

Zero Liquid Discharge Technologies Guidance Manual



Gujarat Pollution Control Board

Prepared by

**ILFS Academy of Applied Development
(IAAD)**

ZLD Guidance Manual

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1. INTRODUCTION

Due to water scarcity, unavailability of disposal points for waste water and stringent regulations, Zero Liquid Discharge (ZLD) concept is widely accepted by industries. There are various challenges to implement this concept including technology selection and techno-commercial feasibility of ZLD scheme. This manual provides guidance for ZLD technology selection with tentative costs involved for various sectors of industries.

1.1. ZLD Globally

In the early seventies, increased salinity of the United States Colorado River, due to Power Plant discharges, created the regulatory context to push for ZLD in the US. ZLD was apparently born in USA, driven by the regulator. Regulations were mainly concerned with power plant discharges from cooling tower blow downs and scrubbers. First ZLDs installed were 500 - 2,000 GPM units based on evaporation/crystallization

For new industrial projects, an approval for a discharge agreement might traditionally take five years, with ZLD it could be a matter of 12 months. As a result, ZLD technology effectively evolved in the US and later grew globally. Initially after RO low cost evaporation ponds were used for RO reject evaporation.

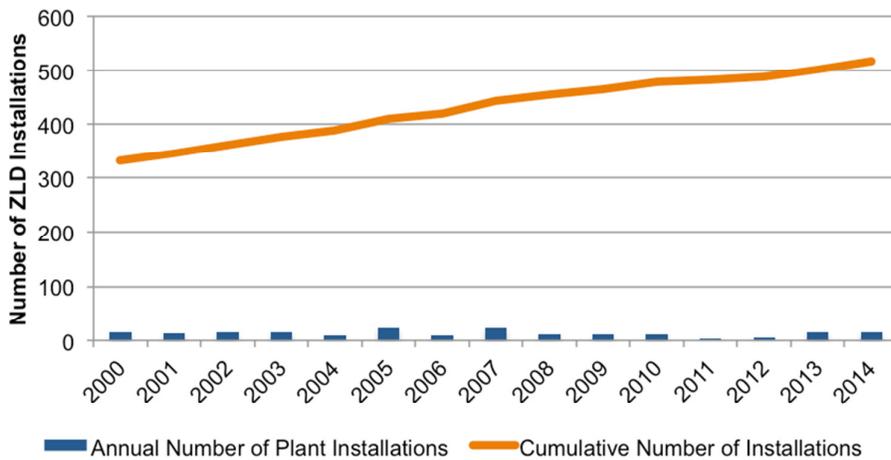
In Germany, stringent regulation in the 1980's resulted in ZLD systems for Coal Fired Power Plants. *(GWI)*

According to a December 2009 study by Global Water Intelligence (GWI)³, today there are thousands of evaporator/concentrator systems around the world in a large range of industries. Worldwide

construction of ZLD equipment represents an average of 100 to 200 million USD of investment annually.

ZLD technology has been mostly developed in Western countries for power plants, but is spreading widely to drought stricken regions such as the Middle East and to highly pollution sensitive environments. Indeed, countries such as China and India where water is scarce and the industrial water recovery ratio is relatively low are potential candidates for the development of ZLD solutions.

The following graph shows cumulative number of ZLD facilities between 2000 and 2014. This indicates that the market is somewhat 'lumpy' with a varying number of plants year. While the cumulative number of installations is building, there is no 'inflection point' visible yet based on the data. The market is however likely to see an increase in activity based on general market trends, a move on the part of industry to minimum liquid discharge and issues around brine management linked to increases in desalination capacity.



Ref : [1]

1.2. ZLD in India

Several states in India including Tamilnadu are water stressed. Competing demands for water from agriculture and domestic use has limited industrial growth. TN has taken a lead on ZLD due to absence of fully flowing perennial river. Most rivers originate from neighbouring states and water sharing is in disputes. Water scarcity, water economics and regulatory pressure are main drivers of ZLD in India. Other States such as Gujarat and Karnataka are going for ZLD concept.

Tirupur Textile CETPs and Tannery CETPs at Chennai have adopted Zero Liquid Discharge concept on large scale.

1.2.1. Textile CETP ZLD at Tirupur

Tirupur is dry region with no perennial rivers. Today Tirupur hosiery and knit wear export contributes nearly 2% of total foreign exchange earnings of the country. Based on the directions of the Madras High Court and TNPCB in 2005, the bleaching and dyeing units in Tirupur implemented CETPs to meet the Zero Liquid Discharge (ZLD) norms. 450 units collectively have set up 20 CETPs while balance 150 units have set up their own individual effluent treatment plants (IETPs). Tamilnadu Water Investment Company Limited (TWIC) was engaged by 9 CETPs. The total investment in this treatment system is estimated to be Rs.800 crores (for 20 CETPs). This investment has been largely funded by the bleaching and dyeing units (20 to 30%) and the balance has been arranged through commercial banks as loans (70 to 80%).

The total effluent treatment capacity of these nine CETPs is 53,000 cum per day, forming the majority of the effluents generated in Tirupur. The cost of this project was Rs. 4200 millions. The Pre-

treatment Section and R.O successfully commissioned and operated since October 2008 in TWIC CETPs. Evaporator commissioned after receipt of TNPCB CTO in Jan 2010. The evaporator which has been installed did not meet the desired requirements and consequently industries had been facing difficulty in operating the ZLD project to full capacity. All the units were closed by High Court Order of 31st January, 2011. Units were reopened with demonstration of modified "Brine Use Technology" and providing additional units in existing treatment.

1.2.2. Tannery CETP ZLD at Chennai

Ambur Economic Development Organization Limited has installed three CETPs of tannery waste water with capacities ranging from 1 MLD to 4 MLD (combined capacities of 7.2 MLD) in Ambur and Vaniyambadi Tannery cluster. These CETPs have Membrane Bio-Reactor as pre-treatment for RO systems and Evaporator for RO reject management. The project cost of approx. Rs. 1000 Million was financed through a mixture of Government grant (50%) commercial loans (25%) and industry contribution (75%).

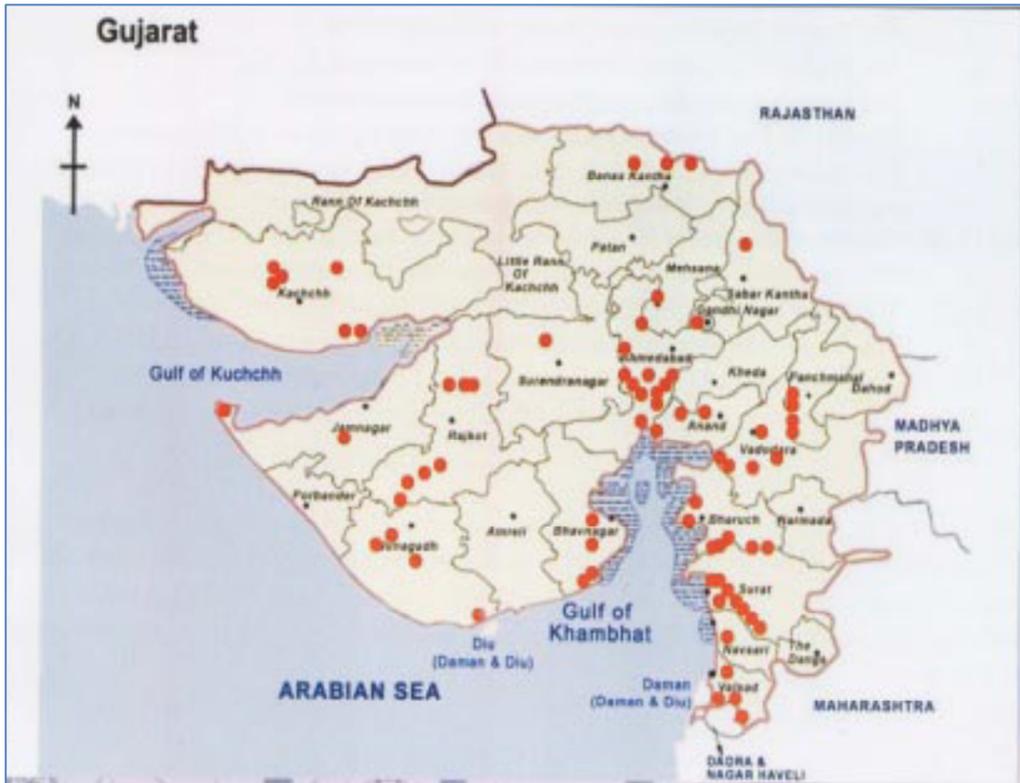
Apart from this many large individual industries like automobile industries, Oil refinery, Steel industries have adopted ZLD to save water, recover valuable product and reduce disposal cost.

In China, a chemical company Yunnan Yuntianhua (YTH Group) for a Coal-to-Chemicals plant in an environmentally sensitive location, one of the largest grasslands in China has gone for ZLD.

1.3. Zero Liquid Discharge (ZLD) in Gujarat

Gujarat state is one of the most developed states of the country and is a leader of industrial development. An entrepreneur skill along with

investor friendly policies of the state has resulted in rapid industrialisation of large number of small and medium scale industries. A state has more than 3 million industries located across 257 industrial estates developed by GIDC.



Ref: [2]

Fig 1 : Location of major Industrial Estates in Gujarat

To overcome operational problems of effluent treatment plants of individual industries Common Effluent Treatment Plant (CETP) near vicinity of cluster of industries were introduced in 1990. Currently 30 CETPs are operational in state, while 7 CETPs are in construction / commissioning stage. The concept of CETP helped to reduce financial as well as manpower burden on individual industry.

1.3.1. ZLD Concept Initiation

Gujarat State has concentration of industrial units in certain areas, which have more pollution potential. In 1997, H'ble High Court order (PIL, for pollution of chemical industries in Ahmedabad), Environmental Audit Scheme was introduced by GPCB for Schedule I and Schedule II industries. Yearly Environmental Audit is made mandatory by authorised auditors. The objective was regular monitoring with a perspective of environmental protection, & sustainable development.

In 2010, after declaration of critically polluted areas by OMs of MoEF, GPCB started quick actions, expanded its infrastructure, declared main points to control pollution at source. Action Plan was prepared for declared critically polluted areas, e.g. Ankleshwar, Vapi, Ahmedabad, Vatva, Bhavnagar and Junagadh. Action Plan was implemented in consultation with stakeholders and necessary directions were issued.

Zero Liquid Discharge (ZLD) concept was included in Action Plan as follows:

- Big units (discharge >100 KLD) should have their own incinerator/ evaporator/ dryer/solvent distillation plant, acid handling or recovery plant etc to make the treated waste reusable or to reduce the load on ETP or CETP.
- All units including zero discharge units should have pH correction and SS removal system, so that they cannot discharge any acidic effluent to CETP or to any unauthorized disposal point. Where spent or mixed acid is generated in large quantity, plan for its recovery or re-use or to send it to authorized place will be required.

- CETP will be required for each industrial cluster for effluent treatment and safe disposal. No direct discharge in GIDC pipeline or any disposal point will be permitted. Narol, Jhagadia, Khambhat, Dahej, Vilayat, Sarigam, Jetpur, Junagadh, Jamnagar etc. need CETP on this principle.

A time bound action plan was asked to concerned industries to install multiple effect evaporator/RO system/Incinerator System/ New technology including cleaner production and cleaner technology.

A seminar was organised on by GPCB jointly with IL&FS Academy of Applied Development (IAAD) on “Zero Liquid Discharge – Policy Experience and Emerging Technologies” to exchange the knowledge regarding ZLD.

1.3.2. Gujarat Today

GPCB has taken concrete steps to implement recycling, reusing and recovering product from industrial waste. Currently 30 CETPs in GIDC industrial estates are operational in state, while 7 CETPs are in construction / commissioning stage (*GPCB Annual report 2013-14*). Many industries are directed to segregate high strength wastewater and treat separately. CETPs are also going for ZLD concept. E.g. Naroda, Ankaleshwar CETP, Zydus SEZ CETP, etc.

All pharmaceutical (API manufacturing) industries, dyes & Dye intermediates industries and pesticide/chemical manufacturing industries are directed to install captive incinerator for high strength waste. Apart from 8 common hazardous waste incinerators, there are 89 captive incinerators in various industries.

[2]

Beyond pollution compliance concept emphasis was given on recover and recycle of useful material from waste. Due to water scarcity, strong enforcement of environmental regulations, unavailability of disposal points, many industries have adopted ZLD technologies. By adopting ZLD, industries are saving water, recover valuable products and protecting environment in large.

Multiple Effect Evaporator (MEE) is finding its place in ETPS in last few years. Gujarat has widely accepted this concept and industries are using MEE for concentrated streams by reducing load of ETP. There are 147 captive Multi Effect Evaporators (MEE) units [2] in industries, which itself is a great initiative towards recycle and recover.

Another concept is co-processing of hazardous waste in cement industry as supplementary resources or for energy recovery. GPCB has taken good initiative and directed many industries to send their wastes for co-processing at cement mills. Cement mills are also convinced to come forward for more and more co-processing of waste in their kilns. Till March, 2014; 935635MT waste have been processed in cement industry [2]. Authorities of the Cement plants in the State have prepared action plan targeting 10 % fuel requirements substitution in the next three years.

Spent acid recovery plant is another initiative in Gujarat. Spent sulphuric acid is generated in the industrial units involved in the manufacture of dyes, dye-intermediates and other chemicals where sulphuric acid or oleum are used as raw materials. The concentration of sulphuric acid in the spent acid is normally in the range of 10-30%. The individual industries find it difficult to store, handle or treat it effectively. Novel Spent Acid Management is established to segregate and collect spent acid received at site in

different tanks depending on the concentration of sulphuric acid and other properties. Supply colourless and concentrated spent acid as raw material in the process or as neutralizing agent in the treatment of wastewater & hydrated lime for the production of Gypsum which is supplied to the cement manufacturing plants to manufacturers of ferrous sulphate, alum, single super phosphate etc. Naroda, Odhav and Vatva industrial estates are working together for putting up spent acid recovery and disposal plant. Spent solvent is sold to consented reusers only.

1.3.3. Challenges in Gujarat

ZLD challenges

Drivers of ZLD are:

- Stringent Environmental regulations on discharge of specific pollutants
- Water scarcity in most of the areas
- Economics : Recycled water becomes more economical than disposal of water and buying water from Municipal Corporation
- Recovery of useful material
- Growing social responsibilities towards environmental issues

Challenges for ZLD are:

- Very high capital cost and operational cost (Capex and Opex)
- Technology selection is a big challenge. ZLD scheme varies from case to case basis. Therefore, technical experts for customised design experts on case to case basis are required for successful ZLD.
- There is difficulty to deal with very complex streams from petrochemical or pharmaceutical industries. There is need of

integration of suitable technologies to achieve recycle, recovery, reuse and reduce.

- Stringent regulations are forcing industries to install ZLD, however, Technical guidance is not available for industries.
- Industries are reluctant to install ZLD due to high Capital cost and Operational Cost. A financial feasible model shall be developed to overcome this problem.

2. ZLD TECHNOLOGIES

2.1 What is ZLD?

Zero Liquid Discharge (ZLD) means zero discharge of wastewater from Industries. ZLD system involves a range of advanced wastewater treatment technologies to recycle water, recovery of useful material and reuse of the treated wastewater and thereby ensure there is no discharge of wastewater to the environment.

CPCB Draft Guidelines, January, 2015; define 'ZLD' as follows:

Zero Liquid discharge refers to installation of facilities and system which will enable industrial effluent for absolute recycling of permeate and converting solute (dissolved organic and in-organic compounds/salts) into residue in the solid form by adopting method of concentration and thermal evaporation. ZLD will be recognized and certified based on two broad parameters that is, water consumption versus waste water re-used or recycled (permeate) and corresponding solids recovered (percent total dissolved / suspended solids in effluents).

In the above ZLD definition, domestic wastewater from industry is separated from industrial wastewater and treated separately. However, recycle / disposal of domestic wastewater is not mentioned.

ZLD is applicable to industries generating wastewater of high BOD and COD load, colour bearing effluents, having metals, pesticides, toxic / hazardous constituents, solvents and High TDS. However, considering water scarcity and reject water / sludge disposal cost, many industries are adopting ZLD irrespective of nature of effluent.

2.2 ZLD Technologies

Zero Liquid Discharge refers to processes that fully removes water from the concentrate stream (in other words, no liquid is left in the discharge). The end product of a ZLD system is a solid residue of precipitate salts that needs to be reused or transferred to an designated solid waste disposal facility for landfill.

ZLD systems range from less complex to highly complex system depending on the nature and various streams of wastewater. Ultimate aim of ZLD system is to recover useful products, recover maximum water for recycle and recover useful salts from rejects. Following are the major ZLD technologies which are used in combination as per requirement:

- Solvent Extraction / Stripper
- Membrane Bio Reactor Technology (MBR)
- Ultra Filtration (UF)/Reverse Osmosis (RO)
- Evaporation Technologies (Multi Effect Evaporators -MEE/
Mechanical Vacuum Re-compressor (MVR)
- Crystallisation / Agitated Thin Film Dryer (ATFD)
- Incinerator

2.2.1. SOLVENT STRIPPER

Solvent recovery from industrial wastewater is usually done by two methods:

- Air stripping
- Steam Stripping

Objectives of treatment are either recovery of solvent or removal of solvents from wastewater to make easy treatment and disposal.

Air Stripping

Many organic solvents are removed from wastewater by air stripping. This applies particularly to solvents that have low solubility in water or a high volatility with respect to water. It is essential to provide air stripping before biological treatment for better efficiency of treatment. Solvent removed from water by air stripping is recovered by adsorption on activated carbon. This method is used only when less quantity of solvent is present in water. Air stripping batch reduces solvent content of water to less than 100mg/l (w/w) and many cases up to 20mg/l. Presence of inorganic salts may affect the efficiency of air stripping. To reduce solvent concentration by 1 mg/l (from 21mg/l to 20mg/l), 1m³ air is required for 1 m³ of water.

Steam Stripping

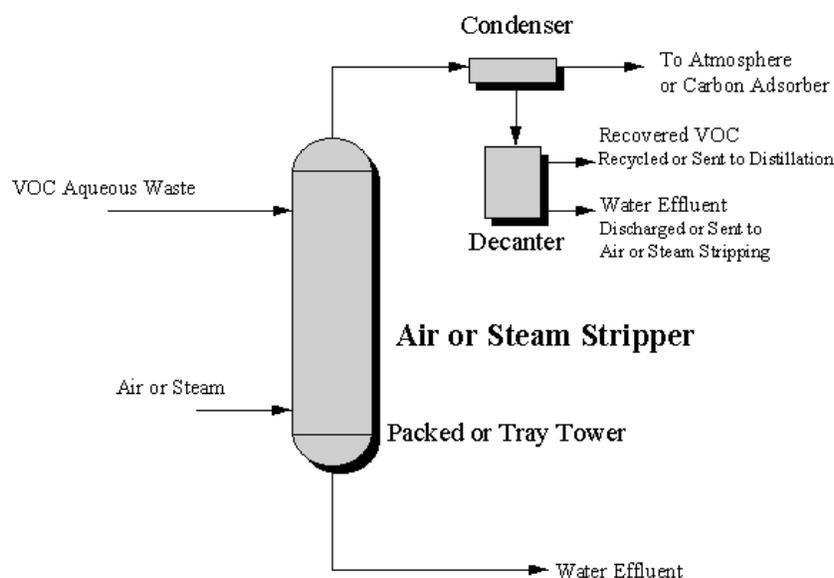
The disadvantage of air stripping as a means of solvent recovery is low concentration of solvent in effluent air, which is difficult to capture. Steam stripping though requires elaborate plant for stripping, needs very simple equipment for trapping the stripped solvent.

In steam stripping, a wastewater stream is heated and put in intimate contact with steam in a packed or tray tower. The combined effects of the steam and heat, or temperature cause organic material to transfer from the liquid to the vapour phase. This material is then carried out with the vapour.

Steam costs are modest provided that good heat exchange is maintained between hot stripped water being discharged and feed to stripper.

It is easy to strip VOC's by this method if they have lower boiling points than water or have limited solubility in water. The concentrated organic product generated by the steam stripping operation is a distillate stream.

Figure 2.1 A typical Air / Steam Stripper



Combination of effluent clean-up and solvent distillation shall be considered in the design of steam stripper. For water miscible solvents like methanol, acetone, etc. the conversion of the stripping column into a fractionating column give rise to few

problems. Similarly, the solvents that are sparingly water miscible can be passed through decanter and the water phase returned to stripper feed. Combination of stripper and distillation unit is favoured when very consistent flows of effluent both quality and quantity are to be processed.

A steam stripping is not suitable for water miscible, high boiling solvents. Steam stripping may give rise to scaling problems at the end of column. A facility to clean scaling or bypassing scaling shall be provided.

Solvent Recovery Columns:

There are two types of columns used in steam stripper.

1. Packed column
2. Grid Column(Tray Tower)

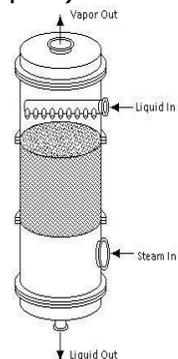
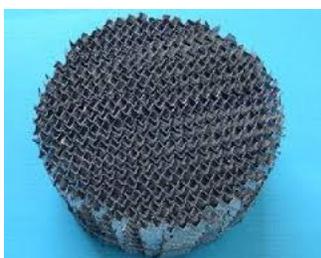
Comparison of Packed column and grid column in solvent stripper:

Sr. No.	Packed Column	Grid Column
1	As only one feed inlet is possible, the column needs to operate at design conditions, giving no flexibility	The column can have multiple feed inlets, providing operational flexibility depending on variation in the feed condition
2.	Being a packed column, the pressure drop is greater and results in a higher steam requirement	The pressure drop is comparatively lower than the drop in the packed column. Hence, less steam is consumed
3	Packed columns have a narrower operating range	Tray columns have a wider operating range
4	If liquid flow rate is too low, the wetting of the packing material may not be adequate	If the liquid flow rate is too high, treatment is tray columns is more economical

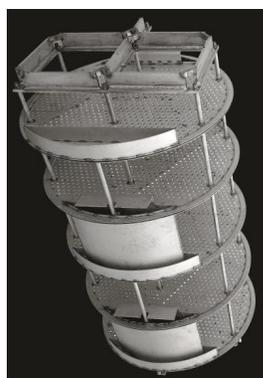
5	If solid particles are present in the liquid, cleaning a packing section is complicated and expensive	Tray columns can handle suspended solids without performance being affected
6	When stressed by temperature variations and pressure, the packing elements are easily breakable	Trays made up of SS316, therefore breaking due to temperature and pressure will not occur
7	Packed columns possess no special design elements for addressing TSS handling	Tray columns are specially designed for more effectiveness

Ref: [3]

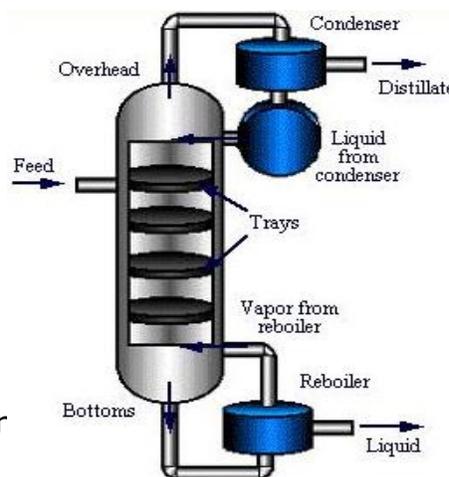
Three factors contribute to economics of solvent stripping as regards ZLD are: Treated water reuse/ recycle potential, Cost of recovered solvent and treatment cost (Capex/opex).



Packed Bed Column media



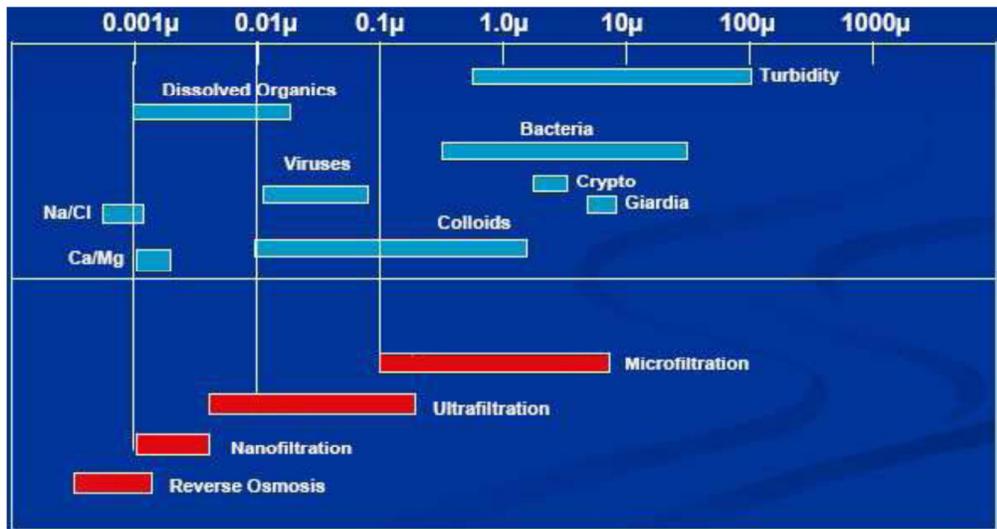
Tray Tower



2.2.2. MEMBRANE BIO-REACTOR (MBR)

Membrane Bio Reactor (MBR) is a process where Microfiltration (MF) /ultrafiltration (UF) membrane is used. MF/UF are low pressure driven processes, where feed water is driven through a micro-porous synthetic membrane and divided into permeate, which passes through the membrane, and retentate or reject containing the non-permeating species. In wastewater treatment applications, these membranes process are more effective in removal of particles and microorganisms.

