Optimisation of water savings and membrane processes

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Abstract The Centre for Industrial Water Management is a co-operation between several technology service institutes, university institutes and water consuming companies in Denmark to promote concepts for cleaner production, water treatment and reduction of effluents in industrial production processes. This investigation focuses on two case studies from two of the industrial partners participating in this centre. The first case study is a texturiser of polyester yarn. Nanofiltration and reverse osmosis (RO) have been tested to clean the water streams from a dyeing bath and a reductive bath. It was shown that only the RO-process guaranteed a high rejection of salts under the process conditions. Furthermore, fouling could be analysed and reduced. The second case study is a manufacturer of functional proteins. An ultrafiltration system was used to concentrate the proteins from pig rind. It could be proved that the declining flux was caused by the adsorption of proteins on the membrane surface. To control fouling, a concept involving operation below the critical flux and a cleaning strategy is presented.

Keywords Cleaning; fouling; hygienic quality; membrane processes; process water

Introduction

Political and ecological issues together with the technical progress have motivated several industries in Denmark to reduce their water consumption. Mainly, two concepts are used to reach this aim. These are the reduction of the water consumption by using new technologies and the reuse of process water. The fast development of these technologies led to the idea of organising a centre where industry, universities and technology service institutes join forces to develop and implement new solutions for improved management of water, substances and energy in industrial production processes. The Centre for Industrial Water Management (CEVI) helps companies to evaluate concepts to save water, to find techniques for treating water and to solve barriers like membrane fouling or hygienic problems.

Concepts for water saving are the optimisation of procedures, the modernisation of equipment, the substitution of chemicals and the treatment of process water to be reused. The presented companies chose membrane processes as water treatment methods. Fouling analysis and development of improved turbulence promoters in spiral wound modules are being carried out. Due to the fact that the composition of process water is different depending on the unit operation, production step or production process, the solutions proposed for treatment differ. To illustrate this, this investigation will focus on two very different types of process water; the first one recovered from a texturiser of polyester yarn, and the second one from a functional protein producing company.

The first case study deals with a polyester yarn texturiser that presently discharges about 630,000 m³/a of wastewater (80% from the dyeing process). To reduce this amount, a process-integrated water saving and recycling system combined with a membrane treatment plant has been considered. The wastewater contains a high dye and salt concentration and should be treated for reuse within the process. To retain salts and dye, two membrane processes, RO and nanofiltration (NF), are established solutions. While the advantages of NF are lower investment and operating costs, the lower salt rejection often limits its
application, when reuse of the permeate in the process is planned. However, both processes have been tested and the fouling was analysed.

The second case study is an example from the food industry. It is within the scope of this study to optimise the production of functional proteins out of pig rind. Ultrafiltration (UF) was chosen to concentrate the proteins. The reduction of the flux could be caused by concentration polarisation or protein fouling, and this has been reviewed by Marshall et al. (1993). This aspect was studied during this investigation. The economic efficiency of a spacer with high mass transfer coefficient or a spacer with low mass transfer and a lower pressure drop along the module will also be investigated. Another aim of this study is to reduce the high demands of water and to control the microbiological or hygienic quality of the water to be reused. The latter issue is a requirement in the food industry.

Results and discussion
Case study 1: texturiser of polyester yarn
After analysing more than 150 different water types, a pinch point analysis leads to several possibilities for saving water within the production plant. It was suggested that a membrane process should treat about 230,000 m$^3$/a of process water recovered from a dyeing bath and a reductive bath. The latter one is required to reduce the oligomers on the surface of the yarn after dyeing. Furthermore, it was planned to recycle the treated process water into the dyeing bath and into the last rinse or cold rinse, where the yarn is cleaned. The water used for the last rinse, which is less loaded, should be directly reused in the process. The proposed process layout is shown in Figure 1.

The process is batch wise, therefore, the chemical conditions of the water change. These are mainly the pH, the salt content and the concentration of organic matter. The removal of salts and organic compounds is required, since the treated water is intended to be reused for the last rinse, which is the last cleaning step for the yarn. The operating temperature in the process is 60–70°C.

