EFFLUENT RECYCLING USING MEMBRANE SEPARATION

Beginning of twenty-first century has witnessed unprecedented interest in membrane separation based effluent recycling systems in India and China. Scarce availability of water, strict environmental laws or lack of disposal option has generally governed this interest, but at the same time, reduction in cost of components and lowering of import tariffs has also helped the cause. While many large plants in excess of 10 MLD capacities are already working successfully for many years, the concept of membrane-based recycling system is now increasingly being adopted by small to medium scale industries also. Membrane Separation Technology has very promising future in the field of effluent recycling, resource recovery and waste concentration.

Manufacturers with experience of water treatment using Reverse Osmosis but no exposure to effluent treatment have failed in their initial efforts while attempting to handle effluent recycling. Industries have been often misguided and confused about type of membrane process that can be used for their particular application. This article aims at creating basic understanding about types of membranes and their application, system configuration, recoveries and rejects and pre-treatment requirements.

Membrane Processes

Based on the pore-size of thin membrane film and corresponding rejection extent, the membrane processes are divided into four groups.

(a)	Microfiltration	:	Pore Size	0.07 microns to 2 microns
(b)	Ultrafiltration	:	Pore Size	0.002 microns to 0.1 microns
(c)	Nanofiltration	:	Pore Size	0.001 microns to 0.07 microns
(d)	Hyperfiltration (Reverse Osmosis)	:	Pore Size	<0.001 microns

FILTRATION SPECTRUM			
PROCESS	**RANGE**	**MOLECULAR WT.**	**EXAMPLES**
Particle Filtration	More than 1✪	-	Suspended Solids
Microfiltration	0.07 – 2 ✪	>100,000	Bacteria, Pigments, Oil
Ultrafiltration	0.002 – 0.1 ✪	10000 – 200,000	Colloids, Virus, Protein
Nanofiltration	0.001 – 0.07 ✪	180 – 15,000	Dyes, Pesticides, Divalent Ions
Hyperfiltration (Reverse Osmosis)	Less than 0.001 ✪	<200	Salts & Ions

Microfiltration generally finds application in drinking water filtration in lieu of conventional clarification and gravity filtration. The flux rates (output per membrane or per unit area) are high and pressure requirement is very low, typically less than 2 bar.

From the viewpoint of effluent recycling or recovery from waste, the other three membrane processes have greater significance. Proper use of either or combination of these processes can reduce the waste quantity and provide higher recoveries at lower operating costs. Interestingly, the desired product can either be permeate or concentrate, depending on the application.

COMMON MEMBRANE APPLICATIONS			
TYP.	**FEED**	**PERMEATE**	**CONCENTRATE**
UF	Milk	Lactose Solution	Protein For Cheese
	Whey	Lactose Solution	Whey Protein
	Antibiotics	Clarified Broth	Waste
	Oil Emulsion	Oil free Water	Concentrated Emulsion
	Colloidal Effluent	Clear Effluent	Concentrated Colloids
	ED Paint Stream	Clear Water	Paint Pigment
NF	Whey	Salty Waste Water	Salt free Concentrate
	Salted Dye ML	Salty Waste	Product Dye
	Hard Water	Soft Water	Concentrated Hardness
	Antibiotics	Salty Waste	Salt free Antibiotics
RO	Saline Water	Salt free Water	Concentrated brine
	Clear Effluent	Clear Water	TDS, Colour, COD, Waste
	Waste Stream	Clear Water	Concentrated Waste For Evaporation / Incineration

<u>Ultrafiltration</u>

Ultrafiltration can be used for following purposes:

(a) To remove fine colloidal solids from effluent, thereby removing turbidity, colour and COD
(b) To remove emulsified oil and polymers from effluent
(c) To remove toxic organics with molecular weight of more than 10000 Daltons from the effluent and make it amenable to biological treatment
(d) To concentrate segregated streams having waste with more than 10000 Dalton MW, whereby the concentrate can be disposed using evaporator or incinerator
(e) As a pre-treatment step prior to Reverse Osmosis so as to eliminate chances of any colloids reaching the sensitive RO membranes

Depending upon pore size of membranes employed, ultrafiltration removes organics above 10000 to 200,000 Dalton molecular weight only. It is not useful in removing COD or colour if the constituents have lower molecular weight.

The most rugged, but the most expensive membrane configuration for ultrafiltration membranes are Flat Sheet (Plate & Frame) and Tubular membranes. Tubular membranes, especially, can tolerate high turbidity in the feed and are robust systems. Because of the very high cost, their application is limited to smaller flows of segregated streams. The operating pressures are higher compared to other configurations and so is the operating cost. Permeate recoveries are lesser than spiral-wound membranes in Christmas-tree pattern. Few manufacturers provide flat sheet or tubular membranes, and some deal only in specialized applications like pharmaceutical processes.

Hollow Fibre Ultrafiltration membranes having bundle of tubes/capillaries of less than 2mm size are widely available but have limited solids and turbidity handling capability. The feed water needs to be pretreated to remove suspended solids and fibres. These membranes are prone to fouling due to organics and have to be designed for continuous or intermittent purge and need to be backwashed with chemicals twice or thrice a day. The in-to-out membranes with bore size of about 1.5mm can withstand higher TSS and Turbidity, and so can out-to-in type Hollow-fibre capillaries, aided by air scouring.