Figure 2.2 gives Membrane filtration spectrum which illustrates the size range of various impurities and the application range of the membrane processes.



Membrane Bioreactor (MBR) systems essentially consists of combination of membrane and biological reactor systems. These systems are the emerging technologies, currently developed for a variety of advanced wastewater treatment processes.

MBR system is essentially a aerobic biological system where air is provided through diffuser membranes for growth of biomass

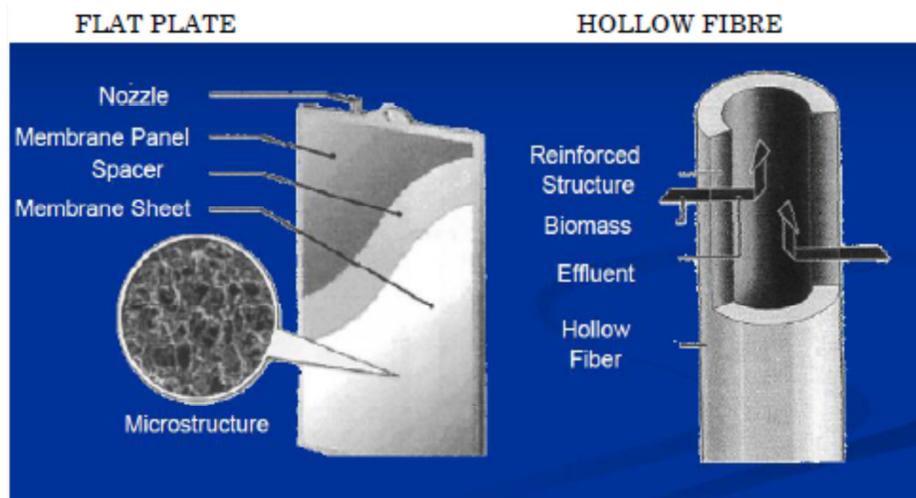
(MLSS). Then wastewater passes through MBR membranes. Therefore, secondary clarifier is not required. Treated water quality is as good as filtered water from sand filters.

MBR Membranes:

MBR membrane pores form barrier to impurities (Suspended and colloidal particles and bacteria, viruses) while allowing water molecules to pass through. Water is drawn through the pores using a gentle suction.

There are two types of membranes. Flat Plate and Hollow Fibre membranes.

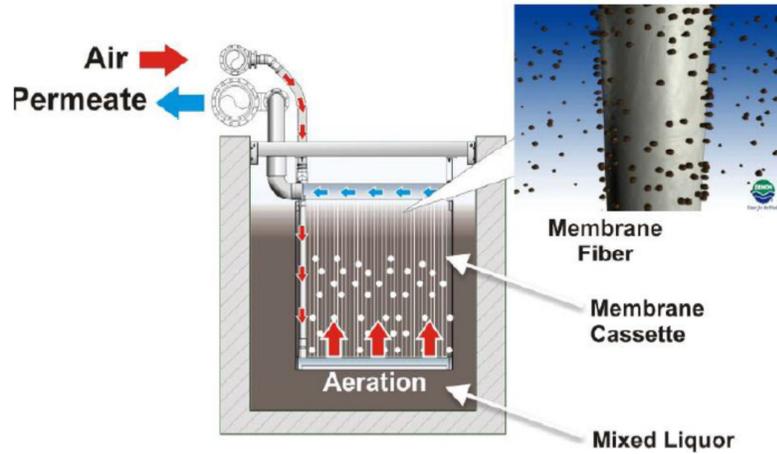
Flat plate membrane sheet is placed on flat plate, while hollow fibre membranes have reinforced structure in the form of fibre.



Hollow fibre membranes are usually used in MBR systems. Modules of MBR are made up of thousands of membranes.



MBR System Schematic Flow Diagram

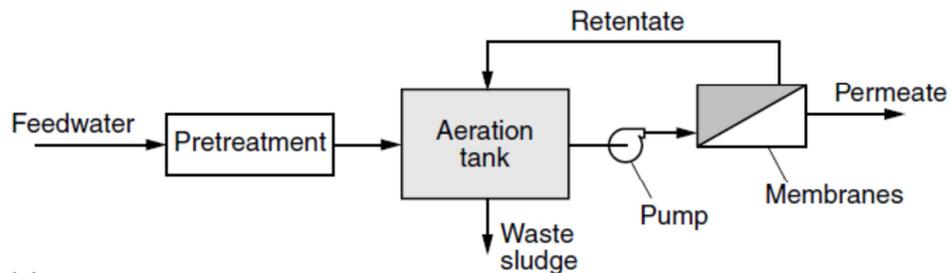


There are two configurations of MBR membranes:

- A. External Membranes
- B. Submerged membranes

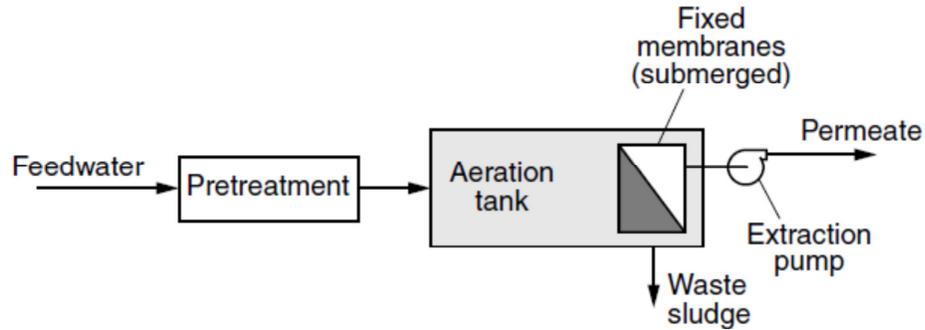
A. External Membranes

External membranes are pressure driven and commonly come in tubular form. They are placed outside the aeration tank.



A. Submerged Membranes

Submerged membranes are submerged inside the aeration tank and are usually vacuum driven.



Operation of MBR

MBR can be operated on either constant trans-membrane pressure (TMP) or constant flux through membrane (constant flow). Constant flux is preferred, since it gives consistent outlet flow.

Vacuum $< 0.5 \text{ kg/cm}^2$ ($< 50 \text{ kPa}$) draws water through membrane, solids retain in the reactor. At the base of the module, there is an air distribution manifold. Air provides oxygen, helps to maintain TSS in suspension within the bioreactor and cleans exterior of membrane surface.

While operating MBR system, continuous backwash is required for membranes after every 10-15 min, and it is done by in-built program of MBR system.

Cleaning of membranes periodically is required. Cleaning chemicals dosing system is to be provided.

MBR operates at higher Mixed Liquor Suspended Solids (MLSS) concentration in MBR Aeration tank than conventional ASP.

- Mixed Liquor Suspended Solids (MLSS) in MBR Tank :
5000 – 16000mg/l
- Treated water Quality:
 - BOD – $< 5 \text{ mg/l}$

- TSS - <1mg/l
- Turbidity - <0.2mg/l

	ASP Treated Effluent	MBR Treated effluent
TSS, mg/l	<30	ND(<2)
Turbidity, NTU	2 to >10	<0.2
Total Coliform, no/100ml	10,000 to 1,00,000	ND to 100
BOD, mg/l	<10 to 30	ND to <5mg/l

Note : MBR process does not remove TDS of wastewater. Therefore, TDS of inlet wastewater remains unchanged.

Membrane flux rate (L/m²h) is an important design and operation parameter. Lower flux rates at higher MLSS.

Fine air bubble diffusers or coarse bubble aeration system is used as per technology provider's design.

Advantages of MBR Sytem

- Secondary Clarifier is not required
- MBR system required smaller foot print than conventional ASP, SBR systems.
- Complete retention of suspended solids and most soluble compounds due to membranes. Post treatment of sand filters can be eliminated
- Independant control of hydraulic and solid retention times
- Ability for slow-growing species to grow (nitrifying bacteria, etc.)
- High loading rate capability
- Combined COD, solids and nutrients removal
- Low sludge production and high SRT
- Eliminates problems of sludge settling, etc
- High biomass (MLSS) concentrations

- Bulking or rising sludge not problem
- Effluent disinfection takes place due to removal of bacteria and viruses

Disadvantages of MBR System

- Membrane costs are very high, therefore MBR system capital cost is high.
- Operational problems due to Membrane complexity and Membrane fouling
- Pretreatment of feed or back flushing with water/air or chemical cleaning is used.
- Operation and maintenance
 - High Energy costs due to high recirculation of inlet flow
 - Replacement of membranes cost
 - Aeration limitations
- Energy consumption is two to four times higher than conventional treatment.

International Leading Manufactureres and comparative data

- Zenon Environmental Inc. (CANADA) (Hollow Fiber)
- General Electric (Hollow Fibre)
- Mitsubishi Rayon Cooperation (JAPAN) (Flat Plate)
- Kubota Cooperation (JAPAN) (Flat Plate)
- US Filter (USA) (Flat Plate)
- Koch Membranes (Hollow Fiber)
- Hydranautics

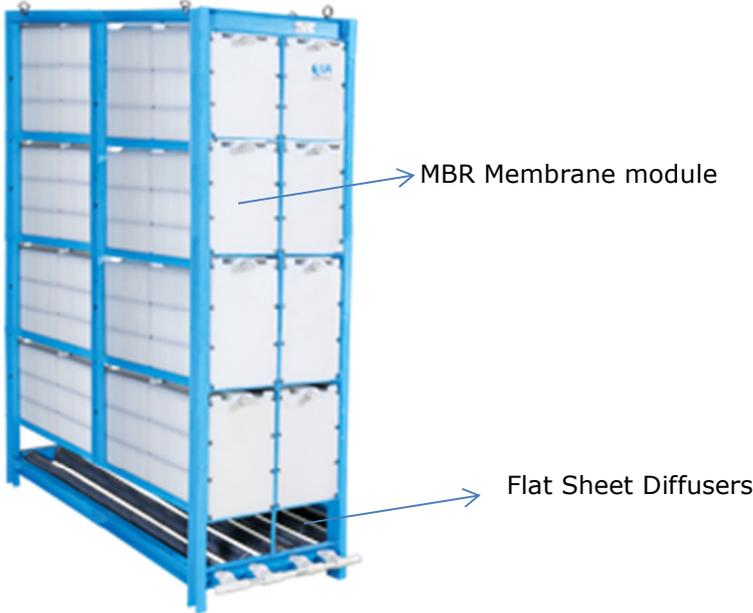
MBR System – Manufacturer’s comparative Data

	Zenon	Kubota	Mitsubishi	US Filter
Membrane				
Type	Hollow fiber	Plate	Hollow fiber	Hollow fiber
Configuration	Vertical	Vertical	Horizontal	Vertical
Pore size	0.04 µm	0.4 µm	0.04 µm	0.04 µm
Module size	31.6 m ²	0.8 m ²	105 m ²	9.3 m ²
Location	Cell compartment	Throughout basin	Throughout basin	Cell compartment
Screening size	≤ 2 mm	≤ 3 mm	≤ 2 mm	≤ 2 mm
Flux management				
m ² /m ³ h	0.37	0.53	0.73	0.18
Aeration cycle	10 sec on 10 sec off	Constant	Constant	Constant
Flux rate				
Average, l/m ² , h	17-25	17-25	8.5-12	17-25
Peak hour (≤ 6 hrs) l/m ² h	<42	<59	equalize	<51
Maintenance				
Clean				
Type	Backpulse and relax	Backpulse	Relax	Backpulse or relax
Frequency	hourly	1 min/15min	2 min/12 min	1 min/15min
Recovery clean				
Type	Chem. Soak	Chlorine Backwash	Chlorine Backwash	Chem. Soak
Location	Drained cell	In situ	In situ	Drained cell
Frequency	≥ 3 months	≥ 6 months	≥ 3 months	≥ 3 months
Biological Parameters				
SRT, days	10-15	15	20	10-15
MLSS, mg/l	≤ 10 000	≤ 10 000	≤ 10 000	≤ 10 000

[source :4] Data compilation by Marmara University, Turkey

Innovations in MBR Technology

- Continuous backwashing to avoid membrane fouling is a operational problem. To overcome this, new membrane material reducing frequency of membrane backwash to once in a week are developed.
- Flat membrane diffusers are used in many cases in place of tubular membranes. Flat membrane diffusers along with membrane cage reduces height of unit.



2.2.3. ULTRAFILTRATION (UF) / REVERSE OSMOSIS (RO)

Filtration is a process of removing particulate matter from water by forcing the water through a porous media. This porous media can be natural, in the case of sand, gravel and clay, or it can be a membrane wall made of various materials. The size of materials that can be removed during filtration depends upon the size of the pores of the filter. In membrane filtration, Figure 2.4 summarises various separation processes and pore sizes and material removed from membranes.

Figure 2.4: Membrane Spectrum

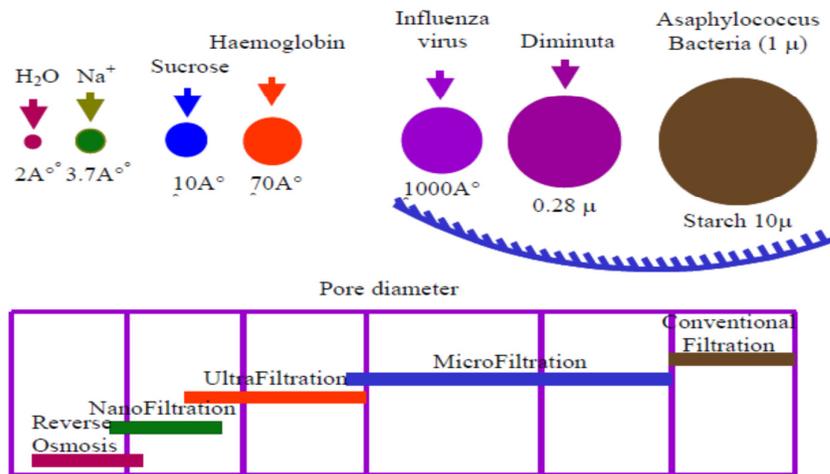


Figure 2.5: Membrane Spectrum with pollutant removals

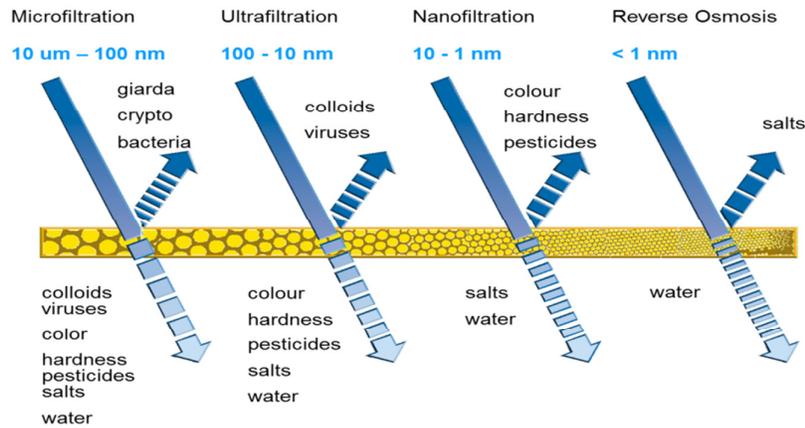


Figure 2.6: Pressure requirement for Membrane processes

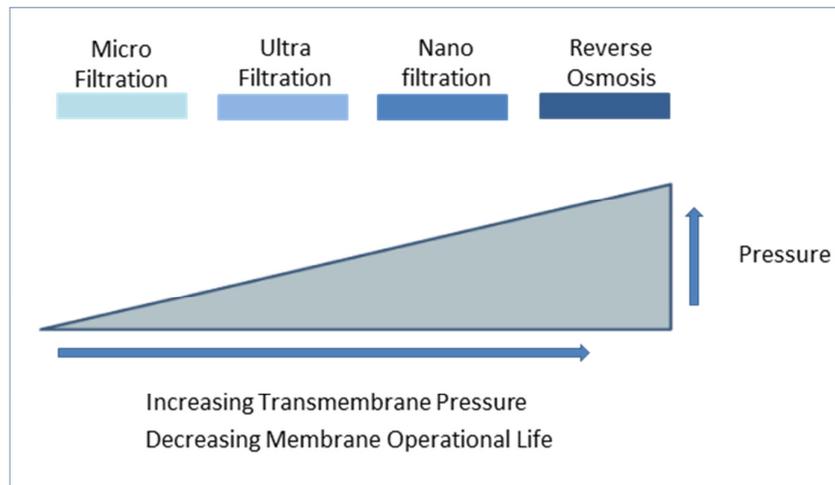


Figure 2.6 shows increase in pressure requirement for membrane processes as we go on reducing pore size of membrane.

A: Ultrafiltration (UF)

Ultra filtration (UF) is a low pressure membrane filtration process which removes bacteria, protozoa and some viruses from the water. Along with this there is removal of colloidal particles from wastewater. When applied for wastewater treatment, it is mostly used as pre-treatment to RO.

A pressure is applied to wastewater to pass through semipermeable membrane. By using ultrafiltration, multimedia

filtration process can be eliminated. Ultrafiltration is also used for applications in industrial wastes for recovery:

Metal industry → Separation of water-oil emulsions

Automotive painting industry → to separate dye from washing water

Pharmaceutical industry → Separation of enzymes

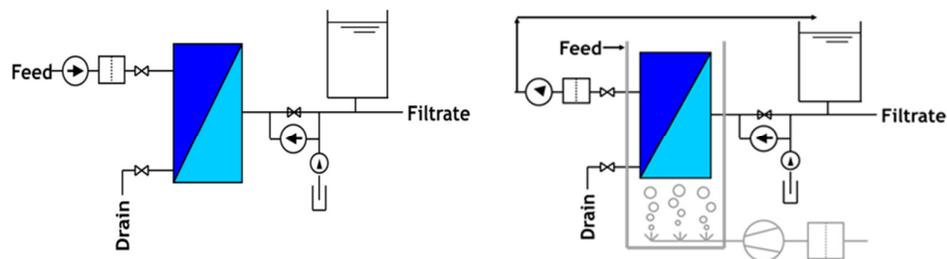
Food industry → Cheese waste

As we have seen in MBR systems, UF membranes are of 2 types:

Submerged membranes & pressurised membranes.

Pressurised UF Membranes

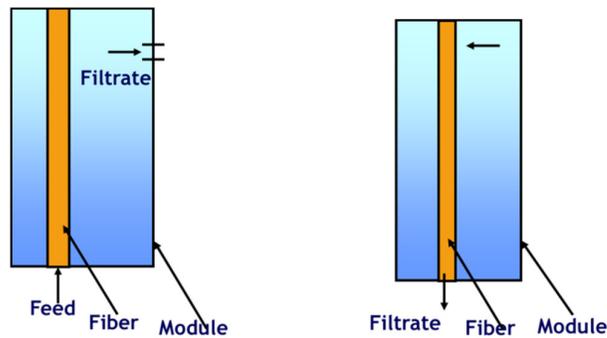
Submerged UF Membranes



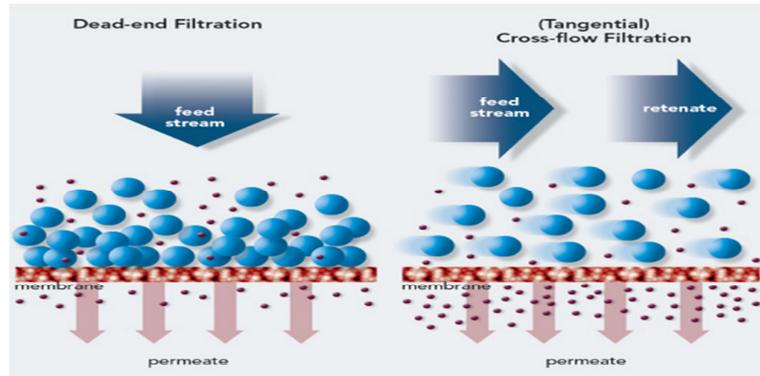
There are two types of membranes as far as filtration mode is concerned:

In to out

Out to in



Dead end filtration and Cross-flow filtration



Dead end Filtration : Operating Flux- 70-130 L/m²/h, Recovery: 90-98%

Cross flow Filtration : Used for Turbidity > 10 NTU / 20ppm, Operating flux: 40 - 70 Lmh, Recovery: 75-90%, Cross flow recommended for very high solid loading (e.g.MBR)

UF membrane Ststem module:



Membrane



Module



Rack



Membranes:

- Hollow fibre capillary membranes
- MOC: Poly Ether Sulphone (PES) / Polyvinylideneflouride (PVDF)

Operating parameters for UF:

- Filtration pressure : 0.1 to 0.6 kg/cm²
- Temperature range: 0 - 40°C
- pH range in filtration: 4 - 11
- Flux : 50-90lmh
- Recovery: 85 to 94%

- Energy requirement: 0.02 to 0.05KWH/m³ (UF as a pre-treatment to RO)

Filtration rate (flux) depends on water quality, pre-treatment, temperature of wastewater.

Treated water quality

- Particles: >1 µm >6 log
- SDI Permeate: < 3
- Virus : >4 log
- Giarda : >5 log
- Cryptosporidium : >5 log
- Turbidity Permeate: < 0.1 NTU
- COD Removal: 0 to 25 %
- COD removal with coagulant : 25 to 50 %

Advantages of UF Technology:

- It the best technology for pre-treatment of RO
- It eliminates pressure sand filtration, Duel media filtration, microfiltration or any other filtration methods for removal colloidal suspended particles.
- Very low pressure and energy requirement
- Very less foot print area as compared to duel media/sand filtration
- Removes small colloids, bacteria, viruses and suspended organics from the wastewater

Limitations of UF Technology:

- Capital cost is comparatively high
- Membrane replacement required after 3-5 years depending on application
- Membrane backwashing and cleaning is required
- Cleaning chemical dosing system is to be provided

Innovations in UF Technology:

- Multi bore system by providing superior mechanical strength, which avoids fibre breakages
- Composite fibres to facilitate better collection system and free flow
- Two stage UF system by diverting backwash water to second stage, thus improving % recovery more than 95% (Inlet COD shall be <150mg/l)
- Micro porous, crystalline structure resulting from thermally induced phase separation (TIPS) provides increased chemical resistance and Increased mechanical strength. Thus reduces maintenance by reducing backwash frequency and membrane replacement frequency

Leading UF suppliers are :

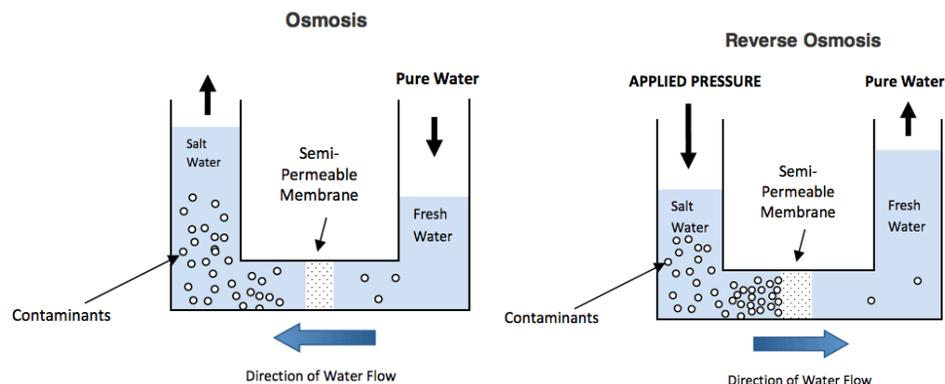
Manufacturer	Membrane Material of Construction
Aquasource	Polysulfone Cellulose Acetate
Hydranautics	Polyethersulfone
Inge	Polyethersulfone
Koch	Polysulfone
Pall	Polyacrylnitrile Polyvinylidene fluoride
TriSep - SpiraSep	Polyethersulfone
US Filter	Polypropylene Polyvinylidene fluoride
X-Flow	Polyethersulfone / Polyvinylpyrrolidone Blend
Zenon	Laminated Polysulfone

Ref: [5]

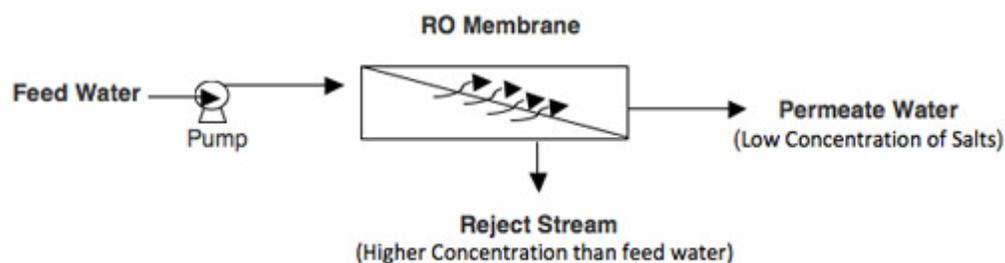
B: Reverse Osmosis (RO)

Since the development of the first practical cellulose acetate membranes in the early 1960's and the subsequent development of thin-film, composite membranes, the uses of reverse osmosis

have expanded to include not only the traditional desalination process but also a wide variety of wastewater treatment applications.



