

MEMBRANE PROCESSES

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ABSTRACT

Membrane processes can be used to treat a variety of aqueous wastes. In some applications the aim is to limit pollution of the environment, in others, wastes are purified to produce water suitable for re-use and there are several examples where valuable byproducts are extracted. Electrical, chemical potential and pressure gradients are used in conjunction with semi-permeable membranes to effect separations in aqueous solutions. Reverse osmosis, ultrafiltration, electro dialysis and transport depletion are all beginning to be employed to process wastes from industries such as pulp and paper, dairy, and metal finishing and also to treat sewage and polluted surface waters.

INTRODUCTION

A membrane can be defined as a barrier separating two fluids. The barriers considered here do not prevent the passage of all species but are permeable to some and impermeable to others. Such membranes are termed semi-permeable and usually are in the form of thin sheets of polymeric material. Since the amount of a species transported across a membrane is inversely proportional to the thickness, it is advantageous to have the thinnest membrane possible. In practice, considerations such as mechanical strength usually determine the lower limit of membrane thickness. In many cases synthetic polymers are used and many have been developed specially to provide the required semi-permeable characteristics.

TYPES OF MEMBRANE PROCESS

In order to drive a species through a membrane permeable to that species a force is required. Such forces are listed in *Table 1* along with processes in which these forces are employed. The types of separations possible are also listed. In all these processes the membranes separate two liquid phases. In a similar way, gas separations can be performed but these are outside the scope of this paper. In *Table 1* only the most important processes are listed though others are known or are being developed. Examples are pervaporation in which volatile species are transported by means of pressure on one side and suction on the other side of the membrane, and piezodialysis where ionic solutes are transported under the effect of pressure. The latter is thus in some ways the opposite of reverse osmosis.

From *Table 1* the potential of such processes is obvious in that various

Table 1. Driving forces in membrane processes

Force	Process	Species passing through membrane	Species not passing* through membrane
Hydrostatic pressure	reverse osmosis	solvent	solutes
	ultrafiltration	solvent and small solutes	larger solutes
Potential difference	electrodialysis	ionic solutes	solvent, non-ionic solutes
	transport depletion	[†] c cations, n solvent, n small solutes	all others, larger solutes
Concentration difference	osmosis	solvent	solutes
	dialysis	solvent, small solutes	larger solutes

* There are two possible reasons for a solute not passing through the membrane

- (i) membrane impermeable
- (ii) force does not cause species to move

[†]c cation permeable membrane
n uncharged porous membrane

separations are possible such as removing solutes from solution and separating solutes. The fundamentals of four of these processes will be outlined and the ways in which they are being used in waste treatment will be described.

REVERSE OSMOSIS¹

In reverse osmosis or hyperfiltration as it is sometimes called the membrane has to be permeable to the solvent, water, and impermeable to solutes, and pressure is used to drive the water through the membrane. The name reverse

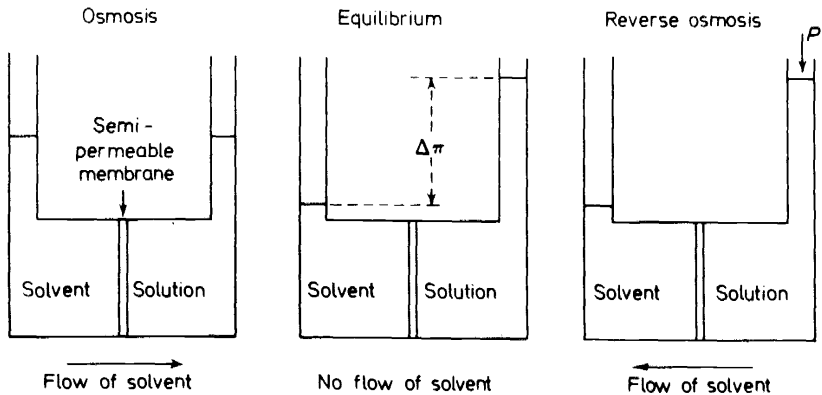


Figure 1. Osmosis and reverse osmosis

osmosis arises from the fact that the direction of solvent flow is the reverse to that occurring in osmosis, as illustrated in Figure 1. The process has been

