The use of dynamic membranes for the treatment of effluents arising from wool scouring and textile dyeing effluents*

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Abstract

Dynamic membrane technology has been extensively researched, with particular reference to industrial effluent treatment. Two major plants have been commissioned in the wool scouring and textile dyeing industries.

The results of the operation of these plants have shown that product water of a reusable quality was produced. In the case of wool scouring effluent, an average flux of 37 $\ell/m^2 \cdot h$ could be maintained under correct operating conditions. Recent trials on the treatment of rinse liquor from a wool processing plant has shown that an average flux of 80 $\ell/m^2 \cdot h$ can be maintained, provided that the membranes are reformed on an approximately two-weekly cycle. An average flux of 33 $\ell/m^2 \cdot h$ was obtained from the dye effluent treatment.

Introduction

Membrane separation techniques have been developed over a number of years for desalination purposes, and, more recently, for the treatment of a variety of industrial effluents for pollution abatement and water reuse.

Industrial effluents often contain a wide range of chemicals including acids, bases, organic chemicals, colloidal material and suspended solids. Incompatibility of the membrane with the chemical nature, temperature, and solids content of the effluent often limit the selection of the membranes available and may make the use of extensive pretreatment of the effluent essential and expensive.

The use of dynamic or formed-in-place membranes may overcome many of these problem areas. The advantages of a dynamic membrane include the following:

- long service life of the support tube;
- ability to be operated at high pressure and temperature;
- in cases of severe fouling, the membrane can be removed by chemical means and re-formed *in situ*; and
- pretreatment to remove solids, whilst always desirable, is not critical in terms of mechanical damage to the membrane.

Formation of dynamic membranes

Dynamic membrane technology was pioneered by the Oak Ridge National Laboratory (Marcinkowsky et al., 1966 and Johnson et al., 1972). Research indicated that membranes of the hydrous zirconium (iv) oxide type were more suitable than many of the other hydrous oxides which were tested.

Zirconium type membranes are formed by the deposition of hydrous zirconium (iv) oxide onto the porous structure of a suitable support from colloidal suspensions. Stringently controlled conditions are necessary for the formation of high performance membranes.

Since stable zirconium chelate complexes form with many organic compounds by co-ordination through oxygen atoms, this enables the deposition of certain polymers onto the hydrous zirconium (iv) oxide membrane layer. This in turn then leads to the possibility of tailoring a membrane for specific duties. The most commonly used polymers for this purpose are of the polyacrylic acid type.

The methods of formation are described in detail by Johnson et al. (1972). It has been proposed by Freilich and Tanny (1978) and Tanny and Johnson (1978) that when a dilute colloidal suspension of hydrous zirconium (iv) oxide, at a pH just below 4, is passed across the surface of a porous substrate, the first stage involves a pore filling, or bridging stage, where colloidal particles of hydrous zirconium (iv) oxide are captured on the walls of the porous support material. This process causes the pores to close after a period and is followed by a surface filtration cake from colloidal particles, as commonly occurs in other types of cross-flow microfiltration. This then represents the hydrous zirconium (iv) oxide membrane which, in acidic solutions, is an anion exchanger.

When a polyelectrolyte, such as polyacrylic acid, is then passed over the hydrous zirconium (iv) oxide, the electrolyte enters the pores of the membrane rather than forming a gel layer on the surface. It is also suggested that at low pH values, the polyelectrolyte molecules are hypercoiled and easily able to penetrate and react with the substrate. If the pH is then raised, the polyelectrolyte molecules expand to block the pores, thereby causing a rapid decrease in flux and increase in rejection. This then represents the composite (Zr/PAA) membrane, which, in a neutral to alkaline solution, has the properties of a cation exchanger.

The hydrous zirconium (iv) oxide membranes are characterised by high water fluxes (150 $\ell/m^2 \cdot h \cdot MPa$) whilst showing a significant salt rejection (40 %). The composite Zr/PAA membranes have lower water fluxes (30 $\ell/m^2 \cdot h \cdot MPa$) but significantly higher salt rejection capabilities (85 %). Actual values will depend on the substrate and formation conditions of either the zirconium (iv) membrane or the composite membranes.

