
Lappeenrannan teknillinen korkeakoulu
Lappeenranta University of Technology

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FOULING MANAGEMENT AND RETENTION IN NANOFILTRATION OF INTEGRATED PAPER MILL EFFLUENTS

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ABSTRACT

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Nanofiltration performance was studied with effluents from the pulp and paper industry and with model substances. The effect of filtration conditions and membrane properties on nanofiltration flux, retention, and fouling was investigated. Generally, the aim was to determine the parameters that influence nanofiltration efficiency and study how to carry out nanofiltration without fouling by controlling these parameters.

The retentions of the nanofiltration membranes studied were considerably higher than those of tight ultrafiltration membranes, and the permeate fluxes obtained were approximately the same as those of tight ultrafiltration membranes. Generally, about 80% retentions of total carbon and conductivity were obtained during the nanofiltration experiments. Depending on the membrane and the filtration conditions, the retentions of monovalent ions (chloride) were between -80 and 95% in the nanofiltrations. An increase in pH improved retentions considerably and also the flux to some degree. An increase in pressure improved retention, whereas an increase in temperature decreased retention if the membrane retained the solute by the solution-diffusion mechanism.

In this study, more open membranes fouled more than tighter membranes due to higher concentration polarization and plugging of the membrane material. More irreversible fouling was measured for hydrophobic membranes. Electrostatic repulsion between the membrane and the components in the solution reduced fouling but did not completely prevent it with the hydrophobic membranes.

Nanofiltration could be carried out without fouling, at least with the laboratory-scale apparatus used here when the flux was below the critical flux. Model substances had a strong form of the critical flux, but the effluents had only a weak form of the critical flux. With the effluents, some fouling always occurred immediately when the filtration was started. However, if the flux was below the critical flux, further fouling was not observed. The flow velocity and pH were probably the most important parameters, along with the membrane properties, that influenced the critical flux. Precleaning of the membranes had only a small effect on the critical flux and retentions, but it improved the permeability of the membranes significantly.

LIST OF PUBLICATIONS

A literature review of the methods of controlling fouling and enhancing the membrane filtration efficiency is presented in paper I. The experimental part of this thesis is based on the papers II-VII. Throughout this text these publications will be referred to by their Roman numerals.

I Mänttäri M., Various methods to improve the filtration performance, *Julkaisu* **92**, Department of Chemical Technology, Lappeenranta University of Technology, Lappeenranta, Finland, 1997, 60 pages.

II Mänttäri M., Nuortila-Jokinen J., Nyström M., Evaluation of nanofiltration membranes for filtration of paper mill total effluent, *Filtration & Separation*, **34**(3) (1997) 275-280.

III Mänttäri M., Nuortila-Jokinen J., Nyström M., Influence of filtration conditions on the efficiency of NF membranes in the filtration of paper mill total effluent, *Journal of Membrane Science*, **137**(1-2) (1997) 187-199.

IV Mänttäri M., Nuortila-Jokinen J., Nyström M., Filtration of paper mill effluents using nanofiltration membranes, *International Symposium on Filtration and Separation II*, Las Palmas de Gran Canaria, February 19-20, 1998, pp. 305-312.

V Mänttäri M., Martin H., Nuortila-Jokinen J., Nyström M., Using a spiral wound nanofiltration element for the filtration of paper mill effluents; pretreatment and fouling, Submitted to *Advances Environmental Research*, 1999.

VI Mänttäri M., Puro L., Nuortila-Jokinen J., Nyström M., Fouling of polysaccharides and humic acid in nanofiltration; effect of pH, crossflow, and membrane hydrophobicity, Submitted to *Journal of Membrane Science*, 1999.

VII Mänttäri M., Nyström M., Critical flux in nanofiltration of high molar mass polysaccharides and effluents from paper industry, Submitted to *Journal of Membrane Science*, 1999.

OTHER PUBLICATIONS ON MEMBRANE FILTRATION

Nyström M., Mänttäri M., Micellar enhanced ultrafiltration, MEUF, as a tool to concentrate metals or hydrophobic pollutants from wastewater, *Proceedings of the 6th World Filtration Congress*, Nagoya, Japan, May 18-21, 1993, pp. 722-725.

Nuortila-Jokinen J., Mänttäri M., Nyström M., Membrane filtration processes as means for internal treatment of paper mill waters, *PTS Symposium*, Chemical Technology in Papermaking, München, Germany, September 17-20, 1996, 18 pages.

Mänttäri M., Nuortila-Jokinen J., Nyström M., Development of a nanofiltration process for flotation treated paper mill waste water, *Julkaisu* **102**, Department of Chemical Technology, Lappeenranta University of Technology, Lappeenranta, Finland, 1998, 51 pages.

Nyström M., Nuortila-Jokinen J., Mänttäri M., Nanofiltration of pulp and paper effluents, In: *Water Management, Purification, and Conservation in Arid Climates*, M. F. A. Goosen and W. H. Shayya (eds.), Technomic Publishing Inc., In press.

OTHER PUBLICATIONS IN RELATED FIELDS

Mänttäri M., Nyström M., Ekberg B., Influence of flocculants on the performance of a ceramic capillary filter, *Filtration & Separation*, **33**(1) (1996) 75-80.

Mänttäri M., Nyström M., Ekberg B., Influence of flocculants on the filtration of copper concentrates with a ceramic capillary filter, *Minerals Engineering*, **9**(4) (1996) 419-428.

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CONTENTS

1. INTRODUCTION

Nanofiltration (NF) is a pressure-driven separation process with performance characteristics between reverse osmosis and ultrafiltration. The name nanofiltration comes from the fact that the spaces in the membrane through which the molecules pass are approximately of one nanometer in size. Nanofiltration membranes can remove multivalent ions and organic molecules larger than 200-1000 g/mol from a solvent. Usually, monovalent ions that are retained by reverse osmosis (RO) membranes can pass through NF membranes. The increased salt passage with NF membranes reduces the difference in salt concentration across the membrane, consequently reducing the osmotic pressure and increasing the available effective pressure. Therefore, an NF process can pass more water during low pressure operation than an RO process (Cadotte et al., 1988; Rautenbach and Gröschl, 1990; Raman et al., 1994; Nyström and Nuortila-Jokinen, 1996; Bowen and Mukhtar, 1996).

Transport through microfiltration (MF) and open ultrafiltration (UF) membranes occurs by convection, but in nanofiltration diffusive transport, like that in reverse osmosis (RO), is also important. Mostly polymeric NF membranes are used today, but ceramic NF membranes have also been developed. All ceramic NF membranes and some polymeric NF membranes are considered porous, but most polymeric NF membranes are dense membranes without fixed pores. These membranes consist of a charged or an uncharged network structure. The morphologies of most dense membranes are asymmetric, with a thin, highly selective polymer on top of an open support structure. This structure minimizes the resistance to transport caused by the membrane. According to the solution-diffusion theory, both the solvent and the solute dissolve into the membrane. The transmission rates through the dense layer depend upon the molecular volume and the amount of the penetrant that can be absorbed into the selective layer. The solute moves through the membrane mainly due to concentration gradient forces, whereas the solvent transport is dependent on the hydraulic pressure gradient. This means that when diffusion is the dominant transport mechanism, retentions in NF improve with an increase in the transmembrane pressure (Petersen, 1993; Koros, 1995; Rautenbach and Helmus, 1994; Peeters, 1997).

Retention in NF can be explained partly by sieving and partly by non-sieving mechanisms. The non-sieving rejection mechanisms are Donnan exclusion, dielectric exclusion, and what is termed a hydration mechanism, which is probably related to the changes in the dissolving ability of water in fine pores (Yaroshchuk, 1998). If Donnan exclusion is the dominant rejection mechanism, the rejection of salts has to increase with increasing co-ion charge (co-ions: ions that have the same charge as the membrane fixed charge) and with decreasing counter-ion charge. Peeters (1997) showed that such a correlation does occur for some NF membranes, while for others that is not the case. Donnan exclusion is the most important non-sieving rejection mechanism in NF. Therefore, it can be said that separation using NF membranes is mostly achieved by a combination of size and charge effects. The tendency of the ions to be solvated influences their retention. The more solvated ions take more space and retain better. Both phenomena influence in similar ways. The higher charged ions retain better. In addition, diffusion coefficients are higher for monovalent ions. This accelerates their transport through the membrane. The retention of dissociated organic substances is higher when there exists charge repulsion than if they are uncharged. The affinity effect may also be important. The difference between their diffusion rates affects the separation of organic compounds (Chaufer et al., 1996; van den Berg and Smolders, 1992).

The unique properties of NF membranes make selective separations possible, including separations of solutes based on their charge differences and separations of high molar mass organics from highly concentrated solutions of monovalent ions (Rudie et al., 1993). Thus, NF is an effective method of separating, for instance, sodium chloride from cheese whey, as shown by Raman et al. (1994). NF membranes are also used in the purification of drinking water (de Witte, 1996; Ericsson et al., 1996) and in the treatment of waste water or process streams (Madireddi et al., 1997; Treffry-Goatley and Gilron, 1993). Furthermore, the food (Cartier et al., 1997), textile (Chen et al., 1997) and mining industries (Awadalla and Kumar, 1994) have also used NF in their processes. In drinking water applications, NF can serve to soften the water, reduce total dissolved solids, and remove color and high molar mass organics. In many cases, it is used instead of reverse osmosis due to its higher flux, thus lowering the capital and operating costs of the process. Nanofiltration has been used for the removal of hardness and organic impurities from textile mill waters. The textile industry uses NF to recover valuable dyes and synthetic sizing agents (Sójka-Ledakowicz et al., 1998). The use of NF means that textile dyes are reused, polluted effluents are avoided, and reusable water is produced. The purification of landfill leachates with NF has been tried by Peters (1998).

The use of NF in the pulp and paper industry has been hindered by fouling and the relatively low fluxes of the membranes. However, NF offers some advantages, like superior retentions, for instance, compared to UF. This means that the permeate quality is in many cases on the same level as chemically treated fresh water, which is the cleanest water used in many mills. Thus the NF permeate can be safely reused in even the most demanding applications in paper mills, like, for instance, for the high pressure showers or the dilution of chemicals. Generally, NF membranes retain divalent ions very well but transmit small uncharged organic components and monovalent ions. As a consequence of this, the osmotic pressure remains significantly lower than in RO, where monovalent ions are also retained. Thus, the pressure needed in NF is markedly lower than in RO and the flux is higher. New module constructions, for example, high-shear modules, will also expand the use of NF. The high retention of organics and multivalent ions, and also a high flux in some cases, are just some of the advantages of using NF in the pulp and paper industry. Hence, NF should be studied further. In the future, NF along with other technologies like ultrafiltration, evaporation, and biological treatment will provide a means of reusing paper industry water streams.

2. OBJECTIVE

The aim of this thesis was to evaluate the performance of several commercially available NF membranes in the filtration of paper industry effluents, and to study how filtration conditions influence the flux obtained, the permeate quality, and the fouling tendency of the NF membranes. The parameters studied were; transmembrane pressure, crossflow velocity, concentration, temperature, and pH. Furthermore, the effects of membrane pore size, charge, and hydrophilicity on the NF performance were evaluated. The causes of fouling were also studied with model substances. Generally, the goal was to determine the filtration parameters that influenced the filtration performance most significantly. The trend was towards non-fouling conditions in NF.

3. BACKGROUND

According to the Chemical Abstract database, the number of nanofiltration studies using pulp and paper industry effluents has increased exponentially during the 1990's. The number of published studies concerning NF in the paper industry is still under 100. Before the term nanofiltration was coined, these membranes were called loose RO or tight UF membranes. Therefore, the term NF membrane has been known about for just over a decade. In many cases, the flux obtained with NF membranes has been considered too low in practical applications. In addition, the fouling of the membranes and modules has restricted the use of NF in the pulp and paper industry.

Review papers on membrane filtration in the paper industry have been written by Jönsson and Wimmerstedt (1985), Kahmark and Unwin (1994 and 1996), and Ramamurthy (1996). In the following sections, results are presented from published studies. The results are divided into mill-scale applications, pilot-scale filtrations, and laboratory-scale tests.

3.1 Mill-scale nanofiltration in the pulp and paper industry

Today, only two industrial-scale applications exist. Both of them are situated in the USA (Lien and Simonis, 1995). These paper mills have utilized spiral-wound NF systems with many pretreatment stages, like chemically enhanced clarification and sand filtration, for example. The driving force for a paper company on the Pacific Rim to start using membrane technology was the lack of affordable, high quality fresh water and the cost of waste water treatment. According to their pilot tests, an increase in the feed volume flow from 1.8 m^3/h to 3.6 m^3/h reduced the fouling and also tripled the flux. It was possible to obtain these results using a wide feed spacer. A 10000 m^3/d water reuse and recovery system was installed there in 1993.

Another plant reported by Lien and Simonis (1995) is situated in Florida. In this case a coal-fired co-generation facility operated in conjunction with a large paper company. In order to comply with the zero discharge permit, the co-generation plant installed a complex water treatment system that included a reverse osmosis system. Reverse osmosis feed water quality problems made the co-generation plant evaluate several different pretreatment technologies, including nanofiltration, activated carbon treatment, tubular microfiltration, and additional chemical treatment. Nanofiltration was found to meet the requirements. It provided the flux, permeate quality, and membrane cleanability necessary for economic system performance and compliance with the zero discharge requirement. Both plants used Desal-5 membranes in spiral-wound modules. Unfortunately, the filtration data from the mills has not been made available.

In addition to the above examples of NF in industry, a vibratory shear-enhanced processing (VSEP) module has been selected for waste water treatment at a recycle mill in the Midwestern US. Mill-scale results are not yet reported (Monroe, 1997).

3.2 Pilot-scale nanofiltrations in the pulp and paper industry

In pilot-scale studies, spiral-wound modules are the most commonly used module types. However, a new vibratory shear-enhanced processing module (VSEP) has also been tested (Monroe, 1997), as well as tubular modules (de Pinho et al., 1995 and 1996, see Section 3.3).

A short review of studies with NF spiral-wound modules is given in Paper V. In the literature studies referred to therein, the retentions obtained were in general high enough. Nevertheless, the restricting factor for the use of spiral-wound NF modules has been the relatively low fluxes. In addition, the complexity of the pretreatment needed has, in many cases, decreased the level of interest in NF. The fluxes obtained with NF spiral-wound modules were in most applications below 30 l/(m^2h), although fluxes of over 100 l/(m^2h) have been measured sometimes.

After both laboratory and additional pilot testing (Monroe, 1997), VSEP modules were selected for waste water treatment at a recycle mill in the Midwestern US. The mill-scale system includes seven units that filter a 760 l/min slip stream. On the pilot scale, a permeate flux of about 110 l/(m^2h) at 24 bar was obtained at a solids concentration of 30%. The membranes used were sulfonated polyethersulfone membranes, one with a 10% sodium chloride retention (probably a NTR-7410 membrane) and the other with a 50% sodium chloride retention (probably a NTR-7450 membrane). The results showed that it is possible to obtain a high concentration of solids with a good permeate flux using the high shear rate module.

3.3 Laboratory-scale experiments with NF membranes

There are some active groups like the Wastewater Technology Centre in Canada, Instituto Superior Technico in Portugal, and the group headed by Professor Ann-Sofi Jönsson in Lund, Sweden, that have studied membrane filtration in the pulp and paper industry. In addition, some papers have also been published by other groups. In our laboratory, effluents from paper machines have been filtered. However, in general NF has not been studied very extensively. The following paragraphs outline some studies where NF membranes were used to treat effluents from the paper industry.

Since the 1980's, the trend has been to evaluate ultrafiltration and nanofiltration performance in the filtration of pulp mill effluents. In particular, alkaline bleaching effluents are produced in large volumes and are a source of severe environmental problems. These streams contain a lot of inorganic load and a wide range of organic solutes resulting from the lignin dissolution and the total organochlorinated compounds (TOCl) formed by the chlorination of different fractions of lignin. Most of the TOCl and color load (50-60%) from the pulp mill is discharged in the first alkaline extraction (E1) effluent. The ultrafiltration of the caustic extraction filtrate for color removal is generally recognized as technically and economically feasible, particularly if the results from three full-scale applications are considered. These applications, in Japan and Sweden, used polymeric UF membranes for the treatment of E-stage effluents. Nanofiltration was not used in the mill-scale applications. However, increasing concerns about the removal of low molar mass (< 1000 Da) organochlorinated compounds led to the investigation of nanofiltration membranes. These small organochlorinated compounds are more hazardous to the environment than the bigger compounds as they are able to penetrate cell membranes, they are more lipophilic and they tend to bioaccumulate. It can also be expected that by moving towards total chlorine-free (TCF) bleaching sequences, more low molar mass compounds, which are responsible for some mutagenicity, will be produced (Afonso and de Pinho, 1995).

de Pinho et al. (1995 and 1996) filtered a bleaching effluent (E1 effluent) with polymeric nanofiltration membranes and with a ceramic membrane. They developed three types of NF membranes and tested them on a laboratory scale and on a pilot scale. On the laboratory scale, they obtained permeability values as high as 10.4 l/(m^{2}h bar) (crossflow velocity 5.0 m/s, 20 bar) using tubular membranes (A) whose active layer was composed of an ampholytic polymer containing ammonium groups and sulfonic acid groups. Another type of polymeric membrane (B) gave a permeability of about 6.6 l/(m^{2}h bar) at 40 °C with a flat-sheet module (DDS Lab-20, crossflow velocity 1 m/s, 20 bar). The active layer of this membrane consisted of a thin film of poly(trans-2,5 dimethyl)piperazinthiofurazanamide (TFZ) formed by interfacial polymerization on a polyethersulfone membrane. The third type of membrane was made from a ceramic material and its permeability was about 4.8 l/(m^{2}h bar). The retentions for the ceramic membrane were lower than for the polymeric membranes. With the polymeric membranes the total organic carbon retentions were 88% for membrane A and 90% for membrane B. The same membranes were also tested on a pilot scale. Table I summarizes the flux data from the results of the pilot-scale tests. In the pilot-scale experiments, the flux values were significantly lower than in the laboratory-scale tests which indicates the existence of fouling. The high crossflow velocity in the tubular membranes prevented fouling and maintained the flux at over 40 l/(m^{2}h) after 100 hours of filtration. The flux of the spiral-wound module (membrane B) was lower, although the feed water was more efficiently pretreated. The relatively low flux was due to insufficient turbulence in the module. de Pinho et al. (1995) depreciated the total costs, including capital and operating costs, for a nanofiltration plant processing 1000 m^3/d of E1 effluent. They concluded that the most economical process would employ the spiral-wound module with membrane B (0.448 ECU/m^3 permeate) in spite of the fact that it had the lowest flux in the pilot-scale experiments.

Table I. Pure water fluxes and permeate fluxes at 40 °C in laboratory-scale and in pilot-scale experiments using three different NF membranes (de Pinho et al., 1995 and 1996).

	Flux, l/(m^{2}h)	Flux of E1 effluent, l/(m^{2}h)	
Membrane	20 bar	Laboratory, 20 bar	Pilot (24 h)
A (tubular)	197 [a]	208, 5 m/s	54, 20 bar, 4.2 m/s, tubular
B (flat sheet/spiral)	167 [b]	131, 1 m/s	20-45, 15 bar, spiral
C (tubular, ceramic)	381 [c]	96, 4.7 m/s	70, 8 bar, 2.0 m/s, tubular

[a] 5 m/s, NaCl: 200 ppm, sucrose: 200 ppm

[b] 1 m/s, NaCl: 2000 ppm, sucrose: 2000 ppm

[c] 4.7 m/s, NaCl: 1000 ppm, sucrose: 200 ppm

The transition from chlorine/chloride dioxide bleaching to only chloride dioxide bleaching affected the nanofiltration performance (Rosa and de Pinho, 1995). Nanofiltration productivity increased 30% with this modification. In the laboratory, a pressure of 20 bar gave a flux of 94 l/(m^{2}h) for the chlorine/chloride dioxide and 124 l/(m^{2}h) for the chloride dioxide bleached effluent. Nanofiltration retentions remained constant with the bleaching sequence modification. The retentions of total organic carbon (TOC) were approximately 90%.

Depending on the NF membrane, the feed content and the filtration conditions, the permeate may contain a lot of monovalent ions, which are detrimental for permeate reuse. Electrodialysis has been tested for the demineralization of NF permeate. Geraldes and de Pinho (1995) filtered alkaline (E1) bleaching effluent using a spiral-wound module and studied the demineralization of a model solution of NF permeate by electrodialysis.

