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Membrane Technologies for Green Industrial Process Separations

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Acknowledgements: All the Members of RO Department

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Presentation- Overview

- Importance of Green Chemical Separation Processes
- Different Type of Separation Processes
- Membrane Separation Processes- Overview
- Application Areas of Membranes
- Membranes in Desalination and Water Purification
- Membranes in Chemical Industry
- Membranes in Biotechnology Applications
- Solvent Resistant Membranes in Organic Process Industry
- Conclusions

Importance of Green Chemical Separation Processes

- Rapid industrialization, modernization in the living standards and increasing population have increased tremendous stress on– availability of safe drinking water, water for agricultural & industrial use, and Environment
- It is essential to design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances which are hazardous to human health and the environment- climate change, energy consumption, and management of water resources.
- Future industrial development will be guided by separation technologies that allow:
  - Less material and low energy consumption
  - Permit recovery & reuse of process streams
  - Least damage to environment
- Separation operations, in fact, occupy a key position in many industries like pharmaceuticals, biotechnology, food, textiles, petrochemicals, etc., to mitigate/minimize some of the problems
- Many technologies already exist and offer immediate opportunities to reduce environmental burdens and enhance economic performance

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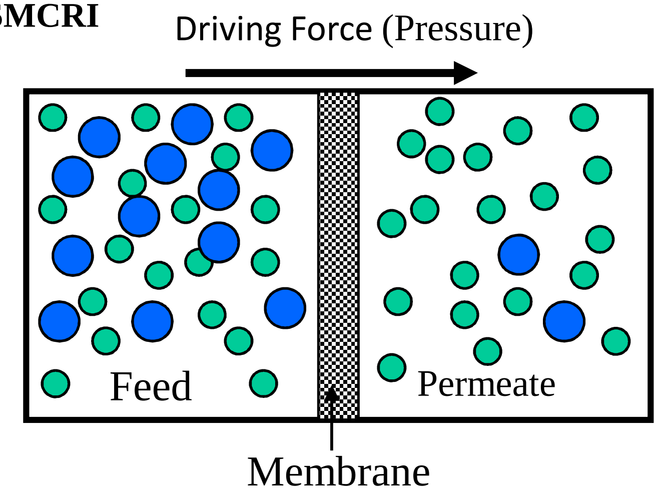
Types of Separation Processes

Separation Process		Driving Force	Possible Separation
Equilibrium controlled processes	Distillation/ evaporation	Differential vapour pressure	• Liquid mixtures, • Salt-water mixtures
	Solvent extraction	Distribution coefficient	• Organics, • Ionic species
	Sorption	Vander Wall's forces, Surface energy	Gases, vapour, organics, as well as some inorganics
	Ion exchange	Charge/size ratio	Charged solutes
Rate governed Processes	Membrane processes	Pressure, Chemical and Electrochemical Potential Gradients	• Dissolved inorganics as well as organic solutes • Suspensions, colloids • Azeotropic mixtures • Gases, vapour

Among the various separation processes, membrane processes encompass nearly all the applications where conventional separation processes are presently in vogue

Membrane Separation Processes



- Membranes are highly-engineered physical barriers with pores of micron/nano size that permit the passage of materials only up to a certain size, shape or character from liquid/liquid, liquid/solid and gas/gas mixture depending on membrane pore size, under certain external driving conditions.
- There are five main membrane separation processes currently employed for liquid/liquid and liquid/solid separation: -

  Reverse Osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF), Microfiltration (MF) and Pervaporation.

Characteristics of the membranes

Membrane Process	Membrane Pore Size (µm)	Applied Pressure (kg/cm^2)	Permeate Solutes Through Membrane	Rejected Solute Size (MW)	Rejected Solutes by Membrane
Microfiltration (MF)	0.15–5	<2	Water Dissolved solutes	>100000	Suspended/colloidal particles, turbidity, bacteria
Ultrafiltration (UF)	0.005–0.2	1–5	Water, Small molecules	>10000	Pathogens , suspended solids, turbidity, macromolecules, enzymes
Nanofiltration (NF)	0.001–0.01	5–15	Water, Monovalent ions	> 500	Sulphates, carbonates, fluoride, some amount of salinity, etc., from water
Reverse Osmosis (RO)	<0.001	15–70	Water	>100	Practically all suspended & dissolved contaminants which include salinity, fluoride, arsenic, hardness, organics, pathogens, etc.,
Pervaporation (PVP)	<0.001	Vacuum	Volatile small organic molecules, water		Nonvolatile molecules, Water

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Transport Mechanism in membranes

Membrane Process	Type of Transport Mechanism
Microfiltration & Ultrafiltration	Separation is a sieving process based on relative molecular size and molecular shape
Nanofiltration	Charge and size
Reverse Osmosis & Pervaporation	• Solution-diffusion model – Both the solute and solvent dissolve in nonporous and homogeneous surface layers of the membrane. – Then each diffuses across it in an uncoupled manner due to its own chemical potential gradient. – Gradient is the result of concentration and pressure difference across the membrane • Preferential sorption-capillary flow model – Membrane barrier layer has the chemical properties such that it has a preferential sorption for the solvent or preferential repulsion for the solutes of the feed solution. – Mechanism of separation is determined by both surface phenomena and fluid transport through the membrane pore. • Solution- diffusion-imperfection model – Both the above 2 models work in tandem

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Application Areas of Membranes

Industry/ Area	Application/ Utility
Desalination and water purification	Production of safe drinking water from brackish water and sea water
Waste water treatment	Water reclamation for industrial use
Electronic industry	Ultrapure water production
Chemical industry	Treatment of effluents from textile, paper & pulp, paint industries
Petrochemical industry	Separation of olefins/paraffins Recovery of solvents from dewaxed lube oil
Biotech and Pharmaceutical industry	Clarification, concentration and purification of enzymes, proteins and antibiotics
Vegetable oil Industry	Recovery of solvent
Dairy & Food industry	Clarification of fruit juice, Purification of beverages, Concentration of vegetable and fruit juice
Medicine	Artificial kidney (hollow fiber membranes)

Highlights of Membrane R & D Activities at CSMCRI

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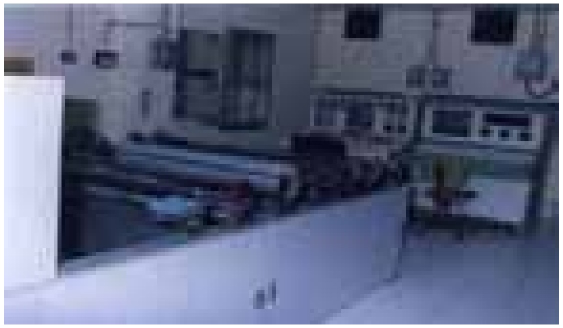


Continuous casting device for making MF/UF membranes by phase inversion process

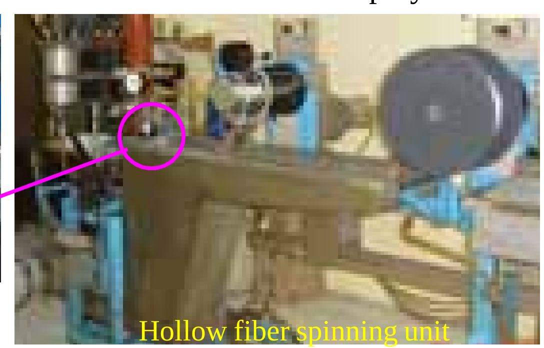
Continuous polyamide TFC RO/NF membrane making unit by interfacial polymerization process

Indian Patent No. 169550 & No.145945. A process for the preparation of high flux, high separation thin film composite reverse osmosis membranes for desalination of highly saline waters

