

CHAPTER 4

MEMBRANE SEPARATION PROCESSES

APPLICATION OF MEMBRANE PROCESSES

Membrane separations, electrodialysis, reverse osmosis, ultrafiltration and other such processes are playing an increasingly important role in waste water treatment.

A membrane is defined as a phase which acts as a barrier between other phases. It can be a solid, a solvent-swollen gel or even a liquid. The applicability of a membrane for separation depends on differences in its permeability to different compounds.

In Table 4.1 a survey is given of membrane separation processes and their principal driving forces, applications and the useful ranges of the separation processes.

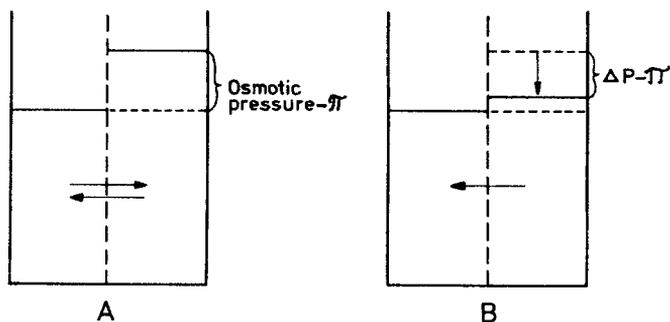


Fig. 4.1. A, illustrates equilibrium. An osmotic pressure appears. B, illustrates the principle of reverse osmosis.

REVERSE OSMOSIS

Osmosis is defined as a spontaneous transport of a solvent from a dilute solution to a concentrated solution across a semipermeable membrane. At a certain pressure, the so-called osmotic pressure, equilibrium is reached.

The osmotic pressure can vary with concentration and temperature, and depends only on the properties of the solution.

For water the osmotic pressure is given by:

$$\pi = \frac{n}{V}RT \quad (4.1)$$

where

n = the number of moles of solute

V = the molar volume of water

R = the gas constant

T = the absolute temperature

This equation describes an ideal state and is valid only for dilute solutions. For more concentrated solutions the equation must be modified by the van't Hoff factor by using an osmotic pressure coefficient.

$$\pi = \phi \cdot \frac{n}{V}RT \quad (4.2)$$

TABLE 4.1

Membrane separation processes

Process	Driving force	Range(μm) particle size	Function of membrane
Electro-dialysis	Electrical potential gradient	<0.1	Selective to certain ions
Dialysis	Concentration	<0.1	Selective to solute
Reverse osmosis	Pressure	<0.05	Selective transport of water
Ultra-filtration	Pressure	$5 \cdot 10^{-3}$ - 10	Selective to molecular size and shape

For most electrolytes the osmotic pressure coefficient is less than unity and will usually decrease with increasing concentrations. This means that equation (4.1) is usually conservative and predicts a higher osmotic pressure than is observed. If the pressure is increased above the osmotic pressure on the solution side of the membrane as shown in Fig. 4.1, the flow is reverse. The solvent will then pass from the solution into the solvent. This is the basic concept of reverse osmosis. Reverse osmosis can be compared with filtration, as it also involves the moving of liquid from a mixture by passing it through a "filter".

However, one important difference is that the osmotic pressure, which is very small in ordinary filtration, plays an important role in reverse osmosis. Secondly a filter cake with low moisture content cannot be obtained in reverse osmosis, as the osmotic pressure of the solution increases with the removal of solvents. Thirdly, the filter separates a mixture on the basis of size, whereas reverse osmosis membranes work on the basis of other factors. Reverse osmosis has sometimes also been termed hyper-filtration.

The flux equations

The permeate flux, F , through a semipermeable membrane of thickness, d , is given by:

$$F = \frac{D_W \cdot C_W \cdot V}{RTd} (\Delta P - \pi) \quad (4.3)$$

where

D_W = the diffusion coefficient

C_W = the concentration of water

V = the molar volume of water

ΔP = the driving pressure (see Fig. 4.1)