Afonso and de Pinho (1997) evaluated the role played by operating conditions in the filtration of bleaching effluent (E1) with tubular NF membranes. The NF performance was strongly dependent on the pH due to the influence of this parameter on the membrane surface charge. The pH affected the retention of conductivity (salts) but did not influence the retention of TOC or TOCl (retention >90%). An increase in pH from 8 to 9 improved conductivity retention from 60 to 74%. At the same time the flux at a pressure of 20 bar decreased from 175 to 75 l/(m^{2}h). The experiments were carried out at a temperature of 40°C with a high crossflow velocity (5.1 m/s). Thus, the rejections were minimal at the isoelectric point of the membrane because the electrostatic forces were weaker at this pH. On the other hand, the flux was at its maximum at the membrane isoelectric point. The same phenomenon was observed, for instance, by Vaija et al. (1993). They concluded that an increase in the surface charge of small pores (D<20 nm) results in a decrease of membrane permeability due to the increasing orientation of the water molecules and the increasing viscosity of the solution in the pores. This phenomenon has also been studied by Huisman et al. (1997). Conversely, an increase in pH was observed to improve the flux in many studies (Jönsson et al., 1988; Berg et al., 1997; Sierka et al., 1997). The reason for this might be increased repulsion inside the pores, which would increase the pore size, or it might be because components in the solution become more dissociated at higher pH. Then there is increased repulsion coagulation. Since dispersion forces are short range, the particles must be close together before a significant attractive force develops. The molecules of the liquid collide with the small particles, which gives rise to the irregular movement of the particles called Brownian motion. This kind of behaviour may bring some particles into close enough proximity to allow the attractive surface forces to bind them together into small agglomerates. The rate of agglomeration only depends on Brownian motion if the electrical repulsion and velocity gradient are absent. This kind of agglomeration is called perikinetic flocculation to differentiate it from the orthokinetic flocculation, which is caused by fluid motion. The charged surfaces of particles may prevent the spontaneous agglomeration caused by the Brownian motion /Halverson and Panzer 1980, Ward 1996, Wakeman et al. 1989, Hughes 1990, Ives 1990/.

The coagulant reagents are added to alter the surface charge to allow the agglomeration to take place. Electrolyte addition can bring about coagulation by two mechanisms. First, addition of any electrolyte increases the ionic strength of the suspending medium, which means that the thickness of the double layer will decrease and the range of interparticle repulsion will also decrease. Ions with similar sign charge as the surface are repelled by the surface, and counter-ions are attracted to its vinicity. As the concentration of counter-ions increases, the volume of the diffuse ionic layer necessary for electroneutrality decreases. If this electrolyte effect is purely electrostatic in nature, the electrolyte is called an indifferent electrolyte. The magnitude of this effect increases with increasing charge on the counter-ion. To counteract the charge in negatively charged suspensions trivalent cations ($Al^{3+}$and Fe^{3+}) are more effective than divalent cations or monovalent cations. Secondly, counter-ions may react chemically with the particle surface and be adsorbed onto it. This specific counter-ion adsorption may reduce the net surface charge to zero, or even reverse the sign of the net surface charge. When the net surface charge is reduced to zero, or close to zero, coagulation is possible. The critical flocculation concentrations (cfc) for destabilisation by specific ion adsorption are considerably smaller than those for an indifferent electrolyte. Hydrolysable metal ions are considered to operate according to this mechanism, although several mechanisms may be involved simultaneously /Amirtharajah 1990, Halverson and Panzer 1980/.

Hydrolysable metal ions are usually added in the pH range and at the concentration level where the metal hydroxide is precipitated. Under appropriate conditions a fluffy aromatic polyamide membranes while the resistance due to fouling was not affected. Thus, these membranes proved to be resistant to fouling by the waste water studied. They also found that the resistance due to fouling for the NTR-7410 membrane increased considerably when the feed was concentrated. The nanofiltration of deinking effluents was also studied by Bredael et al. (1996).

Dal-Cin et al. (1996a) have studied various fouling mechanisms in the filtration of pulp mill effluent. They used membranes of various pore size and material. Results from adsorptive fouling studies are reported by Dal-Cin et al. (1995). The most hydrophobic material had the lowest relative flux or, in other words, the highest fouling. In particular, the thin film composite class of membrane showed widely varying degrees of fouling resistance. Generally, they found that hydrophobic materials, such as polysulfones, polyamide-imide, and polyether-imide, exhibited severe adsorptive fouling. They concluded that ideal membrane materials might be regenerated cellulose or various hydrophilic thin film composites when the adsorptive fouling of a plug screw feeder pressate from a semi-chemical mechanical pulp mill is to be minimized. In other papers (e.g., Dal-Cin et al., 1996b), the relative contributions of various fouling mechanisms in the filtration of the same effluent were reported. These studies showed negligible fouling by adsorption for the Desal-5 and the C30 membranes. Thus, adsorptive fouling can be minimized by the selection of an appropriate membrane material. Pore plugging can be controlled by using a membrane with a suitable, usually small enough, pore size.

Zaidi et al. (1991) evaluated the performance of UF membranes for separating selected organics from pulp and paper mill effluents. The molar masses of the model compounds used were lower than the cut-off values of the membranes. They studied the mechanism by which membranes are able to remove the model compounds and the mechanism which causes fouling of the membranes. They found that toxic organics with a high octanol-water partition coefficient interact strongly with the surface of the organic membrane. Thus, they recommended the use of membranes with highly hydrophilic surfaces.

The adsorption of organic matter onto the membrane was also studied by Crozes et al. (1993). In their study, the highest level of adsorption occurred in the ultrafiltration of aromatic compounds through a hydrophobic membrane. In addition, fouling was significantly reduced when the ring structure of tannic acid was oxidated.

Zaidi et al. (1992) compared the low shear rate flat-sheet module Lab-20 (DDS, Dow Denmark Separation Systems) with the high shear rate CR-250 (cross-rotational filter from Valmet-Flootek nowadays) membrane module. Bleach plant effluent was used in the filtrations. The flux values for the CR-filter were significantly higher, in fact, over three times higher than the fluxes for the Lab-20 filter when UF membranes were tested, and about two times higher with NF membranes. In the CR-250 filter, the linear velocity at the end of the blade was approximately 10 m/s whereas the crossflow velocity in the Lab-20 module was only 1 m/s. Thus, the level of turbulence in these modules varied greatly, which can explain the different fluxes. In the total recycle mode, the NF flux after four hours for the CR-250 filter was about 90 l(m^{2}h) at a pressure of 6.9 bar and a temperature of 50 °C. In addition, they concluded that some membranes seemed to respond more than others to the high turbulence level.

A new high shear rate module, the Vibratory Shear Enhanced Processing unit (VSEP), equipped with NF membranes has also been tested with paper machine effluents. Nuortila-Jokinen (1997) filtered acidic and neutral pH clear filtrates with this type of unit using Desal-5 and PVD-1 membranes. A significant difference between the acidic and neutral pH cases was observed with both membranes: at neutral pH the permeability was around 8 l/(m^2h bar) whereas at an acidic pH it was close to zero at a volume reduction factor of 8. She concluded that the vibration in the VSEP unit is only capable of preventing the fouling caused by adsorption and concentration polarization if electrostatic repulsion forces are also present. In the filtrations of neutral pH clear filtrate, Nuortila-Jokinen et al. (1998) observed a 360% increase in permeate flux for a compact tubular module (WFN4505 membrane) when the crossflow velocity was increased from 2.8 to 8.5 m/s. In addition, with chemical pretreatment the NF flux was significantly increased and irreversible fouling decreased. The modification of NF membranes by UV-irradiation, with NaCl at pH 10 or with 0.1 w-% dextran sulfate, has also been tested with some success in a bid to reduce fouling (Nuortila-Jokinen and Nyström, 1996a).

4. MATERIALS AND METHODS

4.1 The filtered solutions

In this thesis, paper mill total effluent (Papers II-IV, and VII), effluent from a paper and pulp mill, which is referred to as 0-water hereafter (Paper V), and effluent from a mechanical pulp mill, which is referred to as grinder room effluent below (Paper VII), were filtered with commercial NF membranes. In addition, the filtration of model substances was studied (Papers VI and VII). Table II presents values for some measured parameters of the effluents. The effluents have been characterized more precisely in the corresponding papers (II-V, VII). The values presented for the 0-water and the grinder room effluent vary greatly. The 0-water values vary mostly because various pretreatment methods were used. The grinder room circulation water values depended on the proportion of waste water that came from the paper machine to the circulation vessel. The results presented below have been chosen so that the feed content was approximately the same for all membranes and, thus, the membranes could be compared.

Table II. Values for some measured lump parameters and compounds in the effluents studied in this thesis.

	Total effluent	0-water	Grinder room effluent
pH	4.8 - 5.0	7.7 - 7.9	4.5 - 5.3
COD, mg/l	1300 - 1800	120 - 240	600 - 2200
Conductivity, mS/m	145 - 165	75 - 105	30 - 160
UV 280 nm, -	4.6 - 5.4	0.5 - 0.8	3.3 - 7.0
TC, mg/l	400 - 460	40 - 50	170 - 750
Dry solids, mg/l	1300 - 1700	600 - 750	1500 - 3000
Inorganic matter, mg/l	700 - 1100	500 - 650	300 - 1400
Sulfate, mg/l	390 - 540	250 - 320	280 - 330

4.2 Filtration modules and membranes

The experiments were carried out on both a laboratory and a pilot scale. In the laboratory-scale experiments, crossflow flat-sheet modules were used. The pilot-scale experiments were conducted using a spiral-wound module. The membranes used ranged from microfiltration to reverse osmosis types.

4.2.1 Laboratory-scale filtration apparatuses and modules

Two different filtration apparatuses were used in the laboratory-scale filtrations; a one-module filtration apparatus and a new filtration apparatus with three modules. All filtrations in Papers II, III, and IV were carried out using the one-module filtration apparatus. The filtrations in Papers VI and VII were partly conducted with the three-module filtration apparatus (Fig. 1).

In the apparatus with one module, crossflow, pressure, temperature, and permeate flux were measured and controlled manually. The permeate fluxes were measured using a scales. The concentrate flow rate was measured by a rotameter and it was controlled by changing the pump velocity or by adjusting the manual valve on the concentrate pipe or that on the by-pass. The temperature was adjusted and controlled by a heat-exchanger. The apparatus with one module had a feed volume of 8 l.

A new filtration apparatus which contains three flat-sheet modules in parallel was constructed (Fig. 1). This filtration apparatus can also be modified to use other modules, such as tubular ones, for example.

In this apparatus, three membranes can be tested at the same time and under the same conditions. The filtration apparatus with three modules had a feed volume of 18 l. The permeate flux of one module was measured using a mass flow meter and the measured data was collected by a computer using the Labview program. Time-controlled automatic valves were used to switch the flow to the mass flow meter so that the permeate fluxes from the other modules could be measured using the same flow meter. The concentrate flow was regulated by controlling the pump velocity and adjusting manual valves; one to control the concentrate flow and another for the by-pass. The concentrate flow rate was measured by a flow meter outside the feed pipe. The temperature of the feed solution was controlled by a LAUDA water circulation cooler (WK 4600). A peristaltic pump was used to recirculate the permeate back to the feed vessel. The modules were identical in both the filtration apparatuses. The membrane area in all the flat-sheet modules was 0.00529 m^2.

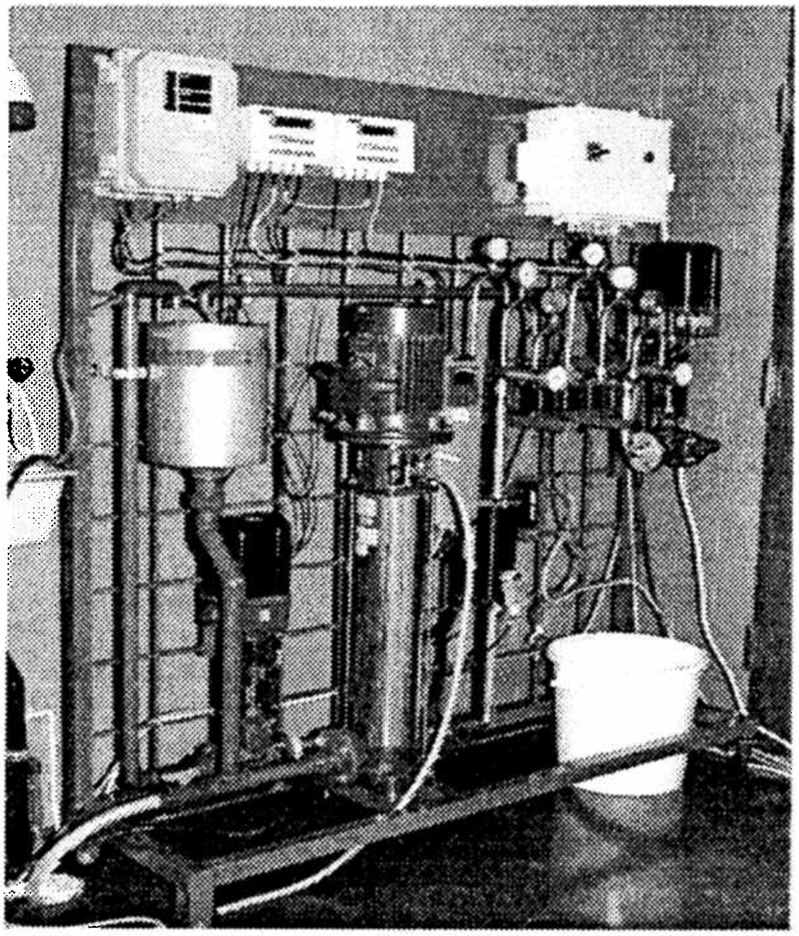

Fig. 1. Laboratory-scale crossflow filtration apparatus with three flat-sheet modules.

4.2.2 Membranes in the laboratory-scale experiments

Several NF membranes were tested in the laboratory-scale experiments. Their respective fluxes, retentions and fouling tendencies were evaluated. Table III summarizes the relevant data relating to the membranes used in this thesis (Petersen, 1993; Raman et al., 1994; Wang et al., 1995; Fu et al., 1995). Mostly Desal-5 DK membranes were used here in the filtrations where the effect of filtration conditions on the NF performance was studied. The DK and DL versions of the Desal-5 membrane are made from the same materials, but different concentrations are used. These membranes consist of four layers: polyester, polysulfone and two proprietary layers (Eriksson, 1999). Previous studies have proven this membrane to work well with many effluents from the pulp and paper industry (Lien and Simonis, 1995; Anonymous, 1997; Salovius et al., 1993; Ekengren et al., 1993).

Table III. Description of membranes used in this thesis (permeability at 25 °C, MWCO = "molecular weight cut-off", data according to membrane manufacturers; Petersen, 1993; Raman et al., 1994; Wang et al., 1995; Fu et al., 1995; Eriksson, 1999).

Membrane	Manufacturer	Material	Retention	MWCO	Permeability	T_{max}	pH
			NaCl	g/mol	l/(m^{2}h bar)	°C	
RO							
Desal-11 AG	Osmonics	PA	99.5% (1 g/l)		2.9	90	4-11
Desal-3 SG	Osmonics	PA	98.5% (1 g/l)		2	90	2-11
TFC ULP	Fluid System	PA on PS	98% (2g/l)		6.1	45	4-11
NF							
TFC S	Fluid System	Mod. aromatic PA	85% (2g/l)	200-300	7.7	45	4-11
N30F	Hoechst		30% (5 g/l)		1.4-4.2		
NF-PES-10	Hoechst	PES	< 15% (5 g/l)		5.6-11.2	95	1-14
ASP-10	AMT	Sulfonated PS on PS	10%		14	50	4-11
ASP-35	AMT	Sulfonated PS on PS	35%		8.3	50	4-11
TS40	TriSep	Fully aromatic PA	40%		5.6	45	4-11
TS80	TriSep	PA	85%	280-300	4.5	45	4-9
PVD-1	Hydranautics	PVA derivative	80%	180	3.5	40	2-8
Desal-5 DK	Osmonics	Proprietary	$MgSO_4$ 98% (2g/l)	150-300	5.4	90	2-11
Desal-5 DL	Osmonics	Proprietary	$MgSO_4$ 96% (2g/l)	300	7.6	90	2-11
NTR-7450	Nitto Denko	Sulfonated PES	51% (5 g/l)	500-1000	9.4	80	1-13
NF 200	Dow Danmark	Polypiperazine	70%	200	7-8	40	
NF 45	Dow Danmark	Aromatic PA	45%		4.8		
UF / MF							
Desal GM	Osmonics	Thin film composite	4%	8000	12	70	2-11
Desal PW	Osmonics	PES		10000	73	50	2-11
C 30	Hoechst	RC		30000	110-230	70	1-12
Desal JX	Osmonics	PVDF		0.3 µm	350	50	2-11

PA	polyamide	PES	polyethersulfone
PS	polysulfone	PVA	polyvinyl alcohol
PVDF	polyvinylidene fluoride	RC	regenerated cellulose

4.2.3 Pilot-scale filtration equipment and module

A spiral-wound NF element was mounted in a portable UF/NF apparatus. In this apparatus three prefilters were used before the spiral-wound element. The first was a 50-µm crossflow bag filter and the next were 10-µm and 5-µm cartridge filters. All prefilters were replaceable. The volume of the feed tank was 1 m^3. The concentrate flow rate was adjusted by regulated manual valves and by controlling the pump velocity. A rotameter was used to measure the concentrate flow rate. The permeate flux was determined by measuring the time that was required to collect a given amount (about 2 l) of permeate.

The Desal-5 DL membrane was used in the spiral-wound element. The element had a 2-mm-thick parallel feed spacer and a membrane area of about 1.1 m^2 (Paper V).

4.3 Methods of filtration and analysis

The filtration procedures, as well as the methods of analysis, are described in the corresponding papers (II-VII). The original waste water, the permeate and the concentrate samples from the filtrations were analyzed for their ionic content (pH, conductivity, ion chromatography, atomic absorption spectroscopy), lignin residuals (UV absorption at 280 nm and 400 nm), sugar content (anthrone-sulfuric acid color method), anionic polyelectrolytes (cationic demand (CAD) titrated with 0.001 N poly-DADMAC using a Mütek particle charge detector), chemical oxygen demand (COD_{Cr}, Hach reactor, standard SFS 5504), turbidity (Hach spectrophotometer), and color (Hach spectrophotometer). The total residue (total solids, drying 105 °C) and the total fixed residue (ash content or inorganic matter, 550 °C) in the waters were analyzed according to the standard SFS 3008. The volatile solids content (total organic matter) was calculated as the difference between the total fixed residue and the total residue. Depending on the case, the total carbon (TC) was analyzed using a Rosemount DC-190 (Dohrmann) or a Shimadzu TOC-5000A analyzer. The suspended solids (SS) were analyzed according to the standard SFS 3037, except that paper filters (Schleicher & Schuell 589) were used instead of glass fiber ones. The samples were stored at a temperature of 5 °C before being analyzed.