- TFC RO membranes for desalination
  - Membranes with high water flux & salt rejection for desalination
  - Large scale on-line optimization of membrane surface modification to improve fouling resistance properties
- UF membranes with precise pore size control
  - Fouling resistant UF membranes for drinking water purification (Removal of pathogens) and for use in other value added biotechnology product separations
- Permselective nanofiltration membranes
  - NF membranes with wide selectivity range for mono- & multi-valent ionic solutes (30-35% for NaCl and >95% for Na_2SO_4) for water purification (Removal of hardness, fluoride, pathogens) & Biotechnology product separations (proteins, amino acids)
- Acid resistant membranes
  - Acid resistant membranes for the recovery of acid/water from acid effluents having LM weight organic solutes like naphthalene sulphonic acid, dyes, etc., up to 20% sulphuric acid
- Solvent resistant membranes
  - Development of polyimide based nanofiltration membranes for non-aqueous solvent separations, e.g., low temperature separation of for MEK & toluene from lube oil mixture
- Structure-Property Relationship in Membranes
  - Characterization of the membranes for surface chemistry by IR, hydrophilicity by contact angle measurements, morphology by SEM/TEM, pore size and its distribution.

    Chlorine stability of the unmodified and surface modified polyamide TFC membranes

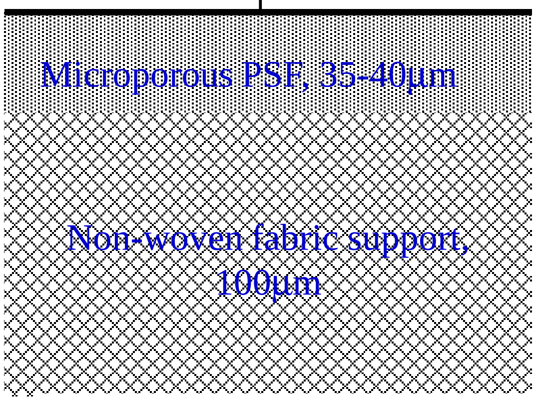
Fiber is coming out from the spinneret & entering the gelation bath



Hollow fiber spinning unit

CSMCRI –Polyamide TFC membrane technology

PA thin layer 0.15-20 µm



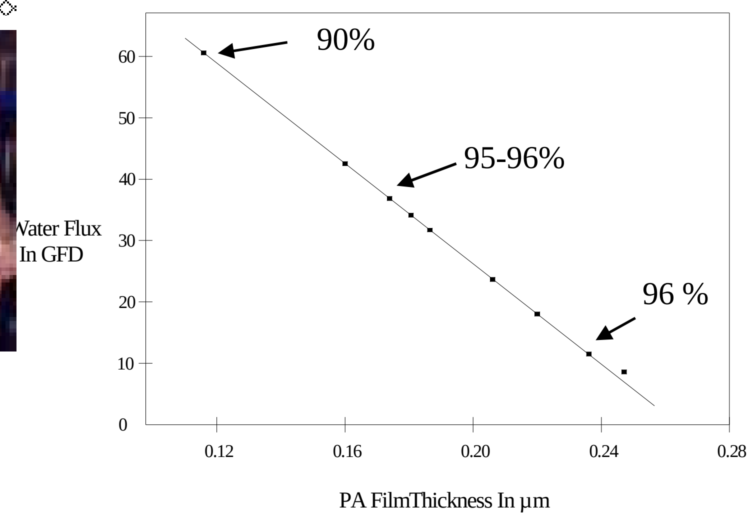
Polysulfone-PA TFC Membrane Process:

(1) Casting porous PSF Membrane, 1m X 100m

(2) Coating of PA layer on PS surface

(3) Post treatment and protective layer coating

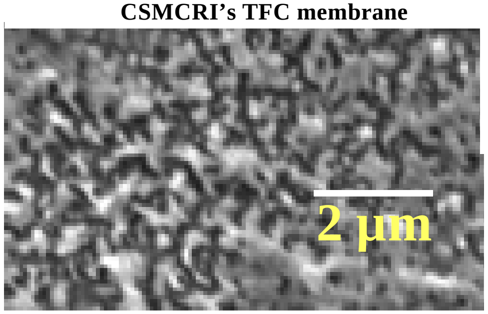
(4) Quality testing of TFC Membrane



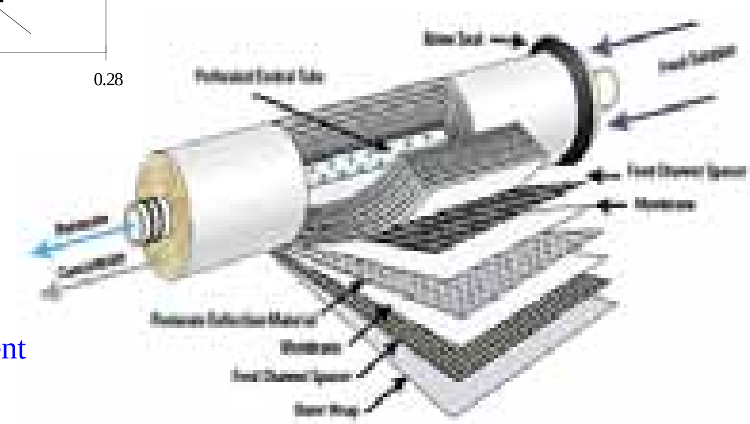
Dependence of product flux with PA thin layer thickness in high flux TFC membrane, *J. Membr. Sci.*, *211*, 2003, 13

Understanding the relationship between the structure-property is the key for the development of membranes for different applications.

CSMCRI's TFC membrane



Top Surface: Hill-Valley Morphology



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Membranes in Desalination and Water Purification

Safe Drinking Water

Water for Industrial use

Aspects Related to Water!

- The need for pure water is a problem of global proportions.
- Water treatment has become an area of worldwide concern to keep this essential resource available and suitable for use.

Options at Hand

- Desalination (Brackish water and Sea Water)
- Removal of harmful impurities from drinking water
- Waste Water Management/Reuse in Production Processes

Several Technology Options Exist.
Membranes is one of the best options.

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"….A survey of national opinion revealed that when asked what would make respondents proud of India, a staggering 73 per cent said that availability of safe drinking water to all our people would truly make them proud of being an Indian…."

Excerpted from the speech of Dr Manmohan Singh, Prime Minister of India, at the Conference of Ministers in-charge of Rural Drinking Water Supply and Sanitation.

January 2006

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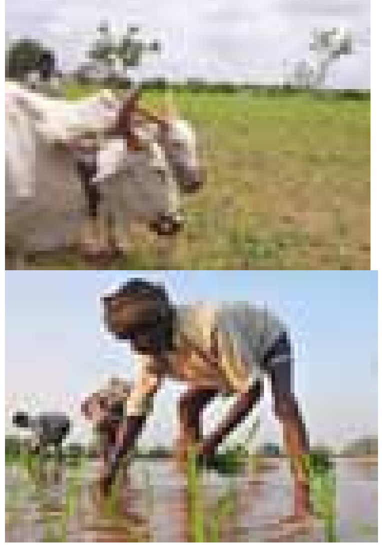
Water Infrastructure Challenges

