Membrane Filtration Techniques –Part II
Scope for minimising effluent load

Purnima Chauhan and Dr. Rekha R.
The Synthetic & Art Silk Mill's Research Associations
Sasmira Marg, Worli, Mumbai-400030

Abstract:

Membrane filtration technique is a practical and cost effective solution to the problems for handling textile wastewater pollution. In earlier article (Man-Made Textiles in India, L(2), 58, 2007) it was illustrated that exhaust dye liquor of reactive dyes could be separated from unfixed dyes by membrane filtration technique at affordable cost. This would enable small process houses to survive and remain competitive. The main thrust area in this paper is the use of membrane filtration technology not only to purify incoming water, but also to recycle used water as many times as is practically feasible so that generation of effluent and treatment costs are reduced.

1. Introduction

In the previous article, it is shown that how large volumes of wastewater from textile industry can be filtered through membrane filtration process to reduce water pollution and minimise hazards to the environment. These effluents have high value of chemical oxygen demand (COD) and is highly alkaline.

SASMIRA has studied this aspect in a perspective to achieve the following objectives viz.

1. To obtain clear water (permeate) through membrane filtration and it's recycling. It would reduce generation of effluent and thus help conserve water.
2. Reducing the volume of wastewater for effective treatment at effluent treatment plant (ETP)

Process houses in Gujarat, Rajasthan and also Tamilnadu are affected by strictly enforced pollution norms. Existing ETP are not able to achieve these norms. By this technology of membrane filtration one can overcome this obstacle by multiple recycling of their effluent speedily without loading ETP.

Sule et. al[1] had mentioned about overcoming the above effluent load, by developing multifunctional reactive dyes. It was concluded that nanofiltration is one of the means for separation of solutes of different molecular sizes. It can also separate hydrolysed reactive dyes from salt solution. This salt solution is obtained as permeate which can be recycled for dyeing[2-4]. Similar aspect of reducing pollution by recycling various wastes from the textile industry has been discussed by Sule and Bardhan[5].

2. Membrane Filtration

Membranes are of different pore size and it is necessary to select membranes of appropriate pore size for specific purpose so that effluent dye liquor (EDL) from different dyes, wash liquors and wastewater could be purified and permeate could be recycled a number of times.

There are three broad categories of membrane filtration. They are Ultra-filtration(U.F), Nanofiltration(N.F) and Reverse Osmosis(R.O). Solute separated by these membranes is given in Table I, while pore size of membranes vis-à-vis approx. molecular weight cut off (MWCO) point is given in Table II.

Table I

Solutes Separated by Membrane Filtration

Type of filtration	Dispersions & Solutes Blocked	Solutes allowed to pass through
Ultra-filtration:	Pigments, Resins, Latex, Sizes, Emsifiers, Enzymes, Oils, Glues, Polymers, Thickeners, Binders	Dyes, Salts, detergents
Nanofiltration:	Polyvalent Salts, Dyes, Detergents	Monovalent salts
Reverse Osmosis:	Salts, Sugar, Ions	None. Only dissolved gases

Table II

Salient Features of Membrane Filtration

R.O. Based	Pore Size (mµ)	Approx. MWCO point	Operating Filtration Pressure(kg/cm^2)
Ultra-filtration	5 – 100	> 1000	10
Nanofiltration	1 - 5	200-1000	15-30
Reverse Osmosis	< 1.0	< 200	30-60

Membrane filtration is not like conventional filtration where under pressure insoluble matter remains on the filter and liquid passes through. If such high levels of pressure are applied to membranes, it will tear apart. Membrane module is so designed that liquid free from particulate matter passes through a rolled up module of membranes and separators, when higher molecular weight compounds slip out as a separate stream of concentrates while lower molecular weight compounds pass through the membrane and are recovered as permeates[6,7].

There are many ways in which membrane modules can be made e.g. tubular, plate and frame, spiral and hollow fibre type but the most common ones are spirally wound modules.