4.4 Calculation methods

The equations used to calculate the various parameters are presented in the corresponding papers. In this section only the equations that are used in Chapter 5 of this thesis are presented. The **retentions** of different species are calculated by comparing the concentration of the substance in the permeate with that in the concentrate as follows:

$$R = (1 - \frac{C_p}{C_c}) \cdot 100\% \tag{1}$$

where R retention, %

C_p concentration in permeate

C_c concentration in concentrate

The flux reduction of the pure water flux, which is assumed to be a measure of membrane **irreversible fouling**, is calculated by comparing the pure water flux before and after the filtration without cleaning as follows:

$$FR_{PWF} = \frac{PWF_b - PWF_a}{PWF_b} \cdot 100\% \tag{2}$$

where FR_{PWF} flux reduction of pure water flux, %

PWF_a pure water flux after effluent filtration, $l/(m^2h)$

PWF_b pure water flux before effluent filtration, $l/(m^2h)$

The **flux reduction** is calculated by comparing the permeate flux with the pure water flux before filtration (3).

$$FR(t) = \frac{PWF_b - PF(t)}{PWF_b} \cdot 100\% \qquad (3)$$

where	*FR(t)*	flux reduction of permeate flux after t min of filtration, %
	PF(t)	permeate flux after t min of filtration, $l/(m^2h)$

The filtrations were performed at a temperature close to 40°C and the flux values were subsequently recalculated to 40°C using a viscosity correction (Equation 4). This procedure was not adopted with the fluxes from the filtrations where the effect of temperature was studied.

$$PF(40) = \frac{\eta(T)}{\eta(40)} \cdot PF(T) \qquad (4)$$

where	*PF(40)*	recalculated flux to 40°C, $l/(m^2h)$
	PF(T)	measured flux at temperature T, $l/(m^2h)$
	$\eta(T)$	viscosity of water at temperature T
	$\eta(40)$	viscosity of water at 40°C

The **recovery** is defined as follows:

$$Y = \frac{PV}{FV} \cdot 100\% \qquad (5)$$

where	Y	recovery, %
	PV	obtained permeate volume, l
	FV	feed volume, l

5. RESULTS AND DISCUSSION

Various filtration parameters were studied and their influences on retention and flux were evaluated. Firstly, the results, which show the existence of different retention mechanisms in NF, will be presented. Subsequently, the effect of parameters such as temperature, pressure, crossflow velocity, and feed solution concentration on the filtration performance will be discussed. The effect of feed pretreatment, as well as that of the pretreatment of the membranes, will be presented. Causes of fouling are discussed and the filtration conditions necessary for a non-fouling process are presented. Finally, the various NF membranes will be compared.

5.1 Retention mechanisms in nanofiltration and their effect on flux

The purpose of membrane filtration, as it is understood in this thesis, is to divide the feed stream into permeate and concentrate streams of various compositions so that at least one of those streams could be reused in the mill. In order for this to be possible, the membrane has to retain some substances and transmit others. Therefore, the retention is a crucially important factor when the performance of the membrane processes is evaluated. In NF, retention occures mainly by a sieving mechanism and by electrostatic interaction. These mechanisms are discussed below.

5.1.1 Size exclusion

The cut-off value or the pore size of a membrane is the most important factor that determines the retentions of microfiltration and ultrafiltration membranes. The molar mass cut-off value is usually defined as being the pore size at which 90% of some test molecule of that molar mass, normally a globular molecule, is retained.

As expected, an increase in the cut-off value (RO → MF) improved the permeability of the membranes here, especially the pure water permeability (not shown here), and decreased the retentions, as can be seen in Fig. 2. The filtrations with the total effluent showed that the ultrafiltration permeate still contained a lot of inorganic compounds as well as low molar mass organic compounds. The permeate from the tightest UF membrane studied (UF 8000) contained inorganic matter over 500 mg/l and its chemical oxygen demand (COD) was over 700 mg/l. Moreover, the fluxes achieved with the NF membranes were equal to the fluxes measured with the tight UF membranes (UF 8000 and UF 10000) when the crossflow velocity was around 3 m/s. If a higher pressure was used with the UF membranes, the flux decreased rather than increasing like with NF membranes due to higher concentration polarization on the membrane surface. An increase in pore size increased the permeability of the membranes studied and increased convective transport to the membrane, which caused a higher concentration polarization on the membrane surface. Larger pores plugged more than smaller ones because more material can penetrate the larger pores which was seen as a decrease in retention using a larger pore size membrane. Furthermore, an increase in the transmembrane pressure increased the concentration polarization if the crossflow velocity was not increased at the same time. Because of the markedly higher retentions of NF membranes compared to UF membranes and their approximately equal permeate fluxes for the same filtration conditions, NF membranes appear to be more attractive for the treatment of total effluent.

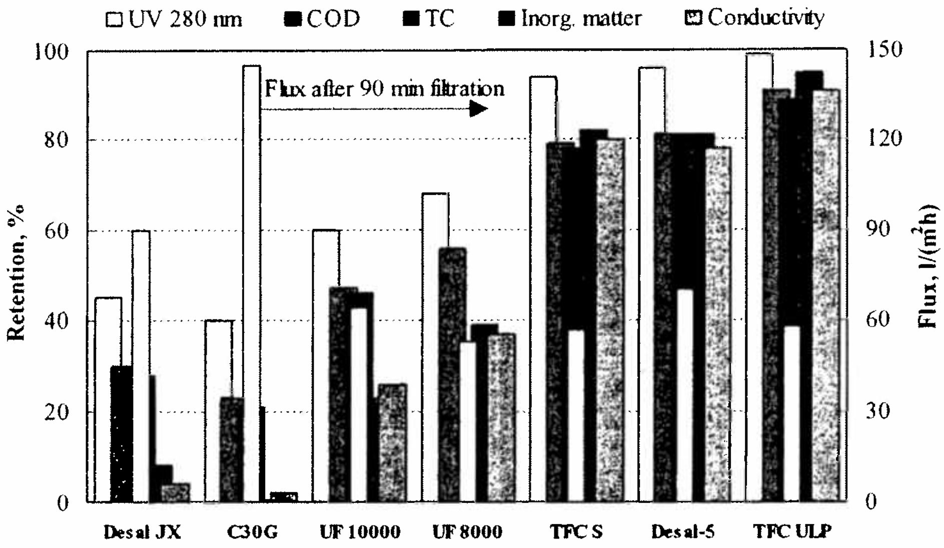

Fig. 2. Permeate fluxes and retentions for various membranes (cut-off decreasing from left to right) in the filtration of paper mill total effluent: pressures (in bar) used with different membranes from left to right 0.5, 1, 1.5, 3, 7, 10, and 10; crossflow velocity 3.5 m/s; temperature 40 °C.

As discussed above, the permeate flux during the filtration with the more open UF membranes dropped more than that with the tighter NF membranes. The same conclusion has been made, for instance, by Sierka et al. (1992 and 1994). They concluded that UF membranes lost a higher percentage (about 65%) of their initial permeate flux than tighter NF membranes (11%).

The same phenomenon is seen when NF membranes made of the same material but with different permeabilities are compared. In Fig. 3 the fluxes for the grinder room effluent filtrations are presented. The flux of the more open NF membranes decreased more and as a result the fluxes for the same kind of membranes were more or less the same at the end of the filtration but the retentions of the tighter membranes were higher, as shown in Table IV. The retentions can be seen to improve when the membrane became fouled and its permeate flux decreased. An exception was the chloride retention. It seemed to depend strongly on the membrane and this phenomenon is discussed in more detail in Section 5.1.2.3.

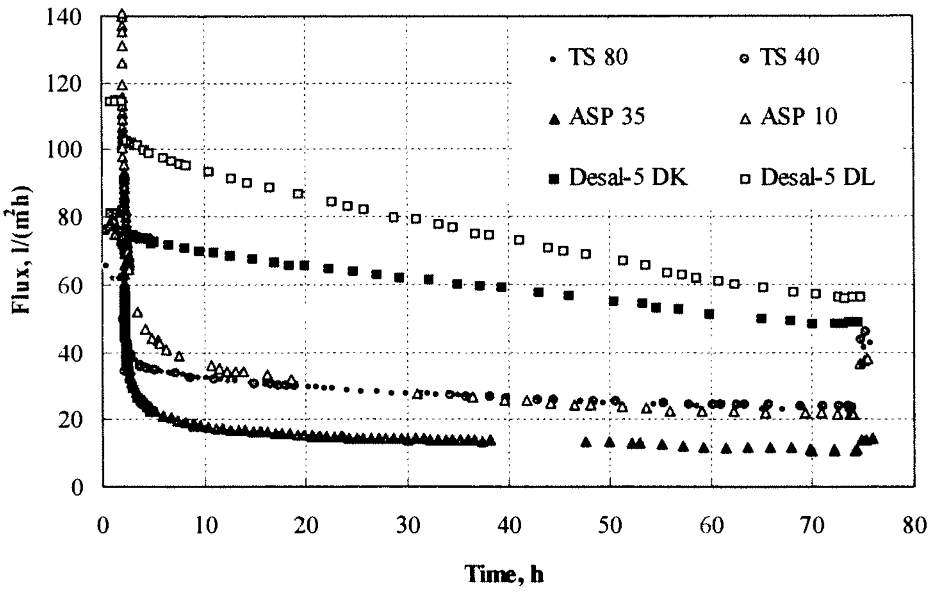

Fig. 3. Permeate fluxes in the filtration of grinder room effluents using NF membranes (pressure, 10 bar; 6 m/s; 45 °C; feed was clarified 3 h before filtered).

Table IV. Fouling and retentions of some lump parameters and compounds at the beginning and at the end of three-day filtrations of grinder room effluent (* average value from three 72-hour filtrations; 10 bar, 6 m/s, 45 °C).

Membrane	PWF $l/(m^2h)$	FR(72 h) %	**FR_{pwf} %**	Total carbon %	Conductivity %	Sulfate %	Chloride %
Desal-5 DK	74 *	47 *	**19 ***	85 → 94	84 → 95	99.7 → 99.9	56 → 11
Desal-5 DL	110 *	65 *	**24 ***	83 → 94	82 → 93	99.7 → 99.9	48 → 3
TS 80	62	63	**31**	96 → 98	94 → 96	99.9 → 99.9	94 → 95
TS 40	76	69	**39**	78 → 83	61 → 63	80 → 77	23 → 13
ASP 35	72	85	**80**	83 → 89	71 → 74	96 → 97	62 → 62
ASP 10	177	88	**79**	70 → 76	59 → 59	84 → 77	29 → 4
TFC ULP	50	77	**28**	91 → 96	86 → 91	97 → 97	88 → 86
TFC S	96	81	**53**	90 → 94	79 → 83	98 → 95	87 → 81
NTR-7450	128	90	**87**	73 → 89	68 → 82	98 → 99	60 → 64
NF-PES-10	52	82	**59**	59 → 69	63 → 69	93 → 93	21 → 4
NF 200	150	71	**53**	94 → 98	84 → 93	100 → 100	79 → 80
PVD-1	80 *	42 *	**26 ***	85 → 94	83 → 93	99.7 → 99.8	87 → 83

5.1.2 Electrostatic interaction in NF

Ionic strength and pH have a significant effect on the charge, stability, and tendency of the solute molecules to aggregate. As a result, these parameters influence the retention and the flux in NF. In this thesis, the electrostatic interactions between the membrane and the components in the solution were investigated by changing the ionic strength and the pH of the solution.

5.1.2.1 Salt addition

The effect of charge on the retentions of three NF membranes is investigated in Paper III. Salt addition reduced the retention of charged components due to decreased electrostatic repulsion between the membrane and the dissociated components in the waste water. The charges of the membrane were shielded by cations. The retentions of a more charged membrane (TFC S) were higher than the retentions of a less charged (Desal-5) membrane when the same amount of salt was added (Paper III, Table 2). The retentions of the TFC ULP membrane were not affected by the salt addition. This means that a steric rather than a charge effect determined the retentions with that membrane.

The flux decreased after the salt addition. Salt addition influenced the solute-membrane interaction as well as the solute-solute interaction. A decrease in electrostatic repulsion between the solute molecules may result in a more closely packed and denser fouling layer resulting in a lower flux (Jönsson and Jönsson, 1996).

The effect of ionic strength (salt addition) on the water flux of the NF membranes studied here varied. When sodium chloride was added during the filtration of pure water (conductivity below 0.2 mS/m) the flux increased for the following membranes: NTR-7450 (sulfonated polyethersulfone), ASP 35 (sulfonated PS on PS), NF-PES-10 (polyethersulfone), and Desal-5 DL. An opposite effect was observed with the following membranes: Desal-5 DK, PVD-1, TS 40, TFC S, and NF 200. Their fluxes decreased after the salt addition. This apparent permeability increase can be explained by electroviscous effects. An increase in salt concentration leads to a lower zeta potential and a thinner double-layer, thus offering lower resistance to water passage (Huisman et al., 1997; Vaija et al., 1993). It seems that this effect most probably depends on the membrane material and the membrane cut-off value.

5.1.2.2 Effect of pH

Both the retention and the flux may be considerably dependent on pH. Even the pure water fluxes of some NF membranes (for instance, the flux of the Desal-5 DK membrane) were found here to vary with pH.

The retention of vanillin, as discussed in Paper VI, showed that more or less the same kind of retention can be achieved by various mechanisms. In the pH range 7-8, the retention of vanillin was the same for the NTR-7450 and the Desal-5 membranes. The NTR-7450 membrane retained vanillin mainly by charge because its retention decreased clearly at acidic pH and because its cut-off value is higher than the molar mass of vanillin. Thus, the retention of vanillin due to size exclusion was not expected. The cut-off value for the Desal-5 DK membrane is close to the molar mass of vanillin. As a result, the retention of vanillin by size exclusion was higher at the acidic pH for the Desal-5 membrane than for the NTR-7450 membrane.

A charge effect was also seen when the pH of the feed solution was changed (Papers III, IV, and VI). In most cases, the pH has an effect on the flux due to the fact that at high pH the components in paper mill effluents become more dissociated and are mostly negatively charged. Also, the NF membranes become more negatively charged with the an increase in pH (Paper VI, Fig. 1). Thus, at high pH better retention may be obtained by electrostatic repulsion forces between the membrane and the dissolved or dispersed substances. With the Desal-5 membrane, the increase in retention of COD and conductivity was almost 15% when the pH was increased from 5 to 7.5, as illustrated in Fig. 4. With other NF membranes the effect of pH was on the same level. However, by increasing the membrane cut-off value, the effect of pH diminished. For instance, with MF or looser UF membranes, pH had a negligible effect on retention. This means that in these membranes separation was due to size exclusion. Furthermore, the flux of the nanofiltration membranes (Desal-5 and TFC S) increased with an increase in pH from 5 to 8 during the filtration of the total effluent.

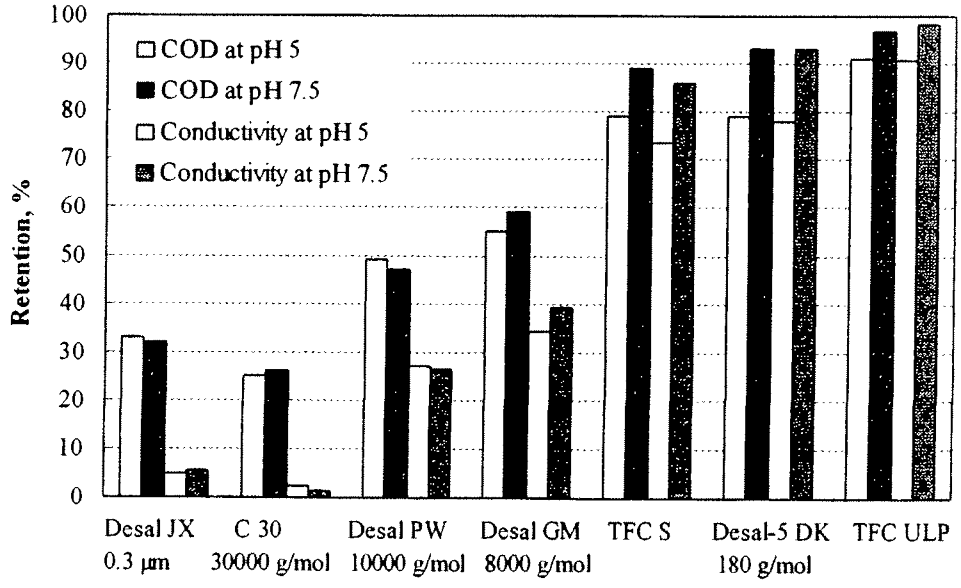

Fig. 4. Effect of pH on the retentions of different membranes (cut-off decreasing from left to right) in the filtration of total effluent (pressures from left to right 0.5, 1, 1.5, 3, 7, 10, and 10 bar, 3.5 m/s, 40 °C).

pH also affected the pure water flux of the NF membranes. For instance, the flux of the Desal-5 membrane increased by about 10% when the pH was increased from 5 to 9. Hagmeyer and Gimbel (1999) reported approximately 10-15% higher fluxes at pH 10 compared to the flux at pH 5-7.

Jönsson et al. (1988) also noticed that the flux of the most dense membranes in their study increased with an increase in pH. The reason for this phenomenon may be a change in the hydrophobic/hydrophilic properties of the membrane material. As the membrane becomes more charged, it also becomes more hydrophilic. It is possible that if nanofiltration membranes contain pore-like structures, at higher pH these may become enlarged due to stronger electrostatic repulsion between the dissociated functional groups of the membrane material (Berg, 1997). Sierka et al. (1997) have also reported an increase in permeate flux with an increase in solution pH. There, the rejections of color by a tight UF membrane (NTR-7410, cut-off 8000 g/mol) were also higher at high pH in the filtration of an acidic stage wastewater.

In the filtration of model substances (Paper VI), pH was found to be crucially important for both the flux and the fouling caused by the charged substances studied. This was clearly seen in the filtration of karaya gum. The pH and the concentration of the karaya gum solution determined the flux and the degree of irreversible fouling. At acidic pH, the NTR-7450 membrane was almost non-charged and the fouling was significantly higher than at higher pH, although the karaya solution had a negative charge at acidic pH. In this case, it seems that decreasing the electrostatic repulsion by changing the pH got the hydrophobic attractive forces between the membrane and karaya gum to overcome the electrostatic repulsion and as a result high irreversible fouling, as well as a significant decrease in permeate flux, was observed. The less hydrophobic Desal-5 DK membrane was not fouled by karaya gum because fewer binding places existed on the membrane surface, and, thus, electrostatic repulsion overcame the hydrophobic interactions.

Salt addition and a change in pH affected the retentions of the charged components. The measured lump parameters, such as COD, TC, and organic matter, consisted partly of charged substances. Their retentions increased with an increase in pH, and decreased when the ionic strength of the feed was increased. On the contrary, the substances that were measured by UV 280 nm absorption were not affected by a change in pH or by salt addition in the filtration of the total effluent or the grinder room effluent with the NF or UF membranes (Papers III and VII). Hence, they constituted the non-charged hydrophobic aromatic compounds (lignin residual) whose molar masses were relatively high (for instance, 50% seemed to be higher than 10000 g/mol in the total effluent).

It can be summarized that both salt addition and a change in pH affected the flux and the retentions. The effects were due to changes in the membrane material as well as to the changes in the solution properties. Generally, a higher pH promotes filtration and a higher ionic strength lowers filtration efficiency.

5.1.2.3 Donnan exclusion

The retention of monovalent ions in nanofiltration depends on both the membrane properties and the solution properties. In Papers II (Fig. 7) and III (Fig. 7), chloride retention can be seen to decrease with increasing sulfate concentration in the feed or with decreasing flow velocity. Ion retention is influenced partly by Donnan equilibrium. This theory was originally developed to describe the distribution of ions between solutions on either side of a membrane when some ions are not free to travel across the membrane. Here, in the filtration of the total effluent, sulfate was the controlling ion. At low salt concentrations, the fixed negative charges on the membrane surface repel all anions. To maintain electrical neutrality, positive ions are retained as well. For a higher ionic strength, the membrane charge will be shielded to a large extent. This results in a lower effective charge and, consequently, a lower retention is obtained. Therefore, Donnan exclusion is reduced at high feed electrolyte concentrations. The higher the concentration of the impermeable ion (sulfate) in the solution, the higher will be the concentration of chloride ions in the membrane. The impermeable sulfate anion will push the chloride in the membrane towards the permeate side. Peeters (1997) investigated the Donnan phenomenon in NF and summarized that Donnan equilibrium is dependent on the salt concentration, the fixed charge concentration in the membrane, the valence of the co-ion, and the valence of the counter-ion. With salt mixtures, like the effluents used in this thesis, the differences in diffusion coefficient and Donnan equilibrium strengthen the effect of each other, for instance, the diffusion coefficient of chloride is higher than that of sulfate. Hence, even negative chloride retentions may be obtained with NF membranes (Comstock, 1989; Rautenbach and Mellis, 1994; Tsuru et al., 1991). In this thesis, the highest negative chloride retention was - 80%.

This special property of some NF membranes, as discussed above, has been used by Levenstein et al. (1996) to enhance NaCl removal from a solution of water-soluble organic dye. They added an ionized polyelectrolyte with a high molar mass to the feed and, as a consequence, salt retention decreased from 50% to -68%. Furthermore, this effect is employed in the separation of sodium chloride from cheese whey (Raman et al., 1994). In this process the cheese whey is retained by the membrane while the salt is passed.