Increasing Droughts

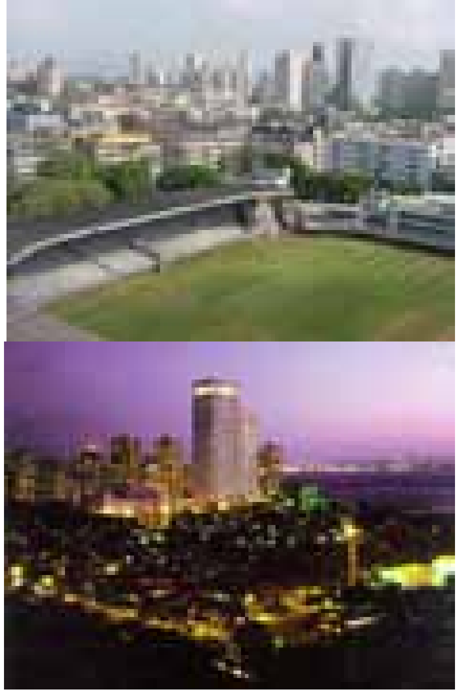
Agriculture



Threat of Waterborne Diseases

Water Pollution

Growth of Cities & Needs



- Providing clean drinking water is emerging as one of the important challenges of the present times
- Presence of high salinity & harmful contaminants like hardness, fluoride, arsenic, nitrate, pathogens, pesticides, etc., in several water sources
- Steady decrease in the available water resources
  - Rapid industrialization
  - Continuous droughts
  - Urbanization
  - Steady increase in population
  - Huge requirement for agriculture

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Desalination & Recovery of waste water and re-use in industrial and civil applications is a necessity while facing an exponential increase of population, long droughts, reduction of the fresh water resources, etc.

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Water treatment processes to obtain safe drinking water

Type of Contamination in Water	Suitable Treatment Process	Effect of the Treatment Process
Salinity (or) Salinity + Other contaminants like Fluoride, Arsenic, Bacteria, etc.	• Reverse Osmosis (RO) (Membrane Pore Size < 0.001μm)	• Removes practically all suspended & dissolved contaminants which include salinity, fluoride, arsenic, hardness, organics, pathogens, etc., from water through physical barrier separation process
Hardness with normal or little excess salinity	• Nanofiltration (NF) (Membrane Pore Size 0.001–0.01 μm)	• Removal of sulphates, carbonates, etc., and some amount of salinity from water through physical barrier separation process
Turbidity	• Alum treatment • Microfiltration (MF) • Ultrafiltration (UF)	• Alum treatment followed by decantation or filtration removes turbidity from water • MF & UF remove turbidity through physical barrier separation process from water
Turbidity + Pathogens	• Alum + chlorine tablet • Bleaching powder • SODIS • Ultrafiltration with 50-75 Kda cut-off value	• Removal of turbidity while killing the harmful pathogens and retaining them in water. • UF removes both turbidity and harmful pathogens form water through physical barrier separation process
Fluoride (or) Arsenic with normal salinity	Ion selective resin or other adsorbents	• Selective removal of fluoride or arsenic but retaining the same salinity of the water

Indigenous TFC membrane based Two Stage Sea water desalination RO plants installed by CSMCRI

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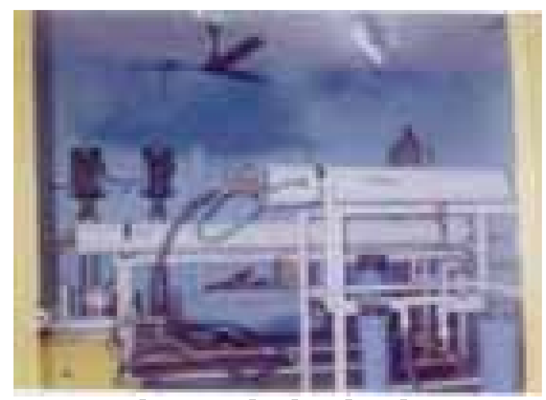
Plant Capacity: 1000 LPH
Stage 1: 600 psi
Stage 2: 300 psi
Recovery: ~33% with respect to seawater intake

Seawater being brought in for RO Plant

Mullimunai

Village people collecting water from RO plant

Karankadu plant



Thirupalaikudi plant

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Providing RO Water to Tsunami Victims at Akkarapettai, Nagapattinam with CSMCRI's "No Frills" RO unit

In the Service of People

Plant at Nagapattinam has 2500 LPH capacity and has been handed over to the TWAD Board.

These are the kinds of situations which have inspired us to develop membranes with superior flux and low energy/pressure demand for low capital investment and operating cost.

Seawater RO Plant

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KENSALT LIMITED

P.O. Box 81665 - 80100, Mombasa,Kenya
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Fax: +254 41 3433719
Email: kensalt@wananchi.com

KENSALT

Our ref: Your ref:

18/06/08
DR P.K.GHOSH, DIRECTOR
CSMCRI
BHAVNAGAR
INDIA.

Dear Sir

We are pleased to inform you that Reverse Osmosis plant supplied by you is working satisfactory since 12th May 2008.

The feed TDS of sea water = 35,000 - 44,000 ppm
The product TDS of fresh water = 325 - 520 ppm
The flow rate of water = 1700 - 2000 litres/hour

We are doing the necessary fresh water washing everyday at the end of the plant working. Also we are maintaining a check on the suspended solids with the feed sea water.

We will let you know the performance of the plant after six and twelve months working also.

Thank You
Yours Sincerely

D.Sengupta
Group General Manager (East Africa)
KENSALT LTD.

Moving beyond Indian shores: 2000 LPH Seawater RO Plant based on Indigenously Developed TFC RO Membrane and Plant Design set up in Kenya.

CSMCRI has setup Six RO brackish Water Desalination plants (including one solar operated) in Afghanistan through Norwegian Church Aid

NORWEGIAN CHURCH AID Afghanistan Program

Kabul, May 13th, 2008.

CSMCRI
Bhavnagar,
Director P.K. Ghosh.

Dear Mr. Gosh,

I would like to take this opportunity to express NCA's gratefulness and thanks for the support you have provided us.

Mr. B.P. Rathod has conducted an excellent job in a very polite and respectful manner and hence ensured the long awaited installation of 6 desalination plants. In addition he has ensured that the plants were tested and he initiated a refreshment course through which the knowledge and ability of the trained community caretakers was assessed.

The result of the support offered and executed is that we have succeeded in the implementation of 6 running and functioning plants.

The cooperation with respectively the communities, the implementing partner and the local authorities was as well conducted in a respectful, cultural sensitive and successful manner.

NCA is grateful for the cooperation with CSMCRI and look forward to a continuous successful relationship.

Yours sincerely,

[illegible]
Program Coordinator,
Acting Country Representative

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RO does more than removing salinity alone

Kasari, Rajasthan

Parameter	Feed (mg/lit)	Permeate (mg/lit)	R (%)
Salinity	1907	148	92.2
Sulphate	110	7.64	93.0
Fluoride	**1.74**	**0.169**	**90.3**
Mg	201	7	96.5
Tot. Hard	261	9	96.5
Ca	60	2	96.6
Nitrate	151	23.4	84.5

Barmer Airforce Base, Rajasthan

Parameter	Feed	Permeate	% R.
Salinity/TDS ppm	4288	570	86.0
Chloride (ppm)	1750	220	87.0
Sulphate (ppm)	476	45	90.0
Fluoride (ppm)	**1.83**	**0.195**	**89.0**
Hardness (ppm)	576	36	93.0

Nalgonda technique is useful for the removal of only fluoride but not salinity and hardness.

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RO desalination & defluoridation

RO feed and permeate water analysis Nalgonda, A.P.

