Small-scale tests to determine the feasibility of reverse osmosis and ultrafiltration for the treatment of industrial effluents[+]

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Abstract

The suitability of membrane processes for the treatment of varied and chemically complex industrial effluents can be assessed by using small-scale laboratory tests. These tests yield information on species rejection, permeate flux, osmotic pressure effects and membrane fouling. Identification of fouling material by X-ray techniques together with accelerated fouling tests allow pretreatment sequences to be tested and evaluated.

Introduction

In recent years membrane processes such as reverse osmosis and ultrafiltration have become increasingly important in the treatment of waste waters and industrial effluents. This has been due to various factors, *inter alia* improved membranes with high temperature stability, apparent simplicity of the process and the adaptability of the process to large- and small-scale applications. These factors, accompanied by increased awareness of the environmental effects of direct discharge of untreated industrial effluents, have resulted in stricter discharge regulations, while economic considerations such as escalating water, chemical and energy costs have promoted research into water reuse and chemical recovery.

Desalination is being used increasingly to provide water for agriculture and domestic use. In this field, membrane processes for saline water treatment have found acceptance. Generally the chemistry of saline water is well characterised and understood. Manufacturers and suppliers of membrane systems have large data banks on factors such as water chemistry, thermodynamic data, membrane performance, design parameters etc. and with the aid of computer programs are able to determine the suitability of a given saline water to a particular membrane system, to such an extent that guarantees can be given with respect to output and quality of the treated water.

With industrial effluents, the position is less certain. Industrial effluents are extremely variable. Frequently complete chemical analyses of the effluents are not available, particularly with respect to trace elements. As a result each industrial effluent must be assessed for the suitability of membrane processes as a treatment technique. Ultimately this will take the form of an on-site pilot-plant investigation but preliminary investigations in the laboratory can yield valuable information.

This paper describes the type of laboratory tests developed by the Pollution Research Group, University of Natal, Durban, over the last 10 years to deal with industrial effluents. The information obtained from these tests can be used to suggest pretreatment sequences and assess the suitability of membrane processes for the treatment of industrial effluents.

Test apparatus

A PCI bench-scale 3-cell test rig, fitted with discs (30 mm diameter) of flat-sheet membrane, is used (Gutman, 1987). The hydrodynamics of the system are similar to those achieved in the PCI tubular membrane systems. Although absolute flux results cannot be compared directly to other module configurations, their relative relationships hold, thus the rejection and fouling characteristics will provide a good indication of the phenomena that would be encountered in large-scale applications.

The components of the rig and the 2 modes of operation are shown in Figs. 1 and 2. During total recycle mode both reject and permeate are returned to the feed tank. Feed temperature can be controlled by means of either cooling coils or a heating element and the loss of water by evaporation is countered by the addition of pure water. In the batch concentration mode the reject is recycled to the feed tank and the permeate is collected separately until the required water recovery is achieved. This may require the processing of several batches to reach high water recovery levels. Membrane permeation rates are measured using a measuring cylinder and stop-watch.

It is desirable to use fresh real effluent rather than simulated effluent. Many trace substances present in the fresh effluent may not be simulated. These trace materials can have a significant effect on membrane performance.

Membrane choice and preliminary set-up

On arrival in the laboratory, the effluent is examined to determine whether any obvious pretreatment, e.g. filtration or centrifugation to remove suspended solids, is necessary. No chemical additions are made at this stage and the raw effluent, or its filtered equivalent, undergoes analysis by standard chemical methods. This provides a chemical base line against which future treated samples can be compared. Depending on the results of these analyses and the particular requirements of the industry concerned, a decision as to the type of membrane required can be made. For example, if complete desalting is required, a reverse osmosis membrane would be necessary, but if removal of organic matter but not complete removal of salts is demanded, an ultrafiltration/charged ultrafiltration membrane may be the preferred choice.

+Revised paper. Originally presented at the SAMSIG Symposium held at Wilderness, Republic of South Africa in November 1989.

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Received 10 July 1991; accepted in revised form 26 August 1991.