NF and RO are two established processes in the textile industry (Porter and Goodman, 1994; van’t Hul et al., 1998; Sojka-Ledakowicz et al., 1998; Rozzi et al., 1999), and these were chosen to treat these process water streams.

The experiments were carried out at laboratory and pilot scale. The membranes used were an NF-membrane (Desal™-DL) and two RO-membranes (Desal™-SG and Desal™-SF). All membranes were supplied by Osmonics (United States).

The laboratory experimental set-up holds up to 4 l. The main volume (2.5 l) is in the glass tank, whereas the remaining volume is found within the system. The heart of the set-up is the cross-flow cell with the membrane. The membrane area is 37 cm$^2$. When running the experiments at pilot scale, a spiral wound 2.5” module with a membrane area of 1.7 m$^2$ was tested.

![Figure 1 The proposed process layout](https://iwaponline.com/ws/article-pdf/3/5-6/289/419253/289.pdf)
The operating pressures were 5–20 bar for the NF/RO-laboratory experiments and 7–21 bar for the pilot-plant experiments. The process water used in the experiments was an average mixture of both process water streams.

The salt rejection was measured by conductivity. First, it was tested, whether NF is suitable for achieving a sufficient salt rejection, even at changing pH. Therefore, the pH dependency of the NF membrane (Desal™-DL) and of one of the RO membranes (Desal™-SG) was evaluated at laboratory and pilot scale. The pH of the process water was changed by adding sulphuric acid, since the process water contained a high concentration of sulphuric ions. In the pilot and laboratory experiments, it was shown that the salt rejection for the RO-membrane was always above 98%, whereas the rejection for the NF-membrane decreased from 93% to 78% at decreasing pH. These significant changes concerning salt rejection made NF not suitable for this treatment process. Therefore, the rest of this investigation focused on RO filtration.

The second goal of this study was to evaluate the fouling and to find solutions to reduce it. One of the options is to find process conditions, where fouling is less severe. In this process, the pH tendency could be controlled by a buffer tank, therefore, the fouling at different pH was evaluated. These experiments were carried out with an RO membrane (Desal™-SG). By observing the flux decline over time, it could be seen that the fouling is less severe at high pH. An explanation for this could be that, at low pH, the particle size is smaller and this leads to faster fouling. Two main foulants were found. The first were cyclic oligomers from the yarn production, which are washed out during the dyeing process. A 10 µm band filter could reject these compounds successfully. The other foulant was an aromatic compound, which forms a dark deposit on the membrane during filtration. The analysis identified this as an UV absorber, which is added during the process. Tests to substitute or remove this foulant by filtration have not yet been successful.

Additionally, the fouling tendencies for the two different RO membranes have been compared. The tested membranes were the SG and the denser SF membranes. Even though the investment cost for these membranes is similar, the fouling tendencies are significantly different. It was shown that the fouling for the Desal™-SF membrane was less severe. After 6 h filtration, the flux was reduced to 80% of the starting value for the SF membrane and to 75% for the SG-membrane, see Figure 2.

Therefore, the Desal™-SF membrane was selected as the more suitable membrane for this application.

**Case study 2: producer of functional proteins**

UF is an established process to treat proteins. In this process, pig rind was dewatered by using an UF system. The feed solution contains a high concentration of fat and proteins and

![Figure 2 Fouling of the SF and SG membrane](image-url)
has a high viscosity. To decrease the viscosity without denaturalising the proteins, the filtration is carried out at 60°C. During filtration, a significant decrease of the flux could be observed. One goal of this research was to analyse the declining flux and to discuss ways to reduce it.

Two phenomena may explain the significant decrease of the flux. The first is the high osmotic pressure of the proteins. However, a higher operating pressure with a denser membrane could solve this problem. The second is the formation of a severe fouling. In this case, the foulants have to be analysed and the possibilities for reducing the fouling by pre-treatment or operating conditions have to be discussed.

The experiments to evaluate the flux decline were carried out in a batch cell with a GR61pp UF membrane and a GRM0.2pp microfiltration membrane both supplied by Danish Separation Systems (Denmark). The required membrane area was 140 cm².

Theoretically the effect of the osmotic pressure should only occur during UF and should be independent of the applied pressure and stirring of the feed. This was not the case.