To distinguish these membranes from conventional phase inversion membrane films prepared by casting or other procedures, the class is designated dynamically formed or dynamic. More recently these membranes have been referred to as "formed-in-place" membranes.

Most of the early research was conducted using porous carbon or ceramic support tubes but problems with the robustness of the

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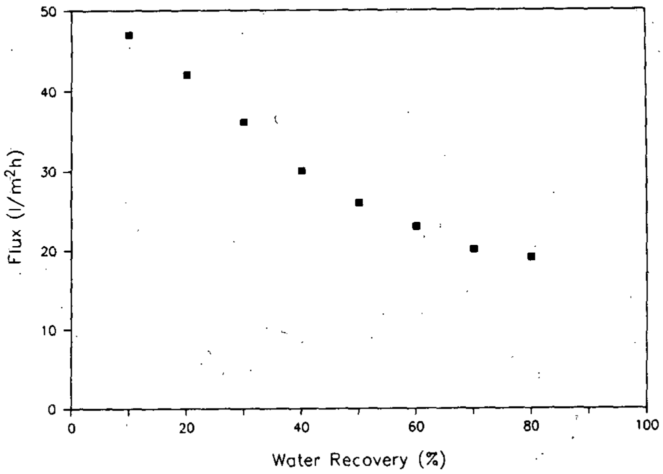

Figure 1
Wool scour effluent: The effect of water recovery on permeate flux

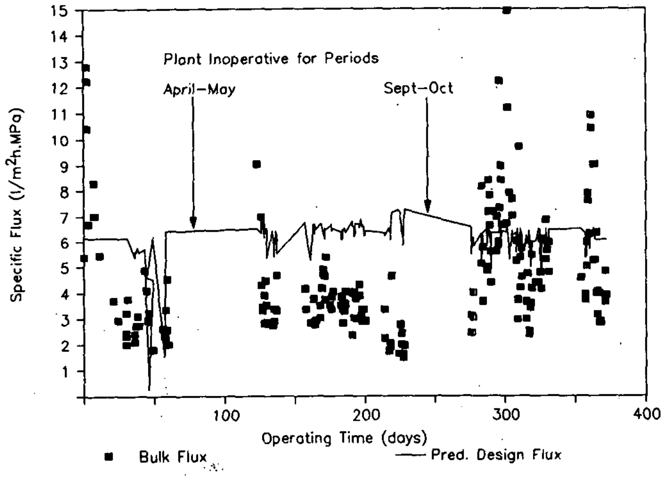

Figure 2
Wool scour demonstration plant performance

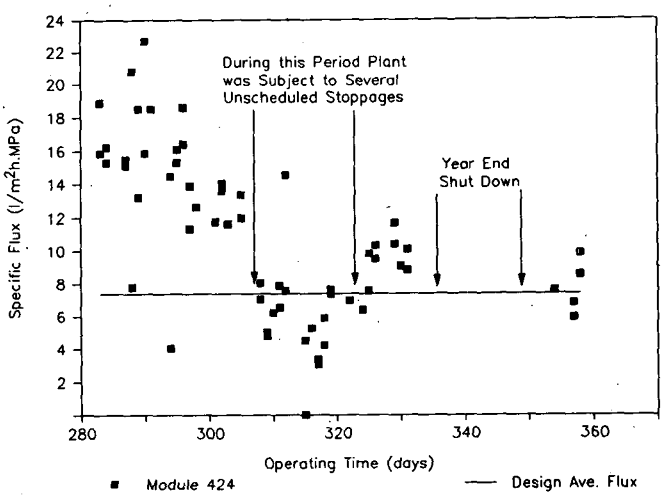

Figure 3
Wool scour demonstration plant: Effect of intermittent operation

tubes limited the applicability of the research. Brandon et al. (1980) and Mott et al. (1977) used porous stainless steel as a support for dynamic membranes which overcame most of the problems associated with the carbon and ceramic tubes. The stainless steel tubes used in the work described in this paper were 14 mm inside diameter. The pore size was variable and ranged from 2 to 7 µm. Carre Inc. (1982) in their brochure refer to the reliability of porous sintered stainless steel as the support material for high temperature dynamic membranes. Because of the integrity of the material, high-pressure operation is possible and single pass tubular dynamic membrane systems were developed. Such systems allegedly overcome some of the shortcomings of other membrane systems, such as prefiltration, low operating temperature, inefficient recirculation, tube breakage and capital expenditure for membrane replacement.