MEMBRANE PROCESSES

widely studied as a means of desalting brackish or sea-water. In practice, useful membranes are not totally impermeable to salt and some compromise has to be reached between flux of water and rejection of salt. The most extensively used membrane material is cellulose acetate though an aromatic polyamide is also used. Thin films—say 10–20 μ thick—of cellulose acetate do not have a high enough permeate flux at reasonable pressures of 30–40 bar to make the process economically attractive but asymmetric membranes have been developed as illustrated in *Figure 2*². The membrane is a very

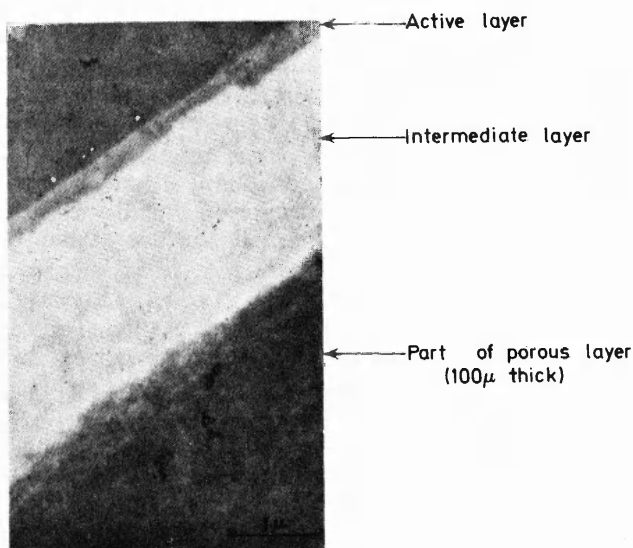


Figure 2. Cross section of membrane

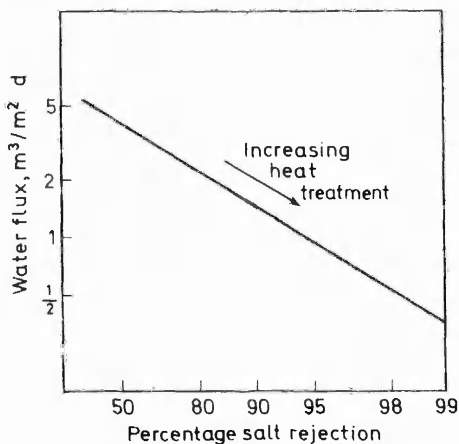


Figure 3. Performance of cellulose acetate membrane at 40 bar on 5000 p.p.m. NaCl

thin semipermeable layer 0.25μ thick on a much thicker non-selective highly porous support. The performance of such a membrane is illustrated in *Figure 3* and the inter-relationship between flux and rejection is clear.

The water flux is proportional to the difference between applied pressure and osmotic pressure whereas salt transport is almost independent of pressure. Thus increasing the pressure results in higher water flux and salt rejection but unfortunately can lead to a reduction in membrane life. Cellulose acetate membranes can be used over a pH range of 3 to 8. Outside this range hydrolysis leads to loss of salt rejection. There is a clear need for more stable membranes particularly for applications other than desalting.

Reverse osmosis membranes reject species other than salts. For cellulose acetate the following criteria can be used.

- (i) the higher the ionic charge, the higher the rejection.
- (ii) the lower the tendency to form hydrogen bonds, the higher the rejection;
- (iii) the larger the molecule, the higher the rejection.

Solutes such as urea are poorly rejected whereas sugars are well rejected.