Reverse Osmosis works by using a high pressure pump to increase the pressure on the salt side of the RO and force the water across the semi-permeable RO membrane, leaving almost all (around 95% to 99%) of dissolved salts behind in the reject stream. The amount of pressure required depends on the salt concentration of the feed water. The more concentrated the feed water, the more pressure is required to overcome the osmotic pressure. The desalinated water that is demineralized or deionized, is called permeate (or product) water. The water stream that carries the concentrated contaminants that did not pass through the RO membrane is called the reject (or concentrate) stream.



RO system employs cross filtration rather than standard filtration where the contaminants are collected within the filter

media. With cross filtration, the solution passes through the filter, or crosses the filter, with two outlets: the filtered water goes one way and the contaminated water goes another way. To avoid build-up of contaminants, cross flow filtration allows water to sweep away contaminant build up and also allow enough turbulence to keep the membrane surface clean.

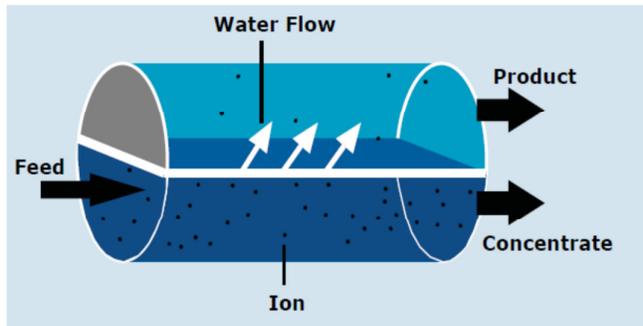
Reverse Osmosis is capable of removing up to 99%+ of the dissolved salts (ions), particles, colloids, organics, bacteria and pyrogens from the feed water. Any contaminant that has a molecular weight greater than 200 is likely rejected by a properly running RO system. Likewise, the greater the ionic charge of the contaminant, the more likely it will be unable to pass through the RO membrane. For example, a sodium ion has only one charge (monovalent) and is not rejected by the RO membrane as well as calcium for example, which has two charges. Likewise, this is why an RO system does not remove gases such as CO₂ very well because they are not highly ionized (charged) while in solution and have a very low molecular weight. Because an RO system does not remove gases, the permeate water can have a slightly lower than normal pH level depending on CO₂ levels in the feed water as the CO₂ is converted to carbonic acid.

Reverse Osmosis is very effective in treating brackish, surface and ground water for both large and small flows applications. Some examples of industries that use RO water include pharmaceutical, boiler feed water, food and beverage, metal finishing and semiconductor manufacturing to name a few.

RO Membranes and configurations:

To significantly reduce the rate of membrane fouling, RO systems employ cross-flow filtration (shown in Figure), which allows water to pass through the membrane while separate flow of concentrate sweeps rejected salts away from the membrane surface.

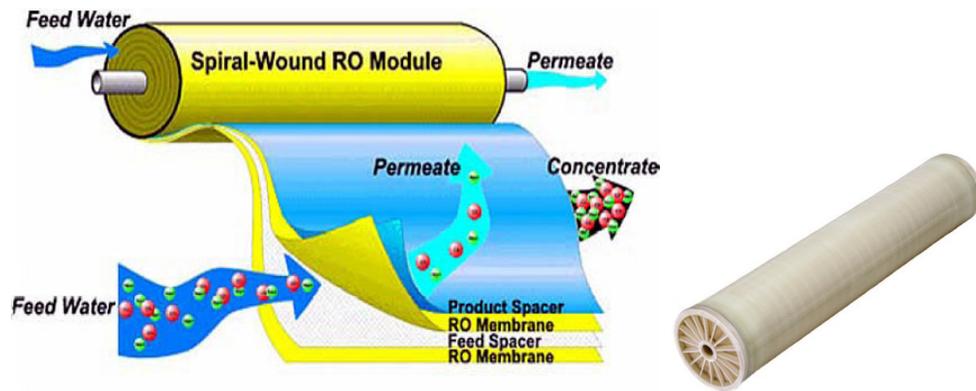
Cross flow filtration:



Common membrane materials include polyamide thin film composites (TFC), cellulose acetate (CA) and cellulose triacetate (CTA) with the membrane material being spiral wound around a tube. TFC membranes have superior strength and durability as well as higher rejection rates than CA/CTA membranes. They also are more resistant to microbial attack, high pH and high TDS. CA/CTA's have a better ability to tolerate chlorine.

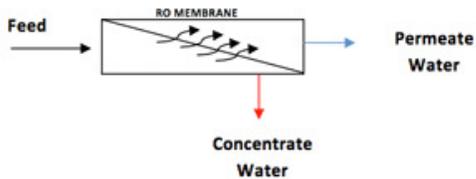
RO membranes are rated for their ability to reject compounds from contaminated water. A rejection rate (% rejection) is calculated for each specific ion or contaminant as well as for reduction of total dissolved solids (TDS).

Spiral Wound Membrane:

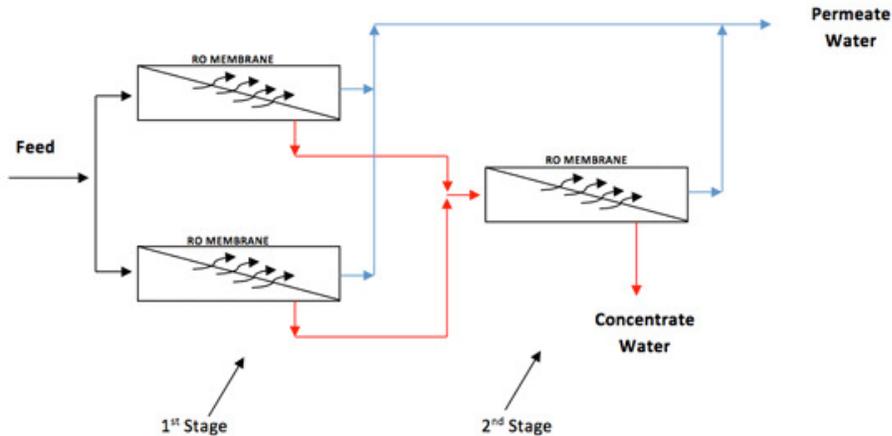


RO system configuration varies as per inlet quality and recovery of water. To increase recovery percentage, reject of first stage RO is subjected to second stage RO and thus overall recovery is increased. Again second stage RO reject can be subjected to third stage. No. of stages depends on reject TDS, silica, etc. Cost of RO system increases with increase in number of stages.

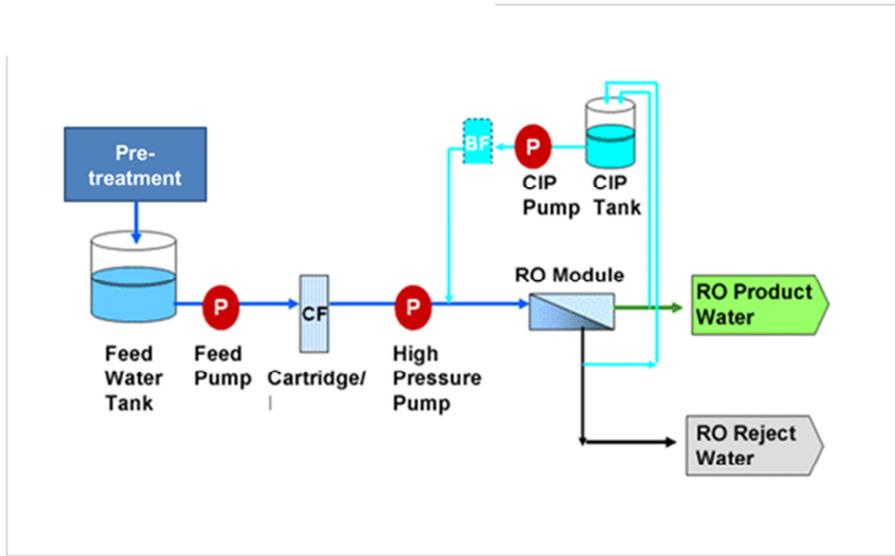
1 stage RO system
 → Feed Water
 → Permeate Water
 → Concentrate Water



2 stage RO system
 → Feed Water
 → Permeate Water
 → Concentrate Water



Typical RO system Flow Diagram



RO System operation:

Proper pre-treatment using both mechanical and chemical treatments is critical for an RO system to prevent fouling and premature RO membrane failure and frequent cleaning requirements. UF before RO is best solution to avoid frequent fouling.

Silt Density Index (SDI) before RO shall be <3.

The performance of RO system depends on factors such as membrane type, flow control, feed water quality, temperature and pressure. Fouling is a major factor affecting performance of the system. Types of fouling are :

Bio-fouling: Fouling can be formed due to the following-

- Particulate or colloidal mater (dirt, silt, clay, etc.)
- Organics (humic/fulvic acids, etc.)
- Microorganisms (bacteria, etc.). Bacteria present one of the most common fouling problems since RO membranes in use today cannot tolerate a disinfectant such as chlorine and therefore microorganisms are often able to thrive and multiply on the membrane surface. They may product biofilms that cover the membrane surface and result in heavy fouling.
- Breakthrough of filter media upstream of the RO unit. GAC carbon beds and softener beds may develop an under drain leak and if there is not adequate post filtration in place the media can foul the RO system.

Damage to membranes can be limited by controlling these substances by use of microfiltration or UF before RO

Scaling: As certain dissolved (inorganic) compounds become more concentrated (remember discussion on concentration

factor) then scaling can occur if these compounds exceed their solubility limits and precipitate on the membrane surface as scale. The results of scaling are a higher pressure drop across the system, higher salt passage (less salt rejection), low permeate flow and lower permeate water quality. An example of a common scale that tends to form on an RO membrane is calcium carbonate (CaCO_3). Scaling can be reduced by limiting salt content by adding acid to limit formation of calcium carbonate and by addition of anti-scalant chemicals.

Chemical Attack

Modern thin film composite membranes are not tolerant to chlorine or chloramines. Oxidizers such as chlorine will 'burn' holes in the membrane pores and can cause irreparable damage. The result of chemical attack on an RO membrane is a higher permeate flow and a higher salt passage (poorer quality permeate water). This is why microorganism growth on RO membranes tends to foul RO membranes so easily since there is no biocide to prevent its growth.

Mechanical Damage

Part of the treatment scheme should be pre and post RO plumbing and controls. If 'hard starts' occur, mechanical damage to the membranes can occur. Likewise, if there is too much backpressure on the RO system then mechanical damage to the RO membranes can also occur. These can be addressed by using variable frequency drive motors to start high pressure pumps for RO systems and by installing check valve(s) and/or pressure relief valves to prevent excessive back pressure on the RO unit that can cause permanent membrane damage.

RO Membrane Cleaning

RO membranes will inevitably require periodic cleaning, anywhere from 1 to 4 times a year depending on the feed water quality. As a general rule, if the normalized pressure drop or the normalized salt passage has increased by 15%, then it is time to clean the RO membranes. If the normalized permeate flow has decreased by 15% then it is also time to clean the RO membranes. You can either clean the RO membranes in place or have them removed from the RO system and cleaned off site by a service company that specializes in this service.

RO membrane cleaning involves low and high pH cleaners to remove contaminants from the membrane. Scaling is addressed with low pH cleaners and organics, colloidal and biofouling are treated with a high pH cleaner. Cleaning RO membranes is not only about using the appropriate chemicals. There are many other factors involved such as flows, water temperature and quality, properly designed and sized cleaning skids and many other factors that an experienced service group must address in order to properly clean RO membranes.

RO Operating parameters:

- Feed water SDI - <3
- Feed pressure – As per membrane type and selection of manufacturer :
 - For brackish water – 10.5 to 42kg/cm² (150-600psi)
 - For sea water – 56 – 70kg/cm²(800-1000psi)
- Salt rejection >99%
- % recovery for one stage -50% - 70%
- Sea water membranes:
 - Inlet TDS – 10,000 to 40,000mg/l

- Feed pressure – up to 70kg/cm² max (1000psi)
- Brackish water membranes:
 - Inlet TDS - <10,000mg/l
 - Feed pressure – up to 42 kg/cm² (600psi)

Advantages of RO Technology

- RO system is very attractive at places where there is water scarcity and permeate water is recycled/reused in industry
- Treated water quality is consistent and water is reused for industrial processes
- RO systems are modular in nature, making expansion of the systems easy
- Simple to design and operate, have low day to day maintenance
- RO technology considerably reduces the volume of waste streams so that these can be treated more efficiently and cost effectively by other processes such as MEE or Incineration

Limitations of RO Technology

- Major limitations of RO processes are the limited recoveries (50-85 percent) dictated by the presence of large concentrations of sparingly soluble salts in the feed water and reject disposal challenges
- High capital cost
- High operating cost due to higher energy consumption of high pressure pumps
- Replacement of membranes required after 3 years depending on application
- If pre-treatment is not proper, membrane fouling results into poor performance of the system, resulting into frequent cleaning and damage of membranes

- Skilled system operation and monitoring is required to maintain the consistent performance

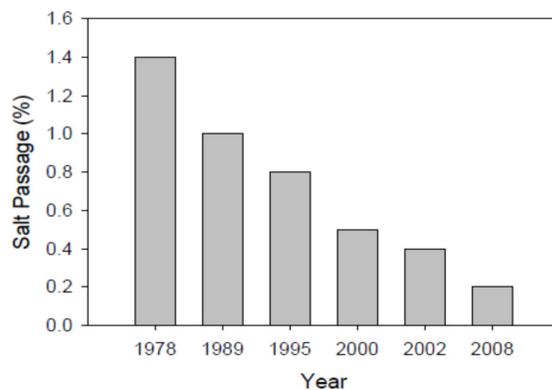
Innovations in RO Technology

Commercial interest in RO technology is increasing globally due to continuous process improvements, which in turn lead to significant cost reductions. These advances include developments in membrane materials and module design, process design, feed pre-treatment, and energy recovery, or reduction in energy consumption.

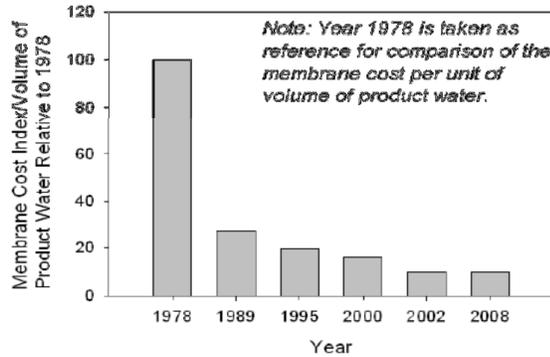
The enhanced mechanical, biological and chemical strength of RO membranes, as well as increased permeability, have reduced the membrane cost per unit volume of water produced by more than 10 times since 1978. The combined effort to minimise fouling and concentration polarization, in addition to maximise permeate flux and energy recovery, has decreased the energy consumption from 12 kWh/m³ in the 1970s to less than 2 kWh/m³ in 2006. There is seven fold increase in salt rejection performance over 30 years.

A study by University of BATH, UK published following graphs[6]:

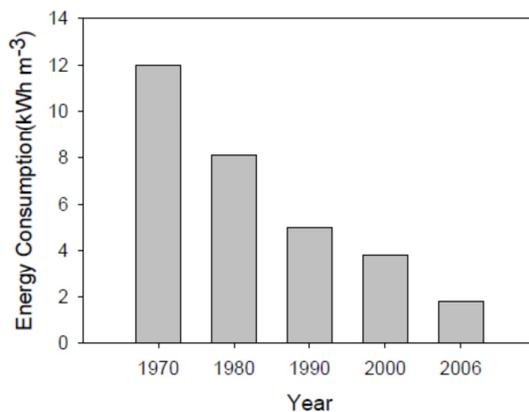
Improvement in salt rejection:



Reduction in membrane cost:



Reduction in energy consumption of RO:



Following are the advanced membranes and improvements by manufacturers:

- Sulphonated polysulphone membranes (SPS) are chlorine tolerant and can withstand higher pH's and are best used where the feed water is soft and high pH or where high nitrates are of concern.
- Low fouling membranes are developed by manufacturers, which are neutrally charged. Unlike negatively charged normal membranes). Low fouling membranes can operate at feed COD of 100-200mg/l.
- Low differential membranes with larger life, more productivity and low fouling are developed
- New development by using spacer with sanitizer to avoid fouling also is innovation in membranes

- Improved spacer design to prevent trapping of small colloidal particles
- The enhanced membrane chemistry of membrane elements helps minimize pressure and energy consumption and provide reliable, long-term permeate quality for single, double pass and inter staged desalination systems.
- EDR membranes : these membranes recover more water from high total suspended solids (TSS) and high silica source water. If your source water is challenging due to high total suspended solids (TSS) or high silica, electrodialysis reversal (EDR) can provide high water recovery. Because of the polarity reversal design, EDR for wastewater reuse is a self-cleaning, durable membrane system ideal for turbid wastewater.

The current RO membrane market is dominated by thin film composite (TFC) polyamide membranes. The spiral wound membrane module configuration is the most extensively used design in RO desalination. This configuration offers high specific membrane surface area, easy scale up operation, inter-changeability, low replacement costs and, most importantly, it is the least expensive module configuration to produce from flat sheet TFC membrane. Although the spiral wound configuration was developed decades ago, improvements in the dimensions of spacers, feed channels and vessels, as well as the materials of construction, have optimised the inter-connection between module design and fluidic transport characteristics, thereby decreasing both fouling and pressure losses.

There are four leading membrane module suppliers which provide RO membranes for large scale desalination plants, namely DOW, Toray, Hydranautics and Toyobo.

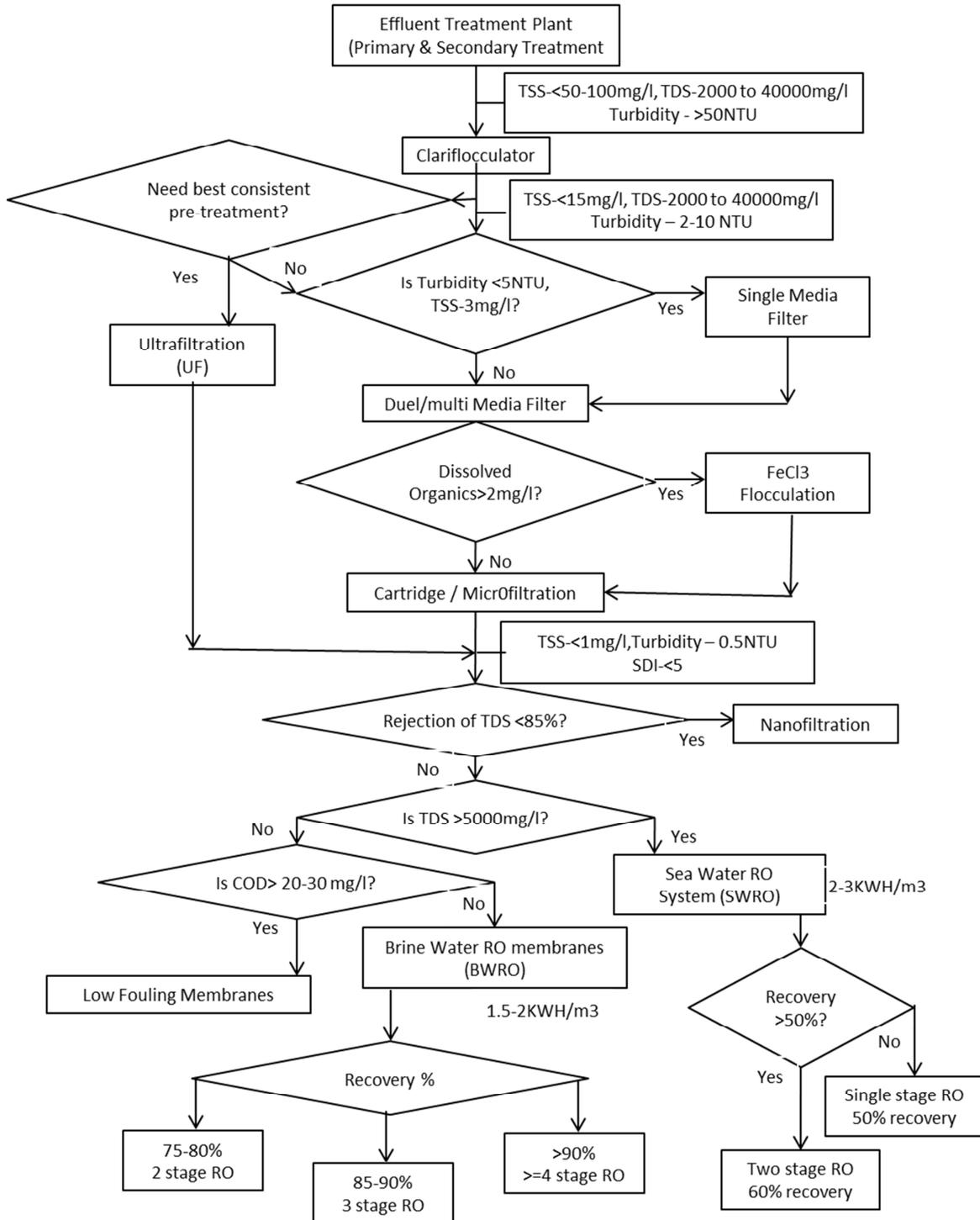
SWRO membrane modules in application:

Membrane module brand name	Material & module	Permeate flux (m ³ day ⁻¹)	Salt rejection (%)	Specific energy consumption ^[d] (kWh m ⁻³)
DOW FILMTEC™ 8 inch SW30HRLE	TFC crosslinked fully aromatic polyamide spiral wound	28.0 ^[a]	99.60 – 99.75 ^[a]	3.40 (2.32) ^[e] at Perth SWRO Plant, Australia [30]
Hydranautics 8 inch SWC4+	TFC crosslinked fully aromatic polyamide spiral wound	24.6 ^[b]	99.70 – 99.80 ^[b]	4.17 (2.88) ^[e] at Llobregat SWRO Plant, Spain [30, 33]
Toray 8 inch TM820C	TFC crosslinked fully aromatic polyamide spiral wound	19.7 – 24.6 ^[a]	99.50 – 99.75 ^[a]	4.35 at Tuas SWRO Plant, Singapore [31]
Toyobo 16 inch HB10255	Asymmetric cellulose tri-acetate hollow fibre	60.0 – 67.0 ^[c]	99.40 – 99.60 ^[c]	5.00 at Fukuoka SWRO Plant, Japan [32]

Note: [a] Test condition: 32 g L⁻¹ NaCl solution, 55 bar, 25 °C, pH 8 and 8 % recovery [29, 35];
 [b] Test condition: 32 g L⁻¹ NaCl solution, 55 bar, 25 °C, pH 7 and 10 % recovery [34];
 [c] Test condition: 35 g L⁻¹ NaCl solution, 54 bar, 25 °C and 30 % recovery [36];
 [d] These numbers should not be compared explicitly because of different operating parameters (e.g. feed water quality, recovery, pre-treatment processes, process design, etc.) at different desalination plants.
 [e] The number in brackets is the energy consumption for the RO unit.

Source: [7]

Reverse Osmosis System Guidelines



2.2.4. Evaporation Technologies

Zero Liquid Discharge (ZLD) has ultimate objective of not discharging wastewater outside the industry. This objective is achieved by evaporation or crystallization of rejects from previous treatment. During these processes, contaminated elements are discharged as solid waste whilst the condensate is recovered. Typically, the effluent is a salty solution and the thermal separation is the final step of ZLD, after ultrafiltration and reverse osmosis units.

Evaporation of reject water is most commonly used treatment for reduction of waste volume, recovery of salts and to recycle the condensate in process. Evaporation plants are used as a thermal separation technology, for the concentration or separation of liquid solutions, suspensions and emulsions.