In our work on the use of such tubes, we have, however, found problems relating to the corrosion of the stainless modules under certain conditions. In general, however, the problem can be overcome by careful design of the modules and system and modification of the upstream process, where possible.

Hydrous zirconium (iv) oxide membranes and the zirconium (iv) polyelectrolyte membranes provide a range of salt rejections from 10 to over 95 %. The membranes can be tailored to suit a particular application.

Because the dynamic membrane is replaceable, fouling considerations are minimised and high strength industrial effluents may often be treated successfully. However, if a component in the effluent has the potential to chelate with zirconium, then the choice of membrane may be the selectively prepared zirconium/polyelectrolyte membrane, rather than a composite or dual layer membrane prepared randomly and fortuitously by passage of the effluent over the hydrous zirconium (iv) oxide membrane. However, it should be recognised that this results in a lowering of the permeate flux compared to the single layer hydrous zirconium (iv) oxide membrane.

Wool scour effluent

Wool scouring produces an effluent considered to be among the most polluting of textile effluents. Typically the effluent contains 10 to 20 g/ℓ wool grease, 7 to 15 g/ℓ suint salts (salts produced by natural excretions) and 10 to 30 g/ℓ dirt (sand, vegetable matter and fibre). The chemical oxygen demand (COD) of the effluent can be as high as 50 000 mg/ℓ (Stewart, 1983). Disposal of these effluents is mainly by solar evaporation or direct discharge both of which has become unacceptable due to environmental considerations.

An important consideration in the treatment of wool scouring effluent by a membrane process was to slightly modify the wool washing process to produce three effluent streams (Groves, 1979): desuint effluent containing mostly the dirt and suint loading (1,0 kℓ/h), scour effluent containing the grease loading (3,2 kℓ/h) and a low strength rinse effluent (2,0 kℓ/h). The low volume desuint stream has been successfully treated by falling film evaporation. The low strength rinse effluent was used as process water in the scour section.

Initial research using conventional ultrafiltration membranes to treat the grease effluent showed these membranes to be unsuitable for wool scour effluents, the characteristics of the effluent being such that permanent damage to the membrane occurred within a very short space of time due to physical damage of the surface of the membrane.

Laboratory-scale experiments and subsequent pilot plant trials at a South African wool scouring company indicated that dynamic membranes of the hydrous zirconium (iv) oxide type could be used successfully to treat the grease effluent. The permeate which was recycled was 85 % of the original feed. The membrane system was capable of rejecting 92 to 96 % of total organic carbon and 85 to 90 % of the total solids. Grease rejection was 100 %. A plot of flux versus water recovery is shown in Fig. 1.

As a consequence of the pilot-plant results, it was decided to construct a modular demonstration plant at a wool scouring factory to treat the grease effluent. The demonstration plant was coupled to one of the factory scouring trains, and incorporated a liquor recirculating system with sludge withdrawal, and a dynamic membrane ultrafiltration plant based on single layer hydrous zirconium (iv) oxide membranes. The permeate was recycled to the scouring train.

The dynamic membrane plant used porous stainless steel tubes as the support for the membrane. A module, which is 3,5 m long and 215 mm in diameter, contains 150 m of 14 mm ID porous stainless tubes and the total porous area is 6,38 m^2. A total of 10 modules was used to treat the effluent from one scour line.

The demonstration plant operated as a factory production unit for approximately 12 months. During this operating period, the need for membrane re-formation was demonstrated as the modules became progressively fouled. In order to maintain the design average flux the membranes were reformed on a two monthly cycle. Re-membraning was accomplished by chemically cleaning the fouled membranes to a bare tube state and re-forming the membrane.

At the end of the 12-months operation, 1 920 t of raw wool had been processed, producing 1,7 Mℓ of scour effluent which was processed by the demonstration plant.

During the plant operation, performance was monitored. The results are presented and various aspects of plant operation are discussed.