Membrane filtration provides solution to these problems. The next aspect is which membrane is to be used. If R.O. is used the permeate will be clear and devoid of all spent dyes and salt which will emerge as concentrate. Nano- filtration is a broad term wherein pore size ranges from 150 MWCO to 500 MWCO. Hence, when processors in many areas tried nanofiltration with modules imported from USA and Europe, it was difficult to separate salt from spent dyes. The ideal pore size lies somewhere between 100 MWCO and 500 MWCO. SASMIRA experimented with three different membranes of MWCO 100, 150 and 250. A clear salt solution was obtained as permeate and spent dye with surface-active agents as concentrate. This concentrate of unwanted components could be further nanofiltered and concentrated and eventually discarded in solid form after evaporation by sun drying or using evaporators. Permeate could be recycled a number of times. To what extent this permeates could be used was studied in detail.

2.1 Membrane Filtration of effluent generated from disperse dyeing

Fresh disperse dyeing of 1% shade was carried out on polyester fabric and the effluent generated after dyeing was nanofiltered to see whether permeate can be used for dyeing medium shades and the results are given in Tables III – VIII.

Table III

Multiple recycling of Coralene Yellow 3G 200%

	L	a	b	C	h	$DECMC_{2:1}$
Fresh water Dyeing	82.57	0.35	80.79	80.8	89.8	--
After 1st Permeate	83.27	1.40	81.74	81.8	89.0	0.69
After 2nd Permeate	82.01	0.64	80.37	80.4	89.5	0.29
After third Permeate	83.20	1.29	81.64	81.7	89.1	0.62

Table IV

Multiple recycling of Coralene Brown 3REL

	L	a	b	C	h	$DECMC_{2:1}$
Fresh water Dyeing	50.02	35.71	29.06	46.0	39.1	--
After 1st Permeate	50.16	35.7	29.20	46.1	39.3	0.12
After 2nd Permeate	49.87	34.62	28.12	44.6	39.1	0.59
After third Permeate	49.87	35.16	28.69	45.4	39.2	0.29

Table V

Multiple recycling of Coralene Scarlet RR

	L	a	b	C	h	$DECMC_{2:1}$
Fresh water Dyeing	52.09	47.99	35.63	59.8	36.6	---
After 1st Permeate	52.07	48.06	35.56	59.8	36.5	0.07
After 2nd Permeate	52.08	46.16	34.9	57.9	37.2	0.79
After third Permeate	52.34	46.14	34.6	57.5	36.9	0.79

Table VI

Multiple recycling of Foron Blue SE2RI

	L	a	b	C	h	$DECMC_{2:1}$
Fresh Water Dyeing	32.65	8.93	-38.04	39.1	283.2	---
After 1st Permeate	32.94	8.16	-37.12	38.0	282.4	0.65
After 2nd Permeate	32.83	8.47	-37.53	38.5	282.7	0.38
After third Permeate	32.45	7.89	-36.5	37.4	282.4	0.91

Table VII

Multiple recycling of Coralene Navy Blue 3G

	L	a	b	C	h	DE $CMC_{2:1}$
Fresh Water Dyeing	34.67	-2.95	-23.93	26.3	263.5	----
After 1st Permeate	34.54	-2.42	-24.12	26.7	264.8	0.50
After 2nd Permeate	34.75	-3.78	-22.88	26.8	261.9	1.00
After third Permeate	34.86	-3.67	-22.85	26.4	262.0	0.94

Table VIII

Multiple recycling of Foron Rubine S2GFLI

	L	a	b	C	h	DE $CMC_{2:1}$
FreshWater Dyeing	42.04	49.91	7.40	50.46	8.46	--
After 1st Permeate	41.33	47.93	5.73	48.28	6.85	1.23
After 2nd Permeate	41.36	47.91	5.80	48.25	6.90	1.21
After third Permeate	41.43	48.00	5.60	48.33	6.65	1.27

Tables III-VIII shows that there is no problem in dyeing medium shades with permeate from nanofiltration. Thus, when multiple recycling of permeate is done by nanofiltering the exhaust dye liquor, some variation in shades may occur but in most of the medium shades, it is mostly less than 1.0 $DECMC_{2:1}$. Dyeing of dark shades poses no problem in multiple recycling.

In any case, permeate from high pore size nanofiltration (e.g. 250 MWCO) can be used for dyeing medium or dark shades and in any case this permeate is quite suitable for reduction clearing and washing or rinsing. This can give enormous savings of water and prove to be a boon in water scarcity areas.