Evaporator design shall have:

- Minimum surface area with highest heat transfer
- Efficient vapour liquid separation.
- Efficient energy utilization –steam/power/thermic.
- Purer condensate/water recovery
- Optimum capital cost
- Optimum material of construction with economic life cycle.
- Least maintenance cost
- Easy operation

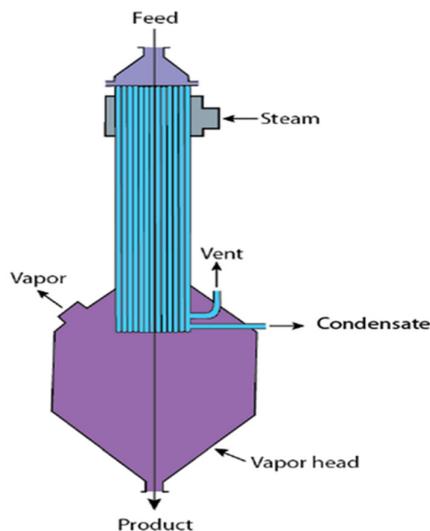
There are various types of evaporators:

1. Falling film Evaporator

This technology is particularly suited for energy-saving, multiple-effect evaporation and mechanical vapour re-compression processes. It only requires a very small operating temperature and thus allows it to be easily controlled and fast to start up and

shut down due to a minimal liquid hold-up. Falling film technology is the right solution for streams which are viscous in nature and contain small concentrations of suspended solids. A falling film evaporator can be used as a pre-concentrator in a combined multiple-effect plant. It has the capacity to treat streams with small to large flow rates.

Unlike rising film, Liquid is fed at the top of long tubes and allowed to fall down the walls as a film. Evaporation occurs on the surface of the highly turbulent film and not on the tube surface. This requires that temperature differences be relatively low. Many times rising film and falling film evaporators are combined into single unit. When a high ratio of evaporation to feed is required and the concentrated liquid is viscous, a tube bundle can be divided into two sections with the first section functioning as a rising film evaporator and the second section serving as a falling film evaporator.



Advantages

- Low power requirement
- Low pressure drop

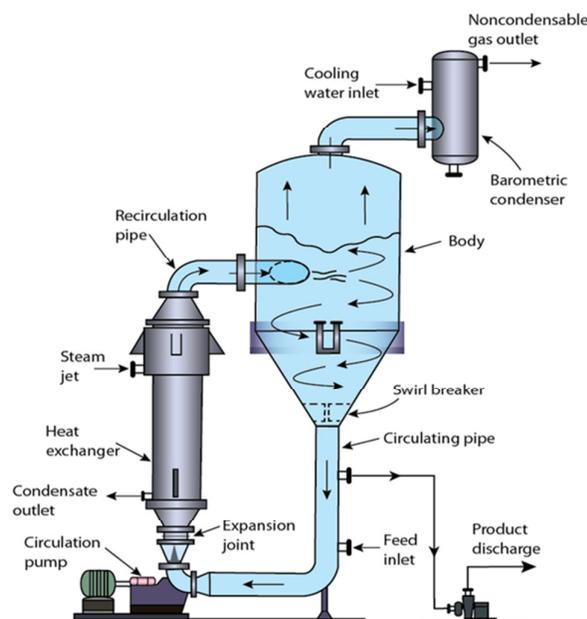
- High heat transfer rate
- Less capital cost

Limitations

- Very sensitive to saturation of ions present in liquid
- Not suitable if any of the component gets saturated during evaporation
- Frequent scaling in case of effluent and crystalline product
- More down time
- Higher cleaning frequency

2. Forced Recirculation

The forced circulation evaporator is used for processing liquors which are susceptible to scaling or crystallizing. Liquid is circulated at a high rate through the heat exchanger, boiling being prevented within the unit by virtue of a hydrostatic head maintained above the top tube plate. As the liquid enters the separator where the absolute pressure is slightly less than in the tube bundle, the liquid flashes to form a vapour.



Advantages

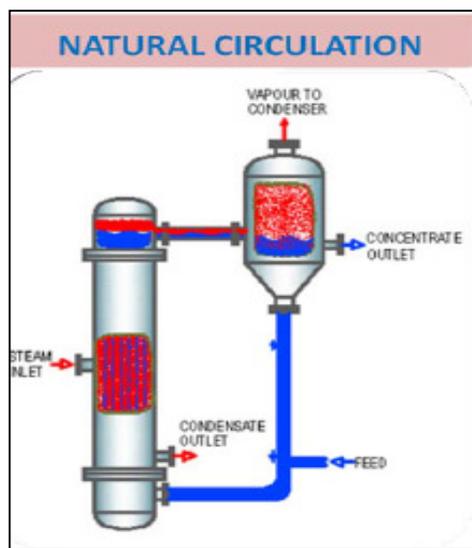
- Suitable for crystalline product
- Can handle slurry
- Very less fouling
- Minimum down time
- Very high heat transfer rate
- Extended cleaning cycle
- Most rugged kind of evaporator

Limitations

- Higher power requirement
- Higher capital cost

3. Natural Circulation

Evaporation by natural circulation is achieved through the use of a short tube bundle or by having an external shell and tube heater outside of the main vessel. The external heater has the advantage that its size is not dependent upon the size or shape of the vessel itself. As a result, larger evaporation capacities may be obtained. The most common application for this type of unit is as a reboiler at the base of a distillation column.



Advantages

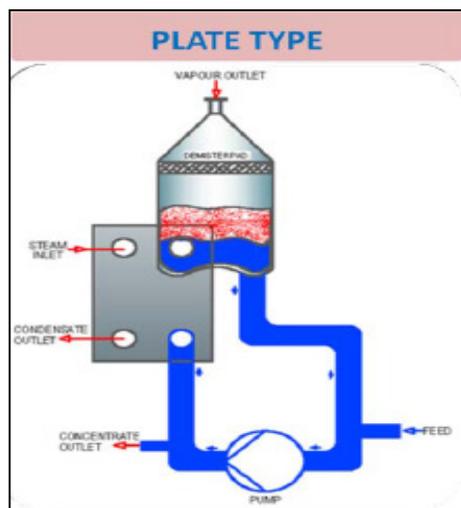
- Minimum power cost
- Easy operation
- Can handle viscous material

Limitations

- Very sensitive to saturation of ions present in liquid
- Not suitable if any of the component gets saturated during evaporation
- Frequent scaling in case of effluent and crystalline product
- Higher cleaning frequency
- Low heat transfer coefficients
- Higher capital cost

4. Plate type evaporator

Principally, plate evaporators are similar to falling film & forced recirculation tubular evaporators. The plate evaporator offers full accessibility to the heat transfer surfaces. It also provides flexible capacity merely by adding more plate units, shorter product residence time resulting in a superior quality concentrate, a more compact design with low headroom requirements, and low installation cost.



Advantages

- Less pressure drop on liquid side & high heat transfer coefficients
- Less height required
- Compact construction
- Less capital cost
- Physical cleaning is easy

Limitations

- Gaskets required to replace periodically
- Not suitable for slurry and crystalline products

Application of Evaporation Technologies:

S.N.	Technology	Application
1	Forced Recirculation	<ul style="list-style-type: none"> • Suitable for evaporation applications containing high levels of hardness, silica, suspended solids & Crystalline slurries • Salt recoveries like NaCl, Na₂SO₄, NH₄Cl, (NH₄)₂SO₄, ZnSO₄, K₂SO₄, KCl, CaCl₂, etc
2	Falling film	<ul style="list-style-type: none"> • Suitable for clear liquors, feeds with low hardness and non-crystalline concentrates with low viscosities • Useful for concentrating milk, fruit juices, if hardness is <150ppm
3	Natural Recirculation	<ul style="list-style-type: none"> • Suitable for concentration of viscous liquids below saturation without hardness • Solid slurry with high viscous liquid, where solids will settle down and clear liquid is recirculated
4	Plate Type	<ul style="list-style-type: none"> • Application is same as Forced recirculation and falling film designs. Used for low level installations

Methodologies for application of evaporator technologies

Above evaporation methods are applied separately or in combination for overall evaporation system depending on application, saving energy and availability of excess heat or steam.

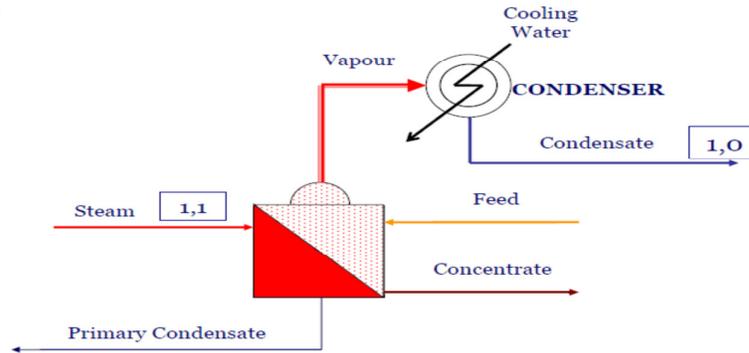
Multiple Effect Evaporator (MEE)

A multiple-effect evaporator is an evaporator system in which the vapour from one effect is used as the heating medium for a subsequent effect boiling at a lower pressure. Effects can be staged when concentrations of the liquids in the effects permits; staging is two or more sections operating at different concentrations in a single effect. The term evaporator denotes the entire system of effects, not necessarily one body or one effect.

A multiple-effect system may be considered as a number of resistances (effects), in series, to the flow of heat. The driving force causing heat to flow is the difference in temperatures of the steam condensing in the first effect and the temperature of the heat sink, often cooling water. Some of the available driving force is lost when the liquid exhibits a boiling-point elevation, the total loss equal to the sum of the boiling-point elevations in all the effect.

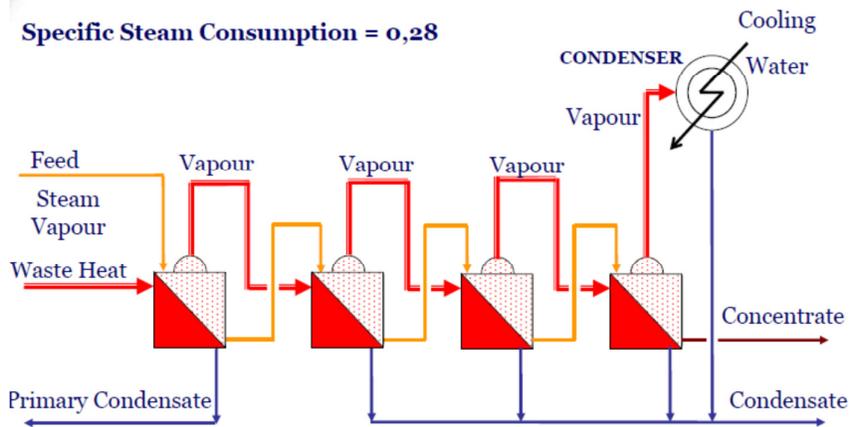
Single Effect Evaporator

Specific Steam Consumption = 1,1



Multi Effect Evaporator

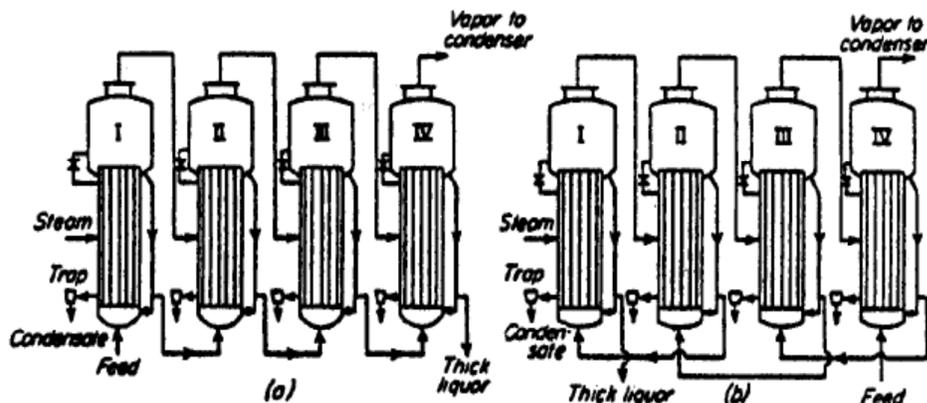
Specific Steam Consumption = 0,28

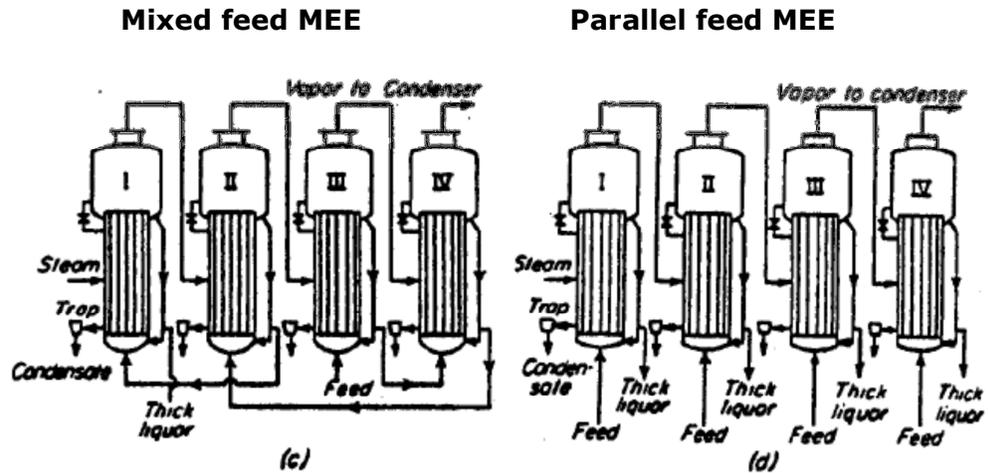


There are 4 types of configurations of MEE:

Forward feed MEE

Backward feed MEE





Ref [9]

Configuration is selected as per temperature and concentration of feed.

The purpose of an evaporator system is to produce the required amount of specified product at the lowest total cost. The designer of an evaporator system must consider a wide range of variables in selecting the system which provides the best balance between operating cost and capital investment. The evaporator type, the number of effects, and the type of compression system are the most important variables.

Operational problems in MEE technology is scaling and fouling of heating surface. Fouling may be defined as the formation of deposits on heat transfer surfaces which impede the transfer of heat and increase the resistance to fluid flow. The growth of these deposits causes the thermal and hydrodynamic performance of heat transfer equipment to decline with time. Fouling is of various types, e.g precipitation, particulate, Chemical reaction, corrosion, biological fouling. Corrosion fouling can be reduced by using Titanium material for construction. Other foulings are eliminated by frequent cleaning.

Some guidelines for design of MEE are as follows:

- (1) the optimum number of effects increases as the steam costs increase or plants become larger
- (2) mechanical vapour compression looks attractive if electrical power is available at reasonable costs and boiling point rises are low
- (3) thermal compression looks attractive when electrical power is costly and boiling point rises are low
- (4) when boiling point rises are large, combinations of vapour compression pre-concentrators followed by multiple-effect systems look attractive
- (5) larger plants enable heat recovery systems to be more easily justified
- (6) mechanical vacuum pumps are generally more energy efficient than steam jets.

Number of effects that can be practically installed depends on pressure of the steam, Boiling point rise (BPR) of the process fluid and Temperature of cooling water

Frequently it is necessary to consider other factors besides the evaporator design. Steam generation, electrical power, and cooling water distribution and supply costs may be sufficiently reduced to justify particular system designs.

Sometimes evaporator efficiency can be sacrificed in order to utilize all of the heat available in a waste heat stream. Final operating pressure may be determined by the ability to recover the heat of condensation in some other part of the plant.

Energy Optimisation in Evaporators:

A. Staging

Often in multiple-effect evaporators the concentration of the liquid being evaporated changes drastically from effect to effect especially in the latter effects. In such cases, this factor can be used to advantage by “staging” one or more of the latter effects. Staging is the operation of an effect by maintaining two or more sections in which liquids at different concentrations are all being evaporated at the same pressure. The liquid from one stage is fed to the next stage. The heating medium is the same for all stages in a single effect, usually the vapour from the previous effect. Staging can substantially reduce the cost of an evaporator system.

- Multi-staging reduces thermal energy requirement
- Suitable with high pressure steam pressure
- Reduces cooling tower power requirement
- Reduces cooling water makeup required in cooling tower.

B. Pre-heating

Pre-heating the feed reduces size of main heat exchange. If forward feed is required and the feed is cold, energy economy can be improved by preheating the feed in stages with vapour from intermediate evaporator effects. Steam economy improves with pre-heating and also minimises thermal losses. If excess heat is available then this option is suitable.

C. Compression Evaporation

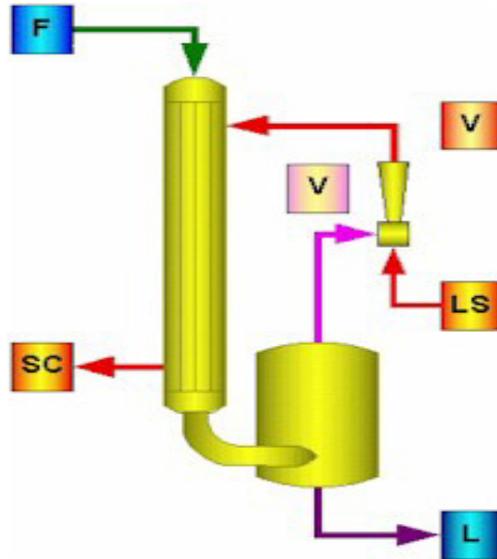
Compression evaporation could be defined as an evaporation process in which part, or all, of the evaporated vapour is compressed by means of a suitable compressor to a higher pressure level and then condensed; the compressed vapour

provides part of all of the heat required for evaporation. Compression evaporation is frequently called recompression evaporation. All compression methods use the vapours from the evaporator and recycle them to the heating side of the evaporator. Compression can be achieved with mechanical compressors or with thermal compressors. Thermal compression uses a steam jet to compress a fraction of the overhead vapours with high pressure steam. Mechanical compression uses a compressor driven by a mechanical drive (electric motor or steam turbine) to compress all the overhead vapours.

Energy economy obtained by multiple-effect evaporation can often be equalled in a single-effect compression evaporation system. To achieve reasonable compressor costs and energy requirements, compression evaporator systems must operate with fairly low temperature differences, usually from 5 to 10°C. As a result, large heat transfer surfaces are needed partially offsetting the potential energy economy.

a) Thermal Vapour Recompressor (TVR) or Thermo Compressors

Thermal compression is the term used to describe the application of a steam jet ejector or thermo-compressor to an evaporator in order to increase the steam economy.



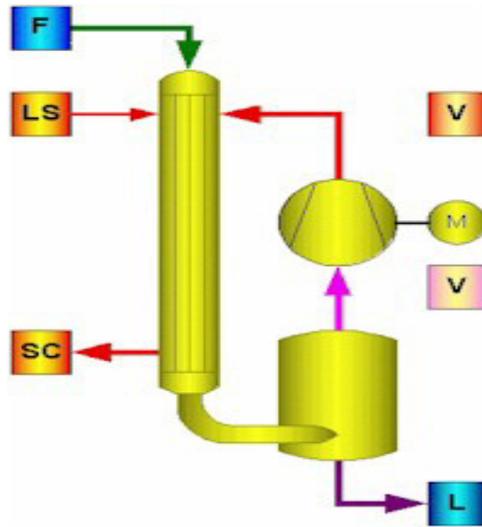
F = Feed
V = Vapour
L = Liquid concentrate
LS = Steam
SC = Steam Condensate

Thermal compression evaporators are well suited for single or double effect systems where low operating temperatures and improved economy are desired. They also find application when space is limited. For practical application the temperature difference across the thermo-compressor should be less than 15%. The application of thermo-compressors is limited when the boiling point rise is high. Thermal Compressors improve steam economy by lowering the operating temperature of evaporation plant. It is suitable for almost all kinds of evaporation plants and liquids excluding high boiling point liquids.

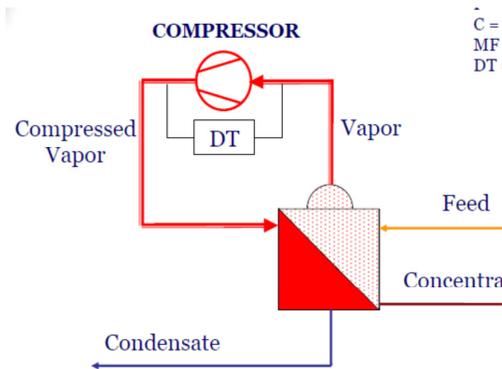
b) Mechanical Vapour Recompressor (MVR)

Mechanical vapor compression evaporator technology has been used for over 100 years and is a proven means to significantly reduce energy required for evaporation. Water vapour generated in the evaporator is compressed to higher pressure. Compressed vapour acts as heat source for evaporation process and

condenses in the evaporator heat exchanger. It is similar to a conventional single-effect evaporator, except the vapour released from the boiling solution is compressed in a mechanical compressor. The compressor adds energy to the vapour to raise the saturation temperature of the vapour above the boiling temperature of the solution by whatever net temperature difference is desired. Compressor power is proportional to the increase in saturation temperature (ΔT) produced by the compressor. An evaporator designer must optimize power consumption and heat transfer surface. Mechanical vapour compression achieves the highest possible energy savings.



F = Feed
V = Vapour
L = Liquid concentrate
LS = Steam
SC = Steam Condensate



MVR eliminates thermal energy requirement. Compressor is heart of the system. System has high efficiency and low operating cost due to low energy consumption. MVR is suitable for liquid with narrow boiling point rise (BPR). MVR is not suitable when steam is readily available in plant.

Selecting the most economical method of evaporation requires knowledge of the costs of energy, capital, operating labor, spare parts, and maintenance over the life of the system. Energy and capital costs dominate and show the greatest variance among evaporator types. It is often difficult to assign true costs to energy sources. Each case must be considered individually. The economics can be calculated only if accurate costs are known; approximations and educated guesses will not provide the correct answer.

The major factors to consider in selecting a compressor are the flow rate, compression ratios, variability of evaporator flow rates and operating conditions, vapour temperature, expected maintenance, and installed cost. Generally, the costs for all mechanical compressors limit their application to situations in which the compression ratio is less than 2, since multistage or a series of single stage compressors would be required at higher compression ratios. Compressors applied to evaporator systems

include positive displacement, and radial-flow turbo and axial-flow centrifugal. Each has advantages for certain applications.

A system of mechanical vapour recompression units for initial concentration where acceptable to remove large quantities of water followed by multiple-effect, steam heated units to finish evaporate the process streams was the solution for the processing and project requirements. Another key factor was that the site had available the necessary electrical capacity to meet the requirements of the MVR system.

Advantages of MVR technology

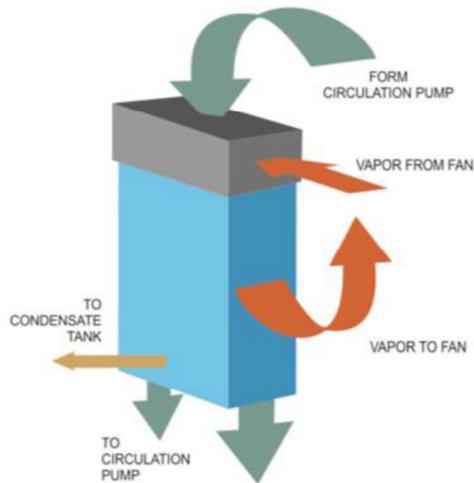
- Steam and overall energy consumption significantly reduces compared to conventional steam heated evaporator systems with the same capacity.
- Substantially lower operational cost than MEE
- Reduction in Cooling water requirements
- The main vacuum pump for the evaporator system was reduced in horsepower, capacity and size compared to one required without use of a MVR
- Higher condensate temperatures provide additional steam savings.

Limitations of MVR technology

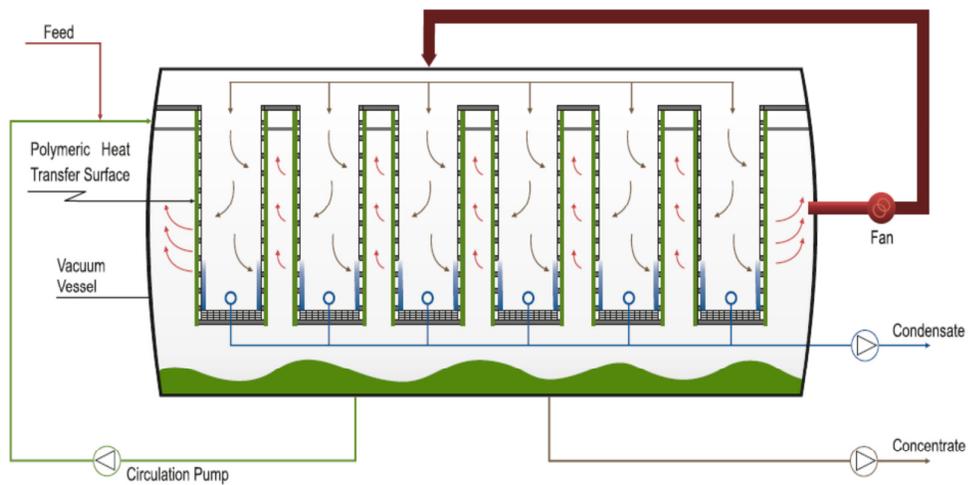
- Very high capital cost
- MVR alone cannot be used for all streams due to its limitation of temperature difference
- Energy consumption is more than conventional evaporation due to high capacity compressor
- MVR is not suitable when steam is available readily

Mechanical Vapour Compression (MVR) Innovations

Conventional MVR uses Stainless Steel material (SS316), hastelloy or titanium for heat transfer. Advanced polymer membranes are developed for heat transfer which have several benefits.