According to Peeters (1997), NF membranes can be classified into two main categories:

a) membranes for which Donnan exclusion seems to play an important role
b) membranes for which retention is neither completely determined by Donnan exclusion nor by size effects

In this thesis, the PVD-1 and ASP35 membranes belong to the first membrane category. Furthermore, the Desal-5 membrane seems to belong to the first category. The NF45 and TFC S membranes belong to the second group. Table 2 in Paper III shows that the Desal-5 and the TFC S membranes behaved very differently when salt was added. The chloride ion retentions for the TFC S membrane were higher than those for the Desal-5 membrane even though the retentions of other substances were approximately the same. The retention of sodium chloride by the Desal-5 membrane decreased significantly in accordance with the Donnan exclusion theory, but the retention of the TFC S membrane was only slightly affected by salt addition. The explanation may lie with the charges of the membranes. The TFC S membrane is more negatively charged than the Desal-5 membrane (Childress and Elimelech, 1996; Väisänen, 1998).

5.2 Effect of filtration parameters on flux and retention

Filtration parameters, such as temperature, pressure, crossflow velocity, and recovery, influence the flux and retention in NF. In addition, the pH and the solution chemistry have a considerable influence on the performance of NF, as discussed above.

5.2.1 Effect of temperature on flux and retention

Most paper machines in use today operate in the temperature range between 45 and 60 °C (Panchapakesan, 1992). In addition, closure of water systems will likely increase the temperature of the effluents. Therefore, it is required to know the temperature resistance of NF membranes with these effluents. In this thesis, the effect of temperature on the pure water flux, as well as on the waste water flux, was studied.

Generally, an increase in temperature improved the flux due to the fact that the viscosity of the solution decreased with temperature. The relatively high temperature of the effluents helps the filtration of these effluents. The effect of temperature on the flux and retention in the filtration of paper mill total effluent is investigated in Papers III and IV. The increase in flux at the beginning of the total effluent filtrations (Paper III, Fig. 3) was very close to what could be expected due the viscosity effect. Nevertheless, the flux decreased more rapidly as a function of time when the highest temperature was used.

An increase in temperature slightly decreased the retention of components in the filtration of total effluent. In the filtrations of grinder room effluent with the Desal-5 membrane, a wider temperature range was studied. The retention of TC decreased from 83 to 68% when the temperature was increased from 23 to 55 °C. Before the effect of temperature on the flux was measured, an 18-hour filtration at a pressure of 8 bar and a temperature of 35 °C was carried out in order to stabilize the flux. Figure 5 shows the retentions of TC and conductivity for three NF membranes and the fluxes when the temperature was increased from 23 to 55 °C.

The retentions of TC for the NF membranes studied here (Fig. 5) clearly decreased with increasing temperature, but the conductivity retentions were not affected. The diffusion of organic substances increased with temperature, thus decreasing the retentions. The conductivity is mostly a measure of dissolved salts and its retention is dependent on the concentration difference in the membrane according to the solution-diffusion model. Therefore, the retention of conductivity decreased negligibly with increasing temperature. Similar results were reported by Sierka et al. (1997). They observed that rising temperature increased the flux of a UF membrane (NTR-7410, cut-off 8000 g/mol) and decreased the retentions of organic matter in the filtration of an acid stage waste water. Furthermore, the retention of total dissolved salts was not temperature sensitive, but the retentions of TOC and color decreased with an increase in temperature due to the higher diffusion of organic matter at elevated temperatures.

When the temperature was subsequently decreased from 55 to 25 °C and the fluxes were measured, the Desal-5 and the PVD-1 membranes were found to have the same fluxes as they had during the increasing temperature part of the cycle. With the NF 200 membrane, the flux was lower than during the increasing temperature part of the cycle. The same phenomenon was seen with pure water. This indicates changes in the membrane morphology. The same effect has been reported by Yao et al. (1994). They found that a high temperature may permanently reorient the polymer chain of an open membrane due to its less dense polymer structure compared to that of a tight membrane. Therefore, the performance characteristics are different when the operating temperature is returned to room temperature.

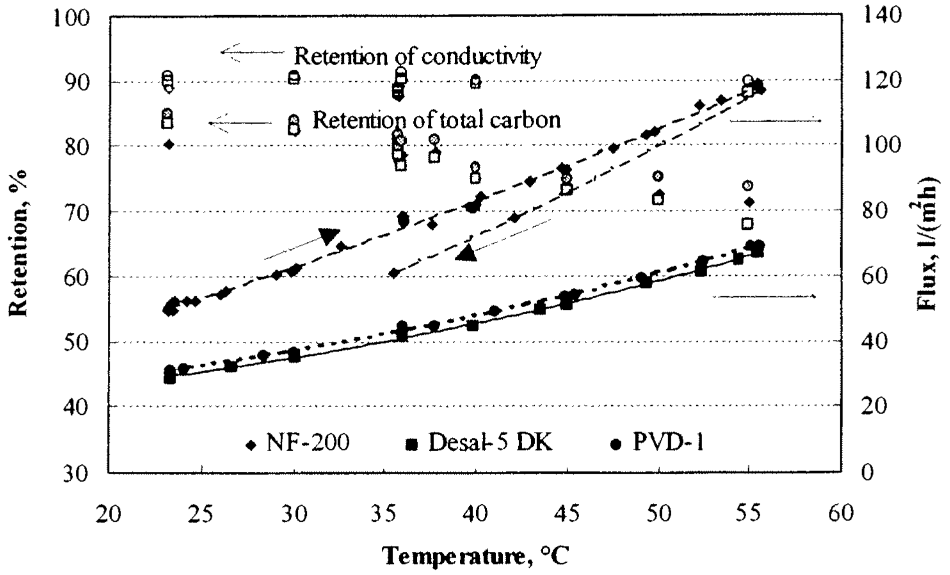

Fig. 5. Effect of temperature on the retentions and the flux in the filtration of grinder room effluent with three nanofiltration membranes (10 bar, 3.2 m/s, pH 4.5; Feed: conductivity, 57 mS/m; TC, 120 mg/l).

Comparing fluxes under constant flow velocity (Paper III, Fig. 3) indicates that increasing temperature increased the flux due to a decrease in viscosity, but, with time, the flux decreases more rapidly than that at a low temperature. It should be noted that if the filtration is operating without fouling at a low temperature, an increase in temperature causes increased concentration polarization and thus may cause increased fouling because the critical flux is exceeded. However, the fouling may still be lower in a temperature-enhanced filtration than in a filtration where pressure is used to obtain the same increase in flux. This is because the increase in temperature also increases the back diffusion and the solubility of the solutes.

5.2.2 Pressure as the driving force in NF

During recent decades, the permeabilities of NF membranes have improved considerably. Today, NF membranes with pure water permeabilities above 10 l/(m^{2}h bar) are available (Table III). Several manufacturers recommend pressures below 10 bar for their NF membranes. In this thesis the effect of pressure on flux and retentions was investigated on a laboratory scale (Papers II-IV and VII) and on a pilot scale with a spiral-wound element (Paper V).

Figure 6 shows the effect of pressure on concentration polarization. Increasing the pressure increases the convection of solute towards the membrane surface, and as a result the flux increases. However, if the solute is retained, the concentration at the membrane surface will increase, which will reduce the flux. In this study, a high pressure was observed to lower the permeate flux more than a low pressure (Papers III and IV). For instance, the permeate flux reductions during the filtration of total effluent increased significantly above a pressure of 10 bar. Thus, the permeate fluxes in the filtration of the total effluent were the same, approximately 70 l/(m^{2}h), after three hours of filtration at pressures of 10, 12, and 14 bar (Paper III, Fig. 4). This indicates that a flow velocity of 3 m/s was not high enough to prevent concentration polarization when pressures higher than 10 bar were used. It was also shown that the use of a high pressure may even decrease the flux. The formation of a gel layer or a cake might be the reason for that phenomenon (Paper VII, Fig.4). This is discussed in more detail in paper VII.

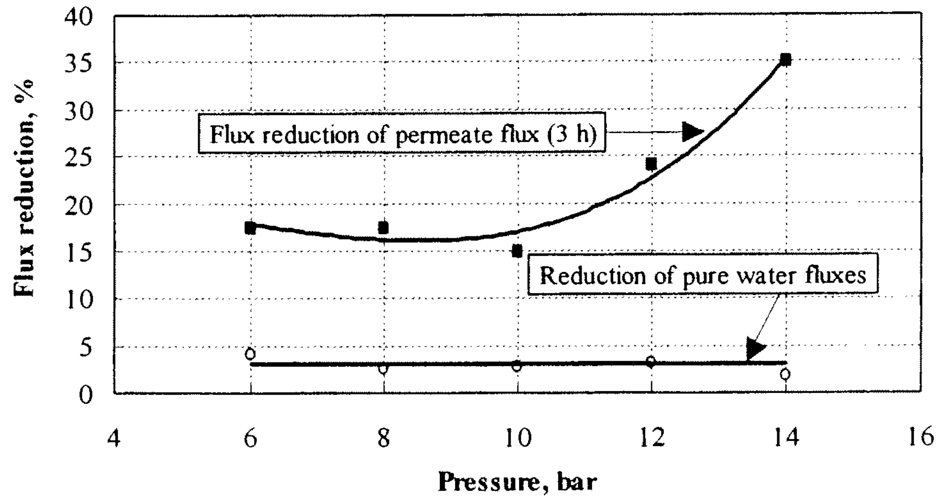

Fig. 6. Reductions of pure water fluxes (irreversible fouling) and flux reduction of permeate flux (relative difference between PWF$_b$ and permeate fluxes at 3 h) as a function of pressure in the filtration of total effluent (Desal-5, 3.1 m/s, 40°C, pH 4.9).

The retentions of COD and conductivity increased somewhat at higher pressures. For instance, the COD retention increased from 72% at 6 bar to 79% at 10 bar. When a pressure above 10 bar was used, the retention of COD decreased slightly due to a higher concentration on the membrane surface, while the concentration gradient inside the membrane increased due to the transport of permeable components.

In the filtrations of the paper mill 0-water (Paper V) with the Desal-5 spiral-wound element, an increase in pressure caused a more rapid decrease in permeate flux. In these filtrations, the optimum pressure seemed to be 5.5 bar, or less. In the continuous mode filtration the high pressure also promoted irreversible fouling, as can be seen from Fig. 7. This was not seen in the batch mode laboratory-scale experiments where irreversible fouling was roughly the same and independent of the filtration conditions (Fig. 6).

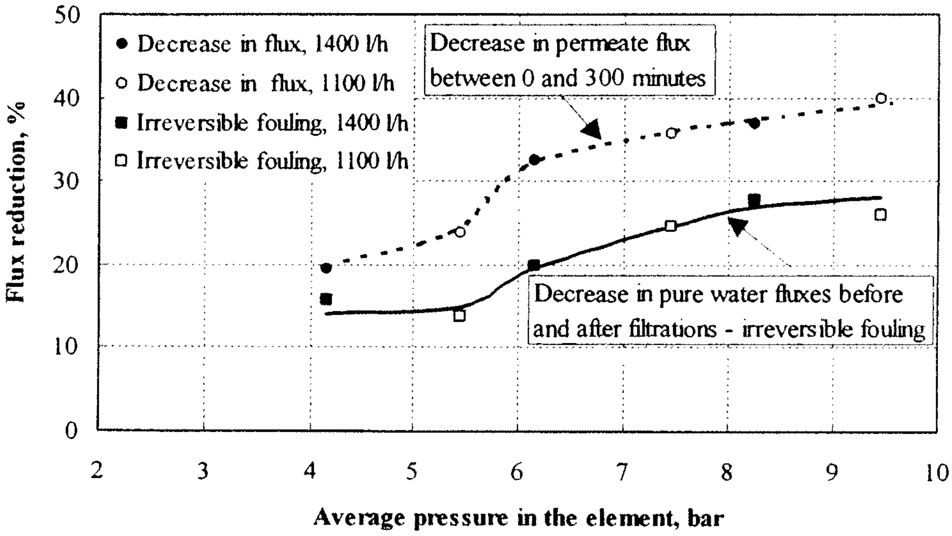

Fig. 7. Flux reductions at different pressures in the filtration of 0-water using a spiral-wound element (Desal-5 DL, pH 7.8, recovery 40%).

5.2.3 Importance of flow velocity

Turbulence (shear rate) is crucially important in the management of concentration polarization and the fouling caused by it. C30 membranes are commonly used in CR-filters for the ultrafiltration of paper mill effluents because of their high hydrophilicity and non-fouling properties. In Finland, at the Kirkniemi paper mill, permeate fluxes for the C30 membrane in CR-filters have been over 300 l/(m^2h) at a pressure below 1 bar (Anonymous, 1997). In this study, on the laboratory scale, the flux of total effluent for the C30 membrane was only 120 l/(m^2h) after three hours of filtration and it was still decreasing. The differences in these cases arise due to the effluent itself and also the crossflow velocity. In the CR-filter the crossflow velocity was about 10 m/s whereas in the laboratory-scale module it was only 3 m/s. This shows how important the crossflow velocity is for UF membranes. Generally, the influence of the crossflow velocity increases as the permeability of the membrane increases (Nuortila-Jokinen et al., 1998; Zaidi et al., 1992). The results in this thesis (Paper III, Fig. 6, and Paper VII, Figs. 4 and 5) show the importance of turbulence, or shear rate, in nanofiltration as well. Thus, new modules and filters with high shears, such as the CR-filter, are also needed in NF.

In the filtrations of paper mill total effluent at 10 bar, concentration polarization was negligible when the crossflow velocity was higher than 3 m/s (Paper III, Fig. 6). Above that crossflow velocity, the turbulence was sufficiently high to minimize the concentration polarization layer and its effect on the flux. It was also seen here that this concentration polarization layer consolidated during filtration at lower crossflow velocities. A consolidation of the secondary layer was very clearly observed when the critical flux was determined in the filtration of the grinder room effluent with the Desal-5 DK membrane (Paper VII, Fig. 12).

In addition, the crossflow velocity had an influence on the Donnan effect (Paper III). At lower crossflow velocities the ionic strength increased on the membrane surface and as a result the chloride retention decreased to a negative value, as discussed in Section 5.1.2.3.

5.2.4 Effect of recovery on flux and retention

Generally, an increase in the concentration of the effluents reduced the flux. In Paper VI, the effect of concentration on the flux of model substances was investigated. In those filtrations a model substance was added gradually to the feed solution and the stabilized flux was measured. The flux decreased significantly with an increase in model substance concentration. For some model substances, the flux was increased by increasing the flow velocity or pH.

Three-day filtrations with grinder room effluent using various NF membranes were carried out by recycling the concentrate and removing the permeate. The volume of the feed solution was kept constant by supplying new feed at the same flow rate as that of the permeate exiting from the system. Figure 8 shows the fluxes as a function of recovery. The flux decreased linearly as a function of recovery up to 60%. After that the concentration polarization layer became more compressed and the flux decreased more rapidly. The fluxes of precleaned membranes were markedly higher than those of virgin membranes. The effect of precleaning on the performance of NF membranes is discussed in the following section.

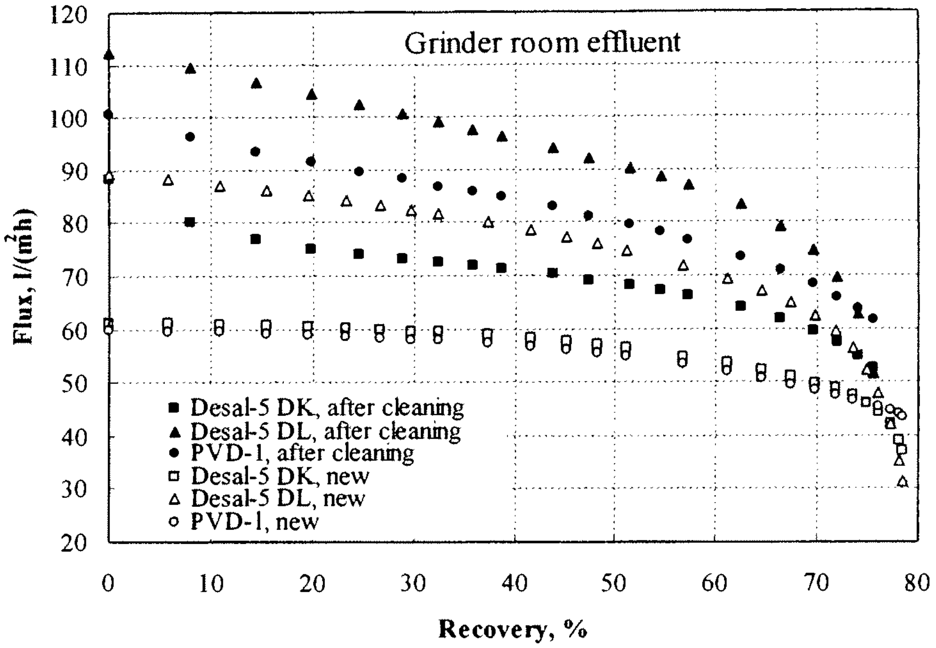

Fig. 8. Permeate flux in concentration mode filtrations of grinder room effluent (10 bar, 6 m/s, 45 °C, pH 4.8-5.2, precleaned using 0.5 w-% Ultrasil 10).

5.3 Pretreatment of membranes and effluents

5.3.1 Effect of an alkaline cleaning agent on the pure water permeability

In this study precleaning the NF membranes with an alkaline cleaning agent (Ultrasil 10) improved the pure water permeabilities (Fig. 9). The increase in the pure water flux was normally between 0 and 30% for an Ultrasil 10 concentration of 0.25 w-%, as illustrated in Fig. 9. A significant (over 20%) improvement in flux was obtained with the Desal-5 membranes (DL and DK) and with the NF 200 membrane. Using higher concentrations of the Ultrasil 10 solution, the pure water flux of the Desal-5 membrane increased even more (Paper II, Fig. 6). The permeabilities of some NF membranes increased after being precleaned with a sodium hydroxide solution (pH 10.5). This increase was lower than that obtained with the cleaning agent.

Jonsson (1991) obtained about a 165% increase in water permeability using an alkaline cleaning agent (Ultrasil 10). However, the selectivity decreased at the same time. This was explained as being related to an increase in the swelling of the membrane material (Jonsson, 1991).

Jönsson et al. (1988) and Nyström and Zhu (1997) used the same cleaning agent and found the flux to increase considerably during precleaning. They assumed that the detergent was adsorbed onto the hydrophobic parts of the membrane and that the charged groups were directed towards the water solution. This means that the membrane became more hydrophilic and more charged after cleaning. The charges then repelled each other and thus opened the pores more. Cleaning agents not only solubilize adsorbed material, but they also serve as wetting agent. Nyström and Zhu (1997) also assumed that the detergent may partly improve the flux by cleaning the pores of materials that remain after the membrane preparation process and cannot be removed by water cleaning. Furthermore, the modifying reaction was more prominent at higher temperatures. When hydrophobic and hydrophilic membranes were compared, they found that the charge in the pores had changed only with the hydrophobic membranes, although the flux increased with both type of membranes.

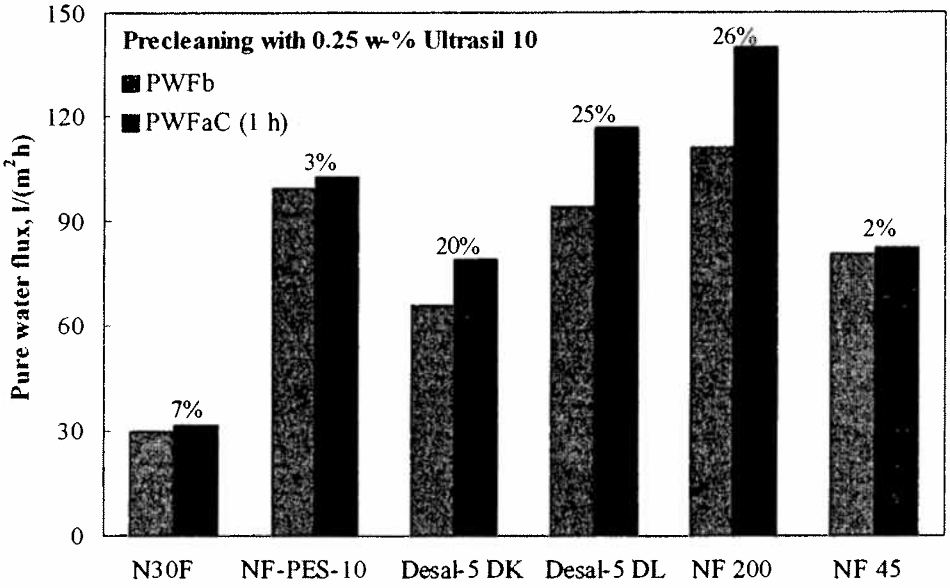

Fig. 9. Effect of membrane precleaning with an alkaline cleaning agent (Ultrasil 10, 0.25 w-%) on the pure water flux of some NF membranes (Precleaning: first 10 min filtration at 2 bar, 3m/s, 40 °C and then 10 min at rest; the values on the top of the columns are the respective increases in pure water flux after cleaning).