Overall plant permeate flux

The overall permeate flux from the plant is shown in Fig. 2.

Because the flux was dependent on the applied pressure, and the pressures were difficult to control, the flux measurements have been presented as specific flux, i.e ℓ/m^2·h·MPa. In addition, flux varied with total solids content of the feed, and in order to compare the measured flux with the predicted design flux, the predicted design flux for the solids content (in g/ℓ) at the time of measurement is included in Fig. 2. The previously established relationship (Simpson and Groves, 1983) between permeate flux *(J)* and total solids *(TS)* content at an applied pressure of 5 MPa is:

$$J = 37 - 0{,}18\ TS$$

It can be seen that, in the latter period of operation (280 d), after introduction of on-site membrane re-formation, there was a scatter of flux measurements about the predicted design flux, whereas previously the flux was below the design flux due to there being no facilities for on-site membrane formation, and hence the plant was operated for extended periods with fouled membranes.

Effect of discontinuous operation

It was found that the design flux could be maintained, provided that the plant operation was continuous. The results of a specific module are presented and compared to the design average flux (Fig. 3). During this period from mid-November 1988 to early December 1988, the plant was subject to numerous unscheduled stoppages. The effects of this were marked and are illustrated in Fig. 3. Several days of operation were required before the flux was restored to the design value. It was concluded that any occurrence which resulted in the scour liquor cooling in the modules would result in module fouling.

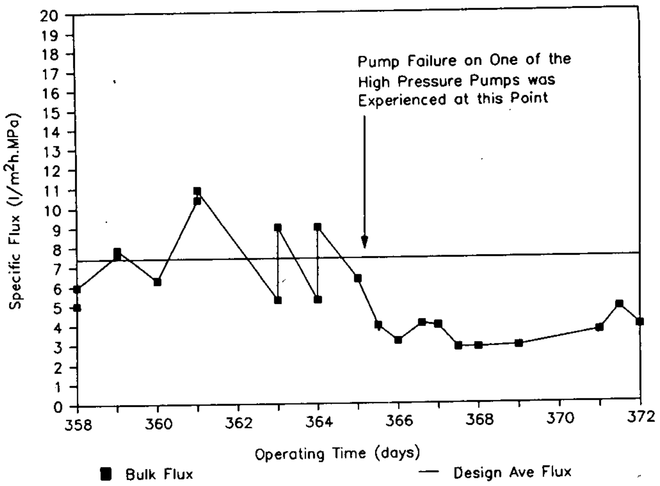

Figure 4
Wool scour demonstration plant: Effect of low cross-flow velocity on flux

Effect of cross-flow velocity on flux

The module configuration comprised 10 modules in parallel, fed by two pumps operating in parallel. With both pumps in operation the tube velocity was 2 m/s, with one pump in operation the velocity was 1 m/s. Previous work, both on the wool scouring plant and laboratory work on synthetic polyvinyl alcohol solutions, indicated that a minimum velocity of 1,5 m/swas required to prevent gel layer polarisation which caused a reduction in permeate flux.

No detailed experiments were conducted on the demonstration plant; however, a failure of one of the two feed pumps presented a period of impromptu tests on low velocity performance. The adverse effect on flux was apparent (Fig. 4).

Subsequent return to higher velocity operation did not restore the flux to the design value within a reasonable time span.

Module cleaning and membrane formation

The effect on a fouled module of chemical cleaning, membrane stripping and subsequent membrane re-formation is shown in Fig. 5. Removal of the foulants and membrane stripping was accomplished by circulating approximately one-molar solutions of sodium hydroxide, sodium hydroxide/hydrogen peroxide mixture, and nitric acid, in turn, through the module. This cleaning technique was carried out at 80 °C. It can be seen that restoration of the flux to that of a clean tube coated with a hydrous zirconium (iv) oxide membrane was possible.