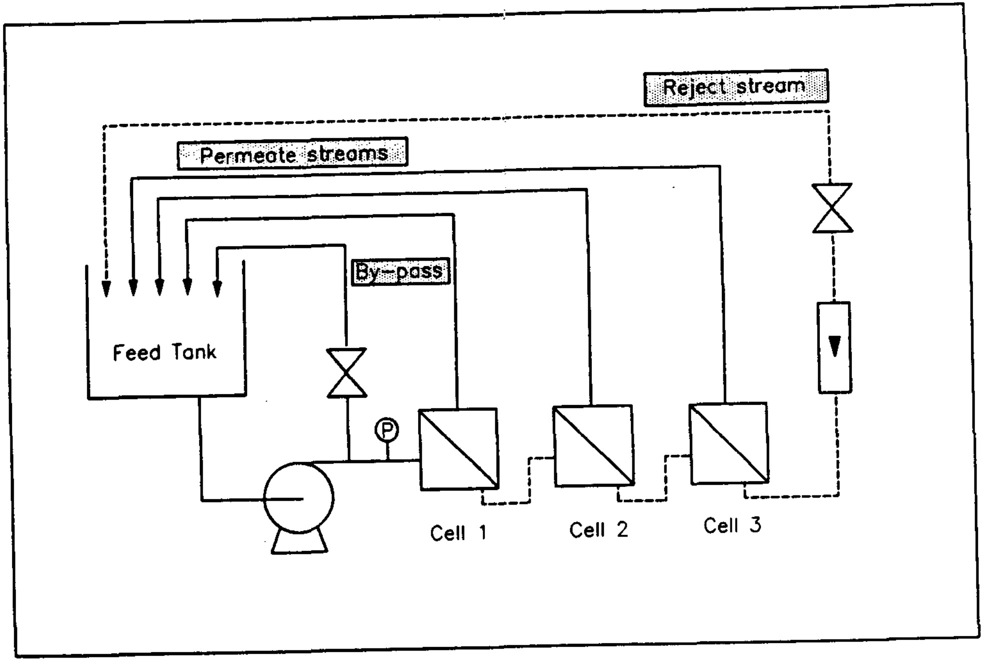

Figure 1
Schematic diagram of test rig in total recycle mode

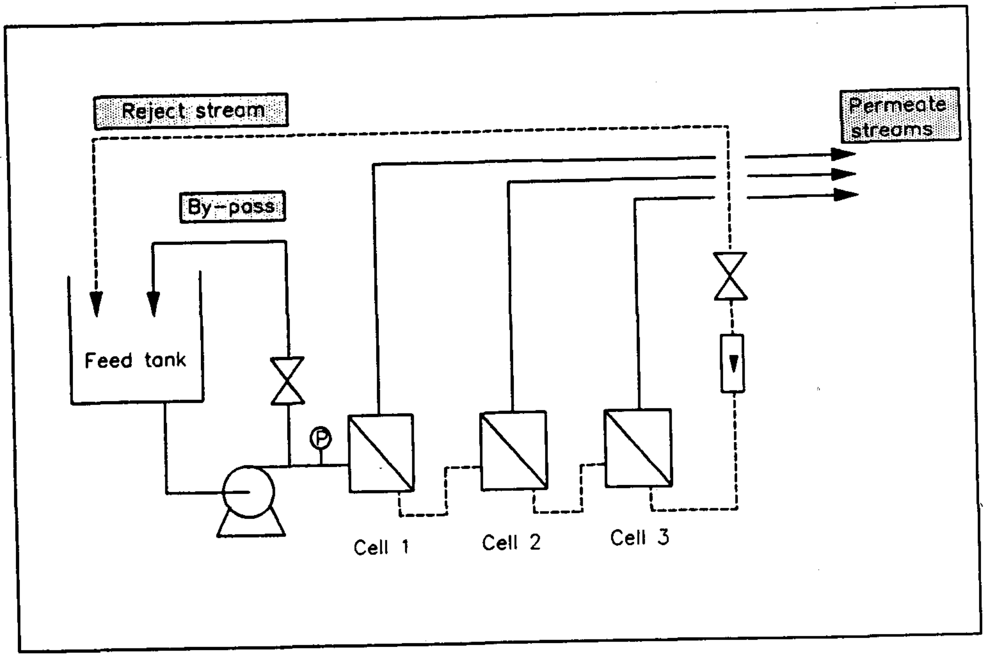

Figure 2
Schematic diagram of test rig in batch concentration mode

Discs are cut from a membrane sheet, and after preconditioning by soaking in deionised water for 24 h, are inserted in the test cells. One advantage of a 3-cell rig is that 3 different membranes of the same class can be evaluated simultaneously at this stage. Before any effluent is tested a pure water flux is determined, initial membrane compaction is quantified and the appropriate flux and rejection characteristics are determifned using pure solutions.

If at any subsequent stage in the experiment, membrane deterioration or a leak is suspected, or if abnormal results are obtained, a water flux or rejection characteristics can be redetermined to assess the state of the membranes. The feed tank is filled with fresh effluent and the rig is run for 24 h in a total recycle mode, with frequent monitoring of the membrane permeation rates.

If different membranes have been used, an assessment can be made as to the suitability of each for the particular effluent. If one membrane proves to be superior to the others, all 3 cells can then be fitted with this membrane. This will allow a check on permeation rates since discs, although cut from the same membrane sheet, may have different performance characteristics. This heterogeneity in the membrane sheet stems from the manufacturing process. On a large scale this effect will be statistically unimportant, but at the small scale it could be critical and lead to erroneous conclusions.

Determination of osmotic pressure

While manufacturers of membranes give specifications as to working conditions, it is useful to check these by experiment since the unique character of each effluent can influence the optimum operating conditions (Groves et al., 1984). The parameters to be determined are pressure, flow rate and temperature.

Under total recycle conditions and with a constant feed flow rate, the input pressure is varied and resultant fluxes are monitored. A plot of pressure and membrane permeation rates should give a straight line since:

$$J = \frac{K_w (P - \pi)}{A}$$

where:

J = permeate flux
K_w = water permeability constant of membrane
P = feed pressure
π = osmotic pressure
A = membrane area