5.3.2 Humic acid as a foulant or as a means of improving flux

An interesting phenomenon was observed when humic acid (from Aldrich, used as delivered) was filtered with the nanofiltration membranes. At an acidic pH, humic acid fouled the membrane slightly (Paper VI). An opposite effect was observed in the pH range 7-8. The same effect was seen after adsorption experiments, as illustrated in Fig. 10. The pure water fluxes increased for the Desal-5 DK and DL, NF 200, PVD-1 and TFC S membranes. Humic acid adsorption was also carried out with other NF and UF membranes. The flux was not observed to increase with polyamide (TFC ULP), aromatic polyamide (TS-40, NF 45), or sulfonated polysulfone (ASP-35) membranes.

The small increase in the flux of the sulfonated polyethersulfone (NTR-7450) membrane may be caused partly by an electroviscous effect (Section 5.1.2.1). The flux of the membrane increased slightly as salt was added to the feed during the filtration of water (conductivity <0.2 mS/m before salt addition). This apparent permeability increase can be explained by electroviscous effects as discussed previously.

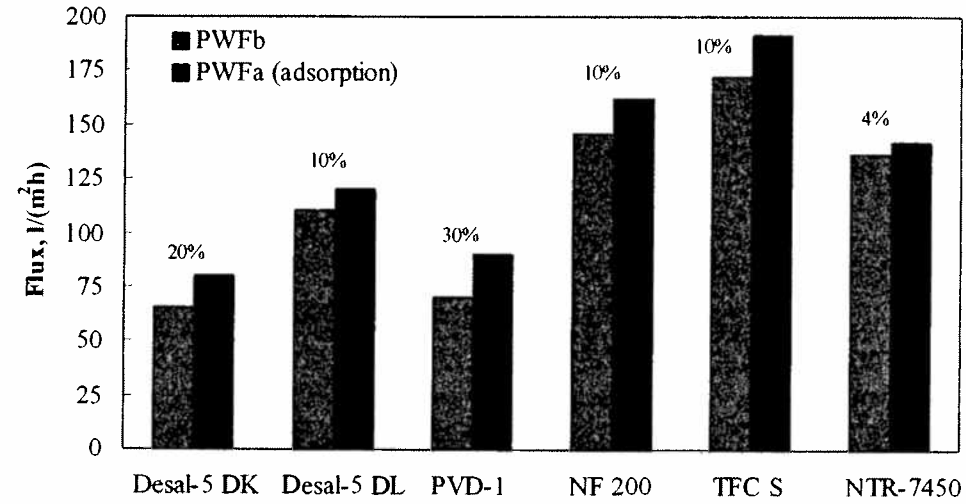

Fig. 10. Effect of humic acid adsorption (600 mg/l) on the pure water flux of NF membranes at 10 bar and 40 °C. Conditions during the 18-h adsorption tests: flow velocity 0.2 m/s, no applied pressure, temperature 40 °C (the values on the top of the columns are the respective increases in pure water flux after adsorption).

The adsorption of humic acid onto the membrane, and its effect on the membrane charge, has been studied by, for instance, Elimelech et al. (1994) and Childress and Elimelech (1996). Using streaming potential experiments, Childress and Deshmukh (1998) showed that humic macromolecules adsorb onto the membrane surface, and that the negatively charged functional groups of the humics dominate the membrane surface charge. In their study, adsorption of the humic macromolecules caused a change in the zeta potential of polyamide- and cellulose acetate-based RO membranes from positive to negative at low pH. According to their results, the adsorption of humic acid occurs at low pH because of both electrostatic and hydrophobic interaction. At higher pH values, where humic acid and the membranes are similarly charged, adsorption is probably dominated by hydrophobic forces. Thus, it is possible that the hydrophobic parts of the humic molecules bind to the similar groups on the membrane and the membrane becomes more hydrophilic on the outside. This causes the increase in flux.

5.3.3 Effect of membrane pretreatment on effluent flux and retention

The precleaning of the Desal-5 DK membrane with an alkaline cleaning agent (Ultrasil 10) was investigated in Papers III, IV, and VII. Although the effluent flux increased by nearly 100%, the retentions for the precleaned membranes remained almost the same as the retentions for the original membranes (Paper IV, Fig. 6). An increase in the chloride retention showed that the charge of the membrane had increased during the pretreatment.

The experiments with the grinder room effluent showed that the permeate fluxes of pretreated membranes were higher than those of virgin membranes. Nuortila-Jokinen et al. (1996b) reported a similar phenomenon with tubular NF membranes. In addition, it was clearly seen that the pure water fluxes of the pretreated membranes after the filtrations were also significantly higher than those of the virgin membranes (Paper VII). As illustrated in Fig. 11, the fluxes of the grinder room effluent increased linearly in the pressure range 2-15 bar. At the commencement of the filtration (i.e., at 2 bar), the permeabilities of the effluents were 17, 22, and 25% lower than the pure water permeability for untreated, humic acid treated, and Ultrasil 10 treated membranes, respectively. These values were significantly higher than what was caused by irreversible fouling. Therefore, it also seems that reversible fouling causes a decline in flux. The amount of reversible fouling did not increase during the filtration, but stayed constant because the relative difference between the pure water and the effluent flux stayed the same (around 25%). This was independent of the pretreatment. Thus, no further fouling was seen after the first 30 minutes of filtration. Therefore, concentration polarization was not the reason for the flux decline as its effect should increase with pressure. The same is true with the osmotic pressure.

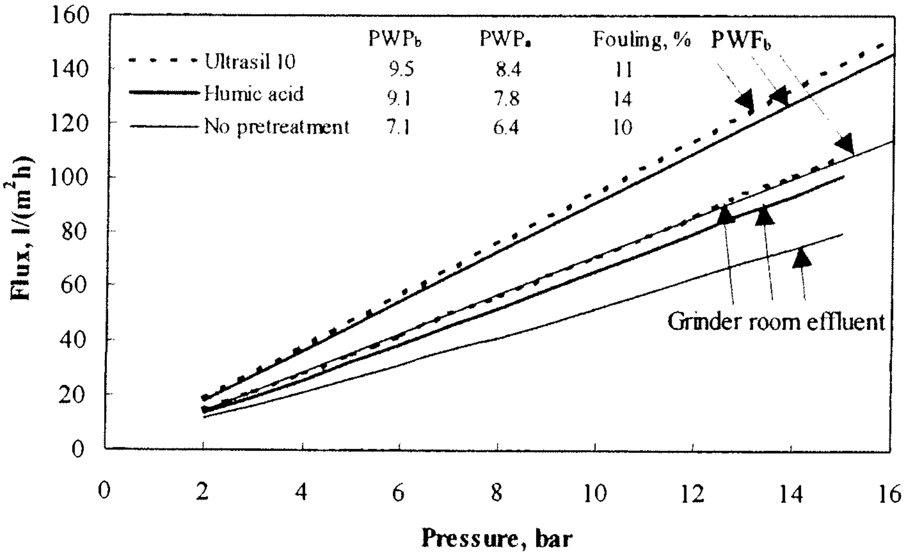

Fig. 11. Fluxes of pure water and grinder room effluent as a function of pressure for the pretreated and untreated Desal-5 DK membrane (3.2 m/s, 40 °C, pH 5-6, Feed: conductivity, 120 mS/m; TC, 700 mg/l).

TC retention increased with pressure (6 → 16 bar) from 87 to 91% for the virgin membrane, and from 86 to 90% for the pretreated membrane. Thus, pretreatment had only a minor effect on the retentions. The effect of pretreatment on the irreversible fouling of the membranes was very small (Fig. 11). Hence, it can be concluded that the modification caused by the pretreatment of the membrane was permanent, at least during the filtration time of 54 h used in these experiments.

5.3.4 Mechanical pretreatment of effluents

One method of decreasing fouling is pretreatment of the feed solution (Paper I). When modules with very thin flow channels are used, proper pretreatment is crucial. These kinds of modules are hollow-fiber modules and spiral-wound modules. In this thesis, the paper mill 0-water was filtered with a spiral-wound element using a multilayer filter as a pretreatment method (Paper V). The multilayer filtration decreased the fouling and improved the flux slightly. However, the flux was still very low, namely about 19 l/(m^2h) at 40 °C and at 5.5 bar after a one-day filtration. The reason for this was insufficient turbulence on the membrane surface. Therefore, the concentration polarization layer restricted the flux and this layer promoted, or even transformed into irreversible fouling during the filtration.

5.4 Irreversible fouling and its management

Different causes of fouling were observed in this thesis. Generally, fouling can be divided into reversible fouling and irreversible fouling. Reversible fouling disappears when the filtration is stopped and the membrane is rinsed with pure water. Thus, it includes the effects of concentration polarization and gel layer or cake formation. Concentration polarization is a common feature in all pressure-driven membrane processes. It is dependent on the operating parameters such as pressure, crossflow velocity, temperature, and feed concentration, for instance. In this study, irreversible fouling includes all that which is not removed by pure water flushing. It includes the effects of plugging of the membrane and adsorption, which is mostly an irreversible phenomenon.

5.4.1 Fouling by the plugging mechanism in NF

The fluxes of the ultrafiltration membranes studied here decreased rather quickly. In addition, the membranes had relatively high degrees of irreversible fouling. This was probably caused by high concentration polarization during the filtration and by pore plugging. For instance, the flux of the C30 membrane during the filtration of total effluent decreased from a pure water flux of over 200 down to 120 l/(m^2h) during 3 h of filtration at 1 bar. The adsorptive fouling of this membrane should be negligible according to Dal-Cin et al. (1996b). Therefore, it can be stated that the decline in the flux of the C30 membrane was mostly due to pore plugging and concentration polarization.

The fluxes in the nanofiltration of effluents in this thesis were always lower than the pure water fluxes before the filtrations. This was clearly seen in the critical flux experiments (Paper VII), which indicated that only a weak form of the critical flux existed in the filtration of the effluents. The decrease in the permeate flux from the pure water flux value occurred immediately after the filtration was started even though a very low pressure was used. Therefore, the decrease in flux was assumed to be caused by adsorption onto the membrane or by plugging of the free space in the membrane material. It can be assumed that tight NF membranes do not contain pores. This means that the fouling caused by pore plugging is negligible and a low degree of irreversible fouling is caused by adsorption. However, on the other hand, the nominal "pore" distributions of commercial NF membranes are not very monodisperse. There may exist larger pores than an average cut-off value indicates. Therefore, it might be so that the lower flux at the very beginning of the filtration was due to the plugging of some of the larger pores or free space in the membrane. Usually, the flux was rather stable after this initial fouling if the filtration was carried out below the critical flux, see, for instance, Fig. 4 in Paper III. Thus, the adsorption or plugging did not increase with time.

Figure 12 illustrates that even in NF membranes plugging exists. The Desal-5 DK and the Desal-5 DL membranes are made from the same material. They differed in their pure water permeabilities. As can be seen in Fig. 12, the membrane, that has a higher permeability immediately fouled to some degree. This decrease in the permeate flux was not due to concentration polarization, as can be seen by comparing the differences in the pure water fluxes and the permeate fluxes at the same permeate flux. Furthermore, in this case adsorption should be the same for both membranes. Thus, it seems that a small amount of fouling is due to a plugging mechanism. Cohen and Probstein (1986) suggested that the initial fouling resulted from a first-order physico-chemical reaction between the foulant and the membrane. The reaction time scale was estimated to be less than a second. This implies that most of the adsorption and pore plugging is essentially instantaneous, as was observed in this study.

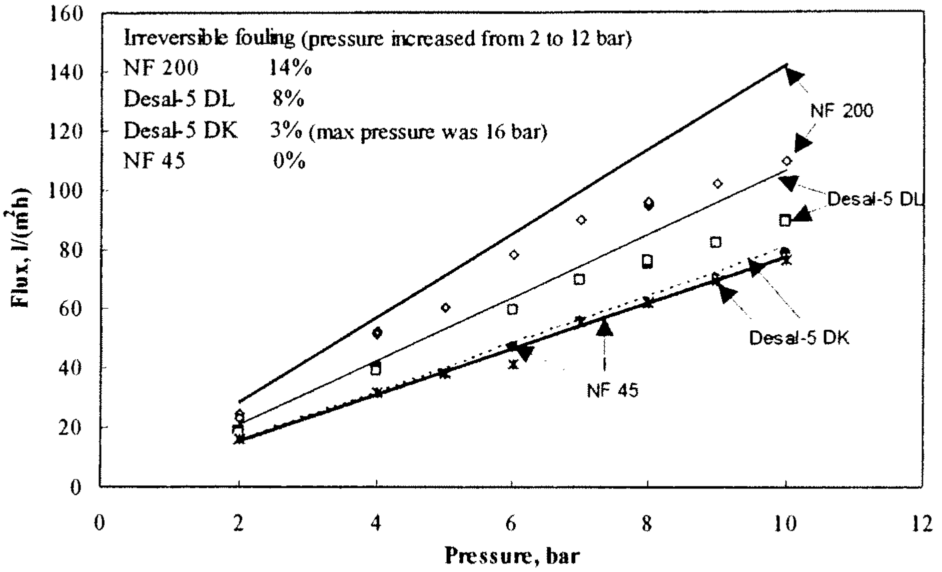

Fig. 12. Effect of pressure on flux in the filtration of locust bean gum at a concentration of 100 mg/l (3 m/s, pH 4.6, 40 °C, straight lines indicate pure water fluxes and points indicate flux values measured with increasing pressure).

5.4.2 Influence of hydrophilicity / hydrophobicity on irreversible fouling

Membrane hydrophobicity has an effect on flux and fouling, and sometimes also on retentions. Generally, hydrophilic membranes have a higher water flux and suffer less fouling by adsorption than more hydrophobic membranes. For instance, membranes like C30 (regenerated cellulose UF membrane) and PVD-1 (polyvinyl alcohol derivative NF membrane) are known to be very hydrophilic in their characteristics (Jönsson C. and Jönsson A.-S., 1995; Väisänen, 1998). Dal-Cin et al. (1995) evaluated a wide range of membrane materials with a pulp mill effluent with respect to adsorptive fouling. Hydrophilic regenerated cellulose membranes experienced negligible adsorptive fouling, whereas they found severe fouling to occur with hydrophobic polysulfone and polyethersulfone membranes. Although the relative fluxes after adsorption at a temperature of 50 °C for the same membrane material (different manufacturers) varied considerably, they found that the most hydrophobic materials had the lowest relative fluxes after the adsorption tests. With the Desal-5 and the C30 membranes no adsorptive fouling was found (Dal-Cin et al., 1996b). Several studies with proteins also show higher adsorption of the proteins onto hydrophobic membranes than onto hydrophilic membranes (Ko and Pellegrino, 1992; Crozes et al., 1993; Jucker and Clark, 1994; Nyström et al., 1998).

In this study, the adsorptive fouling of the most hydrophilic membrane, namely, the PVD-1 membrane, was negligible, as illustrated in Fig. 13. Model substances, such as karaya gum and locust bean gum, were not observed to adsorb onto the surface of the PVD-1 membrane. A small amount of adsorption of the model substances occurred with the Desal-5 membrane, whereas the adsorption was dramatically higher for the hydrophobic NTR-7450 membrane. Irreversible adsorption increased considerably with the hydrophobicity of the membrane studied.

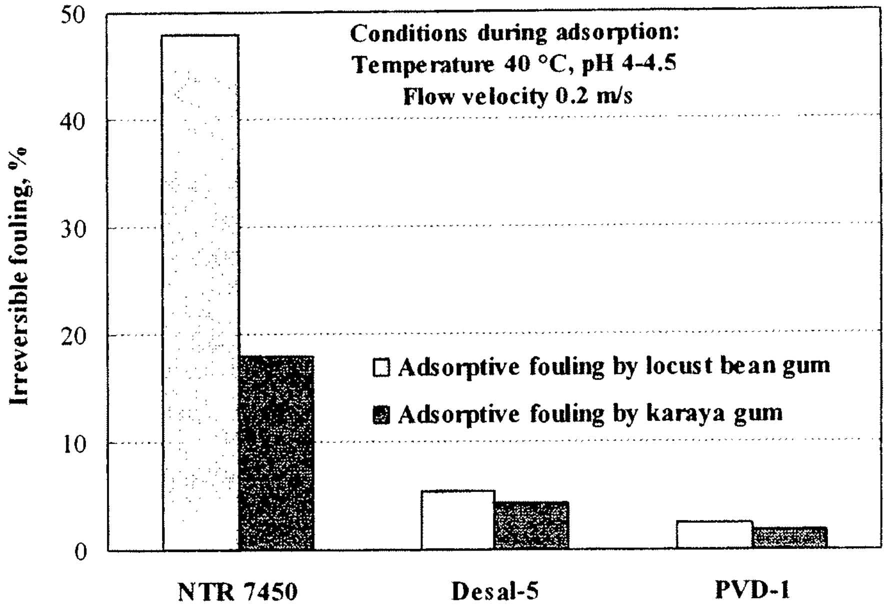

Fig. 13. Adsorptive fouling of locust bean gum and karaya gum (adsorption conditions: concentration of foulant 125 ppm, feed volume 18 l, pH 4-4.5, flow velocity 0.2 m/s, no applied pressure, 40 °C, duration 18 h).

5.4.3 Irreversible fouling in the laboratory- and pilot-scale filtrations

The irreversible fouling was observed to be rather independent of the filtration conditions (crossflow velocity, pressure, and temperature) in the laboratory-scale batch mode filtrations where the foulant concentrations were low. Thus, the decline in flux during the filtration was mostly caused by concentration polarization and other types of reversible fouling. Filtration conditions, such as pressure and flow velocity, markedly influenced concentration polarization and reversible fouling (Fig. 6). Furthermore, pH influenced both the permeate flux and the irreversible fouling, as was seen in the filtrations of the model substances. In the continuous mode filtrations with a spiral-wound element, the filtration conditions affected both the reversible and the irreversible fouling (Fig. 7). An increase in pressure gave a higher concentration polarization and thus promoted irreversible fouling.

The irreversible fouling of the various membranes differed considerably. The higher irreversible fouling was measured for more open NF membranes when membranes of the same material were compared, as was seen in Table IV. The membrane material also has an influence on irreversible fouling. The lowest irreversible fouling values were measured with the Desal-5, the NF 45, and the TFC ULP membranes in the filtration of total effluent. These membranes were also the tightest NF membranes. The irreversible fouling of the hydrophobic NTR-7450 membrane was high with all the effluents and model substances filtered. For instance, the adsorption of locust bean gum at an acidic pH decreased the permeability of this membrane by about 50% (Fig. 13).

The Desal-5 DK and DL membranes experienced the least irreversible fouling in the three-day filtrations of the grinder room effluent. Approximately a 30% reduction of the pure water flux was measured for the PVD-1, TS 80, and TFC ULP membranes. These membranes are tight NF membranes which retained over 80% of the chloride ions at the end of the three-day filtration.

5.5 Methods of improving flux

The decrease in the permeate flux with time is a major drawback of membrane processes. Therefore, numerous methods have been developed and tested to cope with this problem. Paper I is a literature review of various methods of improving the filtration performance. In this thesis the focus is placed on how to determine the filtration conditions at which fouling would be negligible, or at which fouling could at least be minimized. This was done by providing repulsive forces between the membrane and the solutes, by improving the mass transfer from the membrane surface, and by choosing the suitable membrane.

5.5.1 Decrease of concentration polarization

A high solute concentration at the membrane surface increases the osmotic pressure, reduces the effective driving force and, in addition, makes the interaction between the foulants and the membrane possible thus promoting irreversible fouling. Concentration polarization can be reduced by manipulating the flux and the mass-transfer coefficient. The flux can be reduced by decreasing the driving pressure. If a low enough flux is used (i.e., a flux below the critical flux, see Section 5.5.3), it can even be possible to have non-fouling conditions, as was seen in Paper VII.