Spiral-wound configuration is also not so popular in recycling applications. These membranes are best used for removal of bacteria in drinking water applications or in applications with lower recoveries.

UF membranes are available in a variety of material like polysulphone, cellulose acetate, composite polysulphone, PVDF, Ceramic etc. Polysulphone and composite polysulphone are more prevalent and cheaper than others. PSO membranes can not tolerate oil and solvents while composites can not tolerate oxidizing environment.

Nanofiltration

Nanofiltration can be used in waste treatment applications in following area:

(a) Removal of dissolved organics and hardness in cases where only partial removal of TDS and removal of colour, COD and hardness is sufficient to render the permeate reusable.

(b) Recovery or removal of organics with molecular weight more the 300 from salt solution.

Nanofiltration is often confused to be more tolerant to fouling than Reverse Osmosis, which is not the case. The advantage of Nanofiltration is that since it rejects only larger molecules and divalent ions and only partially rejects smaller monovalent ions, the feed pressure to the system is less, and so is the operating cost. This is possible only when the effluent is of low TDS (<1000 mg/L) and permeate with little lesser than feed TDS but without colour, COD and hardness, is acceptable for reuse.

Feed water to the Nanofiltration system should be of similar quality as in Reverse Osmosis. Turbidity and Colloids, as indicated by Silt Density Index should be within permissible limit of 4.0. The presence of carbonates and silica has to be dealt with. The feed should be disinfected for removal of microorganisms. Biodegradable organics should be totally removed if possible. Organics with fouling tendency should also be removed.

Nanofiltration membranes are generally available in cellulose acetate and composite polyamide material and most commonly used as spiral-wound configuration. These membranes are more expensive than RO membranes because of lower volumes of production.

Reverse Osmosis

Reverse Osmosis is the most widely and least expensive desalination process, and preferred system for removal of dissolved salts from brackish or sea-water. About 85% of membranes used worldwide are for RO applications. RO implies the finest level of filtration wherein only water and very low molecular weight compounds (<40 Dalton) pass through as ions.

Reverse Osmosis can be used as end-of-the-pipe recycling system for effluent treatment. After conventional physico-chemical, biological and tertiary polishing treatments, further removal of refractory organics and dissolved salts can be achieved using RO System. In the process, permeate produced from the system is of very high quality and can be recycled for the manufacturing and utility operations. The reject stream from RO system is concentrated with dissolved salts and organics and needs to be disposed by evaporation and/or incineration.

Similar to membranes used for Nanofiltration, RO membranes are highly susceptible to fouling due to organics, colloids and micro-organisms and scaling due to hardness, carbonates and silica. Heavy metals and oil should be totally absent in the feed and there should be no oxidizing chemical like free chlorine or ozone that can damage the membranes. Thus, feed effluent to RO System should be subjected to extensive treatment to bring it as close as possible to "brackish water", with only TDS as the contaminant. Practically, in effluent recycling applications, it is not possible to achieve zero organics and zero micro-organisms, while inorganics like calcium, magnesium, carbonates and silica can either be controlled by pre-treatment or limiting the recoveries. Prudent approach in terms of controlling fouling is to provide extended aeration bio-treatment, chlorination or ozonation, filtration and activated carbon adsorption with a view to bring down at least the BOD to less than 10 or preferably 5 mg/L. The organics, which are not removed in such extensive pre-treatment, are generally well rejected by RO membranes.

The membranes eventually get fouled with some organics, which are deposited on membrane surface and are cleaned by circulating cleaning chemicals. Once the pre-treatment is operated well, the frequency of fouling is less and hence cleaning requirements are fewer. Repeated cleaning reduces the useful life of the membranes. Depending on the characteristics, membrane life of 2 to 5 years are possible.

Recovery in Reverse Osmosis, i.e. amount of permeate per feed, is limited by feed TDS, Hardness and Silica. Normal Spiral-wound Membranes cannot handle pressures in excess of 75 bar, which correspond to handling osmotic pressure of 60-80,000 mg/L TDS depending upon type of salts. Thus, a feed of 3000 mg/L TDS can be recovered 95% and requires a two—stage system for such high recovery. The first stage would employ brackish water membranes with pressure upto 40 bar while second stage will use sea-water membranes. However, TDS is not the only governing parameter for recovery. Concentration of calcium, magnesium and barium salts (sulphates), carbonates and silica in the final reject determine scaling potential of brine and limit the recovery, unless treated. Silica can not be selectively removed and has a saturation limit of 140 ppm in the reject brine. Addition of special antiscalants can permit higher silica in the reject.

Reverse Osmosis Systems can be designed with considerable precision based on effluent analysis using computerized projections from membrane manufacturers. Use of these computer programs needs expertise, as lots of permutations are possible while deciding the system configurations. Such programs require many inputs from designer hence optimization in terms of recovery, no. of passes, no. of membranes, operating pressure, etc. is a skill. Careful considerations are required for saturation indices, concentration polarization and flux levels to develop the best configuration for given application.

Ultrafiltration and Nanofiltration system are best designed after pilot trials to determine levels of recovery and quality of product and reject. Unfortunately, since each trial requires use of at least 4 to 5 different types of membranes, the cost of trials runs high. Such trials become affordable only for larger plants and where enough time is available before the full scale project.