Location (Villages)	Salt Concentration		Fluoride, ppm	
	Feed	Permeate	Feed	Permeate
Wailapally	2500	500	6.50	0.88
Gattuppal	670	75	4.50	0.44
Puttapaka	2300	330	0.90	0.10
Yelama-kanna	4800	527	3.00	0.45
Kalva-kuntla	1875	241	4.00	0.53

Treatment of the RO concentrate is essential before discharge, especially, where Fluoride/As is present in the water

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RO desalination and defluoridation with indigenous 4040 spiral module followed by reject water treatment

Module: TFC, SR = 93%; Flux = 4.5-5.0 liters/min

Parameter	Experiment -1	Experiment -2
Feed solution	2000 ppm NaCl 5.1 ppm Fluoride	2000 ppm NaCl 5.5 ppm Fluoride
Feed volume, lit	150	1800
Permeate volume, lit	105	1350
Reject Volume	45	450
Pressure, psi	200	300
Operating time	25 min	5 hr
Recovery	70	75
Permeate, TDS	200-220	220-250
Fluoride in Permeate, ppm	0.25	0.3
Fluoride in Reject, ppm	17	20
Fluoride in supernatent, ppm	0.05 ppm	0.03-0.04

Treatment of the RO concentrate is essential before discharge, especially, where Fluoride/As is present in the water

RO for desalination & defluoridation for producing safe drinking water

Mobile RO Desalination Plant

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RO Reject Water Utilization

Top: Wasteland adjacent to RO plant prior to cultivation, at Mocha.

Top Right: The same land after cultivation with *Atriplex halophyte* and irrigation with saline reject water (10,000 ppm) from RO plant.

Bottom Right: Use of the harvested *Atriplex halophyte* as fodder.

Nonconventional energy powered RO device for potable water production

500 LPH product water from As and Fe contaminated water, where electricity is not available

Rajasthan

Leprosy Hospital, Vadodara
Gujarat, January 2008

West Bengal

Inset shows wheel and tyre assembly that has greatly enhanced efficiency and reduced load on the animals

Rajasthan

950 LPH, Feed 3500 ppm TDS with 4-5 ppm fluoride

Water	As (mg/L)	Fe (mg/L)	TDS (mg/L)
Raw Water	0.141	1.80	3200
Treated Water	BDL	BDL	400

"Although I have already researched the market with respect to the applicability of various technologies in the region (Africa), I am particularly interested in both the method of desalination that you have developed and the nature of the brackish water RO membranes."

David Farr
Hydrogeologist
Water & Environment
Atkins Limited, U. K.

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I think that the real ingenuity of your ox driven RO units is that they can be placed closer to the local people"

Mathias Zimmermann
Senior Engineer
NTT Europe Ltd.,
Frankfurt Branch

RO for Treatment of Mine Water for Drinking & Agriculture

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- In lignite mining of Rajasthan State Mines & Minerals Ltd at Matasukh and Kasnau, Nagaur district., 50-100 MLD of highly saline (7000-11000 ppm) ground water is being pumped out.
- Institute installed RO plant to recover 75-80% of the water in the form of either drinking water or irrigation water while the reject water—which would have seawater-like salinity—could be utilized for production of salt. The plant produces agriculture water @ 3000 lph with 78% recovery.

Parameter	Stage-1 (Agri water)	Stage-2 (Drinking water)
Feed water TDS ppm	7000	1600-1800
Feed water flow rate, LPH	3600	2400
Operating pressure, psi	575	250
Product water rate, LPH	2880	1860
Product water TDS, ppm	**1600-1800, Agriculture water**	**250-300, Drinking water**
Reject water stream rate, LPH	720	540
Reject water stream TDS, ppm (measured as 2.7 ^{o}Be')	27800	5200
Power consumed, KWH (based on Watt meter reading)	5.5	1.5
Energy cost: paise/liter @ Rs.4.5/KWH	0.86	0.36

Irrigation with 1st stage RO Water

Membranes in Municipal Water Treatment

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Municipal seawage water

↓

Primary treatment

↓

Secondary treatment

↓

Tertiary treatment

↓

RO/NFUF membranes

Low end applications

Toilet flushing,
Gardening,
Floor washing

Agriculture usage

Industrial usage

Boiler feed
Cooling tower makeup
Process water

Water Reclamation using RO Membranes

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Commissioning of 1 MLD Demonstration RO Plant 25-11-2003

1. Commissioning of the 1 MLD Demonstration R.O Plant using indigenous RO membranes was completed on 24.11.03
2. It was operated overnight and after stabilisation its performance was assessed. Results are as follows:

➢	Trains	Two (A and B)
➢	Feed flow per train	24 KL/Hr (400 lpm)
➢	Array	2:2 (4 elements in each pressure vessel)
➢	Feed pressure	16-17 kg/cm^2
➢	Pressure drop	3 kg/cm^2
➢	Product flow	18 KL/Hr
➢	Feed conductance	2310 μS/cm
➢	Product conductance	277 uS/cm
➢	Product recovery	75%
➢	Salt rejection	86-90% (expected to improve after 2 days of continuous operation)
➢	Time of continuous operation	16 hours

This performance of indigenous RO membranes in 2:2 array is nearly matching the projections for imported RO membranes (ESPA-3 of Hydranautics Inc., USA) except for the higher feed pressure needed for indigenous membranes (copy of Hydranautics projections enclosed)

3. In order to improve the quality of permeate, trials were done by routing permeate of train B as feed to train A. After 1 hour of operation conductance of final permeate was found to be 62 μS/cm representing 97.3% salt rejection with respect to feed of 2310 μS/cm. Final permeate quantity was 13.5 KL/Hr (56% product recovery) with respect to 24 KL/Hr. feed flow rate)

4. Operating in permeate recycle mode needs more manpower and continuous attention which is not feasible now. It can be taken up after fixing a level indicator/controller for permeate break tank with interlock trip switch to stop both trains of Demo plant if permeate level in break tank is below the low level mark.

5. **Pending items of CSMCRI/IEIL**. (a) Online conductivity meters (2 nos.) for product need replacement (b) Rotameters need to be fixed rigidly with adequate support and calibrated (c) Minor leakages in pipelines and valves to be arrested (copy of Minutes of Meeting between CSMCRI and IEIL enclosed)

(Dr.M.S.R.SWAMI)
CPCL

(Dr.C.V.DEVMURARI)
CSMCRI

CSMCRI's 1 MLD Plant installed in November 2003

- The plant treats tertiary treated municipal sewage water for cooling tower application.
- CPCL uses about 8% of Chennai's municipal water
- The performance of this plant is comparable to commercial plants
- B.O.D., C.O.D. & organic carbon is reduced by 90 to 88%

Water reclamation from domestic detergent wash water

- Attaining Green Building Environment for Future
- Synthetic soap/detergent water having100 to 500 mg/L of commercial washing powders namely 'Nirma washing powder' or 'Surf excel' treated with indigenous TFC RO indigenous modules at 250 psi operating pressure at room temperature
- The total organic carbon content in the feed and product water were analyzed by TOC analyzer & HPLC

Water type	TOC, ppm		TDS, ppm		Product rate, LPM	Recovery (%)
	Feed water	Product water	Feed water	Product water		
BW	32.90 32.60	8.23 8.25	2150 696	199 79	4.3 4.1	60
BW + Nirma	34.67 35.16	9.60 9.59	2120 837	186 87	4.6 4.2	60
BW + Surf Excel	105.34 89.00	8.80 14.00	701 2270	62 246	3.0 2.8	60

Reusable water could be obtained from domestic detergent cleaning water

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Membranes in Chemical Industry

Water Reclamation

and Product Recovery

Treatment of ACOH-water-Aromatic acids mixture for recovery of process water or concentrated ACOH solution