At $J = 0$ the line will intersect the pressure axis at the osmotic pressure of the feed solution. Thus if no osmometer is available, an indication of feed osmotic pressure can be obtained.

Polarisation effects

Reverse osmosis and ultrafiltration membranes are affected by concentration polarisation (Jonsson et al., 1984). The passage of permeate through the membrane produces an increased concentration of solute at the feed/membrane interface. This can result in:

- the membrane experiencing an apparent increased osmotic pressure (which will decrease the permeate flux);
- an observed rejection which will differ from the *intrinsic* rejection;
- the formation of a gel layer (macromolecular solutions) or of a fouling layer (particulate solutions); and
- *precipitation due to increased concentration.*

To maintain a high flux when the concentration of the feed is high, this polarisation layer must be minimised by operating at high cross-flow velocities. The condition, where the polarised layer has minimum effect, is found by varying feed flow rate at a given pressure until the flux becomes independent of velocity.

Temperature effects

As flux is temperature dependent, it is necessary either to run the rig at a constant temperature or to correct measured fluxes to a reference temperature. The nature of the feed solution may influence the choice of the operating temperature, e.g. if the feed is rich in organic material it is desirable to maintain a high temperature to inhibit bacterial/fungal growth which could alter the character of the feed. In the laboratory, maintenance of the feed at 25°C is convenient. Temperature correction correlations can be used to determine the flux at other temperatures. A typical correlation is:

$$J_{25} = \frac{J_T \, \mu_T}{\mu_{25}}$$

where:

J_T = measured flux at temperature, T
J_{25} = flux at 25°C
μ_T = viscosity of water at temperature T
μ_{25} = viscosity of water at temperature 25°C.

Total recycle experiments

Total recycle experiments are conducted at various water recoveries for a specified period of time. Depending on the nature of the effluent the length of time can vary from a minimum of 24 h to several months.

From these experiments the following information is obtained.

Species rejection

The point species rejection can be calculated from the analysis of feed and permeate samples collected at the same time. Rejection is given by:

$$R = 1 - \frac{C_p}{C_f}$$

where:

C_p = concentration of species in permeate
C_f = concentration of species in feed.