2.2. Membrane Filtration of effluent generated from reactive dyeing

Exhaust Dye Liquor (EDL) from reactive dyeing usually contains 60-80 g/l salt – either sodium sulphate (Glauber Salt) or sodium chloride. It also contains spent reactive dyes devoid of dye reactive groups and are thus useless for reuse. In addition, some surface-active agents and water softening agents may also be present. When this dye bath is discharged into effluent, it is difficult to get rid of salt and colour due to spent dyes. If sodium sulphate is used which is 50% more expensive than common salt, then the only way available till date was precipitation with lime.

$$Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2NaOH$$

Calcium sulphate is gypsum that must be removed before it hardens and sticks to ETP and is difficult to remove and dispose except for land filling. Sodium chloride is cheaper than Glauber salt and now it is widely used by process houses in India. Present dyeing machinery withstands corrosion by common salt and hence there is no point in using Glauber salt anymore.

Colour from spent dyes, however, just cannot be removed. Charcoal, different wood dust, ashes etc. are some of the adsorbents tried by many workers but their efforts were not successful in bulk[8].

Fresh reactive dyeing was carried out on cotton fabric and the effluent of dyeing was nanofiltered to see whether permeate can be used for dyeing medium shades and the results are given in Tables IX – XII.

It was observed that permeate is not suitable for dyeing pastel shades. To what extent medium and dark shades may be dyed in permeate of exhaust dye liquor is tabulated in Table IX to XII.

Table IX

Multiple recycling of permeate of Reactive Navy Blue HE2R

	L	a	b	C	h	$DECMC_{2:1}$
Fresh Water Dyeing	38.36	2.24	-26.09	26.2	274.9	----
After 1st Permeate	37.75	2.20	-26.62	26.7	274.7	0.44
After 2nd Permeate	39.46	1.73	-26.54	26.6	273.7	0.80
After third Permeate	38.85	1.98	-26.17	26.2	274.3	0.36

Table X

Multiple recycling of permeate of Drimarine Turquoise Blue SG

	L	a	b	C	h	$DECMC_{2:1}$
Fresh Water Dyeing	72.16	-28.72	-19.72	34.8	214.5	--
After 1st Permeate	72.51	-28.88	–20.07	35.2	214.8	0.26
After 2nd Permeate	73.11	-28.05	–19.78	34.3	215.2	0.51
After third Permeate	72.87	-28.29	-19.97	34.6	215.2	0.40

Table XI

Multiple recycling of permeate of Reactive Red HE7B

	L	a	b	C	h	$DECMC_{2:1}$
Fresh Water Dyeing	47.90	57.79	-7/76	58.3	352.4	--
After 1st Permeate	48.25	58.56	-7.25	59.0	352.9	0.43
After 2nd Permeate	48.37	58.41	-7.25	58.9	352.9	0.42
After third Permeate	48.16	57.67	-8.0	58.2	352.0	0.22

Table XII

Multiple recycling of permeate Reactive Yellow HE4G

	L	a	b	C	h	$DECMC_{2:1}$
Fresh Water Dyeing	88.26	-1.30	67.45	67.5	91.1	---
After 1st Permeate	87.58	-0.48	66.24	66.2	90.4	0.67
After 2nd Permeate	87.55	-0.58	66.16	66.2	90.4	0.65
After third Permeate	88.27	-1.31	68.01	68.0	91.1	0.19

It is seen from Tables IX to XII that medium shades can be dyed within the colour difference permissible limit of < 1.0 $DECMC_{2:1}$

Multiple recycling exhaust dye-liquor from a tertiary shades developed from few dyes for fresh dyeing of cotton with a same reactive dyes are shown in Table XIII-XIX. The colour difference recorded in these Tables is in $DECMC_{2:1}$ units. Reactive dyes that need salt in stages and those which can be dyed with salt at start were used.