These polymeric film sheets have larger heat transfer surface area and required less foot pint area. Polymeric film evaporation technology works on the same principle as conventional mechanical vapour compressor with lower temperature difference. Energy requirement is typically 10 to 15 kWh per m³ of purified water.



Polymeric Film Evaporation Technology

Preheated effluent is pumped horizontal cylindrical vessel and uniformly distributed on the heat transfer element made up of polymer. The polymeric heat transfer modules are placed one after another along the length of the vessel. As water flows down, evaporation takes place. The vapours are drawn by a high speed centrifugal fan, which compresses the vapour and increases pressure and saturation temperature. The saturated vapours condense on the inner surface of the polymeric heat exchanger modules at the bottom. The concentrated effluent is pumped out for further treatment to crystalliser or disposal.

Advantages of Polymer MVR

- Works on lower temperature difference, therefore less steam consumption than conventional evaporation
- Higher surface area
- No scaling and corrosion problems
- Lower operating cost

Disadvantages of Polymer MVR

- High capital cost

- Replacement of polymers required every year which adds to operational cost
- Since it works on lower temperature difference, fluctuations in design parameters are not accepted by the system.
- Technology is not suitable if steam is readily available

**Operational Cost of various evaporation technologies:
(Excluding Replacement cost)**

Technology	Electricity required (KWH/m3)	Steam required (kg/m3)	Cost Rs/m3 (@6Rs/KWH, 1RS/kg steam)
MVR Polymer technology	12-15	10-15	82-115
Conventional MVR	25	20	170
Conventional MEE – 1 effect	2	1100	1112
Conventional MEE – 4 effects	3	280	298

Combinations of MVR, MEE and crystaliser are used depending on wastewater characteristics, availability of steam and operational cost.

Improvements in Evaporation Technologies

Many improvements have been made in evaporator technology. The improvements have taken many forms but have served to effect the following:

- Greater evaporation capacity through better understanding of the heat transfer mechanisms.
- Better economy through more efficient use of evaporator types

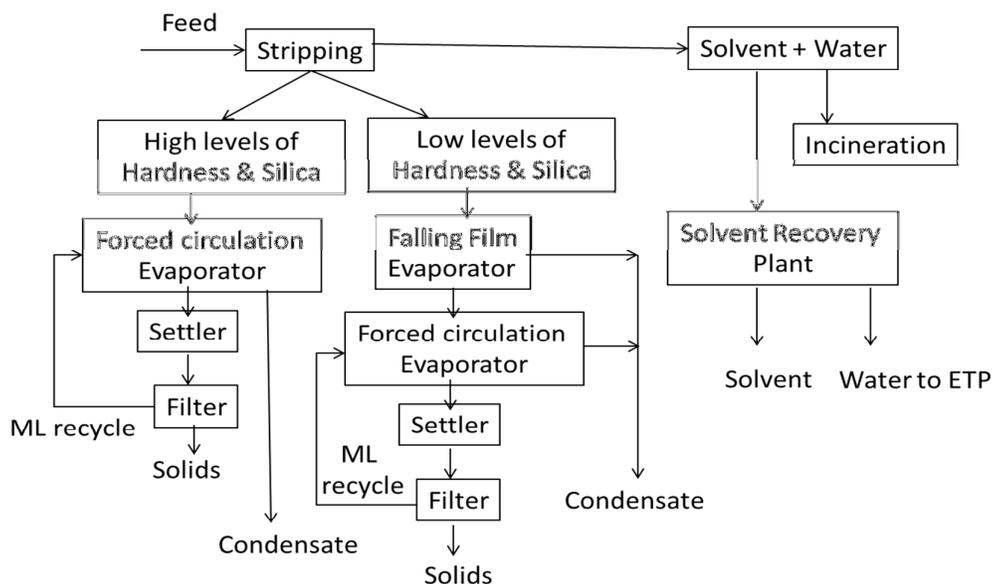
- Longer cycles between cleaning because of better understanding of salting, scaling, and fouling.
- Cheaper unit costs by modern fabrication techniques and larger unit size.
- Lower maintenance costs and improved product quality by use of better materials of construction as a result of better understanding of corrosion.
- More logical application of evaporator types to specific services.
- Better understanding and application of control techniques and improved instrumentation has resulted in improved product quality and reduced energy consumption.
- Greater efficiency resulting from enhanced heat transfer surfaces and better energy economy.
- Compressor technology and availability has permitted the application of mechanical vapour compression.

Selection of Evaporation Technology

Source : [8,9, Vendor data]

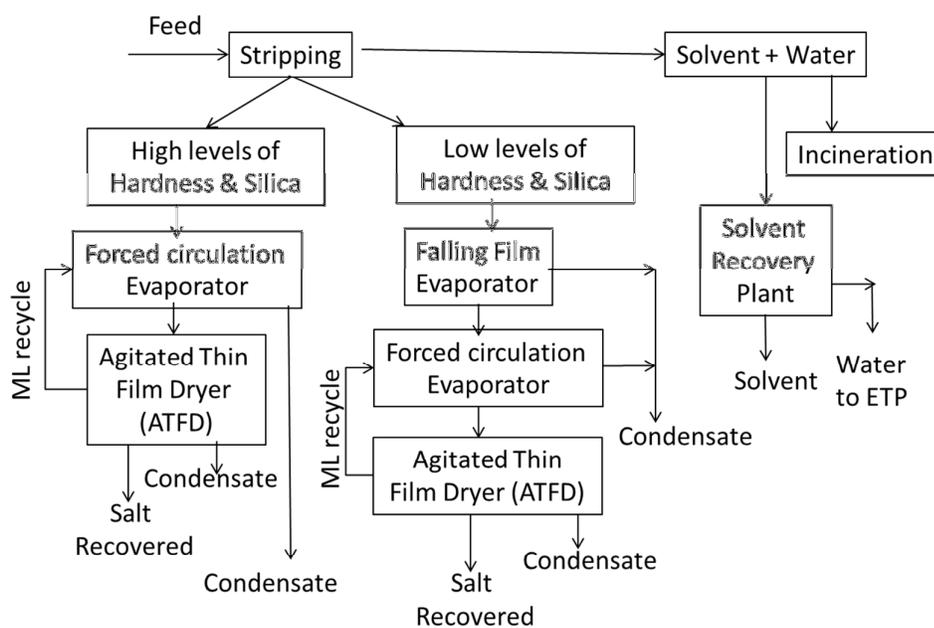
Waste Water with High Volatile + High Boilers + Inorganic Solids- Option 1

(For API, Bulk Drug Pharmaceutical, Chemical & Dye Industries)

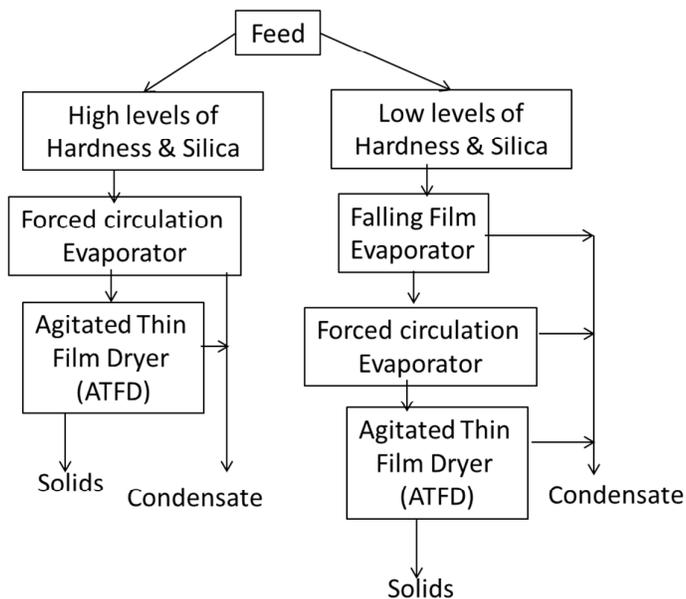


Waste Water with High Volatile + High Boilers + Inorganic Solids – Option 2

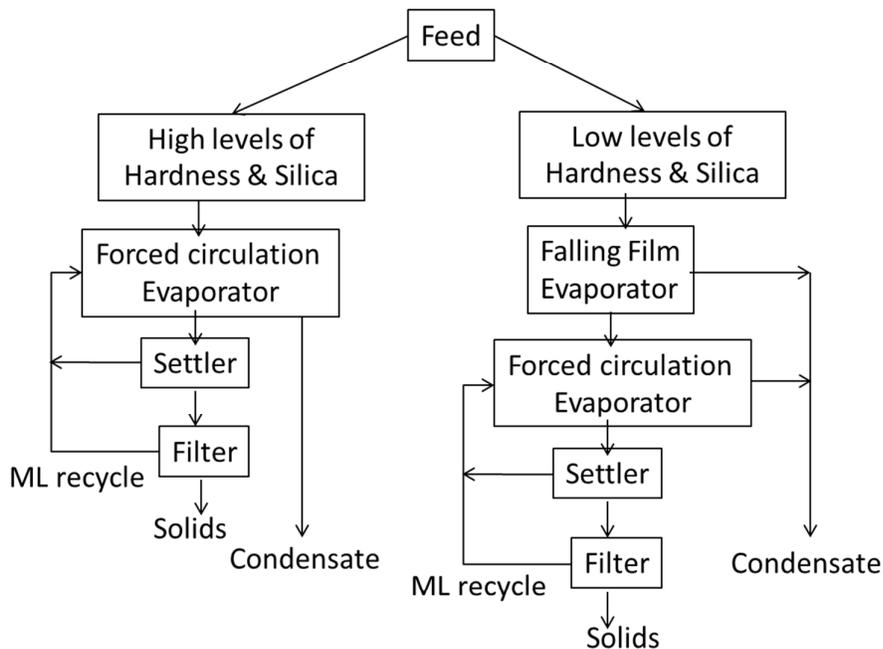
(For API, Bulk Drug Pharmaceutical, Chemical & Dye Industries)



Waste Water with High Boilers + Inorganic Solids
(For Pesticides, chemical & Dye Industries)



Waste Water with Crystalline Inorganic Solids
(For Dairy, Textile, Oil refinery Industries)



2.2.5 Crystallisation / Agitated Thin Film Dryer (ATFD)

Agitated Thin Film Dryer (ATFD)

Agitated Thin Film Dryer is used to dry a solution of high TDS Water or Products. The outlet of ATFD will be in the Powder form having 10-15% moisture. This system will evaporate the solution by thin layer formation on the Surface.

ATFD is stands for evaporation of water/solvents to make concentrated liquid to dry power or flakes. Based on application either recover solvent or dry product in important.

ATFD is the ideal apparatus for continuous processing of concentrated material to dry solids. ATFD is consist of cylindrical, vertical body with heating jacket and a rotor inside of the shell which is equipped with rows and pendulum blades all over the length of the dryer. The hinged blades spread the wet feed product in a thin film over the heated wall.

The turbulence increase as the product passes through the clearance before entering calming zone situated behind the blades as the heat will transfer from jacket to main shell the under the smooth agitation water/solvent will evaporate and liquid will convert to slurry, to cake or to dry power or flex.

The vapours produced rise upward, counter- currently to the liquid and pass through Cyclone separator mounted of vapour outlet of ATFD.

Further these vapours will be condensed in condenser and recovered as condensate. System will be operated under vacuum for temperature sensitive products and atmospheric condition for normal drying.

Due to its inherent design features, it is ideal for thermal treatment of solutions and heat sensitive products, where reduced operating temperatures and vacuum operating pressures are desirable. The typical Agitated Thin Film Evaporator consists of a tubular heat transfer area with an external heating jacket and a fast-revolving, inner rotor with flexible or rigid wiper elements. The driving speed is adapted to the product being handled, its particular specifications and task.

The feed product is evenly distributed by the rotor and its wipers over the heating surface, forming a thin liquid film of uniform thickness. Highly turbulent swirls are produced at the tip of the rotor blades and wipers with intensive mixing and agitation of the product, as it comes into contact with the heating surface. This assures excellent heat transfer combined with constant renewal of the product film and provides an even heating and short residence time of the product through the heated zone.

Key Advantages

- Good heat conductivity (k-value), even when working with highly viscous and contaminated products
- Minimal thermal stress, thanks to low operating capacity, therefore a short dwell time (10-20 seconds of mean dwell time)
- No dead zone, therefore overheating prevented and perpetual high product quality guaranteed
- Continuous mechanical cleaning of the heating surface prevents incrustations
- High evaporation rates, due to highly turbulent film and large difference in temperature

- Gentle evaporation, due to short residence times, rapid conveyance in the heated zone and the constant product film renewal, happens often
- Combined with suppressed boiling points due to operation under vacuum
- Reduced need for maintenance because of sophisticated bearings and shaft sealing parts
- Shorter downtime and assembly time for maintenance and inspection
- No corrosion as outside surface is usually made of stainless steel
- Evaporation in one pass, no circulation
- Small film thickness, no hydrostatic height
- High turndown ratio and high flexibility for variation in requirements
- Low operating pressure down to 1 micron to reduced boiling temperature
- Single step drying because of unique designed combination of vertical and horizontal dryers
- Effective evaporation of concentrated slurries, heat sensitive products, viscous and fouling fluids up to 99% in a single pass
- Simple installation as the equipment is supplied skid mounted with all inter connecting piping, condensers and vacuum system
- Single source responsibility for all project stages because of combined expertise in vacuum technology, heat transfer, evaporation, crystallization and drying – a design mix which gives optimal results

Applications

- Mainly used for difficult vaporization and heat exchange processes, especially where products to be handled are highly viscous and conventional plants can no longer meet user demands because heat transfer is insufficient. Due to the liquid film, mechanically generated on the heating surfaces, thin film equipment achieve much better heat transfer rates, even with highly viscous products containing solids.
- To concentrate highly viscous products, polluted liquids, salt solutions, oils, resins, etc
- As a sump evaporator for vacuum rectification columns
- Sludge drainage
- To continuously dry powdery residues
- Distillation of high-boiling substances under high vacuum
- Degassing and/or removal of volatile components of highly viscous products
- Heating or cooling of viscous solutions
- Improve product quality by removing colour bodies, minimizing impurities and eliminating thermal degradation
- Increase product recovery by reclaiming additional bottoms product from overhead and distillate products from bottoms
- Separation of close-boiling compounds
- Enhance product recovery
- Recovers additional bottoms product from overhead

Crystallization - forced-circulation crystallizers are used to evaporate the water past the crystallization point. Crystals are dewatered and the resulting filtrate/centrate is returned to the crystallizer. Crystallization can be achieved by spray driers to overcome high solubility of certain salts. The clean condensate is returned to the process for reuse and the dewatered crystals are transported off-site for reuse or disposal

Spray Drier:

An evaporator combined with a spray dryer is an ideal solution for small quantities of wastewater. The wastewater is typically (but not necessarily) concentrated in a vapour recompression evaporator. The concentrated brine is fed directly into a spray dryer. During spray drying, an enormous heat and mass transfer takes place within a fraction of time. It starts with the atomization of a liquid feedstock into a spray of droplets. The small droplets are created by an atomizer - either a rotary wheel or a high pressure nozzle, rotating atomizer will be selected for ZLD applications due to the often viscous, crystalline, harsh and corrosive nature of the feed. The droplets are introduced into a hot airstream, which is cooled down due to the evaporation of the water from the concentrate. This now colder and humid air is discharged from the dryer through a cyclone, bag filter or a combination of the two. After separation of the now dry particles, the air is discharged into the atmosphere and the dry particles (solids) can be cooled and landfilled.

2.3 Applicability of ZLD Technologies

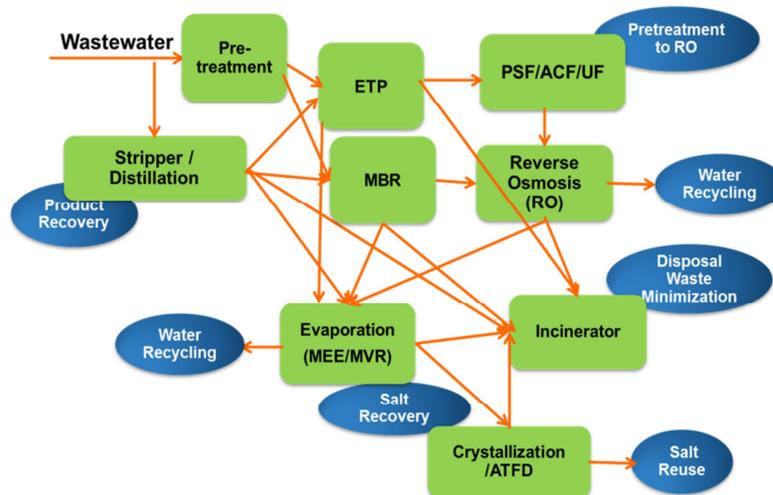
ZLD technologies can be applied to various sectors of industries depending on the quantity of wastewater, characteristics of wastewater streams and sources of generation, recycle and reuse potential for water and salt, etc.

ZLD technologies can be used in variety of combinations with ultimate objective of:

- Recovering useful material,
- Recovering and recycling maximum water and
- Management of reject by evaporation and drying methods.

Various combinations of ZLD technologies and their interconnectivity is shown in following fig:

Fig 3.1: ZLD technology application



A right treatment scheme is to be developed according to type of wastewater to be treated. A matrix is developed as a guideline for applicability of ZLD technologies in various sectors of industries as well as to assess the economic feasibility.

Applicability of ZLD Technologies:

SN	ZLD Technology	Used for	Advantages	Disadvantages	Type/ MOC/ Components	Capital Cost* Rs/m3	Operational Cost* Rs/m3	Applicable for
1	Membrane Bio Reactor (MBR)	Used as biological secondary treatment for reduction of organic load (COD/BOD)	<ul style="list-style-type: none"> Secondary clarifier not required Treated water quality is better than conventional ASP, MBBR and SBR Post treatment of sand filtration not required 	<ul style="list-style-type: none"> Capital cost is more than other aerobic biological technologies (ASP, SBR, MBBR) Membrane replacement after five years 	<ul style="list-style-type: none"> hollow fibre Membranes Pore size 50-10,000nm Pressure < 2 bar Flux - 50-500LMH 	20,000 to 50,000	30-40	<ul style="list-style-type: none"> Textile industry CETPs Oil Refineries Fertiliser industry
2.1	Solvent Recovery-Air Stripper	Used for recovering solvents / Ammonia recovery by providing air	<ul style="list-style-type: none"> Conventional proven method for removal of solvents Economical when solvents with low solubility in water are present in waste water 	<ul style="list-style-type: none"> Applicable only when large quantity of solvent with low solubility in water is present in waste water Difficult to capture solvent when in low concentration 	<ul style="list-style-type: none"> Packed bed column air blowers 	60L-1Cr for 200-400KLD	Depends on Solvent content	<ul style="list-style-type: none"> Recovery of useful solvents, ammonia in pharmaceutical industry pesticide industry Chemical industry.
2.2	Solvent Recovery-	<ul style="list-style-type: none"> Used for 	<ul style="list-style-type: none"> Solvent recovery 	<ul style="list-style-type: none"> Not suitable for 	<ul style="list-style-type: none"> Packed 	1-2Cr for	Depends on	<ul style="list-style-type: none"> Recovery

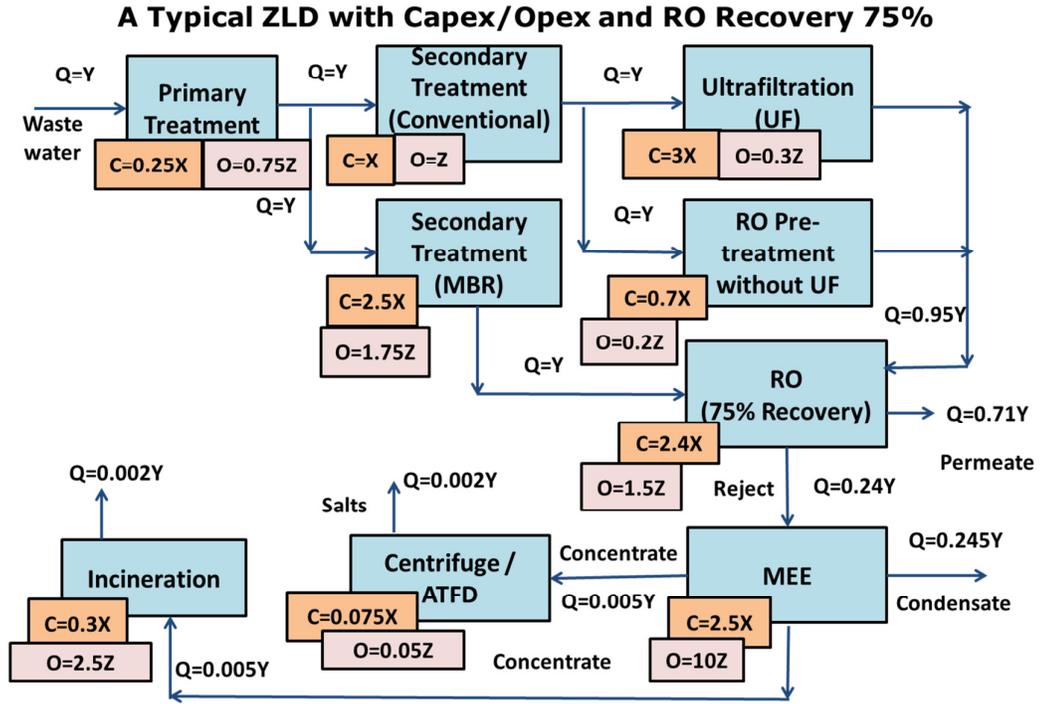
3.1	Steam Stripper	<p>recovering solvents by using steam</p> <ul style="list-style-type: none"> • Solvents can be reused or are saleable 	<p>is more compared to air stripping</p> <ul style="list-style-type: none"> • Useful even less quantity of solvent present in wastewater 	<p>water miscible, high boiling solvents</p> <ul style="list-style-type: none"> • Scaling occurs in column which is to be cleaned periodically 	<p>bed or grid trays in column</p> <ul style="list-style-type: none"> • Steam used 	200-400KLD	<p>ds on Solvent content</p>	<p>of useful solvents, ammonia in pharmaceutical industry</p> <ul style="list-style-type: none"> • pesticide industry • Chemical industry.
3.1	Ultra Filtration (UF)	<ul style="list-style-type: none"> • Used for removal of colloidal matter and bacteria and viruses • Used as pre-treatment to RO 	<ul style="list-style-type: none"> • Removes suspended, colloidal particles, bacteria, viruses. • Best pre-treatment for RO 	<ul style="list-style-type: none"> • Does not filter dissolved solids, gases and organics. • Frequent Backwash, membrane cleaning • Replacement of membranes after 5 years required 	<ul style="list-style-type: none"> • Hollow fibre membranes • MOC : PVDF, PP, PAN • Pore size: 1-100 • Pressure: 1-10 bar • Flux: 10-200LMH 	15,000 to 30,000	2-4	<ul style="list-style-type: none"> • pre-treatment to RO in all ZLD plants
3.2	Reverse Osmosis (RO)	<p>Used for removal of salinity (TDS) and residual organics by passing wastewater through semipermeable membrane by applying</p>	<ul style="list-style-type: none"> • Most Effective treatment for removal of salinity (TDS) with more than 99% salt rejection • Clean technology and no handling of chemicals like acid/alkali like ion exchange technology • Permeate water is free of ions and can 	<ul style="list-style-type: none"> • Very high capital cost • High energy consumption due to high pressure pumps • Membrane replacement required after app. 3 years • Cleaning of membrane frequently due to 	<ul style="list-style-type: none"> • Polyamide with polysulphone support layer • Pore size : < 1nm • Pressure: 10-80 bar • Flux: 5-100LMH 	50000 to 100000	25-45	<ul style="list-style-type: none"> • Used in all industrial sectors for TDS removal and recycling the water

4.1	Multiple Effect Evaporator (MEE)	high pressure Used to evaporate wastewater to separate water and salt by using heat of steam in sequence of vessels	be used in industrial processes • Proven method for recovery of water from saline water and separation of salt	Membrane fouling • Reject water disposal is difficult • Very high Operating cost due to steam requirement	MOC: SS 304, SS316, SS 316L, SS316TI, Titanium	-II Stage (300-1000kg/h r)- 90L -IIIstage (800-2500kg/h r)-1.5Cr -IVstage (2000-6000kg/h r)-3.5-4Cr	600-1000	• Pharmaceutical Industry • Textile industry • Pesticide industry • Dyes & Dye intermediates • Steel industry • Fertiliser industry
4.2	Mechanical Vacuum Compressor (MVR)	Water vapour generated in the evaporator is compressed to higher pressure which acts as heat source for evaporation	• Eliminates thermal energy requirement • Useful when steam not available • Low operating cost	• Suitable only for liquid with narrow boiling point rise (BPR) • Suitable when ready steam is not available in the industry	• Conventional :SS 316/Titanium • Advanced: Polymer	-1000-8000kg/h r – 0.8 to 5Cr	250-400Rs/m ³	• Textile industry

5.1	Crystalliser	Used to dry high TDS water or products using heat	<ul style="list-style-type: none"> Used for recovery of salts like Sodium Sulphate, Sodium Chloride, Sodium Thio-Sulphate, Zinc Sulphate etc.. Simple evaporation method of single effect evaporation 	<ul style="list-style-type: none"> Scaling and corrosion of unit is a problem Requires frequent cleaning 	SS 304 / SS 316	200-300Rs/kg	0.1-0.2Rs/kg	<ul style="list-style-type: none"> All industrial sectors
5.2	Agitated Thin Film Dryer (ATFD)	Used to dry high TDS water or products using fast revolving rotor in a heating jacket.	<ul style="list-style-type: none"> Good heat conductivity, so can be applied for highly viscous fluids Gentle evaporation and high evaporation rate Continuous cleaning of heating surface One pass evaporation 	<ul style="list-style-type: none"> Scaling and corrosion of unit is a problem 	SS 304 / SS 316	200-600Rs/kg	0.5-1.0Rs/kg	<ul style="list-style-type: none"> Applicable for Salt recovery in Dye & Dyes intermediates Textile industry Pharmaceutical industry for final drying before disposal
6	Incinerator	Used for burning the concentrated effluent by thermal energy	<ul style="list-style-type: none"> Useful method for very high strength (High COD) effluent which is difficult to biodegrade No further treatment is required 	<ul style="list-style-type: none"> Requires very high energy Operational cost is high Capital cost is high Viable for only small quantities of effluent 	SS3016 incinerator with air pollution control system	1000-1200Rs/kg	Rs.10-15/kg	<ul style="list-style-type: none"> Pharmaceutical industry Dye and Dye intermediates Pesticide industry

Note : * Costs are on the basis of interaction with ZLD industries, suppliers of ZLD technologies, web references, etc.