In reverse osmosis plant the feed is pumped past the membrane. Water passes through and solute is left behind at the surface. Liquid at the surface is much less well mixed than in the bulk and the solute concentration at the surface increases until the arrival rate is equalled by the combined effects of diffusion and mixing. This concentration polarization results in a reduced salt rejection and can lead to the precipitation of sparingly soluble salts. It

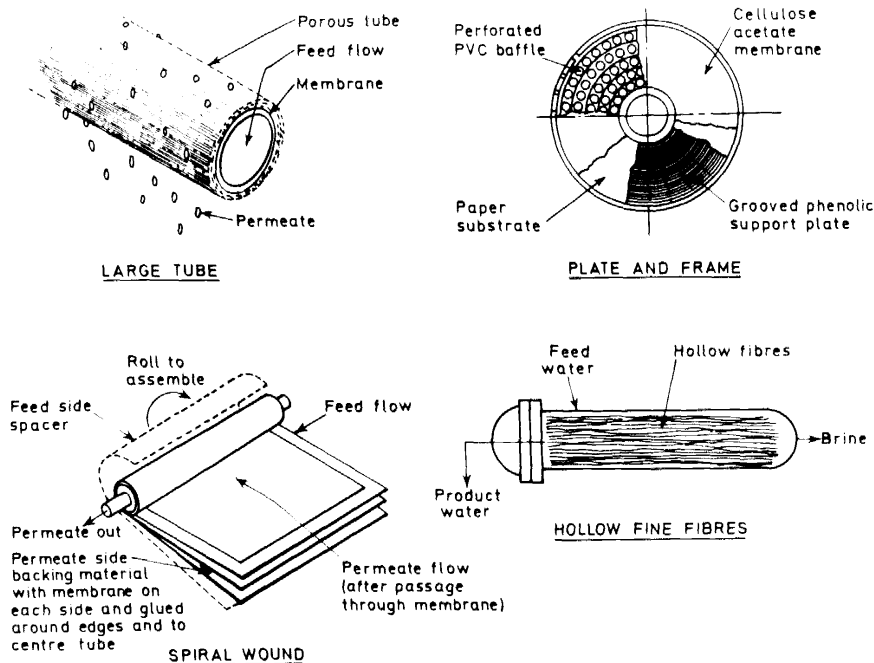


Figure 4. Types of reverse osmosis module¹

can be reduced by more effective mixing but at the expense of pumping power.

Pressures used vary from 30 bar to more than 60 bar, the latter being needed for feed solutions with high osmotic pressure such as sea-water (approximately 30 bar). The membranes have to be supported against this pressure and various types of module have been developed as shown in *Figure 4*.

The different versions can be summarized as follows .

- (i) Flat sheets in plate and frame or spiral wrap.
- (ii) Membranes inside porous tubes.
- (iii) Membranes on the outside of porous supports.
- (iv) Hollow fibres that need no support.

Plants with capacity in excess of 1000 m³ per day are now in use. These are of modular construction and frequently some form of pretreatment is needed to protect the reverse osmosis units from chemical effects or fouling by suspended material.

ULTRAFILTRATION

Membranes are available which reject no salt but do reject larger molecules and colloidal species. These are used in ultrafiltration and the important parameter is the molecular weight cut-off, i.e. the limiting molecular weight beyond which molecules do not pass through the membrane. Values range between 500 and 100000 and a wide range of membranes is available. These are made from various polymers and some are chemically very stable. They are, in effect, polymeric sheets with carefully controlled pore size and, usually, some degree of asymmetry. Typical applications are the fractionation of protein species or the separation of macromolecules from smaller solutes such as sugars.

The membranes used offer much less resistance to the passage of water and much lower pressures can be used (2 to 10 bars). Indeed increasing the pressure frequently achieves nothing as a layer of the rejected species is formed on the membrane and increases in thickness if one attempts to force more water through the membrane. This deposited layer thus limits the flux through the membrane.

The equipment used is similar to that for reverse osmosis though lighter in construction because of the lower pressures. Flat sheet units and modules with membranes on the inside of tubes are most commonly used.

ELECTRODIALYSIS

In electrodialysis, ions move through membranes under the influence of a potential gradient. Two types of membrane are used; one is permeable to cations and impermeable to anions and vice versa for the other. The membranes are made of ion-exchanging materials similar in some ways to those used in cation and anion-exchange beads. The two types are arranged alternately as shown in *Figure 5*. In commercial plant many more compartments are arranged in parallel. Ions move as shown with the net result that

the ionic concentration in one set of alternate compartments is decreased; in the other set it is increased. It is normal to supply the electrode compartments from a separate solution in order to protect the electrodes from injurious species in the feedwater.