Table XIII

Evaluation of dyed fabrics using recycled exhausted dye liquor with standard (6.0%) Reactofix Black HEBL

Recycled	**Colorimetric values**			
	L	**a**	**b**	**ΔE**
Fresh water (standard)	20.05	00.97	-15.01	-
First Recycled	19.88	1.03	-13.87	0.82
Second Recycled	19.78	1.09	-13.71	0.95
Third Recycled	20.10	00.47	-13.54	1.15
Fourth Recycled	19.43	0.84	-13.35	1.26

Table XIV

Evaluation of dyed fabrics using recycled exhausted dye liquor with standard (0.5%) Green (Reactofix yellow HE4G 0.35%, Reactofix Red HE7B 0.04%, Reactofix Navy Blue HERI 0.11%)

Recycled	**Colorimetric values**			
	L	a	b	ΔE
Fresh water (standard)	61.93	-05.56	07.30	--
First Recycled	60.70	-05.31	06.59	0.84
Second Recycled	61.40	-04.85	07.31	0.77
Third Recycled	62.72	-06.67	06.24	1.75
Fourth Recycled	60.57	-05.35	07.54	0.67

Table XV

Evaluation of dyed fabrics using recycled exhausted dye liquor with standard (2.0%) Green (Reactofix yellowHE4G 1.4%, Reactofix Red HE7B 0.16%, Reactofix Navy Blue HERI 0.44%)

Recycled	**Colorimetric values**			
	L	**a**	**b**	**ΔE**
Fresh water (standard)	40.84	-05.04	04.91	-
First Recycled	42.88	-03.96	04.16	1.64
Second Recycled	39.54	-04.80	04.82	0.72
Third Recycled	40.25	-05.47	06.06	1.25
Fouth Recycled	40.55	-03.75	04.18	1.47

Table XVI

Evaluation of dyed fabrics using recycled exhausted dye liquor with standard (5.0%) Green (Reactofix yellow HE4G 3.5%, Reactofix Red HE7B 0.4%, Reactofix Navy Blue HERI 1.1%)

Recycled	**Colorimetric values**			
	L	**a**	**b**	**ΔE**
Fresh water (standard)	29.85	-04.04	2.17	-
First Recycled	28.23	-03.35	2.91	1.60
Second Recycled	28.77	-03.92	03.71	1.96
Third Recycled	30.25	-03.13	03.28	1.77
Fouth Recycled	29.69	-03.04	02.10	1.13

Table XVII

Evaluation of dyed fabrics using recycled exhausted dye liquor with standard (0.5%) Coffee (Reactofix yellowHE4G 0.1%, Reactofix Navy Blue HERI 0.17%, Reactofix Orange HE2R 0.23%)

Recycled	**Colorimetric values**			
	L	a	b	ΔE
Fresh water (standard)	51.85	11.03	7.61	-
First Recycled	50.29	11.36	8.39	1.09
Second Recycled	50.37	1139	8.25	1.05
Third Recycled	51.57	11.44	8.01	0.46
Fouth Recycled	51.79	10.91	7.56	0.11

Table XVIII

Evaluation of dyed fabrics using recycled exhausted dye liquor with standard (2.0%) Coffee (Reactofix yellowHE4G 0.4%, Reactofix Navy Blue HERI 0.68%, Reactofix Orange HE2R 0.92%)

Recycled	**Colorimetric values**			
	L	a	b	ΔE
Fresh water (standard)	32.29	8.44	6.37	-
First Recycled	30.88	8.36	5.89	1.04
Second Recycled	31.98	9.81	7.70	1.59
Third Recycled	31.84	9.23	7.15	0.96
Fourth Recycled	32.53	8.78	6.42	0.38

Table XIX

Evaluation of dyed fabrics using recycled exhausted dye liquor with standard (5.0%) Coffee (Reactofix YellowHE4G 1%, Reactofix Navy Blue HERI 1.7%, Reactofix Orange HE2R 2.3%)

Recycled	Colorimetric values			
	L	a	b	ΔE
Fresh water (standard)	24.09	5.26	3.78	-
First Recycled	24.44	5.13	3.94	0.58
Second Recycled	22.28	5.48	4.60	1.66
Third Recycled	25.36	5.54	3.71	0.99
Fourth Recycled	24.05	4.98	3.94	0.47

It will be seen from Tables XIII to XIX that tertiary shades can be dyed within the colour difference permissible limit of < 1.0 $DECMC_{2:1}$

3. Evaluation of properties

One of the questions that arises in dyeing with permeate from EDL is if it affects fastness of dyeing. In case of polyester, sublimation fastness is important while in case of dyeing with reactive dyes fastness to washing and perspiration is important. It was observed that usage of permeate from EDL has no influence on sublimation fastness of disperse dyes on polyester. Table XX shows that in case of reactive dyes also perspiration, washing and light fastness is not affected by the use of permeates of EDL.