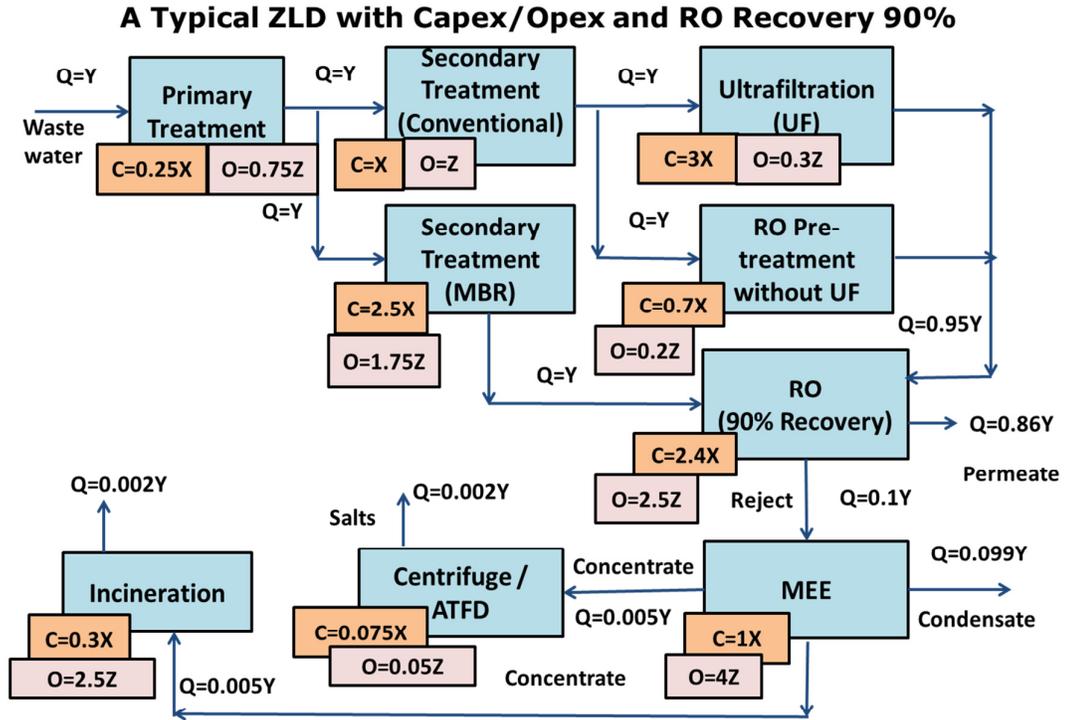
ZLD with 75% RO recovery



Note : Q = Flow (KLD/MT); C & O=Capex & Opex costs are proportionate to respective Q to unit

C = Capital Cost represented as 'X'
 O = Operating Cost represented as 'Z'
 Q = Flow represented as 'Y'

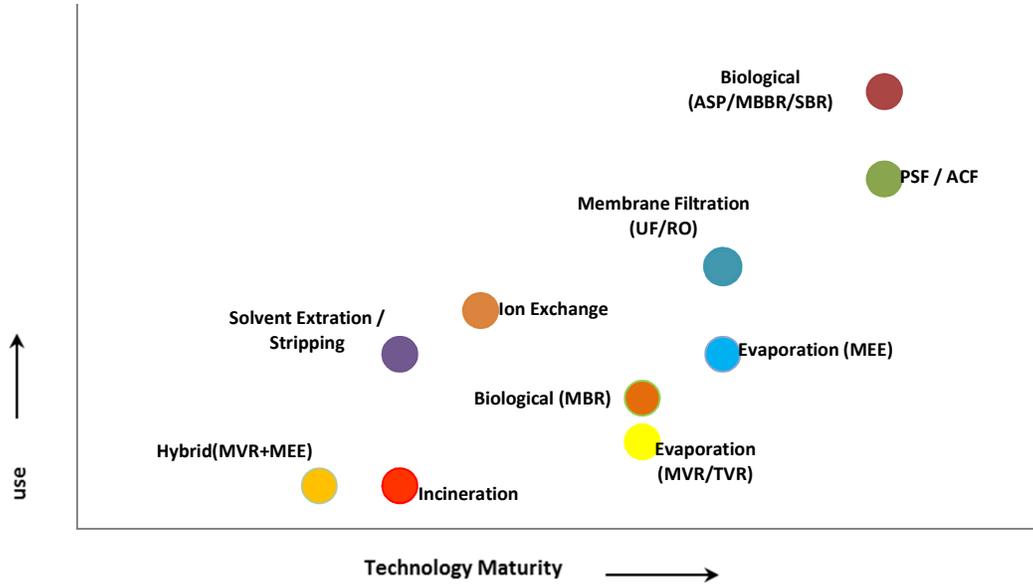
ZLD with 90% RO recovery



Note : Q = Flow (KLD/MT); C & O=Capex & Opex costs are proportionate to respective Q to unit

C = Capital Cost represented as 'X'
O = Operating Cost represented as 'Z'
Q = Flow represented as 'Y'

Technology Maturity:



Note : Technology Maturity is based on its application and age.

3 ZLD INDUSTRIAL APPLICATION

3.1 Pharmaceutical Industry

The Indian pharmaceutical industry can be divided into the bulk drug and formulations segments. Bulk drugs are the active pharmaceutical ingredients (APIs) with medicinal properties, which are used to manufacture formulations. The Indian pharmaceutical industry manufactures about 400 bulk drugs belonging to various therapeutic segments¹. Formulations are the end-products of the medicine manufacturing process, and can take the form of tablets, capsules, injectables or syrups, and can be administered directly to patients.

Major sources and characteristics of effluent

ZLD technologies are mostly applied to API manufacturing industries. The production of special niche API has brought in the problem of specific type of pollution in the effluent. The effluent parameters vary with the niche of product and hence there is no single solution common for all. Pollution control boards are being very strict on the API industry for effluent release outside the premises. Most of the industries are being pushed to adopting a ZLD (Zero Liquid Discharge) regime.

Active Pharmaceutical Ingredients from waste water streams are emerging contaminants in the aquatic environment, because of their adverse effect on aquatic life and humans. The waste from API industries contains high COD, high TSS, other harmful chemicals and high amount of salt along with various nascent chemicals such as bromine & chromium. The chemicals present in the effluent will be dependent on the

product being processed at the manufacturing facility and hence a tailor made solution would be required for making each API manufacturing facility ZLD compliant.

Major sources of generation of wastewater from API industry² are:

- Lean Stream (Low COD-Low TDS)
 - Process Plant -From reactor washings (2nd washing onward)
 - Utility wastewater – From DM plant regeneration, RO reject, Cooling tower blow down, Boiler Blow down, etc.
 - Floor washings
- Mother Liquor Streams (High COD-High TDS, High TDS-low COD, High COD-low TDS)
 - Process plant – product separation, First washings of reactors
- Mother Liquor Stream (high Solvents)
 - From process plant comprising solvent reactions
- Mother Liquor Stream (high Ammonia)
 - From process plant comprising ammonical nitrogen reactions

(Note : High COD:>5000 mg/l, High TDS:>5000mg/l,
Low COD:<5000mg/l, Low TDS:<5000mg/l)

Lean flow is usually 100 to 300KLD depending on size of industry. Mother liquor stream flow is very small (10 to 30KLD).

Ref: [12, 3]

Treatment of Wastewater

Since there are various sources of effluent generation with varies characteristics, the first objective shall be to segregate the streams at source.

A typical treatment of segregated streams shall be as follows:

- Lean Stream (Low COD-Low TDS): Taken to Effluent Treatment Plant (ETP) for primary, secondary biological treatment (ASP/MBR/SBR) and then to tertiary treatment of sand filtration/UF and RO.
- ML-1: Mother Liquor Stream - (High COD-High TDS, High TDS-low COD, High COD-low TDS): Taken to evaporator (MEE) for concentration of the stream. Distillate from MEE is routed to ETP, if not of recyclable quality.
- ML-2: Mother Liquor Stream (with solvents): Taken to Solvent Stripper for recovering solvent
- ML-3: Mother Liquor Stream (high NH₃): Taken to NH₃ Stripper for removal of ammonia. Or it is treated with high grade (>95% lime) and Calcium sulphate is isolated and sent to cement industry.
- RO permeate is recycled back in process, cooling tower, boiler make up water.
- RO rejects are concentrated in MEE, dries by crystaliser / ATFD and mixed salt is sent to designated TSDF.
- Sludge from ETP is dewatered and sent to TSDF

ZLD treatment options are shown in **Fig 3.1, 3.2 and 3.3.**

Figure 3.1: Option 1 - ZLD for Pharmaceutical Industry

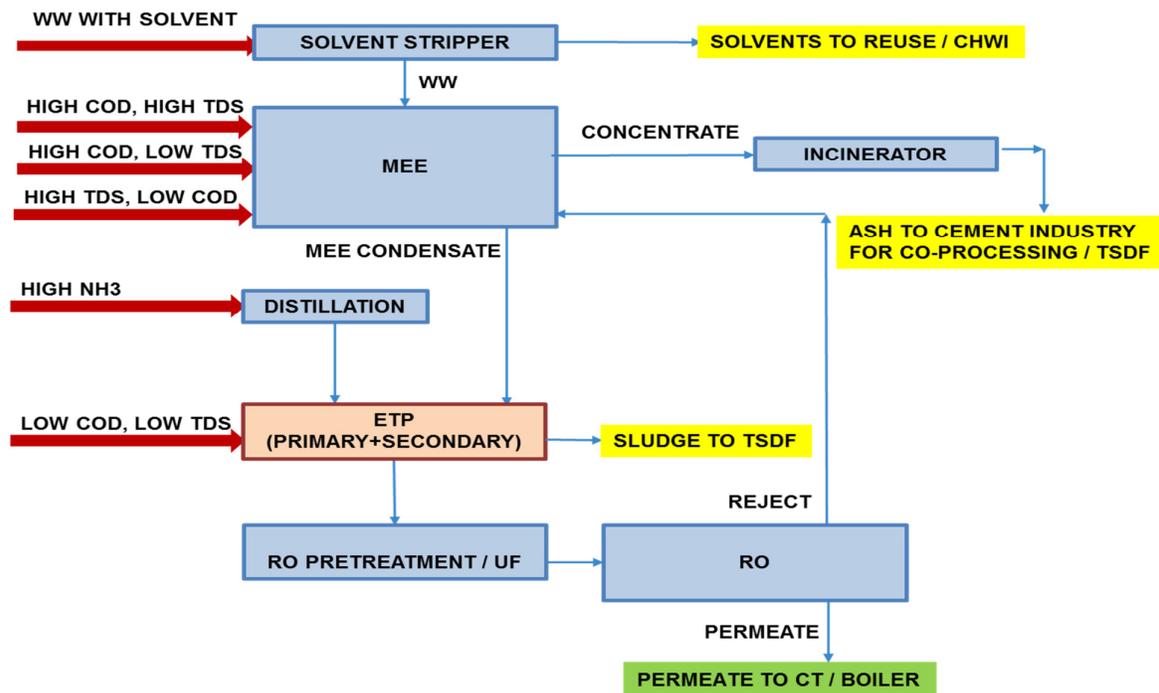


Figure 3.2: Option 2 - ZLD for Pharmaceutical Industry

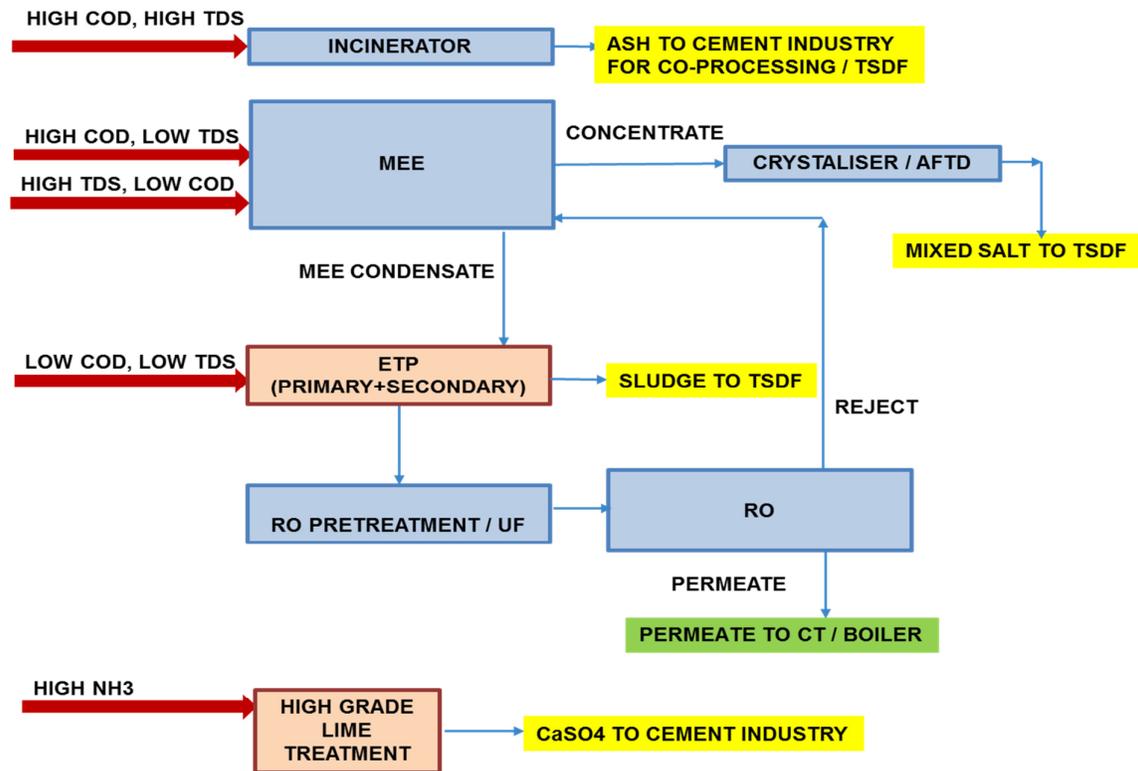
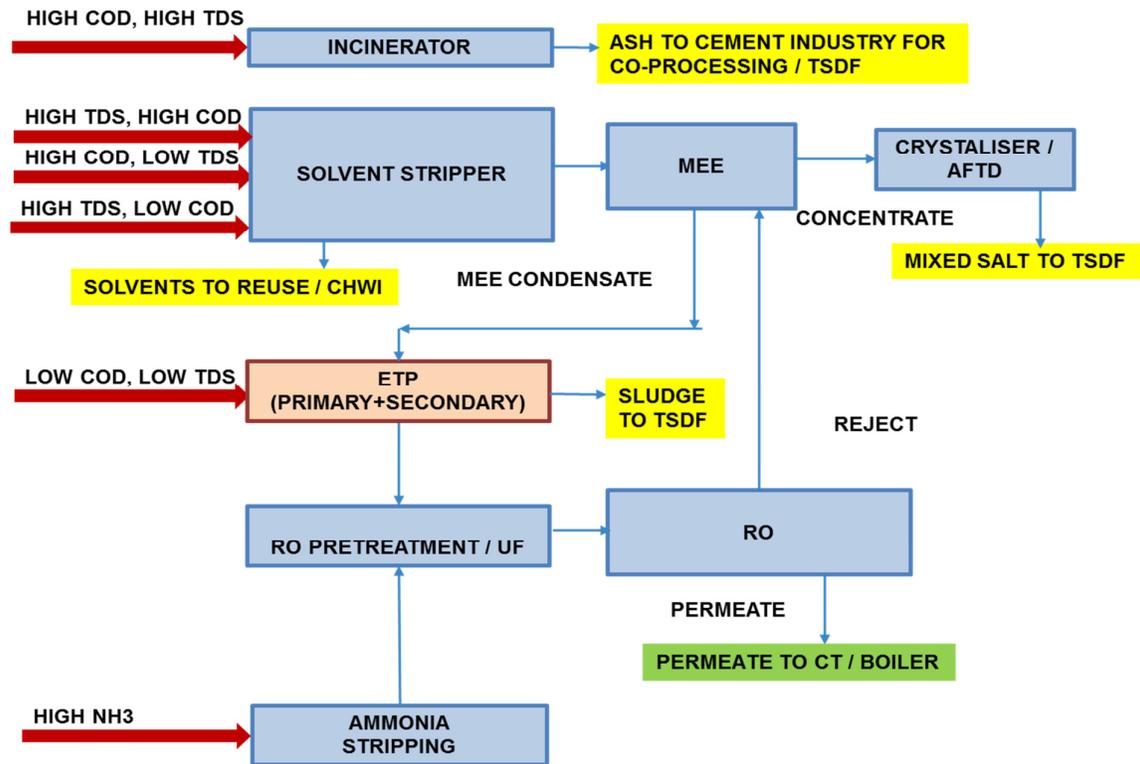


Figure 3.2: Option 3 - ZLD for Pharmaceutical Industry



3.2 Textile Industry

The textile units use a number of dyes, chemicals and other materials to impart desired quality to the fabrics. These units generate a substantial quantity of effluents, the quality of which in most of the cases is unsuitable for further use and can cause environmental problems, if disposed of without proper treatment. At present, due to the increasing resource constraints and the environmental requirements, these textile units need to adopt a sustainable approach, and wastes need therefore to be viewed as unutilised resources. Ways and means must be found to recover water and chemicals from these “waste” resources. Advanced treatment methods, like membrane filtration, appear to be promising because these methods not only help in reducing the pollution but also provide a scope for recovery and recycling of water and chemicals.

Textile industry can be classified into three categories: Cotton, woollen and synthetic fibres upon raw material used. The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is always rich in colour, reactive dyes, chemicals and refractive organic matter. Thus it is complex mixture of inorganic and organic compounds. In synthetic fibre mills use of cooling water is quite high. Final rinse water after mercerising, bleaching and dyeing is only slightly contaminated. And can be recycled for further rinsing.

Major Sources of wastewater generation

Following are the processes generating wastewater:

Process	Effluent composition	Nature
Sizing	Starch, waxes, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), wetting agents.	High in BOD, COD
Desizing	Starch, CMC, PVA, fats, waxes, pectins	High in BOD, COD, TSS, Total dissolved solids (TDS)
Bleaching	Sodium hypochlorite, Cl ₂ , NaOH, H ₂ O ₂ , acids, surfactants, NaSiO ₃ , sodium phosphate, short cotton fibre	High alkalinity, high TSS
Mercerizing	Sodium hydroxide, cotton wax	High pH, low BOD, high TDS
Dyeing	Dyestuffs urea, reducing agents, oxidizing agents, acetic acid, detergents, wetting agents.	Strongly coloured, high BOD, TDS, low TSS, heavy metals
Printing	Pastes, urea, starches, gums, oils, binders, acids, thickeners, cross-linkers, reducing agents, alkali	Highly coloured, high COD, oily appearance, TSS slightly alkaline,

Ref: [14]

Treatment of waste water

Wastewater from dyeing and printing processes is rich in colours which are non-biodegradable and difficult to treat. Mercerizing wastewater has high concentration of salts in wastewater.

It is necessary to segregate the streams. Initial dye bath stream shall be separated from other streams. The dye bath stream is 10-15% of total wastewater.

Dye bath after primary treatment can be directly treated in evaporation technology for reduction of volume. Condensate is recycled in process.

Other wastewater is treated with primary physicochemical treatment followed by biological treatment. After biological

treatment wastewater is subjected to pressure sand and activated carbon filters. Then water is subjected to UF/ RO system for recovery of water for recycling in process. Rejects from RO system are subjected to MEE process. Concentrated slurry from MEE is subjected to crystalliser/ATFD for further drying of salts. Glauber salt is recovered by chilling and then crystalliser. Glauber salt is reused in process again. Mixed salt is either reused or disposed off in designated secured landfill site.

Proper selection and application of individual or combination the advance treatment methods in textile industry can effectively make recovery of water and/or salts from effluent streams for their reuse in production process. Along with the recovery and reuse of water and salt, the advance methods can also be applied to meet stringent environmental or regulatory requirements such as zero effluent discharge. Membrane filtrations can produce treated water with high purity. The evaporator and crystallizer combination can recover salt.

The effluent stream bearing high salt i.e. the spent dye bath is segregated and treated with recovery of salt. This effluent stream has low volume and can be treated using a chemical treatment followed by multi-effect evaporation and crystallization. Glauber salt (Sodium Sulphate decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) based dyeing enables recovery of the salt. The other effluent stream i.e. wash water can be treated separately by primary/secondary treatment methods followed by RO system to recover water.

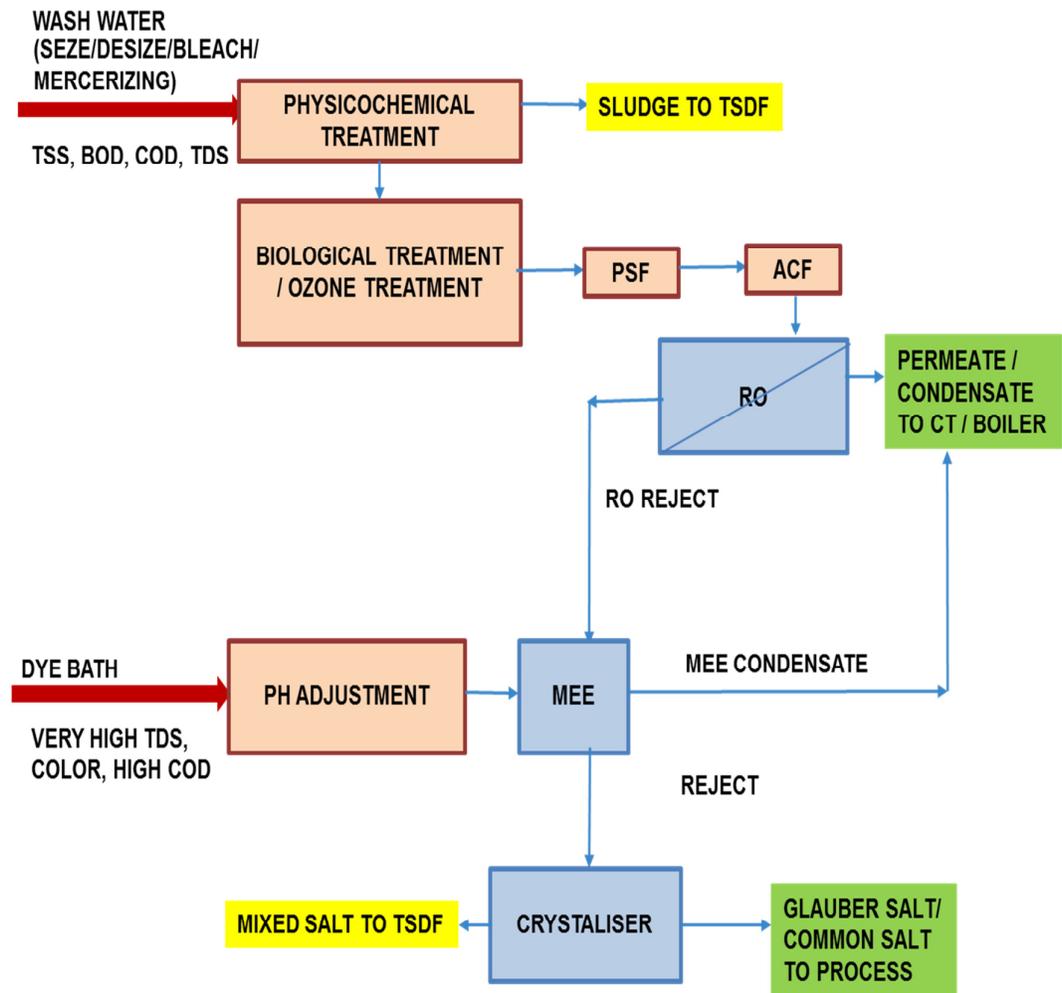
Recovery

- Water recovery upto 98% is achievable by using multistage RO system and proper operation of pre-treatment and evaporation technologies.