The ions transported carry the electrical current and thus increasing the current results in an increased removal of ions. However, concentration polarization occurs here too. The liquid in the centre of a compartment can be stirred effectively whereas that next to the membrane is virtually static. Since anions are transported more readily through the anion membrane than through the solution, the concentration of anions in the layer next to the cathode side of the anion membrane can fall until it becomes comparable with the concentration of hydroxyl ions. Such a low concentration zone has high electrical resistance and leads to higher energy consumption. Also the transport of hydroxyl ions through the anion membrane effectively wastes current and can cause precipitation of basic salts which may be deposited on the membranes. Another problem occurs when the feed contains large organic anions since these become trapped in the anion membranes and alter the semi-permeability.

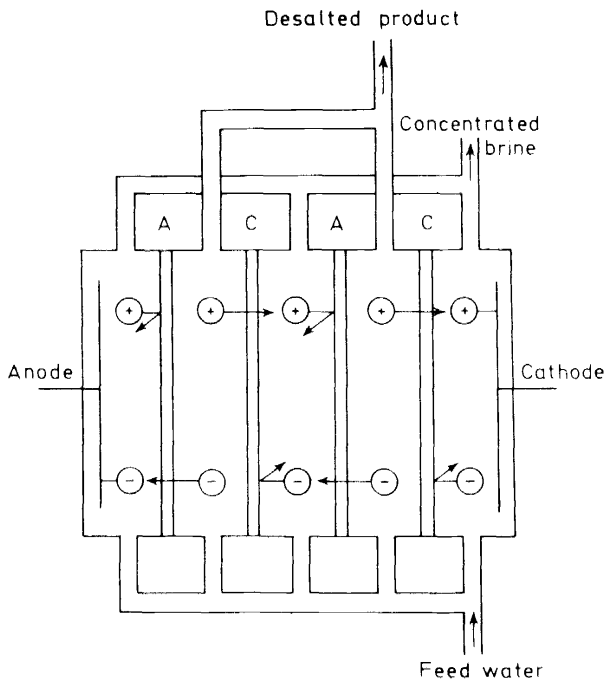


Figure 5. Desalting by electrodesaliation. A is an anion-permeable membrane; C, a cation-permeable membrane

In addition to these problems there are two overall limitations to the process. The ions that are transported take some water molecules with

them—this is called electro-osmosis and limits the degree of concentration possible. If the desalted stream has too low a concentration, e.g. less than 400 p.p.m., the electrical resistance becomes too high for the economic transport of ions.

Electrodialysis plant is made up of a stack of membranes and spacers as shown in *Figure 6*. The whole is clamped together and flow through the two sets of compartments is through the duct and into the compartment via the appropriate port. Each compartment is thus made up of a spacer, two membranes and a screen to separate the membranes and provide a degree of turbulence. Much ingenuity has gone into the design of spacer screen, the prevention of liquid and electrical leaks, and reducing the compartment thickness to decrease electrical resistance. Plants with capacity greater than 1000 m³ are being used for the desalination of brackish water.