4. Characteristic Study of effluents and permeate

Water for textile processing has to meet fairly stringent specifications. It should be free from solid particles in suspension or from material that can give rise to solids during processing and thereby producing stains on end product. Excess acid or alkali can interfere with some textile processes and presence of metals can seriously affect dyeing and bleaching operations. The principle treatments have usually been restricted to filtering to remove suspended solids, correction of pH and removal of metals.

The characteristics study of effluents and permeate obtained from experimental trails are tabulated in Table XXI.

Table XX
Colourfastness Properties

Recycled	Colour fastness properties						
	Perspiration (IS 2454: 2001)			Washings (IS 764:2003)			Light (IS 791:2004)
	Change in Shade	Staining on cotton	Staining on Wool	Change in Shade	Staining on cotton	Staining on Wool	
Fresh water (standard)	4-5	4-5	3-4	5	4-5	4-5	4
1st Recycling	4-5	4-5	4	5	5	5	4
2nd Recycling	4-5	5	5	5	5	5	3-4
3rd Recycling	5	3-4	4-5	5	4-5	5	4
4th Recycling	4-5	2-3	3-4	5	4	4-5	4

Table XXI: Characteristics of effluents and permeate

Sr.No.	Characteristics	Dye Liquor	
		Effluent	Permeate
1	pH Value	Alkaline	Neutral
2	Colour	Pinkish brown	Transparent
3	Total Suspended Solids (mg/L)	185	0.0
4	Total Dissolved Solids (%)	983	0.0
5	Chemical Oxygen Demand (mg/L)	1980	104
6	Biochemical Oxygen Demand (mg/L)	1320	64
7	Dissolved Oxygen (mg/L)	90	81
8	Oil and Grease (mg/L)	350	0.5

There will always be some reject fraction about 15 ± 3% from membrane filtration that may not be suitable for processing or may be harmful for membranes. In such cases, the effluent may be used for non-processing purpose. Only when this also is not possible, can the effluent be sent to ETP on a small sized plant. This fraction is usually less than 10% of the reject fraction. Alternatively, this fraction can be evaporated and incinerated. Thus, of the total quantity of input water, 1.5-2% fraction may have to be discarded. This is a small step towards reducing pollution load as well as water conservation through recycling.

CONCLUSION

Membrane filtration technology has definite utility in reducing the cost of dyeing and reducing pollution. Reactive dyes need 60-80 g/l of salt – usually common salt. 75% - 85% of this salt can be recovered from EDL and first wash liquor free from spent dyes which are rejected as concentrate. This concentrate can be further concentrated and eventually evaporated to dispose off solids by incineration. These solids are non-toxic and except for colour they are harmless. The salt recovered in the process can be recycled.

The age old concept of having huge Effluent Treatment Plants and concentrating all research efforts on efficient washing, new washing machinery development, reduced material to liquor ratio (M:L) for processing are not relevant today. The relevant aspect is to select membrane of appropriate pore size for membrane filtration for specific task. Rather than talking in terms of nanofiltration or ultrafiltration, it is relevant and more scientific to talk in terms of membrane of specific molecular weight cut off (MWCO) for specific task.

REFERENCES

1. A.D. Sule, and J.S. Sawant, Colourage, Vol-50, No.8, 2003, pp 29.
2. A.D. Sule, and J.S. Sawant, Colourage, Vol-50, No.9, 2003, pp 37.
3. A.D. Sule, and J.S. Sawant, Colourage, Vol-50, No. 7, 2003, pp 45.
4. A.D. Sule, and M.K. Bardhan, Indian J. of Fibres and Textile Research, Vol-26, 2001, pp 223.
5. A.D. Sule, and M.K. Bardhan, The Indian Textile Journal, 2004, pp 13.
6. N. Manivasakam, Treatment of Textile processing of effluents, Sakthi publications, Coimbatore, 1995.
7. Padma Vankar, Textile effluents, Ministry of Textile Publications, New Delhi, 2002.
8. Manisha Mathur & Purnima Chauhan, Express Textiles, Jan 31, 2002.