- In the manufacture of TPA, acetic acid is used as the solvent in the oxidation of p-xylene to TPA
- TPA plants generate effluents- containing aromatic acids along with acetic acid in water
- Acetic acid- water mixture with AcOH content approximately 0.4 – 1.2 %
- It is interested to recover ACOH-water with <100 ppm aromatic acids
- Concentration of ACOH-water mixture for reuse in the process and also to reduce caustic consumption for neutralization

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RO treatment of AcOH-Water-Aromatic acids

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Effluent: ACOH & Aromatic acids (TMA-Trimellitic acid, OPA- Orthophthalic acid, IPA- Isophthalic acid, TPA- Terephthalic acid, p-TA- Paratoluic acid, BA- Benzoic acid

Aim: To obtain ACOH-water with about 100 ppm of aromatic acids

TFC 4" module: NaCl rejection = 94%; Water flux = 4.2 l/min

Flux 1.8 l/min; Pressure: 250 psi; Recovery = 70-75%

	ACOH %	Aromatic Acids (AA, ppm)						Total AA ppm
		TMA	OPA	IPA	TPA	p-TA	BA	
Initial Feed 1	0.193	70	7	16	37	362	260	752
RO Permeate	0.10	**10**	**< 5**	**<10**	**<12**	**79**	**<72**	**188**
RO Conc.	0.46	132	19	26	98	758	661	1694
Feed 2	0.07	12	10	<10	12	32	16	
RO Permeate	0.00	**<10**	**<10**	**<10**	**<10**	**18**	**10**	**68**
RO Conc.	0.36	19	12	<10	16	92	58	

ACOH-water with <100 ppm aromatic acids could be obtained for reuse in the TPA process

RO treatment of AcOH-water mixture

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Aim: To get maximum concentration of acetic acid

Pressure: 250 psi; Recovery: 70-75%

	ACOH %	TMA ppm	OPA, ppm	p-TA ppm	IPA ppm	BA ppm	TPA ppm
Initial Feed 1	**0.97**	**<10**	**<10**	**<10**	**<10**	**<5**	**<10**
RO Permeate	0.63	<10	<10	<10	<10	<5	<10
RO Conc.	1.90	<10	<10	<10	<10	<5	<10
Feed 2	0.68	<10	<10	<10	<10	<5	<10
RO Permeate	0.34	<10	<10	<10	<10	<5	<10
RO Conc.	1.70	<10	<10	<10	<10	<5	<10
Feed 3	2.50	<10	<10	<10	<10	<5	<10
RO Permeate	1.93	<10	<10	<10	<10	<5	<10
RO Conc.	4.20	<10	<10	<10	<10	<5	<10

- It is possible to achieve acid concentration up to 4.2% which can be reused in the process

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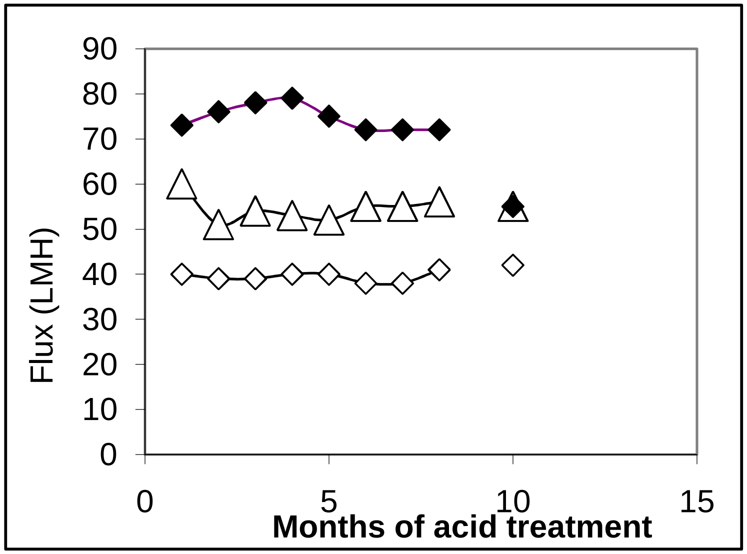
Acid resistant membranes for water recovery from reactive dye effluents

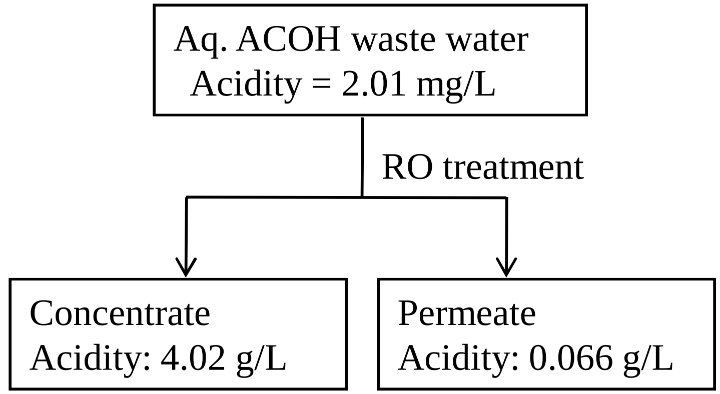
- Preparation of reactive dyes and their intermediates involves sulphonation of naphthalene in sulphuric acid/oleum mixture followed by *in situ* nitration with nitric acid.
- Quenching with water and limestone, filter off the precipitated gypsum- solution containing 1-nitronaphthalene-3,6,8-trisulphonic acid derivatives is further processed.
- Generates large quantities of gypsum and its disposal is a problem.
- Development of alternate separation process to overcome the production of large amounts of gypsum is required.
- Hence, development of membrane based separation of sulphuric acid and nitronaphthalene trisulphonic acid obviates the utilization of limestone for quenching and thereby eliminates the generation of unwanted gypsum.

Acid Stability of the Novel Surface Modified Ultrafiltration Membranes



% Acid concentration	% Separation of PEO 100 KDa
Nil	90.46
1	92.64
3	91.12
5	90.77

Treatment of aqueous-organic solution by membranes



Both the RO concentrate with 4.02 g/L acidity and the permeate can be reused in the process

- Membranes were treated with 5-20% sulphuric acid solution.
- Slight reduction (4-6%) in the rejection (from 99-93%) was observed after 7 months of treatment with 20% acid solution while the flux remains almost same.
- This processes can help in recycling of acid and avoiding unncessary use of alkali for neutralization with consequent problem of salt disposal.

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Desalting of aqueous Dye Solution by NF Membranes

Dye processing industry: Major consumer of pure water

Conventional treatment

Textile dyeing with reactive dyes

15% High TDS water 60000 mg/L NaCl/ Na_2SO_4 & 250–500 mg/L dyestuff

85% Low TDS water 1000 mg/L NaCl/Na_2SO_4

CaO-$FeCl_3$ Flocculation

Colourless supernatent water with ~6000 ppm is discharged in natural water streams

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Membrane Processes

High TDS & colour effluent (60000 TDS) → Nanofiltration → Reject for Incineration

Nanofiltration → Permeate with salt (70-75% water recovery)

Low TDS Low colour → RO, Low Pressure → Reject (salt, colour water) → RO, High pressure → Reject for incineration