R and T are defined above

The equation (4.3) indicates that the water flux is inversely proportional to the thickness of the membrane. These terms can be combined with the coefficient of water permeation, W_p , and equation (4.3) reduces to:

$$F = W_p \cdot (\Delta P - \pi) \quad (4.4)$$

where

$$W_p = \frac{D_W \cdot C_W \cdot V}{RTd} \quad (4.5)$$

For the solute flux, F_s , the driving force is almost entirely due to the concentration gradient across the membrane, which leads to the following equation (Clark, 1962):

$$F_s = D_s \frac{dC_i^1}{dx} = D_s \frac{\Delta C_i^1}{d} \quad (4.6)$$

where

C_i^1 = the concentration of species, i , within the membrane

ΔC_i^1 = measured across the membrane

This equation can be restated in terms of the concentration of the solution, C_i , on either side of the membrane, incorporating the so-called distribution coefficient, K_d , which is a constant for the membranes generally used (Lonsdale et al., 1965):

$$F_s = D_s \cdot K_d \cdot \frac{\Delta C_i}{d} = K_p \cdot \Delta C_i \quad (4.7)$$

where, K_p is termed the coefficient of permeability.

W_p and K_p are both characteristic of the particular membrane type.

As seen by equations (4.4) and (4.7), the water flux depends on the net pressure difference, while the solute flux depends only on the concentration. Therefore as the feed water pressure increases, water flow through the membranes increases, while the solute flow is approximately constant. Consequently the amount and quality of purified water increases as the net driving pressure is increased, but the quality of the water decreases as the feed water solute concentration increases, with a constant pressure, because of an increase in osmotic pressure. As more and more water is extracted from the waste water, the solute concentration becomes higher and the water flux falls. Figs. 4.2 and 4.3 illustrate these relations. The water flux as a function of the water recovery and at a fixed pressure is shown in Fig. 4.2 for two different salinities. The variation of the water quality with recovery is shown in Fig. 4.3. As can be seen, the water quality decreases with increasing feed salinity and increasing recovery.

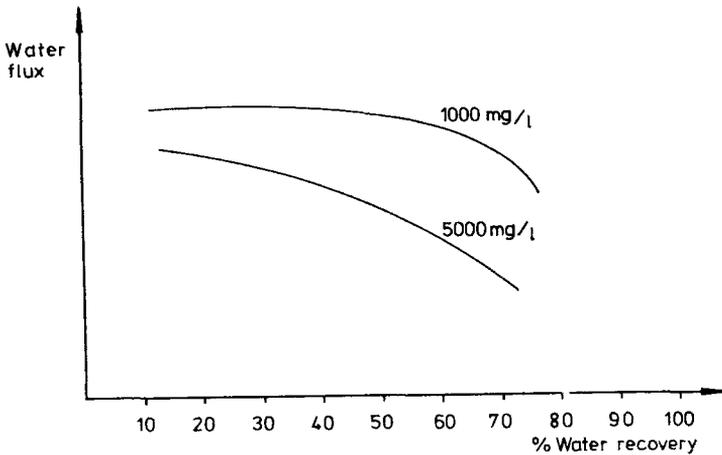


Fig. 4.2. Water flux related to water recovery for two concentrations.

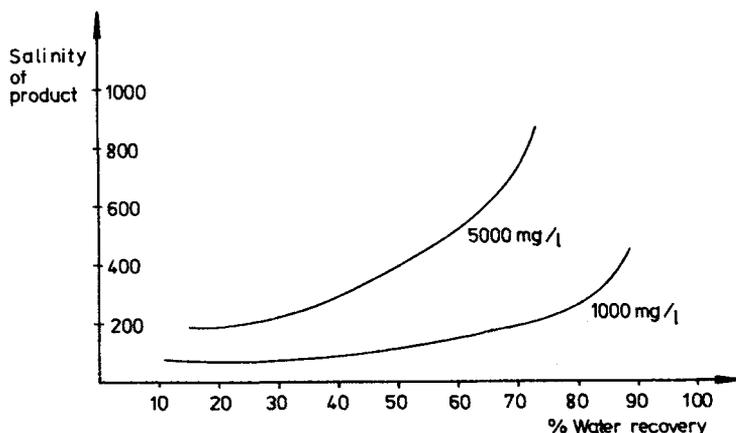


Fig. 4.3. Quality of product related to water recovery for two concentrations.

The rejection ratio in reverse osmosis, R , is defined on the basis of the following equation:

$$R = \frac{C_i - C_{pi}}{C_i} \quad (4.8)$$

where

C_i = the concentration of the species, i , in the concentrated stream (reject)

C_{pi} = the concentration of, i , in the permeate (product).