Concentration polarization can also be minimized through the control of mass transfer between the process fluid and the membrane. The most widely used method is to increase the turbulence at the surface of the membrane. This has been done in this thesis by increasing the crossflow velocity, or by using turbulence promoters, such as spacers. The effect of crossflow velocity is discussed in Section 5.2.3.

The use of spacers reduced concentration polarization and kept the flux stable (Paper II, Fig. 3, and Paper IV, Fig. 3a). Generally, it is assumed that decreasing concentration polarization decreases fouling. In the batch mode laboratory-scale experiments, concentration polarization had an insignificant effect on irreversible fouling. However, the flux decreased remarkably when the concentration polarization layer thickness increased.

Obviously, concentration polarization increased with an increase in recovery (Fig. 8). Therefore, by controlling the recovery it is also possible to prevent reversible concentration polarization from transforming into an irreversible gel layer and to prevent cake formation.

5.5.2 Methods of minimizing irreversible fouling

Irreversible fouling is mostly caused by pore plugging and adsorption. In NF the irreversible fouling caused by plugging is rather low because of the very tight membranes. Pore plugging is best controlled by preventing the solute from entering the membrane matrix. This can be achieved by selecting a membrane with a cut-off much smaller than that of the solute.

Adsorption can sometimes play a significant role, as was seen in Fig. 13 for the model substances. Adsorption can be minimized by choosing the correct membrane material (hydrophilic membranes adsorb less hydrophobic solutes than hydrophobic membranes) or by modifying the membrane and the solute properties so that the interactions between the membrane and the solutes are minimized. In this thesis, less adsorption was observed with the hydrophilic membranes and when electrostatic repulsive forces existed (Paper VI).

5.5.3 Critical and limiting flux in NF

In Papers III, IV, and VII the critical flux in nanofiltration was investigated. This was defined as the highest achievable flux without the occurrence of concentration polarization or fouling. By definition, the flux is equal to the critical flux when the convection towards the membrane is equal to the solute back-diffusion away from the membrane surface. Two forms of critical flux can be distinguished; a strong form and a weak form. The strong form of the critical flux exists when the flux up to a point is equivalent to the corresponding pure water flux at the same pressure. If the flux deviates from the pure water flux, but increases linearly with pressure, its deviation point from linearity is called the weak form of the critical flux (Field et al., 1995). The limiting flux is defined as the highest possible flux that may be obtained by increasing only the pressure.

5.5.3.1 Parameters that affect the critical flux

In this thesis, the critical flux of NF membranes was studied. The effects of parameters such as flow velocity, concentration, membrane precleaning, and pH on the critical flux were investigated. The critical fluxes of total effluent and grinder room effluent, as well as that of a high molar mass polysaccharide (locust bean gum), increased markedly with an increase in crossflow velocity. The forms of back-transport, like lateral migration and shear-enhanced diffusion, for example, are greater at higher crossflow velocities. Therefore, a higher critical flux with an increase in crossflow is expected. An increase in concentration decreased the critical flux as was expected. The critical flux for the grinder room effluent was also somewhat higher at a higher pH. The effect of pH on the filtration performance was discussed in Section 5.1.2.2.

Precleaning the membranes with an alkaline cleaning agent (Ultrasil 10) increased the membrane pure water permeability, as discussed above (Section 5.3.1). The flux decrease at the start of the filtration was slightly higher for the precleaned membrane than for the virgin membrane (Section 5.3.3). Otherwise, the precleaned and the virgin membranes behaved in approximately the same way. The critical and limiting fluxes obtained were more or less the same. In addition, the effect of precleaning on the flux was at least partly permanent.

5.5.3.2 Usability of the critical flux

Both theoretical and experimental determinations of critical fluxes have shown that the critical fluxes are rather low for effluents in membrane filtration. In addition, internal pore plugging and adsorption may also significantly reduce the flux, even when filtering at rates under the critical flux. Pore plugging is more obvious in UF and MF, but it may have some influence on the critical flux in NF. Determination of the critical flux in the laboratory yields a condition where concentration polarization is minimized. However, if the membrane material is sensitive to adsorptive fouling and if the filtered effluent contains only foulants at low concentrations, the critical flux is rather difficult to predict reliably in the laboratory.

However, when carrying out the filtration below the critical flux, fouling is dramatically decreased. Unfortunately, working at this flux usually means that a larger membrane area is needed to obtain the same amount of permeate as when working at higher fluxes. Running a filtration plant at a flux below the critical flux means that the investment costs are higher, but the operating costs are lower than with higher fluxes because cleaning is not needed so frequently and because the applied pressure is lower.

5.6 Comparison of NF membranes

In this thesis, nanofiltration membranes were evaluated on the basis of flux, retention, and fouling. Some of the membranes seemed to work better with the effluents studied than others. However, it should be remembered that the characteristics of the effluents differ. This means that the best membrane for each effluent differed. For instance, the NTR-7410 membrane was found to have the best overall performance with the E-stage effluents from a pulp mill (Buisson, 1998), and the sulfonated polyethersulfone membranes were chosen in the VSEP module for waste water treatment at a recycle paper mill in the USA (Monroe, 1997). However, with the effluents used in this study, those membranes did not work at all well.

The most widely used and tested nanofiltration membrane in the pulp and paper industry is the Desal-5 membrane from Desal/Osmonics. This membrane is used, for instance, in two mill-scale applications in the USA (Lien and Simonis, 1995). It also worked rather well with the effluents filtered in this thesis. Another well-performing membrane was the PVD-1 membrane from Nitto Denko/Hydranautics. Its temperature limit was only 40 °C, but it was used here at temperatures over 50 °C without any damage being done. This membrane is very hydrophilic in its characteristics and its adsorptive fouling is negligible. The Desal-5 DK and the PVD-1 membranes have almost the same pure water permeability, approximately 7 $l/(m^2h\ bar)$ at a temperature of 40 °C. Nanofiltration membranes like NF 200, Desal-5 DL, and NTR-7450 have permeabilities above 10 $l/(m^2h\ bar)$ and can therefore be considered to be loose. Thus, their fluxes decreased more during the filtration experiments because of plugging.

The Donnan effect influenced considerably the retention of monovalent ions of the Desal-5 membrane. Therefore, even a negative chloride retention could be obtained. When monovalent ion retention is required membranes like the PVD-1, NF 200, TFC S, TFC ULP or TS 80 membranes are worth considering. Their retentions did not decrease significantly with increasing concentration.

6. CONCLUSIONS

This thesis has focused primarily on the parameters that influence performance in the nanofiltration of pulp and paper effluents. Parameters such as pressure, crossflow velocity, temperature, concentration of the feed, and pH, as well as the ionic strength of the feed, were studied and their influence on the process efficiency was evaluated. The effects of membrane properties, like hydrophobicity, charge, and pore size, for example, on the filtration process efficiency were also investigated. The filtration efficiency was determined by measuring the retentions and the flux obtained, and by measuring the fouling of the membranes caused by filtering the solution. Three different effluents from the pulp and paper industry and some model substances were nanofiltered.

The special properties of nanofiltration membranes are useful in the paper industry. The high retentions of nanofiltration membranes make them an attractive alternative for closing the water circulation systems of paper mills. The retentions in nanofiltration depend on the sieving effect and the solute-membrane interactions. In particular, negatively charged substances are repelled by the membranes. The retentions of charged substances were clearly dependent on the pH and the ionic conditions in the feed and on the membrane surface. Depending on the membrane, Donnan exclusion may be responsible for really high negative retentions of monovalent ions, perhaps even -80%. The Donnan effect determined the monovalent ion retention of the Desal-5 membranes. Therefore, this membrane is not suitable for applications where a high retention of monovalent ions is needed. Membranes like the TFC ULP, TS 80, NF 200, and PVD-1 membranes retained monovalent ions very well. In addition, at recovery values below 70%, the flux of the PVD-1 membrane was on the same level as the Desal-5 membranes.

With sufficiently high turbulence on the membrane surface, the concentration polarization layer could be controlled and sometimes even non-fouling conditions (after the immediate fouling at the beginning of the filtration) were obtained. Thus, a critical flux exists in nanofiltration. A strong form of the critical flux was found for some high molar mass model substances, but only a weak form of the critical flux was obtained for the effluents from the pulp and paper industry. The critical flux increased with increasing flow velocity and pH and decreased with increasing concentration. Precleaning of the membranes had only a small effect on the critical flux or the retentions obtained, but it improved the membrane permeability significantly.

The fouling of the membranes depended on such membrane properties as hydrophobicity, charge, and pore size. Generally, more fouling was found with the more hydrophobic and more open membranes. For similar NF membranes, higher fouling occurred on the one with the higher permeability. This indicates the existence of a pore plugging type of fouling like in ultrafiltration. Mostly, irreversible fouling was due to adsorption onto the membrane surface. When a strong electrostatic repulsion existed, adsorption onto the hydrophobic membranes was reduced and was even negligible for the most hydrophilic membranes. With the effluents, a small decrease in the permeate flux occurred immediately after the filtration was started. This was probably due to the plugging of larger "pores" and/or very fast adsorption onto the membrane.

By comparing the laboratory-scale filtrations to the pilot-scale ones, it was seen that with the effluents the irreversible fouling was rather low in the laboratory-scale experiments and it depended on the membrane and the effluents, but was mostly independent of the filtration conditions. It seems that a limited amount of foulants in the batch mode filtrations caused a relatively low degree of fouling of the membranes, which means that the differences between the filtrations were small. The pilot-scale filtrations with a spiral-wound element showed the difference in irreversible fouling between a batch and a continuous mode filtration. Although the decrease in the permeate flux was higher in the batch mode filtration of 0-water, the irreversible fouling was three times higher in the continuous mode filtration. Furthermore, in the continuous mode filtrations, the filtration conditions affected the irreversible fouling. An increase in the pressure decreased the flux and increased irreversible fouling in the spiral-wound element. The lower the pressure was, the lower the fouling was.

The performance of nanofiltration can be improved considerably by controlling the filtration conditions. Flow velocity, pressure, recovery rate, solution chemistry, and pH, along with the membrane properties, mostly determine the retention properties and fluxes. The crossflow velocity is especially important in preventing fouling.

With NF a permeate quality close to the quality of chemically treated fresh water was obtained. In addition, considerably less irreversible fouling was observed in NF than in UF. Thus, NF is an attractive alternative for the purification of effluents from the pulp and paper industry. During the filtrations, with NF membranes with a low adsorptive fouling, the decrease in flux was mostly caused by concentration polarization. Therefore, an acceptable flux should be obtainable by minimizing concentration polarization. Moreover, the existence of the critical flux in nanofiltration should encourage development work concerning high shear modules. Another item that requires more study is the search for an effective pretreatment method to be used in front of NF modules. For instance, using UF as a pretreatment method would allow the use of lower shear rate spiral-wound modules. In future, tailor-made membranes for particular effluents will improve the efficiency of membrane technology.

7. REFERENCES

Afonso, M. D., de Pinho, M. N., (1995). Treatment of bleaching effluents by pressure-driven membrane processes - A review, In: Membrane technology: Applications to industrial wastewater treatment, Caetano, A., de Pinho, M. N., Drioli, E., Muntau, H., (eds.), Kluwer Academic Publishers, Netherlands, pp. 63-79.

Afonso, M. D., de Pinho, M. N., (1997). Nanofiltration of bleaching pulp and paper effluents in tubular polymeric membranes, *Sep. Sci. Technol.*, **32**(16), 2641-2658.

Ahn, K.-H., Cha, H.-Y., Yeom, I.-T., Song, K.-G., (1998). Application of nanofiltration for recycling of paper regeneration wastewater and characterization of filtration resistance, *Desalination*, **119**, 169-176.

Anonymous, (1997). PM white water treatment at Metsä-Serla Kirkniemi mill in Finland, *Int. Papwirtsch.*, **3**, 72-108.

Awadalla, F. T., Kumar, A., (1994). Opportunities for membrane technologies in the treatment of mining and mineral process streams and effluents, *Sep. Sci. Technol.*, **29**(10), 1231-1249.

Beaudoin, L., Buisson, H., Zaidi, A., Lavallée, H.-C., Barbe, M., (1992). Treatment of selected CTMP and BCTMP effluents by ultrafiltration, *Proc. TAPPI 1992 Environmental Conference*, Atlanta, USA, April 12-15, Book 2, pp. 721-730.

Berg, P., Hagmeyer, G., Gimbel, R., (1997). Removal of pesticides and other micropollutants by nanofiltration, *Desalination*, **113**, 205-208.

van den Berg, G. B., Smolders, C. A., (1992). Diffusional phenomena in membrane separation processes, *J. Membr. Sci.*, **73**, 103-118.

Bowen, R. W., Mukhtar, H., (1996). Characterization and prediction of separation performance of nanofiltration membranes, *J. Membr. Sci.*, **112**, 263-274.

Bredael, J., Sell, N. J., Norman, J. C., (1996). The use of membrane technology to clean deinking effluent, *Pap. Recycling*, **6**(1), 24-31.

Buisson, H., E-mail, November 23, 1998.

Cadotte, J., Forester, R., Kim, M., Petersen, R., Stocker, T., (1988). Nanofiltration membranes broaden the use of membrane separation technology, *Desalination*, **70**, 77-88.

Cartier, S., Theoleyre, M. A., Decloux, M., (1997). Treatment of sugar decolorizing resin regeneration waste using nanofiltration, *Desalination*, **113**, 7-17.

Chaufer, B., Rabiller-Baudry, M., Guihard, L., Daufin, G., (1996). Retention of ions at various ionic strength, *Desalination*, **104**, 37-46.

Chen, G., Chai, X., Yue, P.-L., Mi, Y., (1997). Treatment of textile wastewater by pilot scale nanofiltration membrane separation, *J. Membr. Sci.*, **127**, 93-99.

Childress, A. E., Deshmukh, S. S., (1998). Effect of humic substances and anionic surfactant on the surface charge and performance of reverse osmosis membranes, *Desalination*, **118**, 167-174.

Childress, A. E., Elimelech, M., (1996). Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes, *J. Membr. Sci.*, **119**, 253-268.

Cohen R. and Probstein D. J., (1986). Colloidal fouling of reverse osmosis membranes, *J. Colloid Interface Sci.*, **114**(4) 186-195.

Comstock, D. L., (1989). Desal-5 membrane for water softening, *Desalination*, **76**, 61-72.

Crozes G., Anselme C., Mallevialle J., (1993). Effect of adsorption of organic matter on fouling of ultrafiltration membranes, *J. Membr. Sci.*, **84**, 61-77.

Dal-Cin, M. M., McLellan, F., Striez, C. N., Tam, C. M., Tweddle, T. A., Kumar, A., (1996a). Membrane performance with a pulp mill effluent: Relative contributions of fouling mechanisms, *J. Membr. Sci.*, **120**, 273-285.

Dal-Cin, M. M., Striez, C. N., Tweddle, T. A., Capes, C. E., McLellan, F., Buisson, H., (1995). Effect of adsorptive fouling on membrane performance: Case study with a pulp mill effluent, *Desalination*, **101**, 155-167.

Dal-Cin, M. M., Striez, C. N., Tweddle, T. A., McLellan, F., Ramamurthy, P., (1996b). Membrane performance with plug screw feeder pressate: operating conditions and membrane properties, *Desalination* **105**, 229-244.

Ekengren, Ö., Bjurhem, J.-E. and Filipsson, S., (1993). Treatment of bleach plant effluents by membrane technology, *Proc. TAPPI 1993 Environmental Conference*, TAPPI Press, Boston, USA, March 28-31, Book 1, pp. 403-411.

Elimelech, M., Chen, W. H., Waypa, J. J., (1994). Measuring the zeta (electrokinetic) potential of reverse osmosis membranes by a streaming potential analyzer, *Desalination*, **95**, 269-286.

Ericsson, B., Hallberg, M., Wachenfeldt, J., (1996). Nanofiltration of highly colored raw water for drinking water production, *Desalination*, **108**, 129-141.

Eriksson, P., E-mail, January 27, 1999.

Field, R. W., Wu, D., Howell, J. A., Gupta, B. B., (1995). Critical flux concept for microfiltration fouling, *J. Membr. Sci.*, **100**, 259-272.

Fu, P., Ruiz, H., Lozier, J., Thompson, K., Spangenberg, C., (1995). A pilot study on groundwater natural organics removal by low-pressure membranes, *Desalination*, **102**, 47-56.

Gekas, V., Persson, K.M., Wahlgren, M., Sivik, B., (1992). Contact angle of ultrafiltration membranes and their possible correlation to membrane performance, *J. Membr. Sci.*, **72**, 293-302.

Geraldes, V., de Pinho, M. N., (1995). Process water recovery from pulp bleaching effluents by an NF/ED hybrid process, *J. Membr. Sci.*, **102**, 209-221.

Hagmayer, G., Gimbel, R., (1999). Modelling the rejection of nanofiltration membranes using zeta potential measurements, *Sep. Purif. Technol.*, **15**, 19-30.

Huisman I. H., Dutré B., Persson K. M., Trägårdh G., (1997). Water permeability in ultrafiltration and microfiltration: Viscous and electroviscous effects, *Desalination*, **113**, 95-103.

Jonsson G., Johansen P. L., (1991). Selectivity of ultrafiltration membranes, Influence of fouling and cleaning conditions, *Filtr. Sep.*, **28**, 21-23.

Jucker C., Clark M. M., (1994). Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes, *J. Membr. Sci.*, **97**, 37-52.

Jönsson, A.-S., Blomgren, Y., Petersson, E., (1988). Influence of pH and surfactant on ultrafiltration membranes during treatment of bleach plant effluent, *Nordic Pulp Paper Res. J.*, **3**(4), 159-165.

Jönsson, A.-S., Jönsson, B., (1996). Colloidal fouling during ultrafiltration, *Sep. Sci. Technol.* **31**(9), 2611-2620.

Jönsson, A.-S., Wimmerstedt R., (1985). The application of membrane technology in the pulp and paper industry, *Desalination*, **53**, 181-196.

Jönsson C., Jönsson A.-S., (1995). Influence of the membrane material on the adsorptive fouling of ultrafiltration membranes, *J. Membr. Sci.*, **108**, 79-87.

Kahmark K. A., Unwin J. P., (1994). Pulp and paper effluent management, *Water Environ. Res.*, **69**(4), 641-658.

Kahmark K. A., Unwin J. P., (1996). Pulp and paper effluent management, *Water Environ. Res.*, **68**(4), 551-564.

Ko, M. K., Pellegrino, J. J., (1992). Determination of osmotic pressure and fouling resistance and their effect on the performance of ultrafiltration membranes, *J. Membr. Sci.*, **74**, 141-157.

Koros, W. J., (1995). Membranes: Learning a lesson from nature, *Chem. Eng. Progr.*, **91** (10), 68- 81.

Levenstein, R., Hasson, D., Semiat, R., (1996). Utilization of the Donnan effect for improving electrolyte separation with nanofiltration membranes, *J. Membr. Sci.*, **116**, 77-92.

Lien, L. and Simonis, D., (1995). Case histories of two large nanofiltration systems reclaiming effluent from pulp and paper mills for reuse. *Proc. TAPPI 1995 Int. Environmental Conference*, TAPPI Press, Atlanta, USA, Book 2, pp. 1023-1027.

Madireddi, K., Babcock, R. W., Levine, Jr. B., Huo, T. L., Khan, E., Ye, Q. F., Neethling, J. B., Suffet, I. H., Stenstrom, M. K., (1997). Wastewater reclamation at Lake Arrowhead, California: an overview, *Water Environ. Res.* **69**(3), 350-262.

Monroe, M., (1997). VSEP: A new approach for treating effluent from recycle mills, *Progr. Pap. Rec.*, **6**(3), 19-21.

Nuortila-Jokinen, J., (1997). Choice of optimal membrane processes for economical treatment of paper machine clear filtrate, Doctoral Thesis, *Lappeenranta University of Technology. Research Papers 58*, Finland.

Nuortila-Jokinen, J., Nyström, M., (1996a). Comparison of membrane separation processes in the internal purification of paper mill water, *J. Membr. Sci.*, **119**, 99-115.