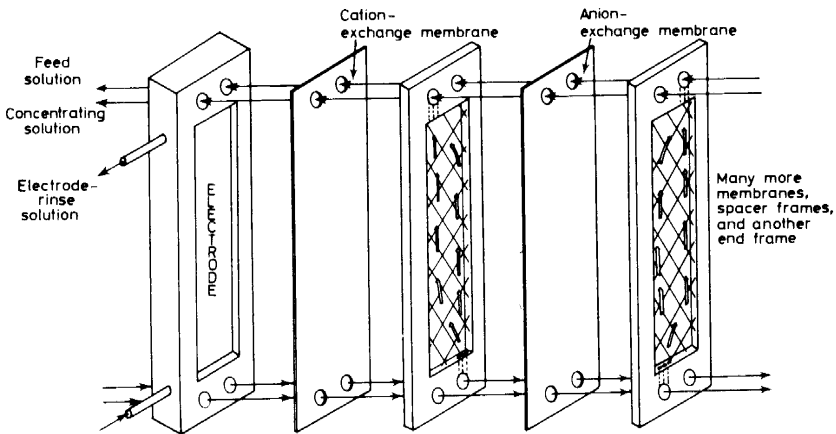


Figure 6. Exploded view of electro dialysis stack⁴

TRANSPORT DEPLETION

Some of the problems encountered in electro dialysis are eliminated in the process called transport depletion where the anion membrane is replaced by a neutral porous film as shown in *Figure 7*. Concentration and desalting still occur but at lower current efficiency. No concentration gradients are established close to the neutral membranes and fouling and precipitation do not occur. With appropriate choice of pore size of the neutral membrane the transport of large anions can be prevented.

The equipment used for this process is the same as that for electro dialysis.

Various other processes are being studied. These include electrogravitation where electrical transport is combined with gravitational transport due to density gradients.

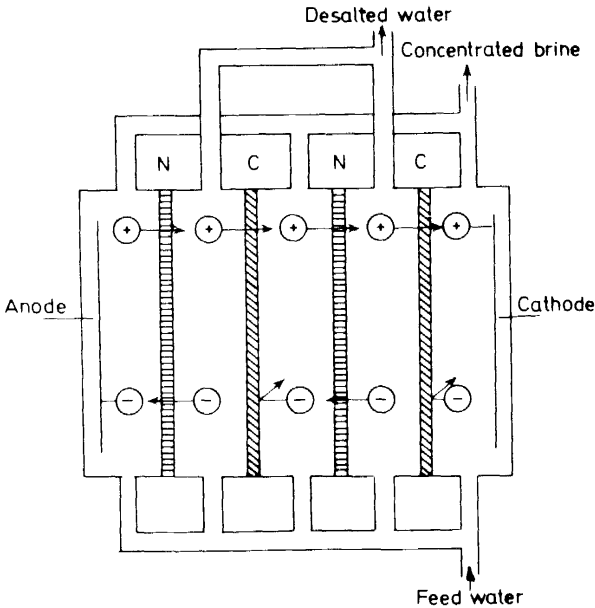


Figure 7. Transport depletion process. N is a neutral, porous membrane; C, a cation-permeable membrane

APPLICATION TO WASTES

The ideal treatment of an aqueous waste would result in water of quality adequate for re-use or safe discharge, recovery of all useful byproducts and an absolute minimum of harmless materials to be released to the environment. Membrane processes are not particularly cheap to operate. For the large scale application to desalination of brackish water, costs are 30p Sterling/1000 gallons treated (or 0.4 DM per m^3). The costs are, of course, higher for smaller scale more specialized applications and this means that, at the moment, there is emphasis either on recovering valuable products or on handling difficult wastes. Moreover, contaminants are not destroyed by membrane processes, they are merely transferred. However, as the cost of process water increases there will be more incentive to use these processes to produce water suitable for recycling.

Some areas of application are listed in *Table 2* along with the current status as derived from published literature. This list is obviously out of date now but it does give an impression of the range of applications and of whether these are being practised on a full production scale.

In general, membrane processes offer the possibility of separating water from various types of solute and of separating solutes either on the basis of size or because some are ionized and others are not. In addition to these cases where a high degree of separation is achieved, there are many instances where the composition of the dissolved material is altered. One example is

MEMBRANE PROCESSES

Table 2. Application of membrane processes in waste treatment

Waste	Processes considered	Current status
Pulp and paper mill effluents	ED, TD, RO, UF	RO 200 m ³ per day pilot ⁵
Sewage	RO, UF	UF 120 m ³ per day production ⁶ RO 70 m ³ per day pilot ⁷
Rinses from electrophoretic painting	UF	UF production ⁸
Effluent from metal-finishing plating	ED, RO, UF	ED laboratory tests ⁹ UF laboratory tests ¹⁰ RO 1000 m ³ per day ¹¹
Acid mine drainage waters		RO 50 m ³ per day pilot ¹²
Whey treatment	ED, TD, RO + UF	ED, TD 10 m ³ per day production ^{1,3} RO + UF 10 m ³ per day production ^{1,4}

ED Electrodialysis RO Reverse osmosis
TD Transport depletion UF Ultrafiltration

in reverse osmosis where the permeate has a considerably reduced salt content and an increased ratio of uni- to multi-valent ions.