The rejection ratio is also expressed by the following equation:

$$R = \left(1 + \frac{K_p \cdot C_{wp}}{w_p (\Delta P - \pi)} \right)^{-1} \quad (4.9)$$

where, C_{wp} , is the water concentration in the permeate. Notice that $K_p \cdot C_{wp}$ and $w_p (\Delta P - \pi)$ must be expressed in the same units.

As $w_p (\Delta P - \pi) = F$ is often expressed as g or kg/cm^2 or $m^2/sec \cdot C_{wp}$ must be expressed as g/cm^3 or kg/m^3 .

The equations given so far are idealized because a good mixing on the brine side has been assumed, so that there is no concentration polarization. However, in reality salt concentrations build up at the membrane surface and a concentration gradient is established.

The increased concentration of the membrane surface raises the local osmotic pressure, so reducing the driving force. Concentration polarization is defined as the ratio of the salt concentration at the membrane surface to the salt concentration in the stream.

Example 4.1

A reverse osmosis membrane has a water permeation coefficient of $2.5 \cdot 10^{-5}$ g/cm²·sec·atm. Find the water and solute fluxes through the membrane at 30 atm. ($t = 25^{\circ}\text{C}$), and the rejection for feeds of 4000 mg/l sodium chloride and magnesium sulphate.

The permeability of the two salts are:

$$K_p \text{ NaCl} = 2.7 \cdot 10^{-5} \text{ cm/sec}$$

$$K_p \text{ Mg SO}_4 = 5.0 \cdot 10^{-6} \text{ cm/sec}$$

Solution

$$\pi = \frac{nR \cdot T}{V_m}$$

$$\text{NaCl: } \pi = \frac{2 \cdot 4000}{58.5 \cdot 10^3} \cdot 0.082 \cdot 298 = 3.34 \text{ atm.}$$

$$\text{MgSO}_4: \pi = \frac{2 \cdot 4000}{120.3 \cdot 10^3} \cdot 0.082 \cdot 298 = 1.63 \text{ atm.}$$

The Permeate flux is found from

$$F = W_p (\Delta P - \pi)$$

$$\text{NaCl: } F = 2.5 \cdot 10^{-5} (30 - 3.34) = 6.67 \cdot 10^{-4} \text{ g/cm}^2/\text{sec}$$

$$\text{MgSO}_4: F = 2.5 \cdot 10^{-5} (30 - 1.63) = 7.07 \cdot 10^{-4} \text{ g/cm}^2/\text{sec}$$

The solute rejected is determined by:

$$R = \left(1 + \frac{K_p \cdot C_{Wp}}{W_p (\Delta P - \pi)} \right)^{-1}$$

$$\text{NaCl: } R = \left(1 + \frac{2.7 \cdot 10^{-5} \cdot 1.0}{6.67 \cdot 10^{-4}} \right)^{-1} = 0.960$$

$$\text{MgSO}_4: R = \left(1 + \frac{5.0 \cdot 10^{-6} \cdot 1.0}{7.07 \cdot 10^{-4}} \right)^{-1} = 0.993$$

The following differential equation describes concentration polarization:

$$\frac{F \cdot C_i}{C_{wc}} - D_s \frac{dC_i}{dx} = K_p \cdot \Delta C_i \quad (4.10)$$

where, C_{wc} , is the water concentration in the reject.

If the membrane is impermeable to the solute, it means that $K_p = 0$, and equation (4.10) can be integrated to give:

$$\frac{C_{im}}{C_{ia}} = \exp\left(\frac{F \cdot d}{C_{wc} \cdot D_s}\right) \quad (4.11)$$

where

C_{im} = the concentration of, i , in the fluid at the membrane surface

C_{ia} = the average concentration of, i , in the reject

The following description for polarization in turbulent flow has been developed:

$$\frac{C_{im}}{C_{ia}} = 1.333 \exp\left(\frac{2F \cdot Sc^{2/3}}{\rho \cdot 0.75 \cdot v \cdot f}\right) \quad (4.12)$$

where

v = the mean velocity

Sc = the Schmidt number

f = the fanning friction factor

ρ = the specific gravity of the solution

The concentration polarization is seen to be a function of the ratio, average product flow rate to average brine velocity, the fanning friction factor and the Schmidt number. Since $\frac{F}{\rho \cdot v}$ is almost proportional to recovery, polarization is favoured by high recovery. However, high recovery can be maintained at low concentration polarization by recirculating the brine. The concentration polarization can be reduced by increasing the friction factor, so promoting turbulence.