Nuortila-Jokinen, J., Mänttäri, M., Nyström, M., (1996b). Membrane filtration processes as means for internal treatment of paper mill waters, *PTS Symposium*, Chemical Technology in Papermaking, München, Germany, September 17-20, 18 pages.

Nuortila-Jokinen, J., Kuparinen, A., Nyström, M., (1998). Tailoring an economical membrane process for internal purification in the paper industry, *Desalination*, **119**, 11-19.

Nyström M., Aimar P., Luque S., Kulovaara M., Metsämuuronen S., (1998). Fractionation of model proteins using their physiochemical properties, *Colloids Surf.*, **138**, 185-205.

Nyström, M., Nuortila-Jokinen, J., (1996). Current trends in membrane technology, *Kemia-Kemi*, **23**(8), 663-672.

Nyström, M and Zhu, H., (1997). Characterization of cleaning results using combined flux and streaming potential methods, *J. Membr. Sci.*, **131**, 195-205.

Panchapakesan, B., (1992). Closure of mill white water systems reduces water use, Conserves energy, *Pulp Paper*, **66**(3), 57-60.

Peeters, J.M.M., (1997). Characterization of nanofiltration membranes, *Ph.D. Thesis*, University of Twente, Netherlands.

Peters, T.A., (1998). Purification of landfill leachate with membrane filtration, *Filtr. Sep.*, **35**, 33-36.

Petersen, R. J., (1993). Composite reverse osmosis and nanofiltration membranes, *J. Membr. Sci.* **83**, 81-150.

de Pinho, M. N., Geraldes, V. M., Rosa, M. J., Afonso, M. D., Figueira, H., Taborda, F., Ganho, R., Creusen, R., Hanemaaijer, J., Gaeta, S., Amblard, P., Gavach, C., Guizard, C., 1995, Water recovery from bleached pulp effluents, *Proc. TAPPI 1995 Int. Environmental Conference*, Atlanta, USA, May 7-10, pp. 883-892.

de Pinho, M. N., Geraldes, V. M., Rosa, M. J., Afonso, M. D., Figueira, H., Taborda, F., Almeida, G., Ganho, R., Creusen, R., Hanemaaijer, J., Gaeta, S., Amblard, P., Gavach, C., Guizard, C., 1996, Water recovery from bleached pulp effluents, *Tappi J.*, **79**(12), 117-124.

Ramamurthy, P., (1996). Application of membrane processes to control dissolved and colloidal matter in pulp and paper water streams, *COST Action E1*, Paper Recyclability, Madrid, Spain, June 6, pp. 153-162.

Raman, L. P., Cheryan, M., Rajagopalan, N., (1994). Consider nanofiltration for membrane separations, *Chem. Eng. Progr.*, **90**(3), 68-74.

Rautenbach, R., Gröschl, A., (1990). Separation potential of nanofiltration membranes, *Desalination*, **77**, 73-84.

Rautenbach, R., Helmus, F. P., (1994). Some consideration on mass-transfer resistances in solution-diffusion-type membrane processes, *J. Membr. Sci.*, **87**, 171-181.

Rautenbach, R., Mellis, R., (1994). Waste water treatment by a combination of bioreactor and nanofiltration, *Desalination*, **95**, 171-188.

Rosa, M. J., de Pinho, M. N., (1995). The role of ultrafiltration and nanofiltration on the minimisation of the environmental impact of bleached pulp effluents, *J. Membr. Sci.*, **102**, 155-161.

Rudie, B. J., Ross, G. S., Harrold, S. J., Paulson, D. J., (1993). Effects of surface interactions on an NF/UF membrane, *Desalination*, **90**, 107-118.

Salovius, L., Söderman, J., Teppler, M., and Jantunen, E., (1993). The zero effluent paper mill, *Proc. the 18th Int. Mechanical Pulping Conference*, Oslo, Norway, June 15-17, Book 3, pp. 433-448.

Sierka, R. S., Avenell, J. A., Angell, H. J., (1992). An evaluation of membrane treatment of a sulfide kraftmill wastewater, *1992 Environmental Conference*, Richmond, USA, April 12-15, Book 2, pp. 705-719.

Sierka, R. S., Folster, H. G., Avenell, J. A., (1994). The treatment of whitewater by adsorption and membrane techniques, *1994 Int. Environmental Conference*, Portland, USA, April 17-20, pp. 249-257.

Sierka, R. S., Folster, H. G., (1995). Membrane treatment of bleach plant filtrates, *1995 Topical Conference*, Recent Developments and Future Opportunities in Separation Technology, Miami Beach, FL, USA, November 12-17, Vol. 1, pp. 485-491.

Sierka, R. A., Cooper, S. P., Pagoria, P. S., (1997). Ultrafiltration and reverse osmosis treatment of an acid stage wastewater, *Wat. Sci. Technol.*, **35**(2-3), 155-161.

Sójka-Ledakowicz, J., Koprowski, T., Machnowski, W., Knudsen, H. H., (1998). Membrane filtration of textile dyehouse wastewater for technological water reuse, *Desalination*, **119**, 1-10.

Treffry-Goatley, K., Gilron, J., (1993). The application of nanofiltration membranes to the treatment of industrial effluent and process streams, *Filtr. Sep.*, **30**, 63-66.

Tsuru, T., Urairi, M., Nakao, S.-I., Kimura, S., (1991). Negative rejection of anions in the loose reverse osmosis separation of mono- and divalent ion mixtures, *Desalination*, **81**, 219-227.

Vaija, P. Random, J., Larbot, A., Cot, L., (1993). Prediction of the flux through an ultrafiltration membrane using fuzzy mathematics, *J. Membr. Sci.*, **83**, 173-179.

Väisänen, P., (1998). Unpublished data. Laboratory of Membrane Technology and Technical Polymer Chemistry, Lappeenranta University of Technology, Lappeenranta, Finland, 1998.

Wang, X.-L., Tsuru, T., Togoh, M., Nakao, S.-I., Kimura, S., (1995). Evaluation of pore structure and electrical properties of nanofiltration membranes, *J. Chem. Eng. Jap.*, **28**(2), 186-192.

de Witte, J.-P., (1996). Surface water potabilisation by means of a novel nanofiltration element, *Desalination*, **108**, 153-157.

Yao, W. X., Kennedy, K. J., Tam, C. M., Hazlett, J. D., (1994). Pre-treatment of kraft pulp bleach plant effluent by selected ultrafiltration membranes, *Can. J. Chem. Eng.*, **72**(6), 991-999.

Yaroshchuk, A. E., (1998). Rejection mechanisms of NF membranes, *Membr. Technol.*, **100**, 9-12.

Zaidi, A., Buisson, H., Sourirajan, S., (1991). Ultrafiltration in the concentration of toxic organics from selected pulp and paper effluents, *Proc. TAPPI 1991 Environmental Conference*, San Antonio, USA, April 7-10, Book 1, pp. 453-468.

Zaidi, A., Buisson, H., Sourirajan, S., Wood, H., (1992). Ultra- and nanofiltration in advanced effluent treatment schemes for pollution control in the pulp and paper industry, *Wat. Sci. Technol.*, **25**(10), 263-276.

8. LIST OF SYMBOLS

C_p	concentration in permeate, mg/l
C_c	concentration in concentrate, mg/l
FR	flux reduction between permeate flux and pure water flux, %
FR_{pwf}	flux reduction of pure water flux, %
FV	feed volume, l
PF	permeate flux, $l/(m^2h)$
PV	permeate volume, l
PWF_b	pure water flux before filtration, $l/(m^2h)$
PWF_a	pure water flux after filtration, $l/(m^2h)$
R	retention, %
T	temperature, °C
t	time, min.
Y	recovery, %
η	viscosity of water, Pa s

Acronyms:

AMT	Advanced Membrane Technology
COD	chemical oxygen demand
CR	Cross Rotational
MF	microfiltration
MWCO	molecular weight cut-off
NF	nanofiltration
PA	polyamide
PES	polyethersulfone
PS	polysulfone
PVA	polyvinyl alcohol
PVDF	polyvinylidene fluoride
RC	regenerated cellulose
RO	reverse osmosis
SPES	sulfonated polyethersulfone
TC	total carbon
TCF	total chlorine free
TFM	thin film membrane
TOC	total organic carbon
TOCl	total chlorinated organic carbon
UF	ultrafiltration
VSEP	Vibratory Shear Enhanced Processing

9. APPENDICES

I	Literature review
II-VII	Publications

I

Mänttäri M., Various methods to improve the filtration performance, *Julkaisu* 92, Department of Chemical Technology, Lappeenranta University of Technology, Lappeenranta, Finland, 1997, 60 pages.

LAPPEENRANNAN TEKNILLINEN KORKEAKOULU
Kemiantekniikan osasto

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Department of Chemical Technology

LTKK

Julkaisu 92

Mika Mänttäri

Various methods to improve the filtration performance

LAPPEENRANNAN TEKNILLINEN KORKEAKOULU
Kemiantekniikan osasto
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Various methods to improve the filtration performance

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Contents

Various methods to improve the filtration performance

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Keywords: enhanced filtration, modification, pretreatment, flocculant, surfactant, hydrodynamic methods, external fields, cleaning

1. Abstract

In the filtration processes the capacity or permeate flux always decreases with time. The decrease of capacity or flux is caused by a phenomenon called fouling. It restricts the use of filtration in many separation processes. Thus, a great number of methods have been developed to decrease fouling and improve the filtration efficiency. The purpose of this literature review is to present some methods, including the use of chemicals, as well as hydrodynamic methods and external fields, to improve the filtration performance. The chemicals discussed in this study include primary flocculants and surfactants. They can improve the cake filtration efficiency increasing the capacity and helping the cake dewatering. The mechanisms of flocculation are discussed.

The flux decline in membrane filtration is known to be caused by concentration polarisation and membrane fouling. Methods to reduce the fouling of a membrane, like membrane modification and feed solution pretreatment are discussed. The use of surfactants for modification of membranes as well as for pretreatment of feed solution is evaluated. A filtration method, which utilises the capability of surfactants to form micelles called micellar enhanced filtration, is presented. The connection between concentration polarisation and fouling has caused the development of many hydrodynamic methods, which are very effective to prevent concentration polarisation and fouling. These methods are based on the increased mass transfer from the membrane surface to the bulk solution. The modules utilising these methods are presented and their advantages are evaluated. Finally, external field enhanced filtrations, such as ultrasonic and electric fields, and cleaning of the membrane are considered.

2. Introduction

Conventional pressure filtration is a mechanical, pressure driven, separation process that can be used to separate particles from fluids and slurries. In membrane filtration mostly dissolved components can be separated from a liquid. A decrease of capacity or permeate flux caused by pore plugging or fouling phenomena is a very common problem in all filtration processes and it limits the use of filtration as a separation process. By controlling the filtration conditions and by using various chemicals blocking of filters and fouling of membranes can be minimised. This means that the filtration process can operate for longer periods without cleaning, and as a result money can be saved. The improved filtration performance can also cause lower power consumption or smaller energy costs during the filtration.

The purpose of this paper is to discuss rather widely the methods used to improve cake filtration and membrane filtration performance. The first part includes chemical methods used to improve the conventional (cake) filtration efficiency. Mainly flocculants and surfactants and their effect on filtration are considered. Coagulation and flocculation phenomena are discussed too. After a brief discussion of the membrane fouling phenomenon various chemicals and hydrodynamic methods to prevent fouling and concentration polarisation are presented. Some methods are used in commercially available modules, but others are under development and are tested only at a laboratory scale. External fields and their effect to reduce fouling and improve membrane cleaning as well as different cleaning methods are evaluated at the end of this literature review. This study has been restricted to pressure driven filtration processes.

3. Cake filtration

The performance of conventional filtration processes (cake filtration) can be enhanced by using flocculants or surfactants. Usually, the goal of cake filtration is to get as much dry solid as economically possible. One example is dewatering of mineral concentrates. Flocculating agents improve the filtration performance increasing the particle size by forming flocs and by binding small particles to the flocs and as a consequence preventing them to plug the filter. The next paragraphs will present flocculating agents, flocculation mechanisms, and how flocculants affect the filtration processes. The optimal use of flocculants will be discussed too. Filter aids are handled very shortly and surfactant effects on the cake moisture content is discussed. In this part of the study operational conditions and their effect on the filtration efficiency are excluded.

3.1 Chemical methods

Many chemicals have been applied to improve the filtration efficiency. The most widely used chemicals are flocculants. They are used to increase the capacity in cake filtration and also to prevent fouling in membrane filtration. Another widely applied class of chemicals in filtration processes is the surfactants. Surfactants can decrease the cake moisture content and in membrane filtration surfactants can improve retention or be used as a pretreatment method to decrease membrane fouling. Adjustment of pH has also sometimes been observed to have a very beneficial effect on the filtration process.

3.1.1 Flocculants

Nowadays, synthetic flocculants are replacing natural products in many processes. Halverson and Panzer (1980) divided the flocculating agents in three classes, inorganic, synthetic and natural materials, table I. Inorganic salts are also known as coagulants. One, but not a very much studied group of flocculants, are micro-organisms such as bacteria. Schulze and Stahl (1996) used micro-organisms to agglomerate fine mineral particles in order to accelerate sedimentation and to improve solid-liquid separation. They showed that micro-organisms represent an alternative to synthetic flocculants used today.

Synthetic organic flocculants are water-soluble polymeric substances with average molar masses ranging from about 10^3 to greater than $5 \cdot 10^6$ g/mol. Polyelctrolytes are polymeric substances which have charged subunits. Also uncharged flocculants (like polyacrylamide and poly(ethylene oxide)) are commercially available. Polyelectrolytes containing both positive and negative charges in the same molecule are termed polyampholytes.

Table I Classification of flocculating agents /Halverson and Panzer 1980, Hughes 1990/.

	Examples	
Inorganic materials	Aluminum derivatives	
	Iron derivatives	
	Silicon derivatives	
	Lime	
	Clays, (bentonite)	
Synthetic organic materials	Polyacrylamides	Nonionic
	Polyethyleneoxide	Nonionic
	Acrylamide co-polymers	Anionic
	Polyacrylics	Anionic
	Polyamines	Cationic
	Acrylamide co-polymers	Cationic
Natural products	Starch	
	Guar Gum	
	Protein colloids	

The earliest and most highly developed group of synthetic polyelectrolytes is based on polyacrylamide and its derivatives, which can be made by the catalytic polymerisation of either acrylamide or acrylonitrile to give a neutral polyelectrolyte, or anionic and cationic derivatives. In commercially cationic flocculants the quadrivalent nitrogen is usually the charged site. In anionic flocculants several types of anionic groups in a polymer are possible but the major type is the carboxylate ion /Ward 1996, Halverson and Panzer 1980/.

The molar mass is very important when considering the effect of polyelectrolytes when reacting with suspended solids. The dispersing agents have a low degree of polymerization (molar mass of about 5000 to 20000). The dispersing agents are usually ampholytic and they solubilise the particles. Their hydrophobic parts adhere to the particles and their hydrophilic charged groups extend into the solution. As a result the surface charge of the particles is strongly increased, which increases the repulsive forces between them accordingly. Thus the average geometrical particle distance in the system reaches the highest possible, for a given particle concentration in the suspension and the dispersity degree of the suspension is increased. On the contrary high molar mass type polyelectrolytes act as flocculating agents and they are used as dewatering agents in filtration /Reuter and Hartan 1986/.

3.1.1.1 The electrical double layer and stabilisation of suspension

The major interactive forces between suspended solids are attractive or repulsive. Attractive forces can operate only when particles are very close to each other. The shortest distance of approach between particles is a direct function of the magnitude of the electrical double layer which is itself a direct function of the charge on the surface of a particle. Therefore, the surface charge has a remarkable effect on the stability of an aqueous suspension of solid particles. In water suspension the solid surfaces tend to have a net electrical charge. There are three mechanisms which can cause this charge. One is the isomorphic substitution in the solid lattice. This behaviour is typical of ion-exchange materials such as zeolites and clays. Another is the ionisation of surface groups (such as an OH group for mineral oxides, carboxyl groups for latex particles and carboxyl or amino groups for proteins). The third method is the preferential adsorption of ions or ionisable species from the suspending medium /Wakeman et al. 1989, Hughes 1990, Halverson and Panzer 1980/. Because of this surface charge, ions of opposite charge in the solution will be attracted towards the surface. There will, therefore, be a higher concentration of counter-ions close to the surface, than in the bulk of the liquid. This concentration falls off with increasing distance from the particle surface. Thus, there is a bound layer of counter-ions at the particle surface and after this layer a more diffuse layer. Only the bound layer (Stern layer) moves with the particles. So there is a plane of shear between the bound layer and the diffusive layers and the potential difference between the plane of shear and the bulk solution is called the zeta potential. The zeta potential is of special importance since it can be measured with different methods. The shear plane is located further from the surface than the Stern plane but its place is not well defined. These phenomena give rise to the electrical double layer which surrounds colloidal particles. The double layer is composed of the Stern layer and diffusive layers, as shown in fig. 1. Because of the repulsive forces between particles charged this way the suspensions can be stabilised.

In addition to electrostatic stabilisation of suspended particles also other kinds of stabilisation may be present. The surface characteristics of particles range from hydrophobic to hydrophilic. Suspensions of hydrophobic particles, such as minerals, tend to be stabilised primarily by surface charge. Hydrophilic particles, such as sewage sludges, are stabilised by solvation as well as by charge /Halverson and Panzer 1980/.

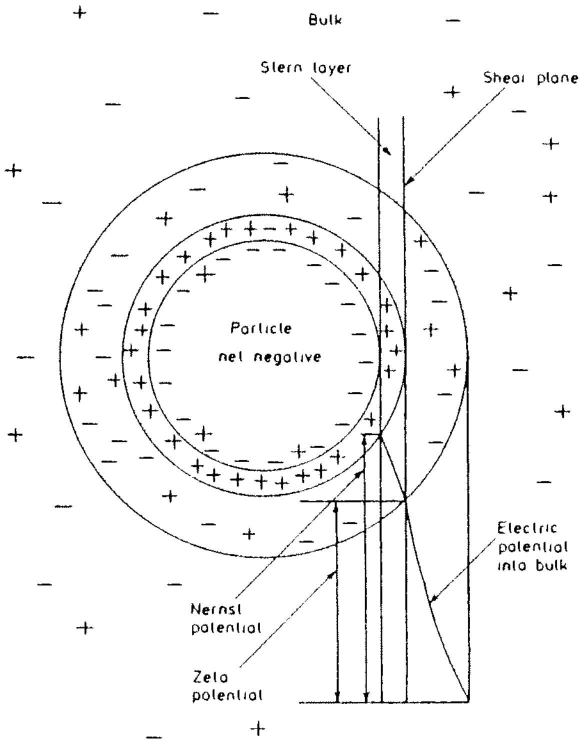


Figure 1. Electrical double layer /Hughes 1990/.

3.1.1.2 Coagulation and flocculation

The terms coagulation and flocculation are both used in connection with the formation of aggregates. The differences of these terms are shown in table II.

Table II Distinction of coagulation and flocculation /Halverson and Panzer 1981/.

	Coagulation	**Flocculation**
Mechanism	Compact aggregates	Loose or open network aggregates
Chemical agents	Inorganic materials	Organic polymers
Engineering process step	Conditioning the particles	Mechanical particle transport step
Engineering usage	Aggregation process	Particle transport step

Coagulation is the adhesion of particles by forces of molecular and atomic origin. The balance between the attractive London dispersion forces (van der Waals attraction) and the repulsive electrical forces, double layer forces, determine the presence or absence of coagulation. Since dispersion forces are short range, the particles must be close together before a significant attractive force develops. The molecules of the liquid collide with the small particles, which gives rise to the irregular movement of the particles called Brownian motion. This kind of behaviour may bring some particles into close enough proximity to allow the attractive surface forces to bind them together into small agglomerates. The rate of agglomeration only depends on Brownian motion if the electrical repulsion and velocity gradient are absent. This kind of agglomeration is called perikinetic flocculation to differentiate it from the orthokinetic flocculation, which is caused by fluid motion. The charged surfaces of particles may prevent the spontaneous agglomeration caused by the Brownian motion /Halverson and Panzer 1980, Ward 1996, Wakeman et al. 1989, Hughes 1990, Ives 1990/.