WHEY TREATMENT

Whey is the byproduct of cheese-making and, since it contains about five per cent of lactose, it has a very high biological oxygen demand. It has some value as a pig food but considerable quantities are discharged to waste and the lactose content causes problems. Whey also contains protein of high nutritive value and inorganic salts; various membrane processes are used to recover useful products and to alleviate the pollution problem. These are listed in *Table 3*. Removal of inorganic salts prior to drying yields a product that is suitable for use in a number of foods. This demineralization is accomplished by electrodialysis or transport depletion and both processes are in use in the USA.

With electrodialysis the high calcium content can result in the formation of precipitates on the cation membranes while protein fractions can be

Table 3. Processes used in the treatment of whey

Effect required	Process used
Partial removal of water	Evaporation or RO
Almost total removal of water	Above + spray drying
Removal of salts	ED or TD
Removal of lactose and salts	UF

deposited on the anion membranes. Operation at low current density and high liquid velocity is used to control precipitation of calcium salts and polarity reversal is an effective means of limiting the deposition of proteins. In addition, the inorganic deposits can be removed by washing with acid, and alkaline cleaning solutions proteinaceous fouling.

These problems do not occur with transport depletion and though, under ideal conditions, the current efficiency of this process is only about half that in electrodialysis, the difference largely disappears in the treatment of whey.

The whey can be processed at its starting concentration of six per cent solids or after prior concentration which results in lower energy consumption. The compromise between amount of salt removed and processing cost usually results in 60-70 per cent salt removal.

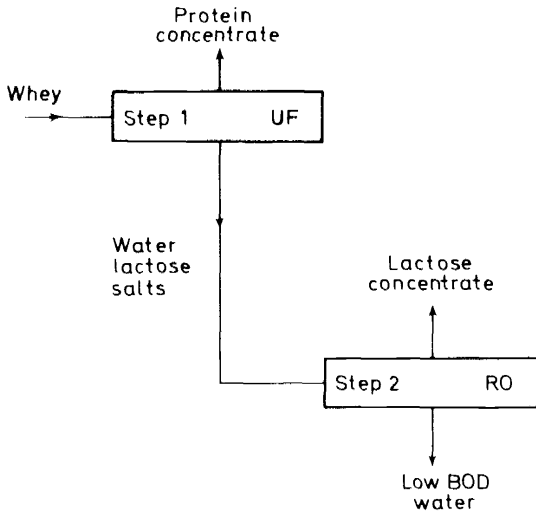


Figure 8. Dual process for treating whey

Simple removal of water from whey is not much used. Instead ultrafiltration alone or in conjunction with reverse osmosis is preferred. The dual process is depicted in *Figure 8* and yields concentrates of proteins and lactose and water of low enough BOD for disposal without further treatment. In ultrafiltration, water, lactose and salts are removed in equal percentages and products with a range of protein to lactose ratios can be made as shown in *Table 4*. The product with ratio of 0.67 has a composition close to that of skim milk powder and can be used as a substitute for this. Products with different ratios could be used in a number of ways but the markets for such products are not yet developed.

The ultrafiltrate contains a large fraction of the lactose and this can be extracted using reverse osmosis. This sugar has a number of uses but, if it were extracted from all the whey produced, new markets would have to be identified. Plants for the fractionation of whey are operating in Europe and the USA. Flux can be maintained by using suitable cleaning procedures and adequate sanitary standards can be achieved.

MEMBRANE PROCESSES

Table 4. Composition of whey protein concentrate

% water removed	% total solids	Protein to lactose ratio in dry solids
0	6.2	0.14
50	6.9	0.28
75	8.2	0.56
90	11.7	1.40
95	17.3	2.80

SEWAGE TREATMENT

The treatment of whey is already performed in small plants whereas the treatment of domestic sewage would generally require very large plants. The steps used in conventional sewage treatment are outlined in *Figure 9* and reverse osmosis has been applied at each stage in pilot-scale trials. Considerable fouling occurs leading to a reduction of permeate flux but the magnitude of this effect decreases as more pretreatment stages are used.