RO, Low Pressure → Permeate (Pure water) for reuse

RO, High pressure → Permeate (Pure water) for reuse

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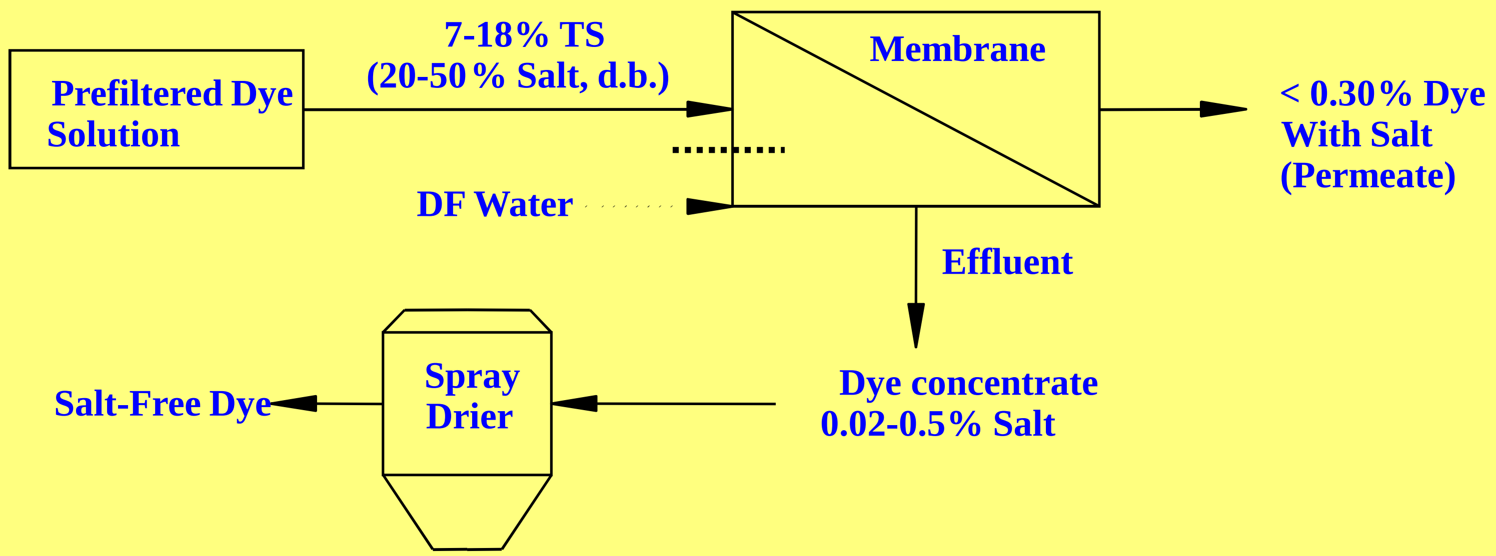
Water recovery from dye-effluent by Nanofiltration

Details of Dye – effluent:

1. pH : 7.3
2. TDS : 17.6 W/V (%)
3. COD : 6015 PPM
4. Hazen Value : 75,000
5. Cl as NaCl : 16.7%

Details of Operational results

1. Initial permeate flux: 30 GFD
2. Rejection of dye : 100%
3. Rejection of NaCl : 25%
4. NaCl in permeate: 75%
5. Operating pressure : 100 psig
6. Feed Flow Rate : 660 ml/min



Flow Diagram for treatment of dye effluents by Nanofiltration

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Desalting of aqueous Dye Solution by NF Membranes

Performance of different Membranes

Mem. code	Flux (gfd)	Rejection (%)				
		NaCl	Na_2SO_4	$CaCl_2$	$MgSO_4$	Dyes
SPA1	75	14.04	69.20	3.97	21.10	97.00
SPA2	65	10.20	75.51	8.68	19.23	98.60
AM1	12	21.00	68.23	22.48	26.20	98.65
AM2	10	25.94	71.59	31.40	28.50	94.80

Polyamide based TFC NF membrane unit

Dye solutions containing about 500 mg/L of dye and 5% salts have been concentrated to about 80% and the concentrate was evaporated to get solid dyes and salts. Reusable water has been obtained.

Optimum performance is found with NF membranes modified to have negative surface charge.

F: Initial feed
P: final permeate after 80% recovery
R: Concentrate
Reactive red 2; Reactive red 120
Reactive orange 4; Reactive orange 13

Treatment of dye-effluent (by NF membrane

It is the most suitable option for concentrating and desalting of dyes

Nanofiltration of Dye effluents by PIPA TFC Membrane

Membrane	Name of the Dye	MW of the dye	Flux, GFD	% Dye separation	% Salt in permeate
NFM 198	Acid Orange II	327	89	95	65
	Indigo Carmine	466	68	90	
	Indigo Carmine	466	73	85	75%
	Atul dye effluent	Mixture of 4 dyes	25	100	75%
NFM 209	Rhodamine B	347	60	98	
NFM 210	Acid Orange II	327	95	97	

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Treatment of dye effluents with submersible membranes

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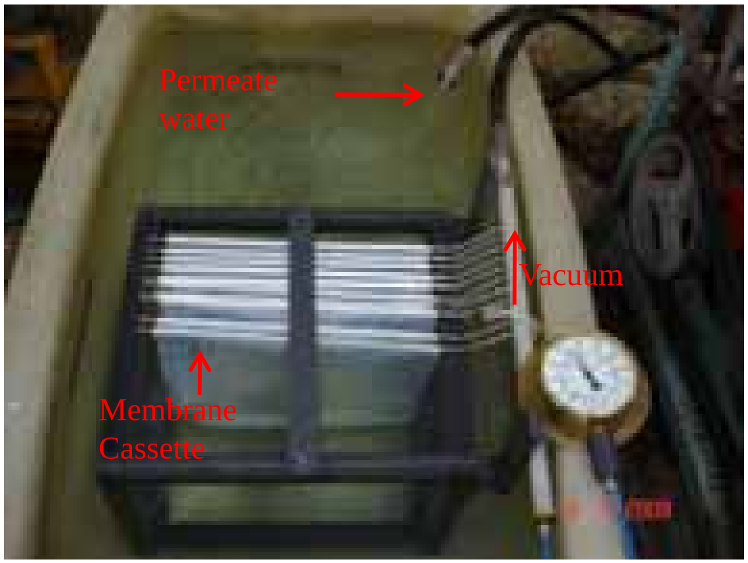
Membrane: Indigenous NF membrane
Water flux: 125 liters/m^2/hour at 600 mmHg vacuum



- Reactive dye separation of 60-85% was observed with flux of 5-10 liters/m^2/hour at 600 mmHg
- Colorless solution was obtained in presence of PVA due to molecular association
- Water with <1 NTU could be obtained from water containing up to 200 NTU

Submersible Flat Sheet Membranes for Water Reclamation

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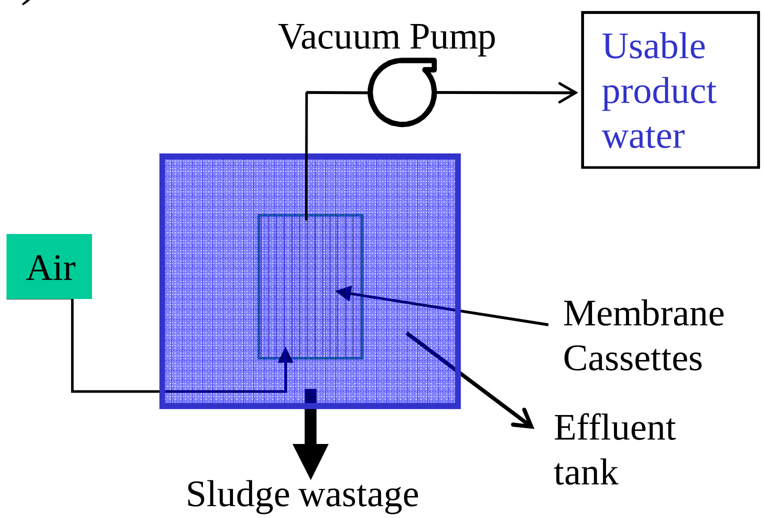
- Submersible membrane systems have several advantages over conventional treatment of municipal wastewater and waters containing excess turbidity & organic matter