Trials have been conducted on membrane cleaning techniques, without membrane re-formation. High temperature (80 °C) and

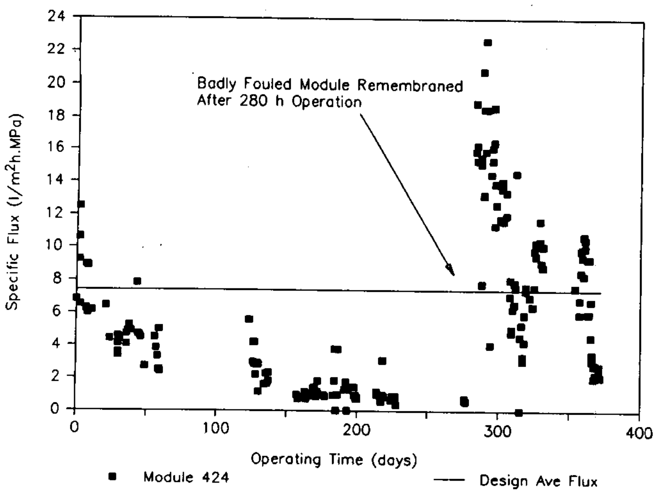

Figure 5
Wool scour demonstration plant: Effect of membrane re-formation

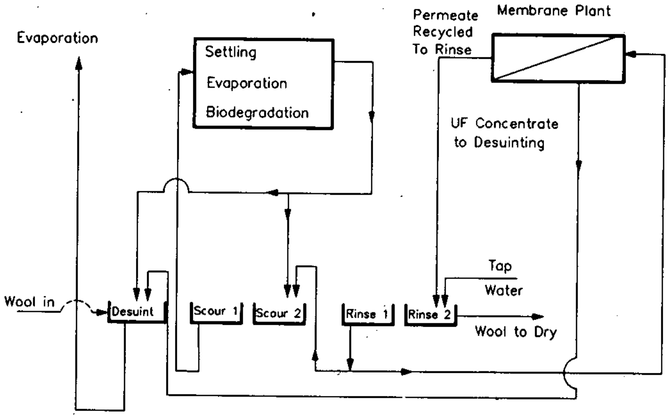

Figure 6
Simplified diagram of wool rinse effluent treatment process

high strength sodium hydroxide (pH 13) proved effective in removing grease from the membrane surface; however, the permeate flux was not significantly improved. This implied that the foulant was imbedded or chemically bonded in the matrix of the membrane/substrate and significant flux restoration would not be possible without an alkali wash followed by an acid wash and subsequent membrane re-formation.

Operation of the demonstration plant on wool rinse effluent

Because the permeate resulting from the treatment of scouring effluent required tertiary treatment in order to be suitable for use in rinsing wool, as opposed to scouring wool, and because of economic considerations, it was decided to conduct trials on the treatment of the rinse effluent (as opposed to scour effluent) using the hydrous zirconium (iv) oxide membrane on the porous stainless steel substrates. A simplified schematic diagram of this process is shown in Fig. 6. Initial results on reasonably fouled membranes showed that higher fluxes might be obtainable on rinse water compared with scour effluent. The clarity of the permeate was obviously better than when scour effluent had been used as the feed liquor.

Longer term trials were then implemented on re-formed hydrous zirconium (iv) oxide membranes, using the demonstration plant in the same configuration as for the scour effluent process. During these trials it was evident that although starting flux was high, a high rate of flux decline was experienced. In addition to this, bacterial slimes were forming on the modules and on the walls of the module trays. Checks on the bacterial count of the rinse liquor feed water also revealed relatively high counts of bacterial colonies. The bacterial organisms were identified as those belonging to the Sphaerotilus group (*Sphaerotilus natans*).

During later trials the feed liquor was dosed with calcium hypochlorite, but this only suppressed bacterial activity to approximately 300 colonies per mℓ. Subsequently the feed liquor was dosed (100 mg/ℓ) with a biocide (Anikem 7330) which proved effective in suppressing bacterial growth to below 10 bacterial colonies per mℓ.

However, despite control of the bacterial growth, flux decline was still marked, and plant fluxes are shown in Figs. 7 and 8 for the calcium hypochlorite- and biocide-treated liquors respectively. Initial flux rates were good (80 to 140 ℓ/m^2·h) but in both cases flux decline was rapid, declining to between 20 to 30 % of the initial flux within 21 calendar days of operation. The quality of the permeate proved completely satisfactory for recycle to the rinsing bowls. No deterioration of the product wool was detected. It has not been fully established which constituent(s) of the effluent are responsible for the rapid flux decline.