Design of the reverse osmosis unit

A reverse osmosis plant consists of a series of module arranged in parallel. The design data include recovery, pressure, brine, flow rates, product water quality and flux maintenance procedure.

To be able to design a reverse osmosis unit one must know the feed water composition, its temperature and osmotic pressure. The capacity requirements of a plant are usually based on a certain reject flow rate at a given temperature or, in the case of waste water treatment, on the feed flow rate.

Based on mass balance for the water as well as the solute, the following equations can be set up:

$$Q_f = Q_r + Q_p \quad (4.13)$$

$$Q_f \cdot C_{if} = Q_r \cdot C_i + Q_p \cdot C_{ip} \quad (4.14)$$

where

Q_f = flow rate of feed stream

Q_r = flow rate of reject

Q_p = flow rate of permeate

C_{if} = concentration of, i, in the feed stream

C_i = concentration of, i, in the reject

C_{ip} = concentration of, i, in the permeate

The mean concentration of i, C_{ia} , on the one side of the membrane is given by:

$$C_{ia} = \frac{Q_r \cdot C_i + Q_f \cdot C_{if}}{Q_r + Q_f} \quad (4.15)$$

The water quality in the permeate (product) can be expressed by means of C_{ia} and the average rejection ratio, R_{av} :

$$C_{ip} = C_{ia}(1 - R_{av}) \quad (4.16)$$

The average salt rejection is given by:

$$R_{av} = 1 - \frac{K_p \cdot C_{wp} \cdot \Delta C_i}{W_p(\Delta P - \pi)C_{if}} \quad (4.17)$$

This equation can be solved most easily by an iteration. If we assume $C_{ip} = 0$, we have:

$$Q_f \cdot C_{if} = Q_r \cdot C_i \quad (4.18)$$

$$C_{ia} = \frac{Q_f \cdot C_{if}}{Q_f \cdot Q_r} = \frac{C_{if}}{2 - R} \quad (4.19)$$

where

$$R^{\dagger} = \frac{Q_p}{Q_f} \quad (4.20)$$

C_{ip} is then estimated:

$$C_{ip} = \frac{C_{if}}{2 - R^{\dagger}} (1 - R_{av}) \quad (4.21)$$

A better approximation can be obtained by utilizing the value given by equation (4.21) as next C_{ip} -value etc.

The minimum free energy requirement is determined (Johnson et al., 1966) by means of:

$$\Delta G = -RT \int_0^1 \ln a_w \cdot dn_w \quad (4.22)$$

where

a_w = the chemical activity of water
 n_w = number of moles of water recovered

a_w can be calculated from:

$$\ln a_w = \sum \frac{\theta}{55.5} \cdot C_i \quad (4.23)$$

where θ = coefficient (see 4.2).

Example 4.2

It is desired to produce 1000 m³/24h of potable water (500 mg/l dissolved salts) from water containing 3000 mg/l of dissolved salts, mainly NaCl. Design a reverse osmosis unit for this job. A membrane is available that has shown sodium chloride rejection of 0.95 at 45 atm. pressure. The permeability is 2.5 · 10⁻⁵ g/cm²/sec/atm.

Solution

$$\pi = \frac{2 \cdot 3000}{58.5 \cdot 10^3} 0.082 \cdot 298 = 2.5 \text{ atm.}$$

$\theta \cong \text{ca. } 1$

To be conservative we use: $R^{\dagger} = \frac{Q_p}{Q_f} = 0.9$

Therefore the osmotic pressure of the concentrate is approximately 10η feed or 25 atm.

$$Q_p = 1000 \text{ m}^3/24\text{h}$$

$$Q_f = 1110 \text{ m}^3/24\text{h}$$

$$Q_r = 111 \text{ m}^3/24\text{h}$$

$$C_p = \frac{2C_{if}}{2 - R} (1 - R_{av}) - \frac{2 \cdot 3000}{2 - 0.9} (1 - 0.95) = 272 \text{ mg/l}$$

$$C_i = \frac{Q_f \cdot C_p - Q_p \cdot C_p}{Q_r} = \frac{1110 \cdot 3000 - 1000 \cdot 272}{111} = 27577 \text{ mg/l}$$

$$C_{ia} = \frac{Q_r \cdot C_i + Q_f \cdot C_p}{Q_r + Q_f} = \frac{111 \cdot 27577 + 1110 \cdot 3000}{1222} = 5232 \text{ mg/l}$$

$$C_p = C_a (1 - R_{av}) = 5232 (1 - 0.95) = 262 \text{ mg/l}$$

$$F = 2.5 \cdot 10^{-5} (45 - 2.5) = 1.06 \cdot 10^{-3} \text{ g/cm}^2/\text{sec}$$

$$A = \frac{Q_p}{F} = \frac{1000}{1.06 \cdot 10^{-3} \cdot 10^{-6} \cdot 10^4 \cdot 3600 \cdot 24} = 1092 \text{ m}^2$$

