Fig. 2. Effect of concentration on membrane performance for reactive dyes.

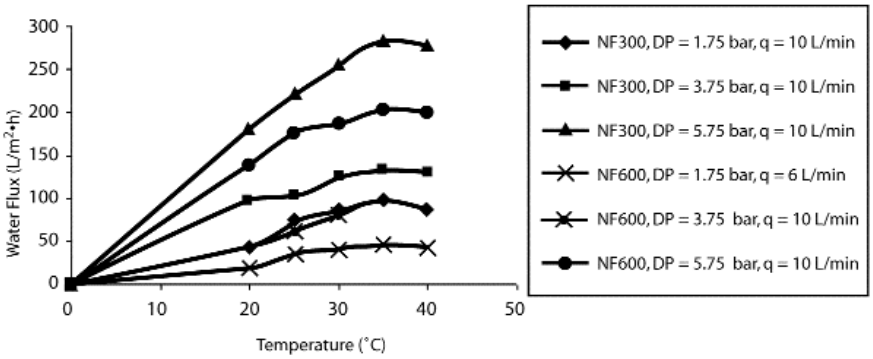


Fig. 3. Effect of temperature on membrane performance for reactive dyes.

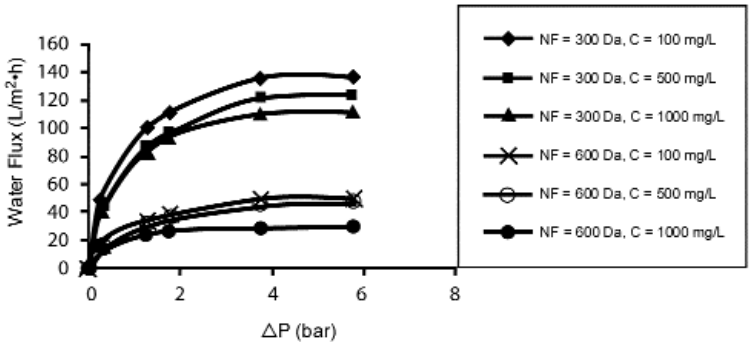


Fig. 4. Effect of pressure on membrane performance for reactive dyes.

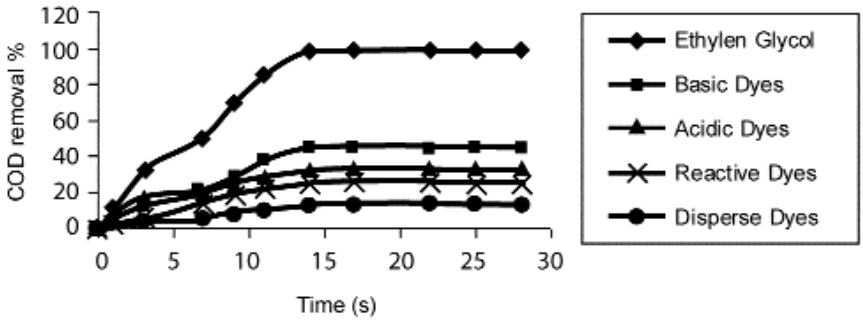


Fig. 5. COD removal percentage versus time for different types of dyes by biological degradation.

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 NF = 300 (92.5%). COD removal efficiency with this type of membrane was 50%. Compared 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, NF = 600 and RO, respectively. On the other hand, COD removal percentage was significant only with RO 85%.

For basic dyes, application of ISO-9888 (1999) 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 ISO-9888 (1999) 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 clearly shows the high potential of RO membranes for simultaneously removing dyes and COD from textile effluents.

Conclusions

Based on experimental results, the following conclusions can be drawn. The highest possible dye rejection coefficient with NF membranes obtained was 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 3. Permeate fluxes and COD removal percentage at different pressures, constant temperature (30–35°C) and a dye concentration of 100 mg/L

Type of membrane (MWCO) (Da)	Types of dye	ΔP (bar)	J_{wi} L/m²·h	J_{MF}[a] L/m²·h	J_{ww}[b] L/m²·h	J_{wc1} L/m²·h	J_{wc2} L/m²·h	%COD removal
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

[a] Dye permeate flux after 20 minutes.
[b] Distilled water flux before washing steps.

Table 4. Comparison between ADMI values, R% and COD removal percentage with biological and membrane filtration methods (dye concentration 100 mg/L)[a]

Methods	Biological			Membrane filtration								
				NF = 300 Da			NF = 600 Da			RO = 50 Da		
Types of dyes	ADMI VALUE	R%	% COD Removal	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			

[a] Operation conditions: temperature is 30–35°C, $\Delta P = 4$ bar for NF, and $\Delta P = 7.5$ bar for RO.

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