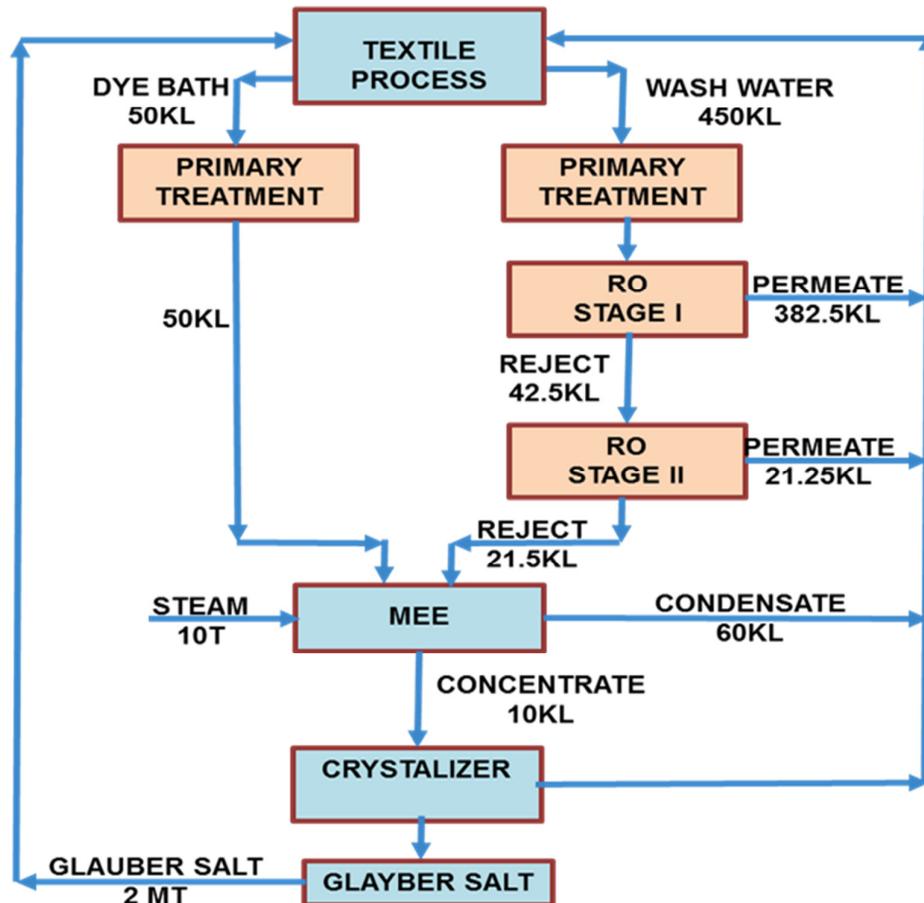
- Glauber salt is recovered from the system and is reused in the process

Following are ZLD treatment options for textile wastewater:

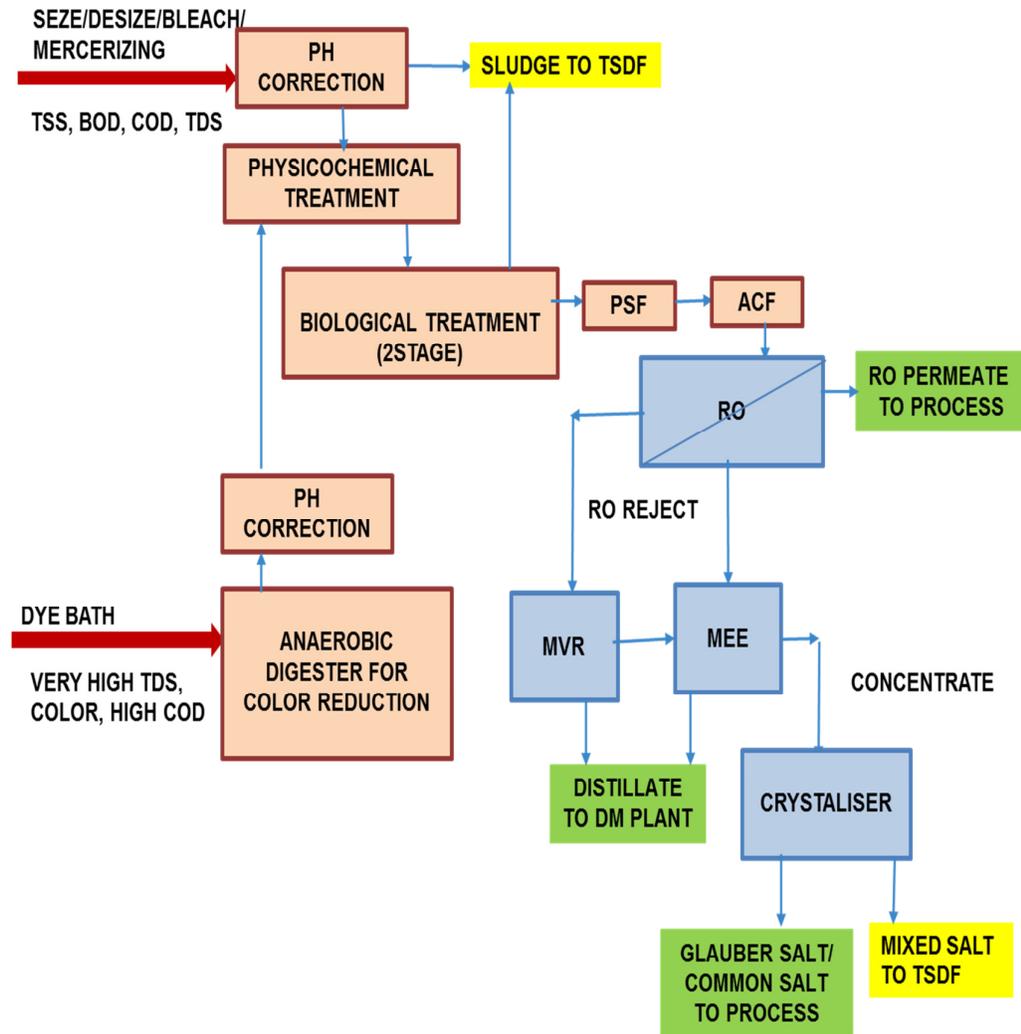
Textile ZLD : Option 1



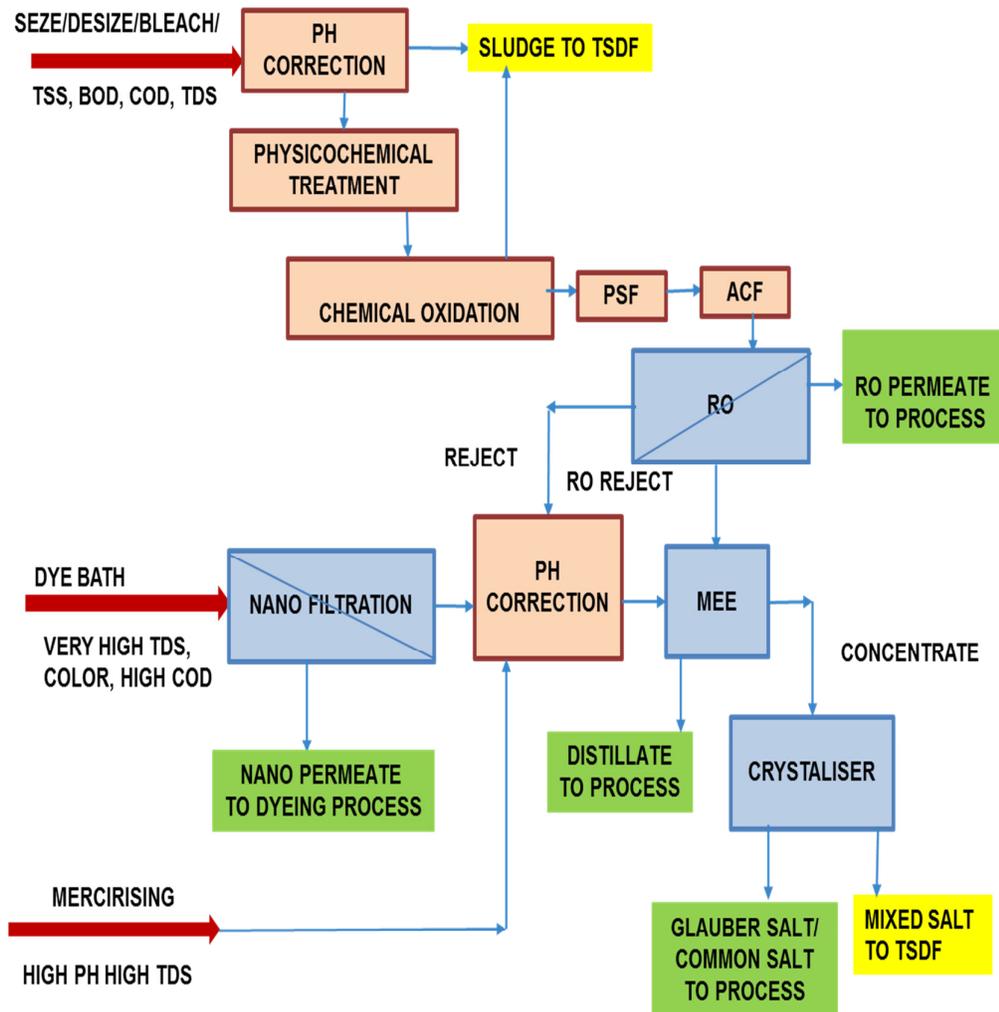
TYPICAL MASS BALANCE FOR 500 KLD TEXTILE ZLD



Textile ZLD : Option 2



Textile ZLD : Option 3



3.3 DYES AND DYE INTERMEDIATES

In dyes and Dye intermediates industry, H acid production and Vinyl Sulphone manufacturing are two major units.

H- Acid Plant

Manufacturing of H-acid involves various processes and generates two types of effluent.

Acidic Stream:

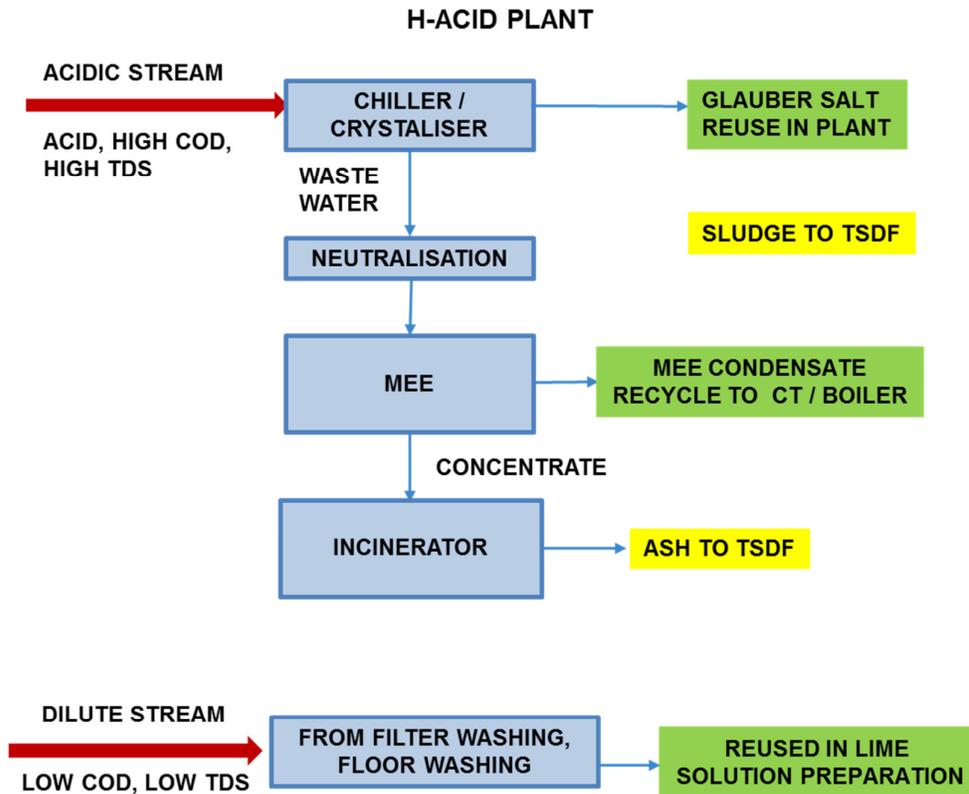
This is generated from isolation stage of H-acid during Filtration and centrifugation process. Effluent generation is 15-18 l/kg of product, having High COD and TDS values as Mother Liquor. This waste water is passed through crystallizer, where mother liquor is chilled to recover Glauber salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). This Glauber salt is reused in H-acid manufacturing plant. Waste water which is acidic is then neutralized. The neutralized effluent is passed through the Multiple Effect Evaporator. Condensate generated is reused back in the process for hot water wash /cooling tower make up, and the concentrate having specific gravity 1.3-1.35 , is high in organics , is incinerated or spray dried .

Thus in above treatment there is recovery of Glauber salt which is reused in H acid manufacturing, reduction of salt in waste water for better MEE operation, reuse of condensate water from MEE. Concentrate from MEE are incinerated in Incinerator.

Dilute stream:

It is mainly generated during gypsum cloth, filter washing and floor washings. This dilute stream is reused in lime solution preparation, gypsum washing, etc.

Ref : [14, 15]



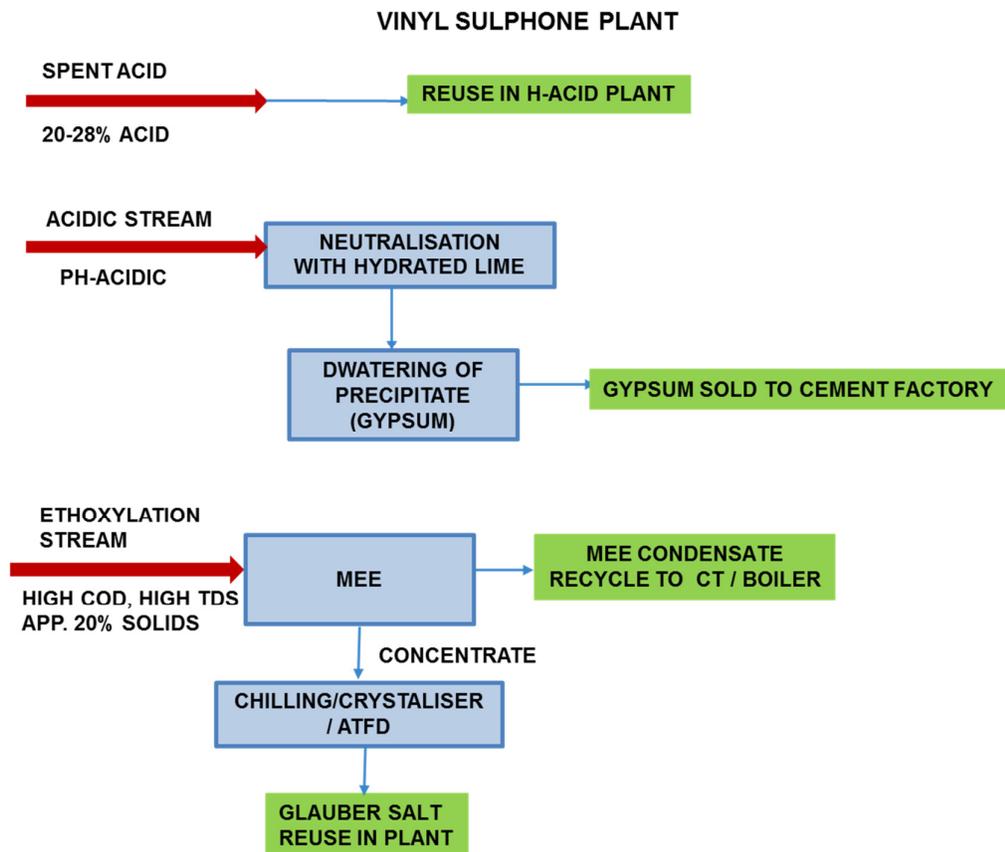
Vinyl Sulphone Plant

The manufacturing of Vinyl Sulphone effluent is generated at two stages. The stage one is of acidic effluent of Acetyl Sulphonyl Chloride (ASC) and stage two is neutral ethoxylation effluent.

Acidic Stream: Acidic waste water of 20-28% acidity sulfuric acid (6 l/kg) is generated from drowning of sulpho mass in Ice chilled water in ASC manufacturing. This spent acid effluent is reused in H-acid plant at isolation stage.

Washings of ASC are neutralised with hydrated lime. Neutralised sludge can be dewatered resulting in Calcium sulphate (Gypsum), which is sold to cement industry.

Ethoxylation Wastewater: The other stream is Ethoxylation waste water generated during the condensation stage of reduction mass with Ethylene oxide. The Ethoxylation waste water generated @ 6-6.5 ltrs/kg is having high COD/TDS. The Ethoxylation waste water (20% solids) is passed through the Multiple Effect Evaporator to recover sodium sulphate (Glauber Salt) after chilling. Glauber salt is reused in dyes manufacturing. Condensate water from MEE is recycled back in cooling tower makeup.



3.4 Chemical Industry

The chemical industry comprises the companies that produce industrial chemicals. Basic chemicals or “commodity chemicals” are a broad chemical category including pharmaceutical products, polymers, bulk petrochemicals and intermediates, other derivatives and basic industrials, inorganic/organic chemicals, and fertilizers. The chemical industry is of importance in terms of its impact on the environment. Chemical industrial wastewaters usually contain organic and inorganic matter in varying concentrations. Many materials in the chemical industry are toxic, mutagenic, carcinogenic or simply almost non-biodegradable. This means that the production wastewater also contains a wide range of substances that cannot be easily degraded.

A ZLD scheme for pesticide and aromatic chemical manufacturing processes can be designed as follows:

Major Sources of Wastewater Generation:

There are various chemical processes carried out in manufacturing of chemicals according to type of chemical. Generally for pesticide, aromatic chemicals manufacturing industry wastewater is broadly divided into high strength and low strength wastewater streams.

High strength wastewater streams:

- High TDS (>10,000 mg/L) with High COD (non-volatile organics >10,000mg/l)
- High TDS (>10,000 mg/L) with High COD (volatile organics > 10,000mg/l)
- High TDS (>10,000 mg/L) with low COD (volatile organics- <10,000mg/l)

- High COD (volatile organics or mixed organics >10,000 mg/L) with low TDS (<10,000mg/l)
- High COD (non-volatile non-biodegradable organics >10,000 mg/L)
- Very High COD (>10% volatile organics, 1,00,000mg/l) low TDS (<10,000mg/l)
- Very High COD (>10% non-volatile organics) with Very high TDS (>1,00,000mg/l)

Low strength wastewater streams:

- Low TDS (<10,000 mg/L) without organics
- Low TDS (<10,000 mg/L) with low COD (<10,000 mg/L) without volatile organics
- Low TDS (<10,000 mg/L) with low COD (<10,000 mg/L) with volatile organics (solvents)

ZLD Treatment Scheme:

It is necessary to identify, characterise and segregate the streams before treating. High strength streams are usually from various chemical processes, first washings of reactors, etc.

Lean or low strength streams are generally utility streams such as cooling tower and boiler blow-downs, DM water plant regeneration, rejects from RO, et. and process plant reactor washings and floor washings, etc.

Treatment of each stream is given below:

High strength wastewater treatment:

- High TDS (>10,000 mg/L) with High COD (non-volatile organics >10,000mg/l)
 - Multiple-effect Evaporator with dewatering of residual salt; this stream can be mixed with RO Reject

- High TDS (>10,000 mg/L) with High COD (volatile organics > 10,000mg/l)
 - Single effect Evaporator with dewatering of residual salt and thermal oxidation of vapours (ensuring air pollution control); heat can be recovered by pre-heating the vapours using exhaust gases
- High TDS (>10,000 mg/L) with low COD (volatile organics-<10,000mg/l)
 - Multiple-effect Evaporator with dewatering of residue and treatment of condensate in bio-treatment system
- High COD (volatile organics or mixed organics >10,000 mg/L) with low TDS (<10,000mg/l)
 - Single-effect Evaporator with dewatering & incineration of residual salt and thermal oxidation of vapours (ensuring air pollution control); heat can be recovered by pre-heating the vapours using exhaust gases
- High COD (non-volatile non-biodegradable organics >10,000 mg/L)
 - Multiple-effect Evaporator with incineration of residue
- Very High COD (>10% organics, 1,00,000mg/l) low TDS (<10,000mg/l)
 - Incineration, followed by heat recovery
- Very High COD (>10% non-volatile organics) with Very high TDS (>1,00,000mg/l)
 - Multiple-effect evaporator with incineration of residue
 - Single-effect evaporator with thermal oxidation of vapours and dewatering of residual salts.

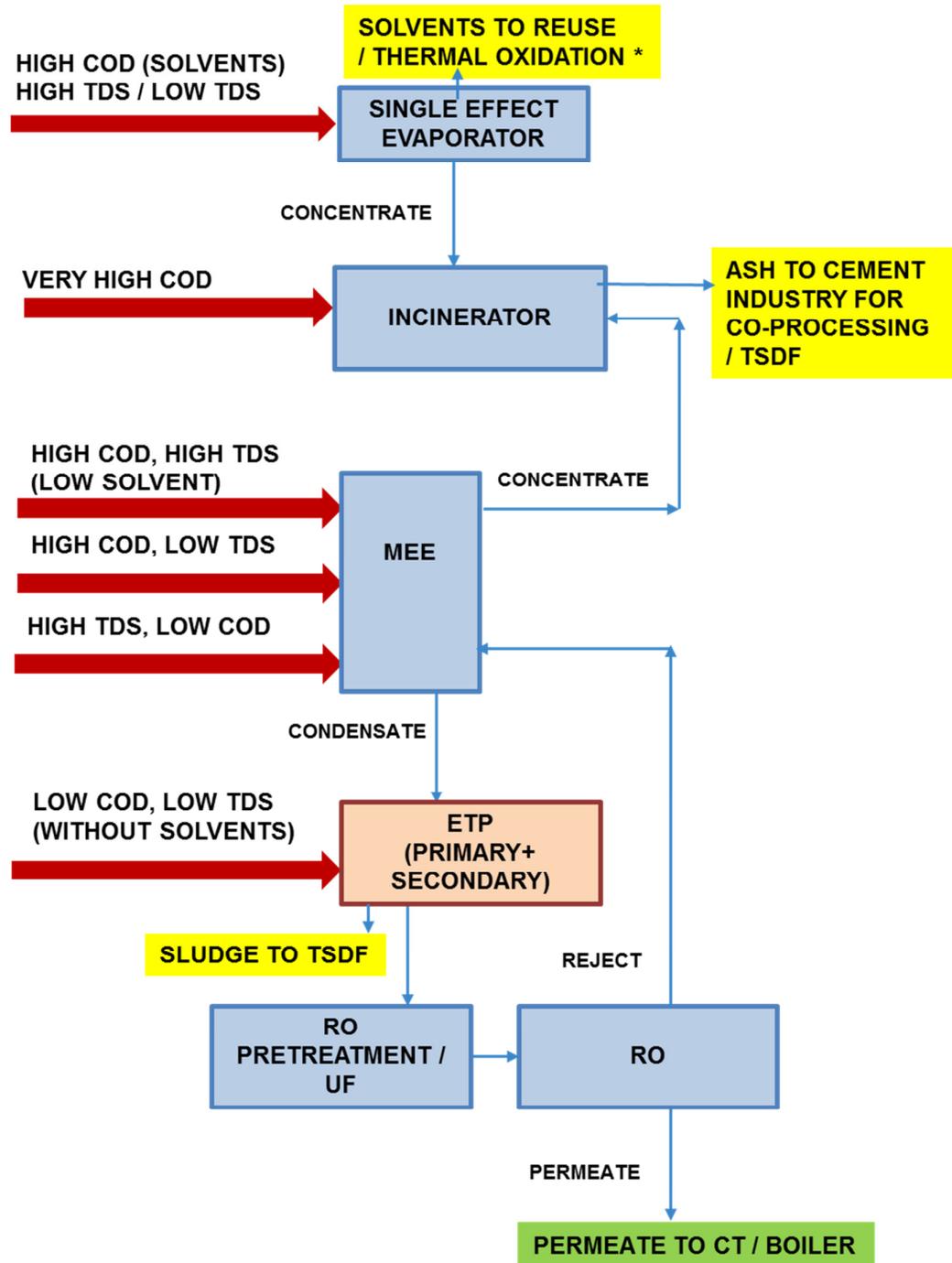
Low strength wastewater treatment:

Low strength wastewater is first treated by primary and / or secondary treatment for removal of suspended particles and biodegradable organics. Further water is treated in tertiary treatment to remove TDS for recycling the permeate water in the process. Rejects are treated by MEE and salt is dewatered by centrifuge / ATFD.