It is suggested that $\underline{1400 \text{ m}^2}$ be used to allow for compaction and fouling of membranes.

Reverse osmosis system

In constructing a system for reverse osmosis many problems have to be solved:

- 1) The system must be designed to give a high liquid flux reducing the concentration potential.
- 2) The packaging density must be high to reduce pressure vessel cost.
- 3) Membrane replacement costs must be minimized.
- 4) The usually fragile membranes must be supported as they have to sustain a pressure of 20-100 atm.

Four different system designs have been developed to meet the solution to the latter problem. The plate and frame technique, large tube technique, spiral wound technique and the hollow fine fibre technique.

The various techniques are compared in Table 4.2.

TABLE 4.2

Comparison of the various techniques

Module concept	Packing density (m ² /m ³)	Useful pH range	Ease of cleaning	NaCl rejection	Water flux at 40 atm. (m ³ /m ² /day)
Plate and frame	450	2-8	fair	very good	0.5
Large tubes	150	2-8	very good	very good	0.5
Spiral	750	2-8	good	very good	0.5
Hollow fine fibres	7500-15000	0-12 ⁺)	fair	good/fair	0.05-0.2

+) Polyamide

The most widely used membrane is the cellulose acetate membrane by the Loeb-Sourirajan technique. This membrane is asymmetrical and consists of a thin dense skin of approximately 0.2 μ on an approximately 100 μ thick porous support.

As shown in Fig. 4.4, these membranes are not resistant to high or low pH, and a temperature range of 0-30°C must be recommended.

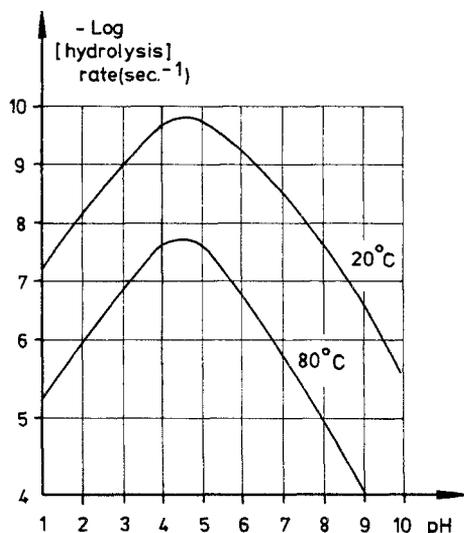


Fig. 4.4. Hydrolysis rate of cellulose acetate membrane as function of pH at 20°C and 80°C. (see Vos et al., 1966).

Polyamide membranes have also been developed. They are considerably more resistant to temperature and pH, but give a smaller flux. During the latest decade there has been intense research activity in the development of membranes, resulting in several new types of membrane. Cellulose acetate-butyrate resin, cellulose acetate-methacrylate, polyacrylacid and cellulose nitrate-acetate, are among the recently developed membrane materials, which are more resistant to pH and temperature, but do not reduce the initial fluxes. Several natural materials could also be of use as membranes and extensive laboratory investigations may hold promise for the application of such natural membranes in the near future (Kraus et al., 1967).

ULTRA-FILTRATION

Both ultra-filtration and reverse osmosis depend on pressure as the driving force and require a membrane which is permeable to some components and impermeable to others.

The difference between the two processes is that, while ultra-filtration is usually used to separate solutes above a molecular weight of 500, which have a small osmotic pressure (this includes bacteria, starch, protein, clays, etc.) - reverse osmosis is used to remove material of low molecular weight, which has a high osmotic pressure.

The flow through an ultra-filtration membrane depends on the pressure drop, as shown in Fig. 4.5.