The effect of variations in pH on species rejection can also be examined at this stage, by repeating the total recycle experiment at different pH levels. If pH is shown to have an effect on species rejection, then pH control will be a factor of importance in any proposed pretreatment schedule.

The species rejection data obtained at various water recoveries can be compared.

Permeate flux

After an initial flux decline, membrane permeation rates should remain constant with time for a given concentration. A continuous decline in flux could indicate feed/membrane interaction with physical and/or chemical modification of the membrane by the feed. An increased flux could indicate hydrolysis of the membrane.

Steady flux decline with increasing feed concentration may be attributable to increasing osmotic pressure of the feed or to membrane fouling.

In order to investigate the reasons for variation in permeate flux, a pure water flux should be determined between total recycle experiments. If this does not differ significantly from the initial water flux, then a decline in permeate flux or species rejection with feed concentration, is most likely due to osmotic pressure effects. If no osmometer is available, osmotic pressure can be determined experimentally as described earlier.

If, compared to the initial value, the water flux is considerably reduced, then membrane fouling is indicated.

Batch concentration experiments

During batch concentration tests the permeate is collected separately and not returned to the feed tank, resulting in an increased feed concentration. Depending on the volume of the feed tank, generally 6 to 8 batches of fresh effluent are concentrated to 50% water recovery. The concentrates are combined and concentrated further.

Species rejection and membrane permeation rates are monitored throughout the experiments. A pure water flux should be determined at the beginning of every batch. In this way the effects of osmotic pressure and membrane fouling can be monitored. If membrane performance should deteriorate below acceptable limits, various cleaning techniques can be implemented between batches. The effectiveness of such cleaning cycles is assessed by the pure water flux.

Batch concentration tests are time consuming but offer examination of the behaviour of the membrane over a range of feed concentrations. Further information may be gained on the effects of osmotic pressure on permeate flux and quality, the occurrences of concentration-dependent fouling and the possibility of progressive permanent membrane fouling.

Membrane fouling

Frequently during total recycle or batch concentration experiments, membrane fouling is indicated. Efforts should be made to identify the cause and nature of this fouling. Based on successful identification of the foulant, steps may then be taken to eliminate or minimise its fouling potential.

Concentration-dependent fouling may occur during batch concentration tests when, with increasing feed concentration, solubility limits are exceeded and precipitation occurs. Examination of the concentrates at various water recoveries, together with collection and analyses of any precipitates, will enable identification of the foulant and the water recovery level at which it occurs.

The data can be used to suggest:

- Further pretreatment steps; for example, would the addition of a sequestering agent or crystal inhibitor prevent fouling, or can the foulant be removed from the effluent prior to membrane processing.
- The frequency of cleaning cycles; for example, can the fouling be controlled sufficiently by frequent cleaning cycles so as to allow the required fluxes and water recovery levels to be achieved.
- The upper limit of water recovery; for example, if the formation of the foulant cannot be prevented or controlled by cleaning, the water recovery level at which precipitation occurs will represent the upper limit for successful functioning of the membrane.

Generally concentration-dependent fouling can be minimised or eliminated by adequate pretreatment measures. To this extent it can be thought of as reversible fouling. A more serious form of fouling is progressive membrane fouling. This is somewhat similar to feed/membrane interaction (compaction/hydrolysis) in that it is an irreversible process. The mechanics of this type of fouling are not well understood and its existence can only be identified with certainty when all possibilities of cleaning/pretreatment sequences have been examined.

Because batch concentration tests are time consuming and concentration-dependent fouling may not become obvious until fairly high water recovery levels have been achieved, it is useful to undertake accelerated fouling tests.

Accelerated fouling tests

A batch evaporation technique enables rapid screening of potentially fouling effluents.

The feed is evaporated under vacuum either at a temperature similar to that at which the effluent will be treated, or by utilising a cold trap at ambient temperature. At different water recoveries the concentrate is passed through 0,22 μm filters in order to detect and allow identification of precipitates. Verification should be made that any precipitates, formed in this way, are identical to those formed on the membranes during batch concentration tests.