- SM systems can be used as pretreatment system to produce good quality water from highly turbid water for treatment by RO

- Can produce high quality effluent water suitable for low end applications

- Membranes: Polysulfone (PS), Polyethersulfone (PES), Polyvinylidene fluoride (PVDF), Polyacrylonitrile (PAN)

  - High chemical stability
  - High mechanical stability
  - Easily cleanable
  - Rejection for solids and bacteria
  - Long lifetime
  - High flux



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Membranes in the treatment of extreme acidic/basic industrial wastewaters

Sucrose rejection and flux of membranes in 20% H_2SO_4

Membrane	Temp (^0C)	R(%)		Flux (lmh)	
		Initial	After 2-3 months	Initial	After 3-4 months
NF-45	80 20	83 80	--- 2	6 7	---- 19
Desal-5DK	80 20	89 91	--- 28	11 11	---- 15
BPT-NF1-015	80 20	88-97 88-91	6-10 92	2-5 2-5	86-129 5
BPT-NF1-006	80 20	83-92	9-13	2-4 2-4	61-65

J.M.Sc., 239 (2004) 91

* RO system for reprocessing hydrofluoric (HF) acid etch waste in semiconductor industry.
(Gill, W., et al. Advances in Environmental Research, 2 1998, 333

Membranes in Biotechnology and Pharmaceutical Applications

* Membranes play a critical role in successful development of many new **Biotechnology and Pharmaceutical** products and processes with cost savings and improved yields.

* For broth clarification, cell harvesting and cell debris removal

* Concentration of dilute product streams and final purification

* Production of enzymes, growth harmones, amino acids and antibiotics (pencillanic acid, clavulanic acid, cephalosporin)

* Concentration factors from 10 to as high as 100 can be achieved. **RO, NF or UF membranes can be used depending on the type of separation required.**

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Ultrafiltration for Simultaneous Purification, Concentration and Fractionation of *Biomacromolecules*

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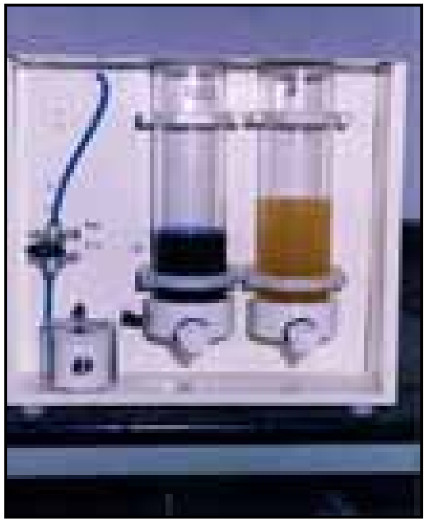

- Extract is a mixture of CPC, proteins, amino acids, inorganic salts, carotenoids, plant growth hormones, allophycocyanin
- Ultrafiltration of CPC extract at 50 psi could be carried out up to 80% concentration.
- CPC is used as colorant in food, cosmetics, etc

Membrane	Flux, LMH	% Removal of other proteins	CPC purity ratio after UF (A_{620}/A_{280})
PES 85K	115	4.5	0.43
PES 35K	94	32.0	1.21
PES 9K	37	1.7	0.35
PES-SM40K	290	34.0	1.35

Suitable as food grade material

Ultrafiltration of Phycoerythryn

Solvent Resistant Membranes in Organic Process Industry

* **Solvent-resistant membranes can bring about step change in organic process chemistry.**

- Petrochemical Industry
- Vegetable oil extraction
- Catalyst recovery
- Pharmaceutical Industry

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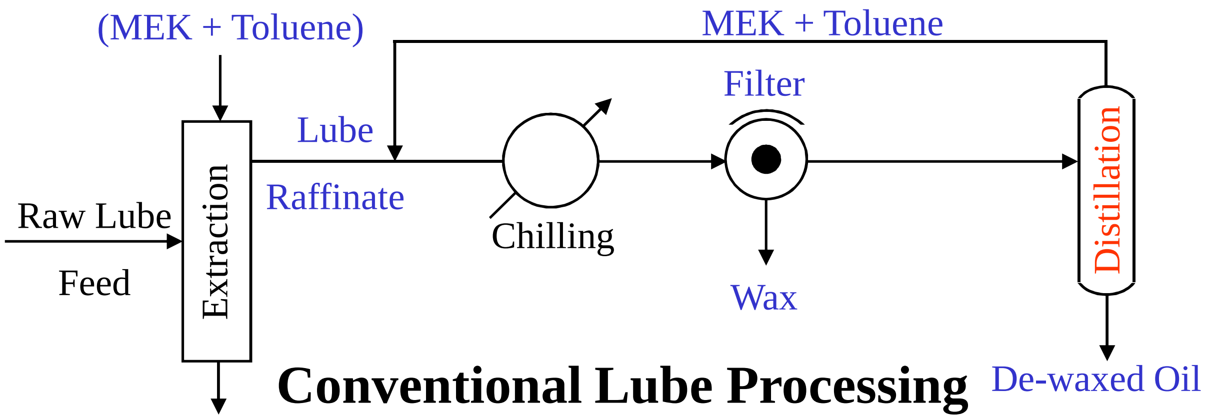
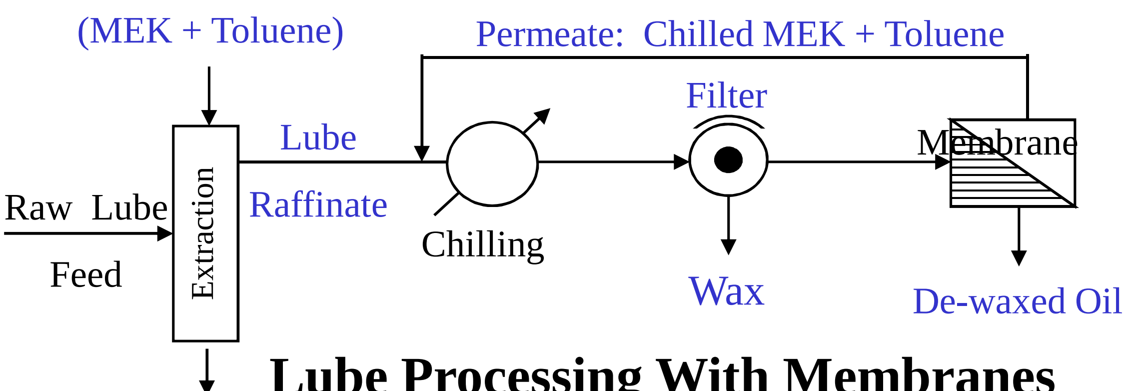
Membranes in Organic Solvent Separations



Conventional Lube Processing



Lube Processing With Membranes

Polyimide Membrane Based Organic Solvent Separation Demonstration unit

Lube oil separations up to 90% could be achieved at –10 to –15^{0}C using indigenously developed polyimide membranes.