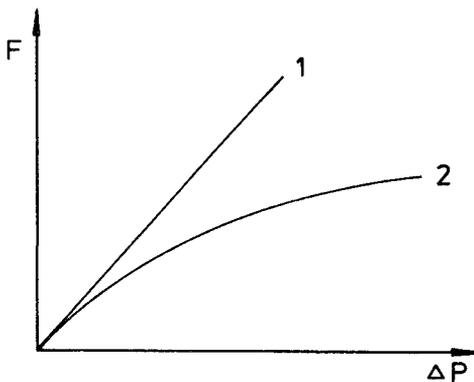


Fig. 4.5. Curve 1 illustrates the relation between flux and driving pressure by membrane permeability control, and curve 2 the same relation by membrane permeability- and concentration polarization control.

At relatively small pressure drops the flux is proportional to a pressure driving force ΔP and is inversely proportional to the membrane resistance R_n :

$$F = \frac{\Delta P}{R_n} \quad (4.24)$$

When the concentration adjacent to the membrane surface exceeds a critical value, the flux begins to level off with increasing Δp . The flux is then controlled by the membrane permeability as well as the concentration polarization (see Fig. 4.5).

The polarization is usually greater in ultra-filtration than in reverse osmosis because the diffusion constant is two or three orders of magnitude smaller for the macro-molecules than for salts. The flux usually decreases logarithmically with increasing concentration of retained substances; the following equation describes the observed flux:

$$F = k \cdot \ln \frac{C_c}{C_i} \quad (4.24)$$

where

k = an overall mass transfer coefficient

C_c = the concentration of retained species adjacent to the membrane surface

C_i = as defined above in conjunction with reverse osmosis

Ultra-filtration is used to remove clays, micro-organisms and vegetable matter and for de-watering sludge.

DIALYSIS AND ELECTRODIALYSIS

Dialysis involves the separation of solids by making use of unequal diffusion through membranes. The rate of diffusion, F_d , is related to the concentration gradient, Δc , across the membrane:

$$F_d = k_d \cdot A \cdot \Delta c \quad (4.25)$$

where

k_d = the overall dialysis coefficient

A = the area of the membrane

A good approximation to Δc is given by:

$$\Delta c = \frac{\Delta c_1 - \Delta c_2}{2.3 \log \frac{\Delta c_1}{\Delta c_2}} \quad (4.27)$$

where Δc_1 and Δc_2 are the concentration gradients at the inflow and outflow points.

Electrodialysis is accomplished by placing cation and anion selective membranes alternatively across the path of an electric current. When the current is applied, the electrically attracted cations will pass through the cation-exchanging membranes in one direction and the anions will pass through the anion-exchanging membranes in the other direction (see Fig. 4.6).

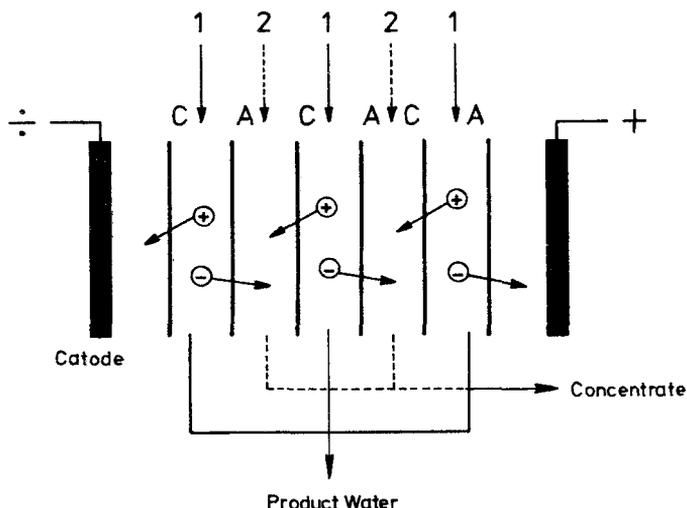


Fig. 4.6. Principles of electrodialysis. 1 and 2 could be two different feeds - respectively more diluted and more concentrated - obtained from another set of membranes.

The result is that salinity decreases between one pair of membranes and increases between the next pair, etc. Water can then pass through several such membranes until the required salinity is achieved.

Dialysis has been used to recover acids and metal salts and sodium hydroxide (Keating et al., 1960).

Electrodialysis has been investigated as a method for denitrifying agricultural run-off water, but has also been used for recovering acids, for lignin from pulping waste water and for chromate from plating waste water.

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