Precipitate identification

Non-destructive X-ray techniques are most useful in identifying the fouling phase. Where it has been possible to collect precipitates, X-ray diffraction (XRD) provides rapid and precise identification of the crystalline phases present.

Where the foulant is attached to the membrane surface, a scanning electron microscope (SEM) with an energy-dispersive attachment (EDAX, KEVEX etc.) or an electron microprobe analyser (EMPA) can be used. Such examination can provide evidence of any changes in membrane morphology, the location of foulant material within the membrane structure and an element analyses of the fouling material. These methods cannot identify the fouling phase, only its chemistry, but in conjunction with computer speciation programs (Flemy et al., 1984; Westall et al., 1976), the phase/s present can be determined.

The accurate identification of fouling material is a prerequisite in determining pretreatment steps to prevent membrane fouling.

Pretreatment assessment

Based on identification of the fouling material various pretreatment steps may be proposed. Rapid screening of their effectiveness can be conducted by treating some effluent in the suggested way and undertaking further evaporative tests. If satisfactory results are obtained, then batch concentration experiments can be repeated using pretreated effluent, in order to verify the success of the pretreatment to the membrane process.

Case histories

While the use of small-scale tests is not a substitute for pilot-plant studies, the information obtained can be utilised in the overall design of pilot plants, and help to alleviate many of the teething problems associated with pilot-plant trials. If unforeseen problems do occur in the pilot plant, then simulation of such problems in the laboratory using small-scale tests or installation of small test cells in the reject stream of the pilot plant can be a cost-effective way of problem solving. Some case studies where small-scale tests have proved useful are given.

Reverse osmosis of textile effluents

A pilot plant was used to treat textile effluents (Treffry-Goatley et al., 1983). Despite extensive pretreatment, the reverse osmosis membranes fouled rapidly. Small test cells fitted with reverse osmosis membranes were inserted into the reject line. Analysis of these membranes by electron microprobe indicate the presence of iron, chrome and nickel. This allowed the source of fouling to be traced to corrosion of sections of the plant which were fabricated from 304 grade stainless steel. Replacement of these items with the correct grade of steel eradicated the problem.

Pulp bleach effluent treatment

Results of laboratory-scale work with bleach effluent from a pulp and paper mill were utilised in the development of a pretreatment sequence to a reverse osmosis pilot plant. Success was achieved in preventing fouling due to:

- Organic constituents, by their removal with calcium hydroxide flocculation.
- Calcium sulphate formation, by careful control of sodium bisulphate dosing (used to remove free chlorine).

However, membrane fouling still occurred in the pilot plant. Laboratory-scale evaporation tests (to high water recoveries) were undertaken with pretreated effluents. Precipitates, collected on 0,22 μm filters and analysed by X-ray diffraction, were shown to be calcium oxalate (Buckley et al., 1987).

Subsequent analyses of raw effluent found oxalic acid to be present at approximately 7 mg/ℓ. As the concentration of oxalic acid required for calcium oxalate precipitation in the effluent was 5 mg/ℓ, the mass of calcium oxalate able to form was small. Increasing concentration of the feed, together with an already elevated calcium concentration from the effluent pretreatment, resulted in continuous precipitation of calcium oxalate which caused fouling of the reverse osmosis membranes.

A revised pretreatment sequence, involving the removal of excess soluble calcium with soda lime, was suggested and tested in the laboratory. Water recoveries greater than 90% were achieved without any further precipitation of calcium oxalate, and the necessary modifications were made to the pilot plant.

Conclusions

Industrial effluents are usually chemically complex and variable. Thus prediction of possible precipitation at high water recoveries is difficult. Often a complete chemical analysis, particularly of trace substances, is unavailable. Frequently it is these species which are responsible for membrane fouling especially at high water recoveries.

Small-scale laboratory concentration and evaporation tests can help to highlight problems, such as flux decline, decline in species rejection, osmotic pressure effects and fouling. These problems can then be engineered out at the pilot-plant stage by adequate pretreatment and plant design.

Acknowledgements

The techniques described have been developed during the course of a number of research grants from the Water Research Commission, SAPPI and David Whitehead and Sons.

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