- Low TDS (<10,000 mg/L) without organics
 - Primary treatment for removal of TSS, metals and hardness, followed by ultrafiltration(UF) and Reverse Osmosis(RO). Reject from RO to MEE.
- Low TDS (<10,000 mg/L) with low COD (<10,000 mg/L) without volatile organics
 - Primary treatment for removal of TSS, metals and hardness, followed by membrane bio reactor (MBR) and Reverse Osmosis(RO). Reject from RO to MEE.
- Low TDS (<10,000 mg/L) with low COD (<10,000 mg/L) with volatile organics (solvents)
 - Solvent stripper followed by Primary treatment for removal of TSS, metals and hardness, followed by membrane bio reactor (MBR) and Reverse Osmosis(RO). Reject from RO to MEE.
 - Primary treatment for removal of TSS, metals and hardness, followed by high rate bioreactor followed by membrane bio reactor (MBR) and Reverse Osmosis (RO). Reject from RO to MEE.

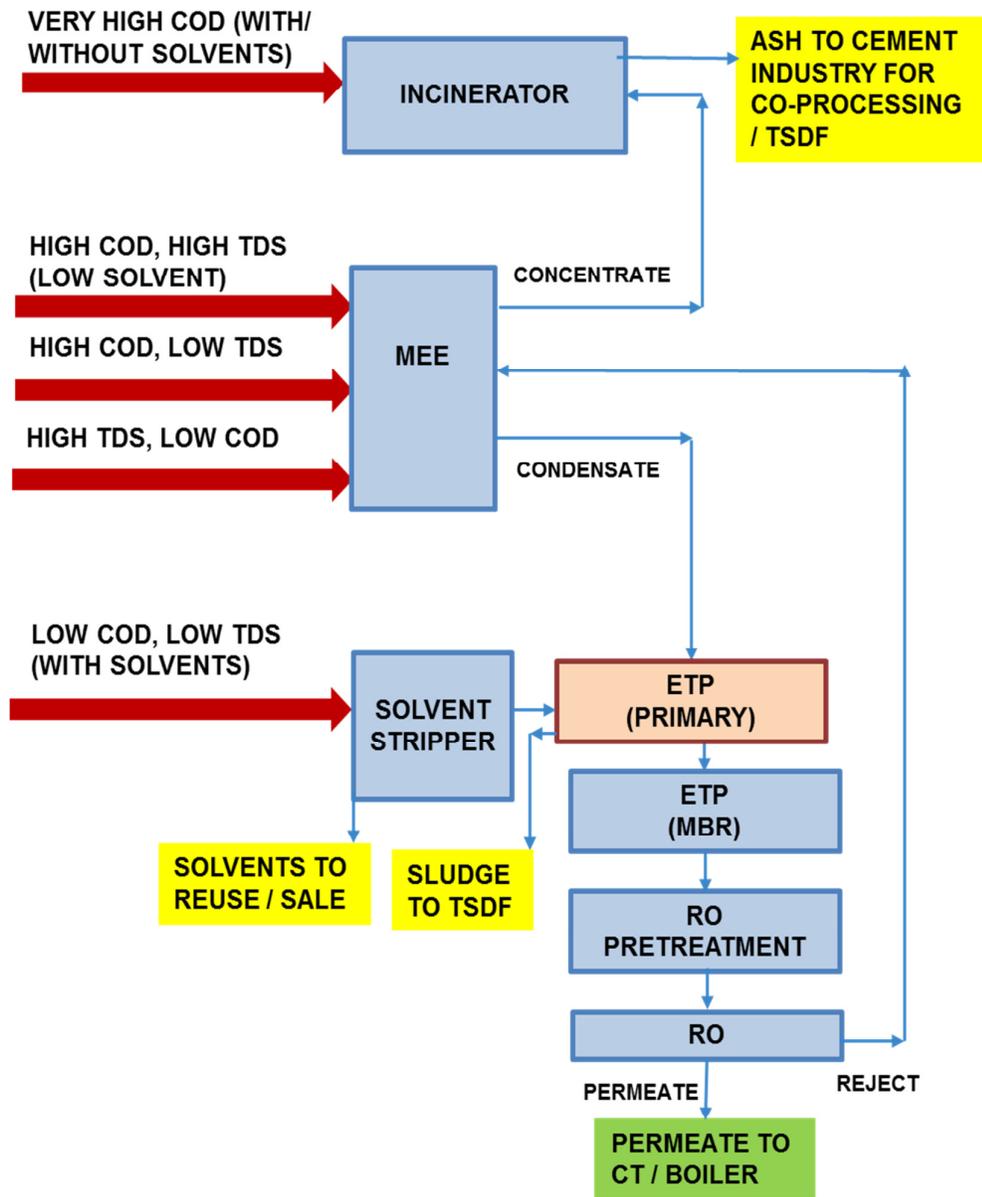
Ref : [16]

Option 1 : ZLD treatment flow-chart for Chemical Industry

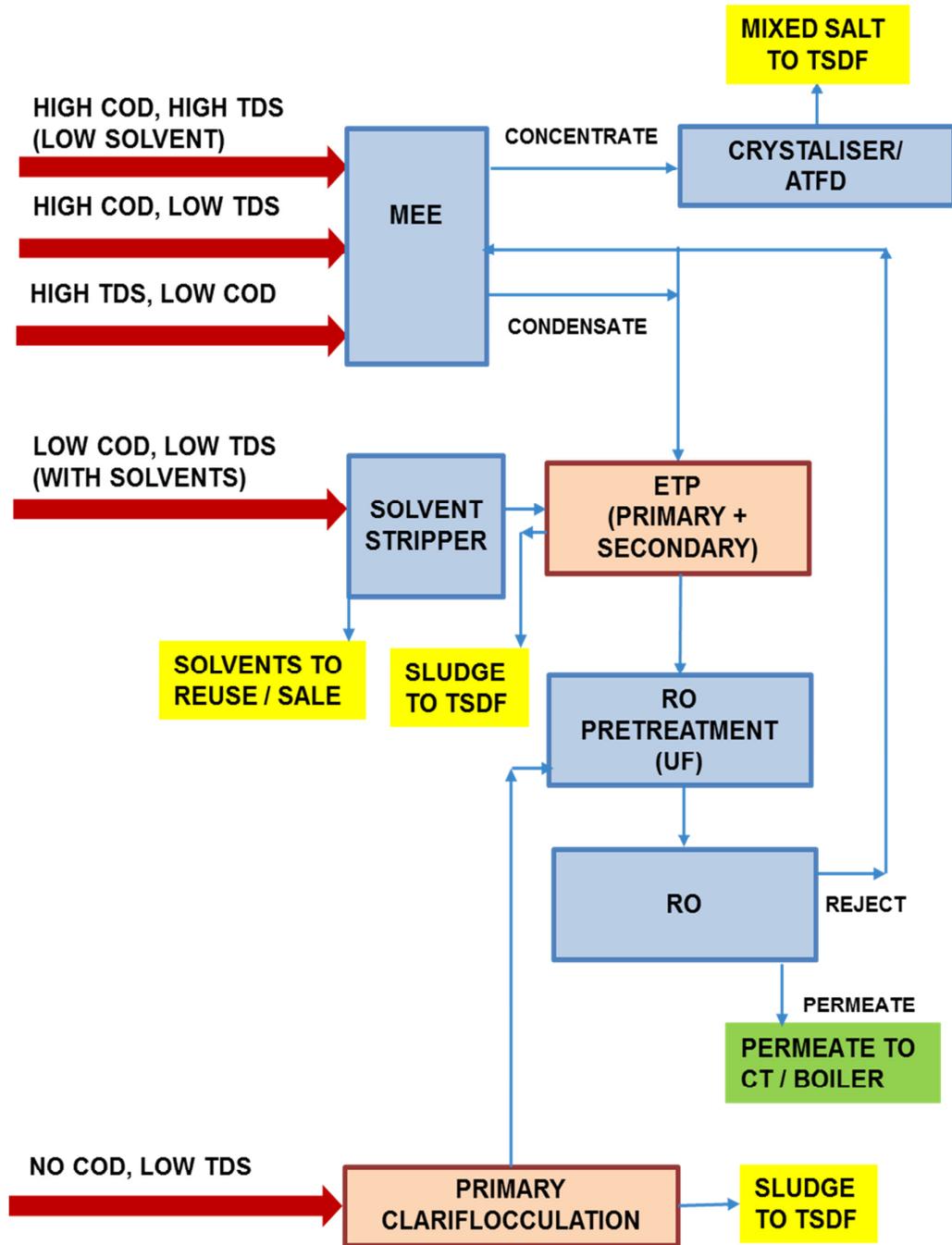


NOTE: * - THERMAL OXIDATION WITH STIPULATED AIR POLLUTION CONTROL NORMS

Option 2 : ZLD treatment flow-chart for Chemical Industry



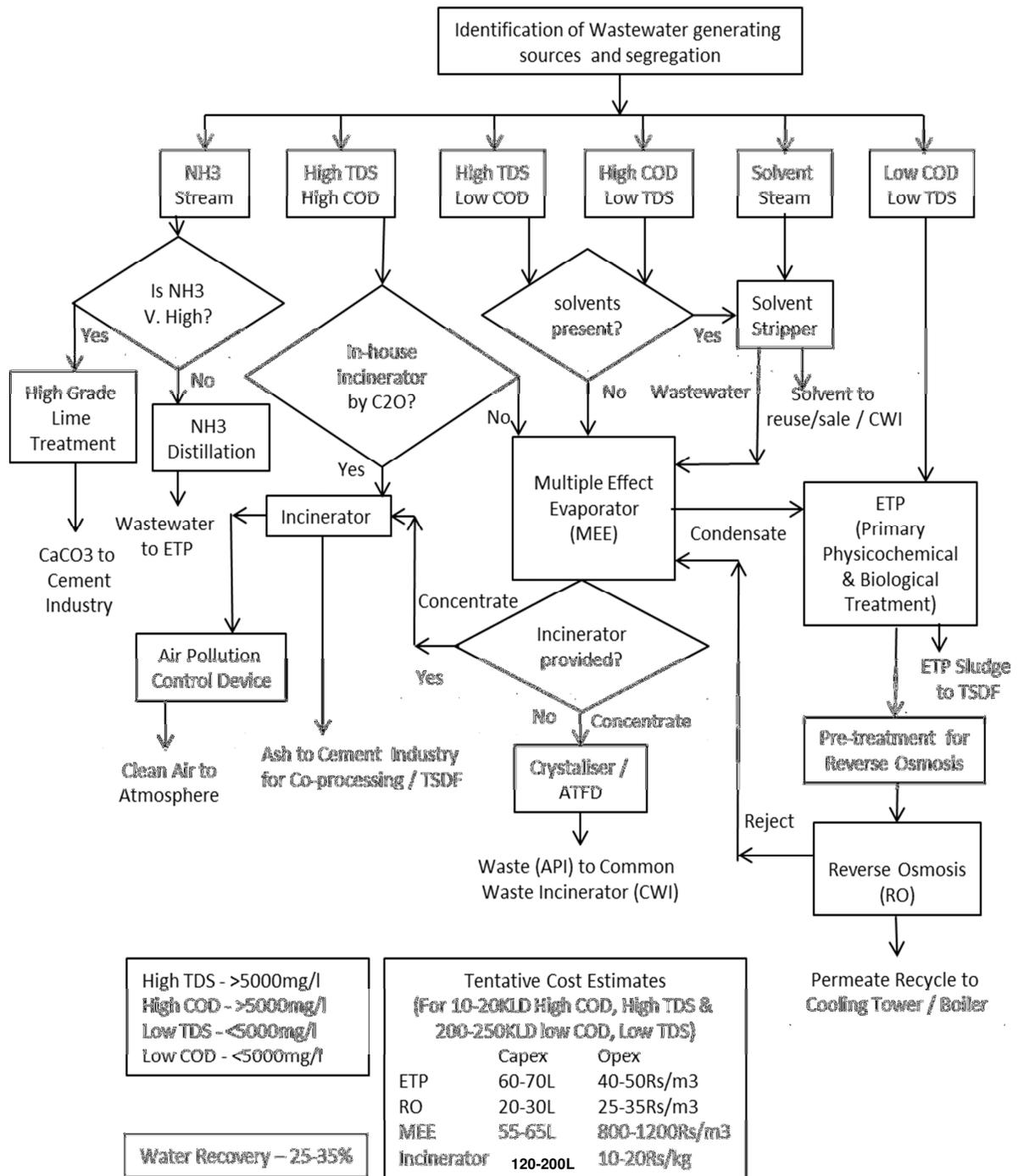
Option 3 : ZLD treatment flow-chart for Chemical Industry



4. SELECTION OF ZLD TECHNOLOGY

4.1 Selection of ZLD Technology for Pharmaceutical Industry

ZLD Treatment Selection for Pharmaceutical (API) Industry



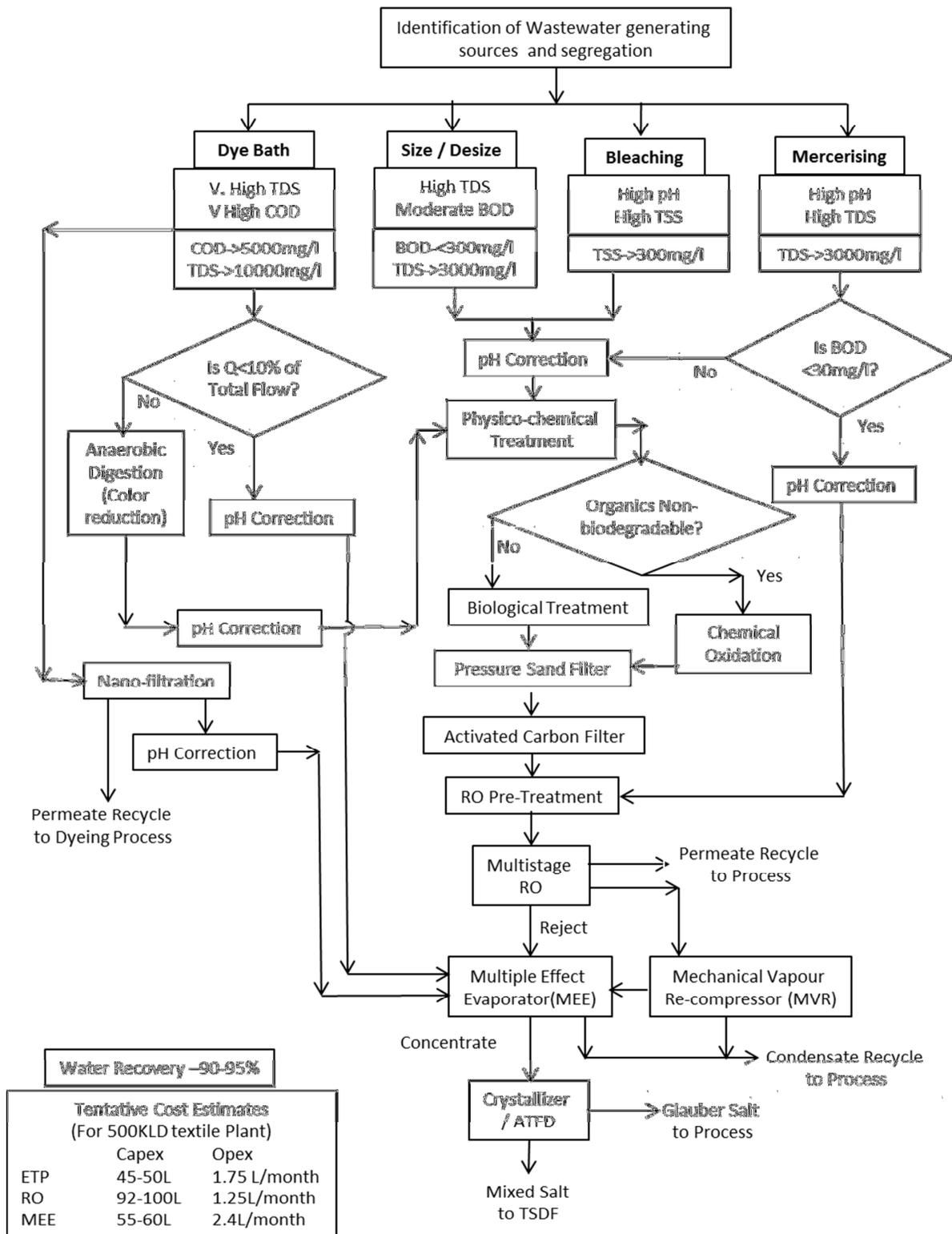
High TDS - >5000mg/l
High COD - >5000mg/l
Low TDS - <5000mg/l
Low COD - <5000mg/l

Water Recovery – 25-35%

Tentative Cost Estimates (For 10-20KLD High COD, High TDS & 200-250KLD low COD, Low TDS)		
	Capex	Opex
ETP	60-70L	40-50Rs/m3
RO	20-30L	25-35Rs/m3
MEE	55-65L	800-1200Rs/m3
Incinerator	120-200L	10-20Rs/kg

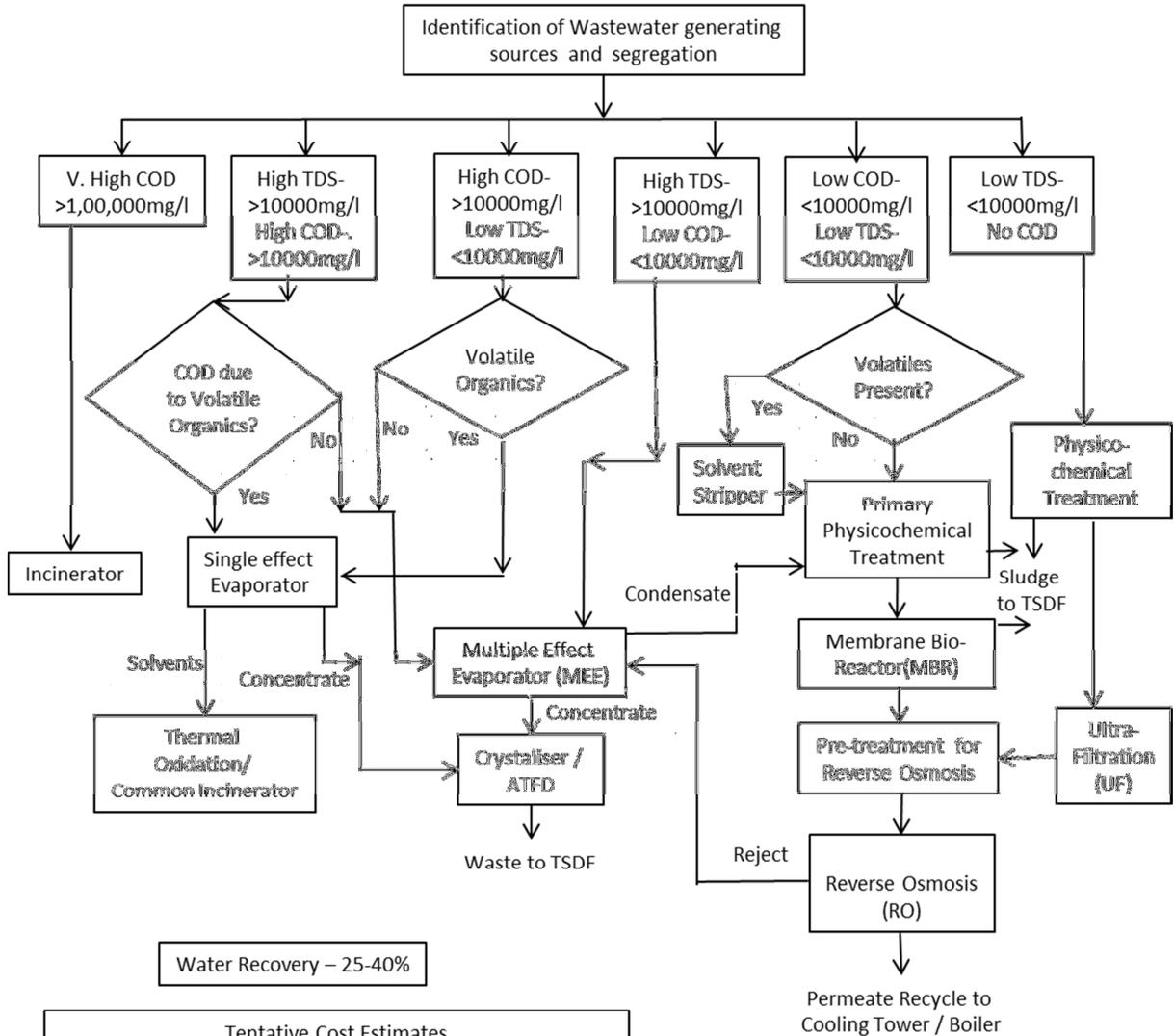
4.2 Selection of ZLD Technology for Textile Industry

ZLD Treatment Selection for Textile Industry



4.3 Selection of ZLD Technology for Chemical Manufacturing Industry

ZLD Treatment Selection for Chemical Industry



Tentative Cost Estimates (For typical 500 KLD Effluent ZLD Plant)		
	Capex, Rs	Opex
ETP (conventional)	100-120L	10-15 Rs/m ³
ETP(with MBR)	250L-300L	15-20Rs/m ³
UF	50L-80L	5-10Rs/m ³
RO	80-120L	25-40Rs/m ³
MEE (150KLD)	250-500L	600-800Rs/m ³
Single EE (30-50KLD)	100-300L	3000-5000Rs/m ³
Incinerator (100kg/hr)	50L-60L	10-20Rs/kg

5. WAY FORWARD

Zero Liquid Discharge systems in the industry are fast becoming a mandatory necessity due to stringent enforcement of regulations. This is a result of past many years of non-compliance. Indiscriminate pollution and extraction of water over the years has had devastating impact on water bodies. Due to water scarcity, river and ground water pollution and landlocked locations for discharge of effluent, Zero Liquid Discharge (ZLD) framework is being imposed on industries through regulations.

Challenges to Face:

1. High Capex and Opex

Major challenge for installing ZLD system is Capital cost (Capex) and operational cost (Opex) is very high. It is a financial burden on small or medium scale industry. Therefore feasible and Attractive Financial Models should be developed to promote ZLD and make it successful.

- Financial institutions would come up with a more amenable solution which is a BOOT model whereby the investment into implementing a ZLD unit would be made by a third-party investor who would recover their return on investment by charging a tariff over a long concession period, typically 10-15 years.

There are two risks involved for investor. One Technology & Operations Risk and other credit risk. Once these parameters are well identified and the risks quantified, a risk premium is priced which is then built into the financial model. The risk premium is the return on investment the investor is seeking.

- Government should come up with attractive incentives to promote ZLD schemes. There shall be special incentive or reward to industry that is installing ZLD system and operating it successfully.
- Financial support shall be extended from Central or State government similar to Common Effluent Treatment Plant (CETP) model.

2. Technology Selection

Technology selection is a big challenge. Effluent from every industry is unique and ZLD scheme varies from case to case basis.

- Every ZLD system is unique. A proper technology selection and customised ZLD system for the specific industry shall be developed. It is necessary to involve technical experts for tailor made design of ZLD scheme.
- There are many developments and innovations in ZLD technologies. It is essential select a technology innovation according to nature of effluent and economics on long term basis.
- Trainings for awareness and guidance of ZLD scheme shall be conducted. Seminars / workshops shall be organised through common platforms or forums of think tanks for sharing technology innovations, experiences and guidance to industries.

3. Technology Improvement

Operational cost of ZLD technologies is very high due to energy and replacement cost.

- A research and developments in new products to minimise energy, replacement cost, cleaning frequency, etc. shall be carried out.
- A development of ZLD technology products to handle specific difficult waste waters e.g. pharmaceutical & dyes industry shall be promoted with cost benefit analysis.
- Energy efficient technologies shall be developed to recover specific useful products.
- Material of construction for ZLD technology products shall be long lasting with minimum maintenance requirement.

4. Process Change

- It is necessary to look back to manufacturing processes which are generating wastewaters. By making process technology change, by changing raw material, catalysts and by adopting advanced energy efficient methods it is possible to minimise waste. It is also possible to recover maximum useful material from waste. This will reduce burden on ZLD scheme.

By efficient combination of economic modelling; use of advanced energy efficient technologies, by adopting technology/process change and financial innovation, the implementation of Zero Liquid Discharge systems will become a norm and not an exception.

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30. Vendor Data:
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 - c. M/s Ion Exchange
 - d. M/s Hydraunautics Nitto Group Company
 - e. M/s Forbes Pro Water Solutions data
 - f. M/s Chem process India Ltd.
 - g. M/s Arvind Envisol Ltd.
 - h. M/s GE India Industrial Pvt. Ltd.
 - i. M/s Thermax Ltd.
 - j. Praj Industries Ltd
31. Visit to ZLD plants in pharmaceutical, dyes and textile industrial units