The results show that the main reason for the flux decline is not the osmotic pressure, but the formation of a gel layer on the membrane surface.

By making a dead-end filtration and analysing the cake and the membrane, it could be seen that the cake is mainly formed by fat, while the proteins were attached to the membrane surface. In order to reduce the fouling, the concept of the critical flux was used. The critical flux is defined as a flux below which a decline of flux with time does not occur; above it, fouling is observed. This flux depends notably on the hydrodynamics of the system. Using the strong form of this hypothesis is the same as saying that the flux is equal to the corresponding clean water flux. However, below the critical flux, the pressure flux relation is linear and reversible, meaning that the pressure can be reduced and the same flux can be measured (Field et al., 1995). One explanation for this effect is that the transport of particles to the membrane is similar to the back-diffusion to the bulk. Operating below the critical flux leads to less fouling and minimises cleaning. On the other hand, higher membrane area is required.

The measurement of the critical flux was carried out in a cross-flow cell using the GR61pp membrane. The required membrane area was 37 cm². For 10 minutes, the pressure was kept constant and the flux was observed. The reversibility was proved by repeating the previous experiment, see Figure 3.

The experiment shows that the formation of a gel layer may be reduced by working at a flux below 55 l/m²·h⁻¹. It should also be mentioned that operating at this low flux required the use of a large membrane area. Therefore, an economic evaluation of this procedure should be done in order to evaluate its feasibility.

Another way to decrease the fouling tendency is to improve the performance of the membrane module. In this case, spiral wound modules were chosen due to their good
membrane area versus price relation. The module can be improved by using the optimal spacer. Therefore, the performance of three different spacers (fishbone, parallel and diamond) was evaluated in a flat test-cell operating at the same pressure drop along the channel. Polyethylene glycol (PEG) and dextran were used as test solutes. It was shown that diamond spacers had the best pressure drop versus flux relation. The diamond spacer decreased the effect of concentration polarisation, and, therefore, the fouling tendency. The next step of this investigation will be to evaluate this tendency at pilot scale with real process water.

An efficient strategy to reduce fouling should also include a concept for cleaning the membrane. Cleaning is also an issue of especial importance in the food industry where the microbiological or hygienic requirements are high when compared to other types of industries. Usually, three steps for cleaning the system are recommended: enzymatic, acid and caustic cleaning. In order to evaluate whether these steps are necessary or sufficient, the hygiene in the system will be evaluated by analysing the permeate after the different cleaning steps. Conventional microbiological methods are not suited for rapid intervention. It should also be mentioned that traditional and modern microbiological methods, equipment, facilities as well as qualified personnel capable of performing this type of analysis are not always available within food industries. Therefore, other types of rapid methods based on chemical and physical procedures are suggested. ATP bioluminescence is a widely used indirect method based on the detection of the high-energy molecule adenosine triphosphate (ATP) extracted from cells. ATP is present in all viable cells and the ATP amount is measured as the light energy released by the luciferin-luciferase system in the presence of magnesium ions (Stanley, 1989). The amount of light generated is proportional to the ATP concentration, and this is proportional to the number of cells present. ATP bioluminescence has become a widely accepted method for hygiene monitoring in the food and beverage industries. This method is being currently tested for evaluating the efficiency of both treatment and cleaning.

Conclusions
The case studies described in this paper demonstrate that co-operation between different companies, research institutes and technology service institutes is beneficial for all parts involved regarding improved water management.

RO was found to be suitable for guaranteeing stable salt rejection when treating process water from a polyester yarn texturiser. The treated water can be recycled within the same unit operation. Fouling was found to be less severe at high pH. Two main foulants were found: cyclic oligomers and an aromatic compound. The first foulant could be removed by pre-filtration.

The production of food functional proteins was optimised by concentrating those by means of UF. The decrease of the flux was mainly caused by the high osmotic pressure of the proteins and the adsorption of proteins on the membrane surface. However, fouling was reduced by operating below the critical flux. The UF module was improved by selecting the proper spacers. A cleaning procedure is currently being developed and a rapid method for microbiological or hygienic control is being tested for the evaluation of the efficiency of both treatment and cleaning.

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References