Effluents from polyester/viscose dyeing

The standard approach to textile effluent treatment has been extensively researched by organisations such as the Environmental Protection Agency, USA. The proposed treatment involves biological oxidation followed by operations such as flocculation, settling, filtration, carbon adsorption, ozonation, resin adsorption, ion exchange, reverse osmosis and electrodialysis. The characteristics of effluent, however, differ with mills and processes. Textile effluents containing colloidal dyestuff are difficult to treat by biological systems and are not decolourised effectively by activated carbon adsorption or ozonation. One of the most promising techniques for the treatment of dyehouse effluents has been shown to be the use of a membrane separation process (Brandon and Porter, 1976; 1977) as it is a one-step process and gives good removal of salt, organics and colour.

The effluent from any mill's dyehouse is a function of the major fibre utilised by the mill because the techniques employed during the processing of any fibre are fairly universal. Viscose tends to be dyed with direct, vat or reactive dyes by methods essentially the same as for cotton giving a similar effluent. Disperse dyes are applied to the polyester fibre at temperatures up to 130 °C in the presence of some dispersing/levelling agent.

Viscose/polyester dyeing effluent contains both soluble and colloidal dyestuffs, acetate, alkali, salt and organic auxiliary chemicals. Processing conditions result in an effluent varying in pH from 4 to 9, with temperature up to 75 °C and total dissolved solids up to 4 500 mg/ℓ. The colour in ADMI units can be above 10 000.

A typical example of a viscose/polyester dyehouse effluent from a textile finishing and dyeing mill was investigated. The effluent varied depending on the dyeing process but generally had a pH of between 7,0 and 9,0 and was high in chemical oxygen demand (COD) with a dark colouring. This effluent was being discharged to sewer but became a problem as it was affecting the biological performance of the sewage works and subsequently polluted the river to which the sewage works discharged. The textile effluent was a high proportion of the total flow to the sewage works.

A dynamic membrane ultrafiltration plant was installed at the mill in November 1984. At that stage it was believed to be one of the biggest of its type in the world with a total membrane area in the region of 280 m^2. The plant employs a closed loop system with the permeate being reused in the dyehouse and the concentrate treated by evaporation. Whilst the membranes were capable of rejecting the deleterious components from the effluent so as to make the permeate suitable for partial reuse in the dyehouse there were some shortfalls in the design of the plant.

The two major problems that existed at the ultrafiltration plant were the low fluid velocity past the membranes and the stagnant conditions which developed in some areas of the membrane separation modules. These conditions led to severe fouling and corrosion problems which obviously adversely affected the performance of the plant.

This was rectified and the plant now consists of three independently operable units (viz. DYE-l, DYE-2 and DYE-3), each with its own feed pumps and membrane bank. Two units (DYE-2 and DYE-3) from this plant have been refurbished with new pipe sections connecting the porous elements, and the modules re-membraned under the supervision of the Pollution Research Group.

The membraning technique employed was similar to that developed by the Pollution Research Group (Townsend and Neytzell-de Wilde, 1989) and consisted of pretreating the porous stainless steel tubes with either a suspension of precipitated hydrous zirconium (iv) oxide, (DYE-2 unit), or a suspension of fumed silica (DYE-3 unit).

The performance of the refurbished DYE-2 plant was monitored closely during the first three months of operation, and results are represented in Fig. 9. The module configuration on the plant is a 6:4:2 series taper with a semi-batch concentration operation.

It was possible to maintain an average flux of 33 ℓ/m^2·h, with colour removal, measured by the ADMI method, consistently better than 95 %. Ionic rejection was generally 75 to 85 %. A chemical clean using a cleaning agent consisting of a non-ionic detergent and sequestering agent at pH 10, followed by a nitric acid rinse at pH 2 was necessary at three- to four-day intervals to maintain this performance.