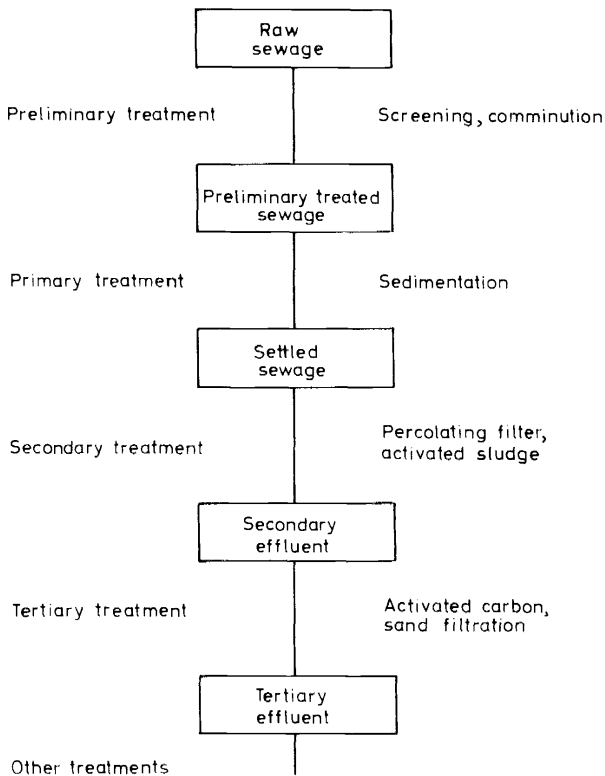


Figure 9. Steps in conventional treatment of sewage

Various trials on plants of capacity up to 70 m³ per day have been reported and considerable progress has been made in devising suitable cleaning methods. Periodic flushing with enzyme detergent is particularly successful and typical results are shown in *Figure 10*.

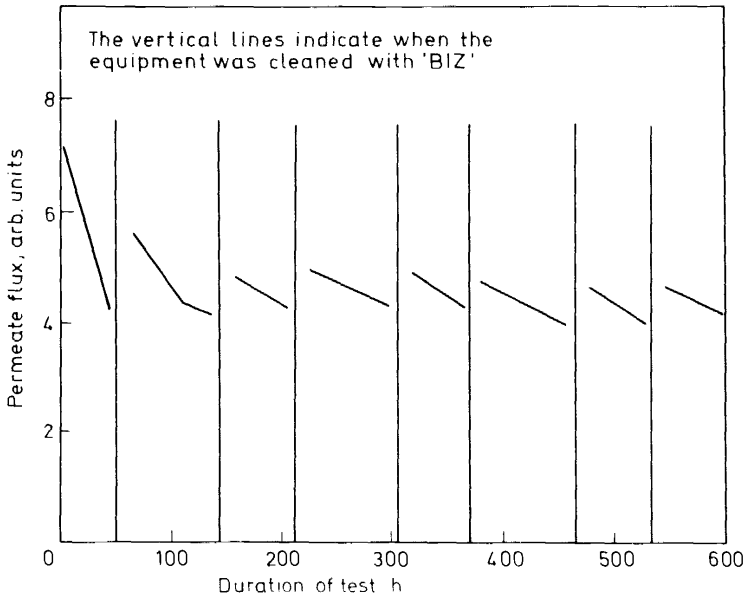


Figure 10. Treatment of secondary sewage effluent by RO

This application is at too early a stage in development for reliable cost estimates to be available. Indeed there is considerable discussion as to the most useful role reverse osmosis can play in sewage treatment. Possibilities vary from the extraction of water for purposes such as horticulture to reduction in salt content of the effluent. The latter role is one particularly suited to reverse osmosis and will be required as the salinity of rivers increases. In addition to salt removal, high removals of BOD and COD are obtained by reverse osmosis. Microbiological species such as bacteria and viruses do not pass through the membranes.