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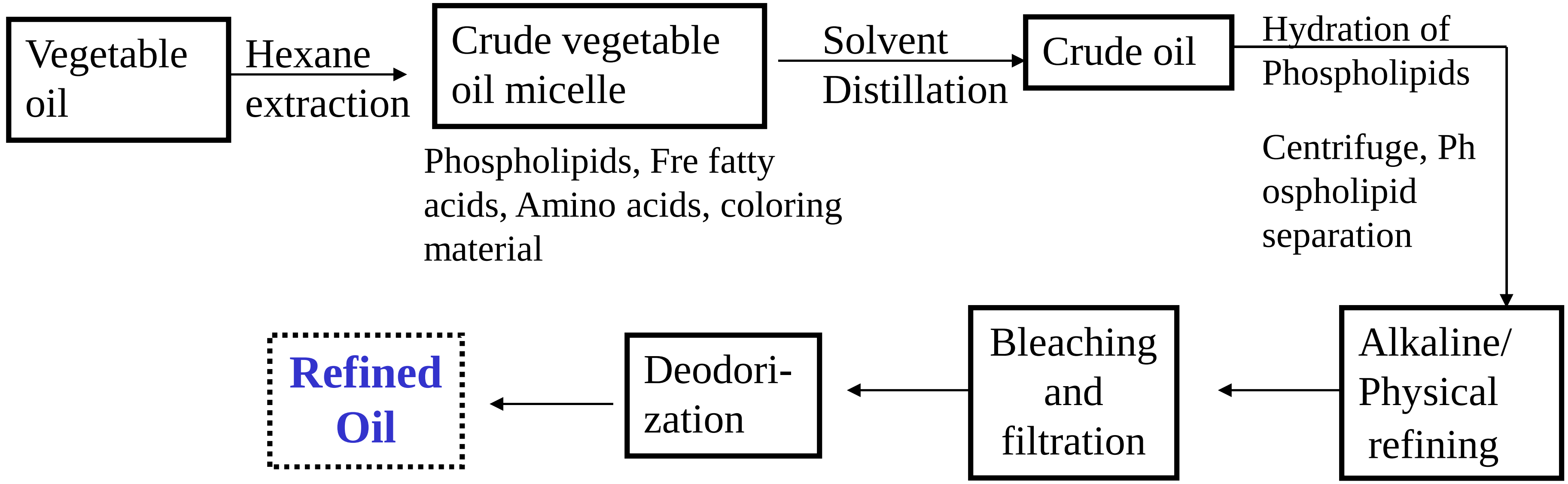
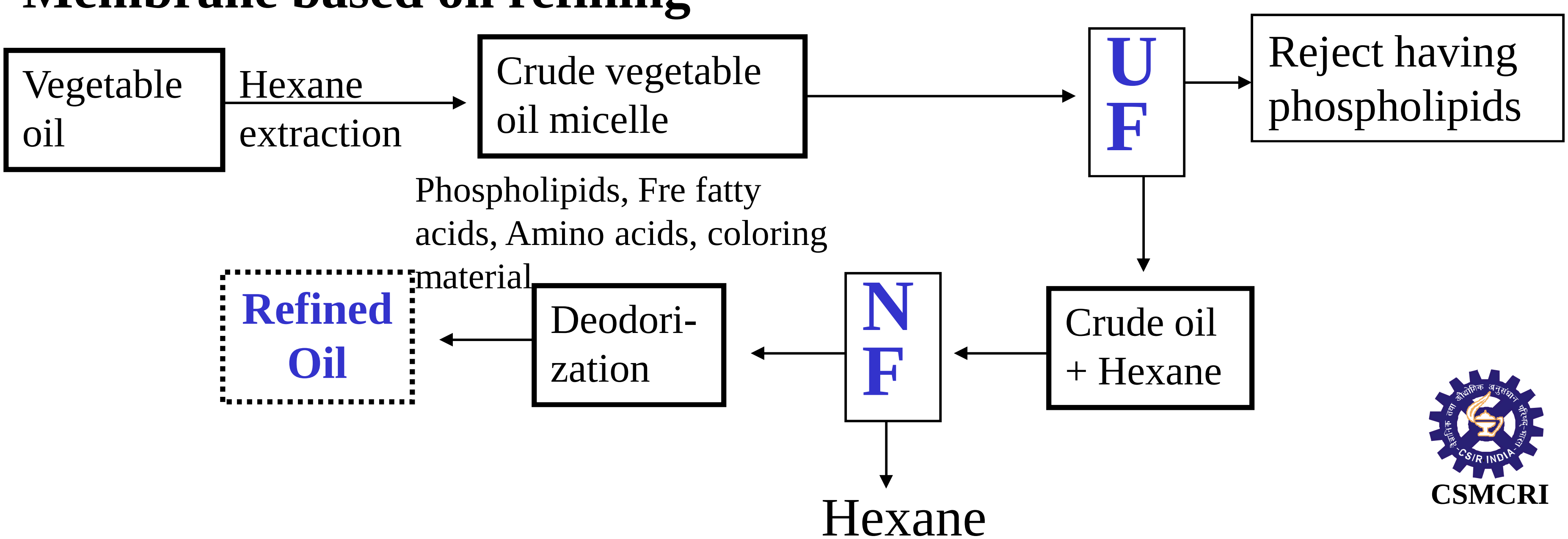
Conventional oil refining process



Membrane based oil refining



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Separation of lube oil-MEK-toluene mixture

Membrane	Feed concentration (%)		Permeate concentration (%)		Solvent Flux (l/m^2-hr)	R (%) Lube oil
	Lube oil	Solvents	Lube oil	Solvents		
BTDA-PPB	33	67	5	95	12.8	84.8
IDPA- DAM	30	70	2-3	98-97	5-6	92-94

Test conditions: Feed temperature: -15 to -20^{0}C; Pressure: 600 psi

Separation of hexane from edible oil

Membrane Code	Feed (%) composition		Permeate (%) composition	
	Oil	Hexane	Oil	Hexane
IDPA-DADM 5/5	25	75	6	94
PIM- 7	30	70	9	91
PIM-5	24	76	8	92

Pressure 500 psi; Ambient temperature

- Lube oil separations up to 90% could be achieved at –10 to –15^{0}C using indigenously developed polyimide membranes.
- Dewaxing aides are removed completely.

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Advantages of Solvent Resistant Membranes

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Petrochemical Industry	Low temperature (-15 to -20 degree C) recovery of methyl ethyl ketone toluene and from de-waxed lube oil mixture
Vegetable oil industry	Degumming and Recovery of hexane from vegetable oil extract

- Delivers cold pure solvent without requiring the distillation and additional refrigeration in MEK-Toluene recovery- **Saves energy and greenhouse gas emissions**
- De-bottlenecks refrigeration, solvent recovery and filtration sections of the conventional unit
- Capital investment is substantially reduced

Technical challenge

- Develop appropriate polymeric membranes/systems that both separate out the desired components and are resistant to organic solvents at low & high temperatures

Recovery of phase transfer catalyst for re-use by solvent resistant membranes

$$Br\text{-}C_7H_{15(org)} + KI_{(aq)} + PTC \longrightarrow I\text{-}C_7H_{15(org)} + KI_{(aq)} + PTC$$

PTC: tetraoctylammonium bromide in toluene

Membrane	MWCO	Flux LMH	R(%) TOABr MW 546	R(%) Br-C_7H_{15} MW 179	R(%) I-C_7H_{15} MW 226
142 A	220	25	>99	20	22
142C	400	32	>99	8	5

Membrane: Matrimid 5218 Polyimide, *(S.D.Luthra et al., Chem Commun 2001, 1468)*

Product is recovered from permeate (35 mL) while PTC-containing retentate (5 mL) is recycled with fresh charge of reactants and solvent.

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Conclusions

- Green separations occupy a key position in future industrial development
- Less material and low energy consumption, recovery & reuse of process streams, Least damage to environment are essential
- Among the various separation processes, membrane processes encompass nearly all the applications
- Membranes can be utilized for recovery of acids/alkali enabling processing of fluids over wide pH range
- Membranes play a critical role in successful development of many new Biotechnology and Pharmaceutical products and processes
- Solvent-resistant membranes can bring about step change in organic process chemistry, e.g. Petrochemical Industry; Solvent recovery in vegetable oil extraction; Catalyst recovery


Thank You
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