Conclusions

Dynamic membranes have proven to be operable under the most harsh conditions of temperature, mechanical and chemical abuse. The capital cost of a dynamic membrane system using porous stainless steel supports, is high. A recent cost from one supplier of the stainless supports was approximately R6 000,00 per m^2 of membrane area (Du Pont Separation Systems, 1989). The cost of a conventional cast film membrane is approximately R300,00 per m^2 (Hart et al., 1983). Cost benefits occur by way of the decreased need for expensive pretreatment techniques such as centrifugation, and membrane replacement. The cost of chemicals used in membrane formation is approximately R0,50 per m^2 for a hydrous zirconium (iv) oxide membrane.

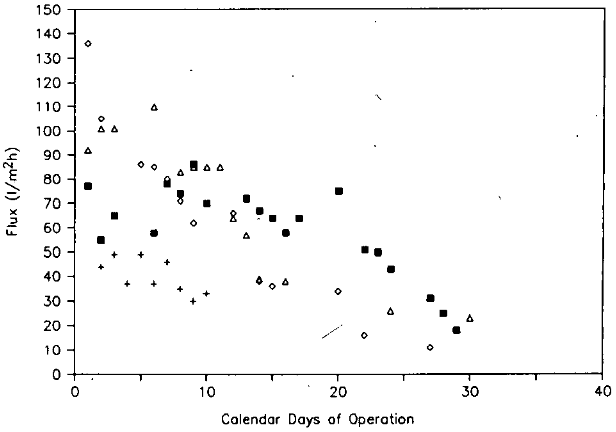

Figure 7
Wool scouring plant. Dynamic membrane treatment of wool rinse effluent. Rate of flux decline with time. Feed dosed with calcium hypochlorite

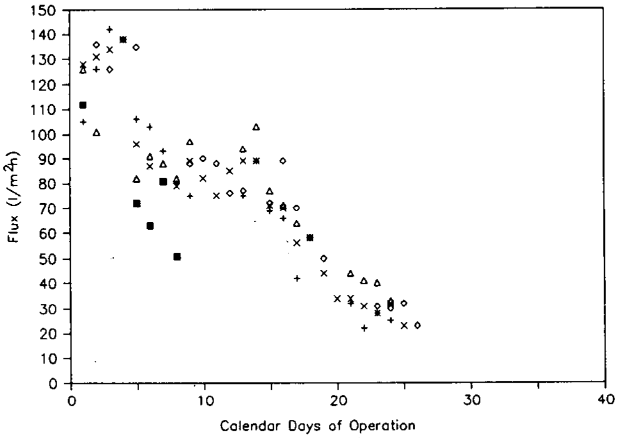

Figure 8
Wool scouring plant. Dynamic membrane treatment of wool rinse effluent. Rate of flux decine with time. Feed dosed with Anikem 7330, 100 mg/ℓ

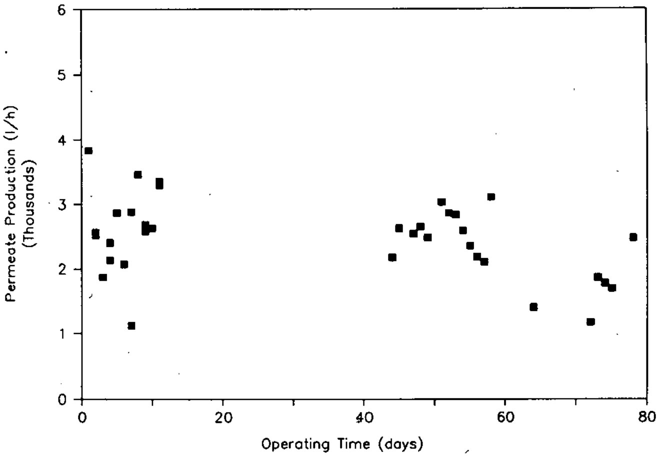

Figure 9
Polyester/viscose dyehouse effluent. Overall permeate production, DYE-2 unit

Membranes can be tailored to suit the requirements of the product water. For instance, a dual layer zirconium/polyacrylic membrane when used to treat wool rinsing effluent produced a permeate with a conductivity equivalent to that of the municipal supply. However, a higher flux can be maintained with a product of lesser quality (but still quite suitable) when using the single layer hydrous zirconium (iv) oxide membrane. Similarly, when using dynamic membranes to treat certain types of dyehouse effluent, a dual layer zirconium polyacrylic membrane is necessary for the production of reusable permeate.

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