WASTES FROM METAL FINISHING

Wastes from electroplating, etching and pickling can be, in principle, processed by electrodialysis, reverse osmosis and ultrafiltration. Various laboratory scale studies have been reported and recently the use of reverse osmosis in a zero discharge system has been described. The process is used in two ways; the first is to extract chromium from rinse baths and return it to an electroplating solution 30 m³ per day; in the second the effluent from a flocculation process is treated to produce water suitable for recycle

--1000 m³ per day—and a concentrate that can be used, after drying, to de-ice roads. The value of the recovered chromium counterbalances the costs of the recovery process.

In a similar way 99 per cent of the nickel can be recovered from rinses subsequent to plating in Watts or sulphamate baths. The limited pH stability of cellulose acetate membranes is a disadvantage in many plating applications.

Electrodialysis has also been investigated as a means of recovering nickel in electroplating. Amongst other possibilities is the maintenance of a constant zinc concentration in an etch bath by removing excess by electrodialysis.

Membrane processes are more likely to be used where the recovered species can be re-used easily. This does not apply for pickle effluents and precipitation is preferred unless there is a high quality effluent required for recycling as in the example quoted earlier.

EFFLUENT FROM ELECTROPHORETIC PAINTING

Electrophoretic painting is used extensively in the automotive industry as well as for domestic appliances and office furniture. The paint is basically an aqueous solution of a resin solubilized by alkali and to which pigments and organic solvents are added. After electrodeposition, undeposited paint is washed off before the deposited paint is cured. The undeposited material can represent a drag-out loss as high as 50 per cent which is unacceptable in terms of both loss of paint and production of high BOD effluent. Ultrafiltration has been used extensively to solve these problems. It would be possible simply to concentrate paint from the water rinse and return it to the dip tank but this is not the most useful procedure. Impurities gradually build up in the paint dip tank and these, particularly those that are ionic in character, adversely affect electrodeposition. In addition, the use of water alone can cause instability and precipitation in the material that is washed off. Thus it is preferable to use an integrated system as shown in *Figure 11*. In this the contents of the dip tank are treated by ultrafiltration when the higher molecular weight species such as paint and pigments are separated from water, ionic impurities and organic solvents. The paint and pigments are returned to the dip tank, some of the ultrafiltrate is bled off to control the level of impurities and the rest is used for washing off excess paint. The solvents exercise a stabilizing influence on the paint and are more effective than water alone for washing.

The throwing power of the paint is improved at high paint concentrations and the use of ultrafiltration encourages this. This application imposes fairly severe conditions on the membrane namely pH up to 9.5, high content of solids, some of them abrasive, and the presence of organic solvents. The first plants in use on the production line were marketed by Dorr Oliver but now equipment from various manufacturers is employed.

CONCLUSION

Various other applications in waste treatment have been studied but these few will suffice to indicate the usefulness of the membrane processes described.

At the moment, membrane processes are beginning to play an increasing role in waste treatment and it is clear that this increase will continue as industry becomes more familiar with relatively new processes such as reverse osmosis. Tighter control on pollution and demand for water exceeding available supply will further accelerate the use of membrane processes.

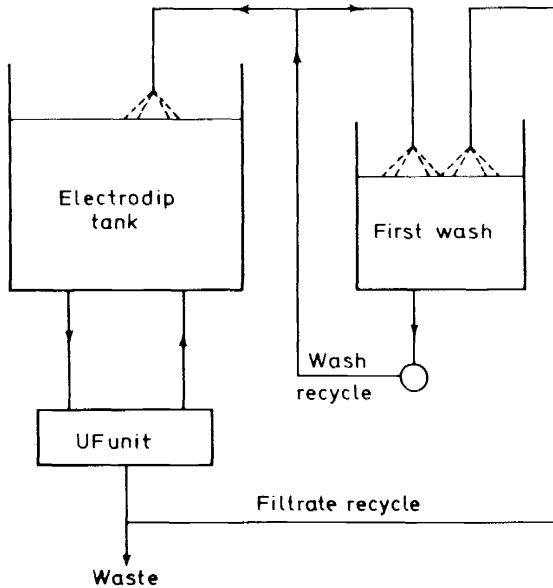


Figure 11. Use of UF in electrophoretic painting

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