The coagulant reagents are added to alter the surface charge to allow the agglomeration to take place. Electrolyte addition can bring about coagulation by two mechanisms. First, addition of any electrolyte increases the ionic strength of the suspending medium, which means that the thickness of the double layer will decrease and the range of interparticle repulsion will also decrease. Ions with similar sign charge as the surface are repelled by the surface, and counter-ions are attracted to its vinicity. As the concentration of counter-ions increases, the volume of the diffuse ionic layer necessary for electroneutrality decreases. If this electrolyte effect is purely electrostatic in nature, the electrolyte is called an indifferent electrolyte. The magnitude of this effect increases with increasing charge on the counter-ion. To counteract the charge in negatively charged suspensions trivalent cations ($Al^{3+}$and Fe^{3+}) are more effective than divalent cations or monovalent cations. Secondly, counter-ions may react chemically with the particle surface and be adsorbed onto it. This specific counter-ion adsorption may reduce the net surface charge to zero, or even reverse the sign of the net surface charge. When the net surface charge is reduced to zero, or close to zero, coagulation is possible. The critical flocculation concentrations (cfc) for destabilisation by specific ion adsorption are considerably smaller than those for an indifferent electrolyte. Hydrolysable metal ions are considered to operate according to this mechanism, although several mechanisms may be involved simultaneously /Amirtharajah 1990, Halverson and Panzer 1980/.

Hydrolysable metal ions are usually added in the pH range and at the concentration level where the metal hydroxide is precipitated. Under appropriate conditions a fluffy amorphous hydroxide forms rapidly, trapping and enmeshing colloidal particles as it settles. This mechanism is called sweep flocculation and it works well only when the suspended solids concentration is very low /Halverson and Panzer 1980, Wakeman et al. 1989, Penniman 1981/.

The mechanisms of flocculation by polyelectrolytes are surface charge neutralisation and bridging. If the charge of flocculants is opposite in sign to the suspended particles, addition of such a polymer to the suspension will result in aggregation caused by specific ion adsorption. If the flocculants have a high density of charge also Charge Patch attraction exists. This is usually the situation, when the charge density of the polymer is much higher than that on the particle surface. The polymer will neutralise all the negative charge within the geometric area of the particle on which it is adsorbed, and will still carry an excess of unneutralised cationic charge. This means that positively charged patches will be formed and these patches are surrounded by regions of negative charge. Thus, there is electrostatic attraction between this positive charge and negatively charged areas on the surfaces of other particles. The most common types of polymers to operate by this mechanism are relative low molar mass polyamines. The formed flocs have fairly small particle sizes and slow-settling /Halverson and Panzer 1980/.

Polymer bridging is shown in Fig 2. When very long polymer molecules are adsorbed on the surface of particles, they tend to form loops that extend some distance from the surface into the aqueous phase, and their ends may also dangle. These loops and ends may come into contact with, and attach to, another particle, forming a bridge between the two particles. The particles must come close enough together so that the bridging can occur but charge neutralisation is not required. It should be remembered that electrostatic bonding is only one possibility how water soluble polymers can bond to a particle surface. Other types include hydrophobic bonding, van der Waals bonding, and a group of rather specific physico-chemical interactions ranging from hydrogen bonding to covalent bonding /Luttinger 1981, Halverson and Panzer 1980, Hughes 1990, Ward 1996/.

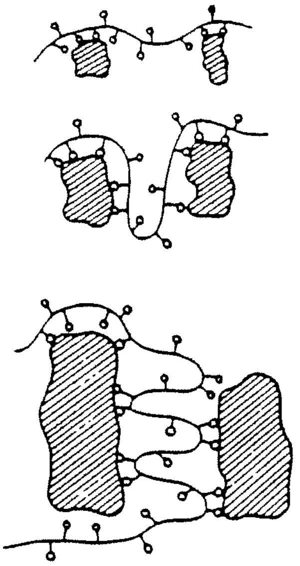


Figure 2. Polymer bridging /Leja 1982/.

3.1.1.3 Flocculants in the filtration processes

Flocculants may improve filtration rates by up to 100 times. Thus, they can be used to make impossible slow filtering slurries filterable at reasonable rates. They bind small particles together preventing them to plug the filter medium. Thus, they can increase the capacity and also prevent plugging. On the other hand faster filtration rates usually cause higher cake moisture too. This can be overcome by using surfactants.

3.1.1.4 Dewatering

Cake filtration is a commonly used process in dewatering of mineral concentrates /Pearse and Allen 1983/. The difficulties in dewatering can be due to the presence of ultrafine particles (<10 μm) and clay material. With the addition of flocculant, the filtration rate can be significantly increased, and filter medium plugging may be reduced due to enlarged particle sizes. Especially the flocculant effect on the dewatering of fine coals in filtration has been studied widely /Cheng et al. 1991, Fang et al. 1988, Mehrotha et al.

1982/. Flocculants improve the dewatering process primarily by increasing the extent of flocculation of the coal fines /Mehrotha et al. 1982/. Flocculants increase the effective particle size of the coal fines and change the structure of the cake. Mehrotha et al. (1982) also concluded that flocculation may eliminate stratification of coarse and fine particles during a cake formation and consequently improves the overall dewatering process of coal fines.

The flocculation performance highly depends on the properties of the flocculants, the particulate suspension and the flocculation conditions. The *nature of the functional group*, which determines the type of flocculant is one important characteristic of the polymeric flocculant. An efficient flocculant must contain a functional group that can interact with sites on the surface of suspended particles. There are many mechanisms how flocculants and solids can interact. Electrostatic attraction is one possibility. Flocculants with high ionicity can adsorb on the oppositely charged particle surface through electrostatic attraction. Adsorption of flocculant molecules at the surface of lightly charged particles may occur due to covalent interactions. Sometimes also hydrogen bonding can enhance adsorption. Bridging is the main mechanism for nonionic flocculants and for those with the same charge as the particles /Cheng et al. 1991/.

The *dosage of flocculant* is the most important factor in slurry treatment. An optimum concentration of a flocculant exists for a given slurry sample /Cheng et al. 1991/. It has been suggested that optimum flocculation occurs when half the area of solid is covered with polyelectrolyte. At higher concentrations the degree of flocculation decreases, and the particles may be completely covered by the adsorbed polymer layer. Thus overdosing can be a serious mistake in that it may create a well-stabilised suspension that is extremely difficult to separate /Ward 1996/. Cheng et al. (1991) showed that coarser particulate samples need less flocculant to obtain the best performance. This is not surprising because coarser particles have smaller surface area, and therefore, smaller amounts of flocculant are needed.

The *molar mass of the flocculant* is another important factor to be considered when selecting a flocculant. The molar mass determines the size and shape of the flocs, and thus, the filtration characteristics and the dewatering properties. Generally increasing the molar mass of flocculants leads to increased flocculation efficiency and floc strength, but at the expense of an increased cost of polyelectrolyte owing to the greater quantities required. There is an optimal polymer chain length for efficient flocculation. The type of solid-liquid processes dictates the molar mass of the chosen polyelectrolyte, as seen in Table III /Hughes 1990, Ward 1996/.

Table III Choice of molar mass of flocculants for different processing techniques /Ward 1996, Hughes 1990/.

Process type	Molar mass range
Sedimentation and centrifugation	High (in conjunction with highly cationic electrolyte for overflow clarity)
Vacuum filtration	Medium to high
Pressure filtration	Low to medium
Pressure belt filtration	Medium to high (in conjunction with low molar mass, highly cationic electrolyte)
Low solids clarification	Very low to high

In addition to the properties of the flocculant and the particulate suspension, flocculation performance depends on the physical variables of the flocculation conditions. It is necessary to *mix the suspension* in order to disperse the polymer and to increase the collision rate of the particles. For a given flocculant and particulate sample the intensity of mixing and the time of mixing determine the size and shape of the flocs and thus the filtration characteristics /Cheng et al. 1988/. Hogg (1988) studied floc formation and growth under various conditions and found that the limiting floc size decreases with mixing intensity. In general, low mixing speeds generate large but loose flocs, which may provide a good filtration performance. The higher mixing speeds produce smaller flocs which result in better dewatering /Cheng et al. 1991/. But evidently, a too high mixing speed breaks the flocs.

The effect of *solution pH* is complex. In general it could be expected that the presence of high charge will inhibit the adsorption of a polyelectrolyte having a charge of the same sign and enhance that of a polymer bearing the opposite charge.

The *hydrophobic interaction* is found to be the very important factor, which controls the aggregation behaviour of hydrophobic particles in aqueous solution. Fine particles can be made hydrophobic by the adsorption of surfactants. Thus, strong attractive hydrophobic interaction exists in water between hydrophobic particles. Hydrophobic flocculation is an important way to aggregate colloidal and fine particles. In filtration made with hydrophobic polymers the final moisture content of the filter cake is expected to be lower than that achieved with hydrophilic flocculants /Attia and Yu 1991, Song and Lu 1994, Lu and Song 1991/.

3.1.2 Surfactants

Surfactants can be used for further dewatering of a flocculated filter cake (post-treatment). All surfactants consist of a hydrocarbon chain, which is the hydrophobic (nonpolar) part of the surfactant, and one or several hydrophilic (polar) groups. The water solubility of the surfactant is caused by the hydrophilic group. The hydrophobic parts try to avoid the interaction with water. This bifunctionality leads to an accumulation of the surfactants at the interfaces. Thus, they lower the liquid-air interfacial surface tension, change the wettability of particle surfaces and reduce the capillary forces holding water in the fine pores.

The surface tension of an aqueous solution depends on the surfactant concentration. In the case of a low surfactant concentration, surfactants accumulate at the air-water interface until the interface is completely covered. In this concentration range surface tension decreases with increasing surfactant concentration. If the surfactant concentration in the solution is increased above this range, the hydrophobic parts of the surfactant tend to avoid the interaction with water and tend to form micelles. Above this limiting concentration (critical micelle formation concentration) the surface tension remains stable /Stahl and Stroh 1990, Stroh and Stahl 1990/.

In dewatering processes surfactants can be added in two ways: in the premixing stage with the slurry before filtration or in the cake washing water. Inside the cake the quantity of the interparticle water, which fills the voids between the particles, depends on the wetting angle and the surface tension of the liquid. The surfactants reduce the surface tension remarkably and also slightly improve the surface wetting properties.

Köster et al. (1992) have studied surfactant effects on the dewatering of fine-grained solid materials. Their results clearly show that a suitable nonionic surfactant can reduce the residual water content of small coal and of iron ore concentrate up to 2% in the case of mechanical dewatering. This means, that sometimes thermal drying is not necessarily needed any more.

3.2 Filter aids

The performance of the filtration operation can be improved by addition of another powdered solid, termed a filter aid, to the system. Filter aids extend the areas of surface filtration economics, the ranges of particle sizes removed, concentration limits and types of particles to be filtered. With filter aids particles as fine as 0.1 µm can be removed in surface filtration. Filter aids may be used in two ways, either separately or in conjunction with the suspension. In the first of these methods the filter medium is precoated with a layer of a filter aid cake. Precoat aids must filter quickly without bleeding or penetrating through the cloth and must give a uniform thickness with a reproducible filtering surface. The suspension is then filtered onto the precoat by surface and depth filtration mechanisms. Filter aid powder may also be mixed with the suspension. Such material is called "body aid". The object is to change the properties of the suspension so that the pores remain open in the filter cake during the filtration and as a consequence of that it provides a faster filtration.

Filter aids must have a high permeability and they should be inert to the liquid being filtered, which means, that their chemical resistance should be rather good. The surface properties of the filter aid may be a major factor to be considered for the successful applications of a filter aid in some processes. The most commonly used ones are diatomite and perlite filter aids /Ward 1996, Smith 1990/. Also cellulose and unactivated carbon can be used as filter aids. Pulverized fuel ash, saw dust, spent lime and many other waste products can and have been used in some applications, where a rough separation is required. Other specially prepared solid powder materials such as hydrated magnesium silicate, hydrated calcium silicate, bentonite, fuller's earth or activated carbon are used also to act as filter aids in the separation of the particulate solids from a suspension /Ward 1996/.

4. Membrane filtration

The efficient use of membrane filtration technology is hindered by two factors: fouling and concentration polarisation. The management of these phenomena is a necessity for the economical use of membranes. The methods to manage fouling and concentration polarisation and to improve the membrane filtration performance can be classified into four categories including pretreatment of the feed solution, modification of the membrane, modification of the hydrodynamic conditions and cleaning of the membrane.

Firstly, a pretreatment of the feed solution can be used to improve the filtration performance. For instance, addition of a surfactant can improve the separation efficiency of membranes due to the formation of micelles, which can solubilise small species and retain them in the concentrate. This method is named micellar enhanced filtation and is discussed more precisely later.

An adjustment or tailoring of membrane properties has also been studied widely in order to improve filtration efficiency. Modification of hydrophobic membranes with hydrophilicity increasing agents has been observed to decrease fouling and increase flux.

The third class includes various methods, which are used to modify the operating conditions (hydrodynamics) of the filtration. These methods are efficient in reducing the concentration polarisation and as a consequence also fouling. Concentration polarisation is the accumulation of the solute species at the upstream surface of the membrane. This layer on the surface of the membrane increases membrane fouling. Because of concentration polarisation the foulant concentration in the vicinity of the membrane is high enough to cause fouling and this stable layer also gives more time for the foulants to react with the membrane. The viscocity on the surface of the membrane increases too and as a result the flux decreases.

Although all the above methods reduce fouling to some extent, cleaning methods will always be employed in practice. The choice of the cleaning methods depends mainly on the module configuration, the chemical resistance of the membrane and the foulant type encountered. The cleaning can be carried out as hydraulic cleaning, mechanical cleaning, chemical cleaning and electrical cleaning or as combinations of these methods /Mulder 1995/.

4.1 Fouling mechanisms

If membrane filtration should be improved by modification of the membrane, the fouling mechanisms have to be known. Fouling of membranes has been studied very widely, but the phenomenon is still not well understood. Fouling is determined to be a phenomenon in which a membrane adsorbs, interacts with, or becomes coated with a foulant. The pores of the membrane can become plugged by solutes and/or by precipitates in the feed stream, resulting in a decrease in membrane performance by lowering the flux and/or affecting the rejection of solutes. Flux decline can be caused by several factors, such as concentration polarisation, adsorption, gel-layer formation and plugging of the pores. Concentration polarisation is a reversible phenomenon that occurs immediately when the process has been started and will reach an equilibrium value, which depends on the filtration conditions. Fouling is often an irreversible long-term process. Therefore, both phenomena should be reduced or managed in order for the flux to be maintained as high as possible and stable.

The fouling mechanisms of ultrafiltration and microfiltration membranes are not directly applicable to RO because of the great difference in membrane pore sizes and permeation rates. For instance microfiltration and ultrafiltration membranes are more sensitive to pore plugging by colloids and macromolecules than reverse osmosis membranes. Fouling of RO membranes comes primarily from precipitate fouling and biofouling. Normally, the different types of fouling occur at the same time, influencing each other, which means that it is sometimes really difficult to find out the reasons for fouling /Flemming 1993, Nyström 1992, Zhu and Elimelech 1995/.

One way to classify fouling is according to the foulants as shown below:

1. Inorganic deposits (scaling)
2. Organic molecule adsorption (organic fouling)
3. Particulate deposition (colloidal fouling)
4. Microbial adhesion and growth (biofouling)

Fouling caused by inorganic deposits are often observed on RO membranes. If the concentration of inorganic species on the membrane surface increases over the solubility limits precipitates are formed. The most common scalants are calcium sulphate and calcium carbonate.

Colloidal fouling is caused by small particles ranging from 0.01 to 1.0 μm. They can form a thin cake on the surface of the membrane. The colloids may be fine clays, iron hydroxides or biological solids. Membranes are most susceptible to fouling by particles 0.01 μm to 10 μm in size since the influence of both diffusive forces (Brownian motion and shear-induced lift) is small. Generally, the shear-induced lift increases with increasing particle size (above 10 μm). On the contrary, the diffusivity caused by Brownian motion increases with decreasing particle size (below 0.01 μm). Thus, the colloidal particles may be accumulated on the membrane surface. Colloids can also cause pore plugging. Pore plugging seems to be more depending on the pore sizes of the membranes, the pressure and the pore size distribution than actually on the membrane material or the foulant properties. Pore plugging is best controlled by preventing the solute from entering the membrane matrix. This can be done by selecting a membrane with a cut-off much smaller than the solutes /Nyström 1992, Ramamurthy et al. 1993/.

The membrane material and the foulant properties and their concentration are very important factors that determine the extent of adsorption. The adsorption process starts as soon as the membrane is in contact with the feed solution due to physico-chemical interactions, e.g., hydrophobic interactions (dispersion forces), polar interactions (dipole-dipole and dipole-induced dipole forces and charge transfer (hydrogen bonding). Adsorption can be minimised or reduced choosing the suitable membrane material (hydrophilic membranes adsorb less than hydrophobic) or modifying the membrane and solute properties so that the interactions between membrane and solute are minimised. Also solute properties can be changed so that the conditions are not favourable for adsorption /Mulder 1995/.

Biofouling is the result of complex interaction between the membrane material and fluid parameters (such as dissolved substances, flow velocity, pressure, etc.), and microorganisms. Biofouling is basically a problem of biofilm growth. Bacteria are the most likely biofoulants. If they enter the membrane system in sufficient quantities they attach to the membrane surface and spread by colonisation. They excrete exopolymers which are incorporated in the biofilm of bacteria. Algae are another reason for biofouling. Algae and bacteria are also the main source from which humic acids are formed. They foul the membranes as shown in many studies /Nyström 1996, Ericsson and Trägårdh 1996/.

Bacteria fouling may be controlled by disinfection (chlorination, UV, etc.) followed by filtration (sand media or multilayer filtration, or cartridge microfilters). Algae can be removed by filtration and careful design of water intake, such the use of a sand spear for a seawater intake. A sand spear is simply a perforated pipe, mesh-covered to prevent ingress of sand, burried a metre or more in the sand on the sea bed. Feed material entering the spear is prefiltered as it is drawn through the surrounding sand /Dal-Cin et al. 1996, Fane 1994, Flemming 1993/.

With polyelectrolytes fouling is decreased if the electrolyte has the same sign of charge as the membrane. The charges of the polyelectrolytes and the membrane depend on pH. Thus, an adjustment of solution pH changes the species charge and the membrane charge too.

Some fouling is totally irreversible. Substances present in the feed at low concentration having an affinity for the membrane is the usual culprit. Especially troublesome is a sparingly soluble substance at or near its saturation concentration. Such a material can slowly sorb into the membrane, and in the worst case, change the membrane structure irreversibly. Antifoams are examples of a class of materials responsible for occasional destructive fouling. This kind of fouling is very unusual today, because the membranes in use are chemically robust /Eykamp 1995, Fane 1994/.

4.2 Pretreatment of the feed solution

The fouling ability of a solution may be diminished by a suitable pretreatment. The pretreatment can be mechanical, thermal or chemical. The feed solution can be pretreated with chemicals as surfactants or its pH can be changed. Mechanical or physical methods like sedimentation, biological treatment, flotation and deep bed filtration are as well utilised as pretreatment steps for membrane processes. Some oxidation methods such as ozonation can also be tried out to destroy foulants in the feed solution. A thermal pretreatment is often necessary in order to avoid undesirable changes, especially when processing biological materials, which are sensitive to biodegradation. Thermal pretreatment is not included in more detail in this study.

4.2.1 Mechanical pretreatment of the feed solution

Mechanical pretreatment is especially important when using thin-channel membrane modules. The danger of plugging the flow channels is greatest for spirals, hollow-fibre and plate and frame modules. Centrifugation, sedimentation, clarification, flotation, screening and media filtration are used to pretreat the feed. The efficiency of these methods can be increased by chemicals. Colloids and particulates can cause blockage of the feed channels between the membranes. This can be avoided by careful pretreatment and removal of solid particulates. Another aspect is that pretreatment can also improve the performance of the membrane itself. However, sometimes pretreatment can also decrease the filtration performance. This is true when a secondary layer on the membrane surface has caused the retention of foulants and has prevented them from interacting with the membrane. If this layer, or the species that causes the secondary layer, has been removed during the pretreatment, the membrane performance can be decreased remarkably /Nuortila-Jokinen 1997, Murkes 1986, Jönsson and Trägårdh 1990/.

Pretreatment methods can as well include ozonation or various kinds of irradiation, like UV irradiation to kill bacteria and decrease biofouling. Ozonation integrated into the membrane filtration process for drinking water production has been studied by Takizawa et al. (1996). They observed that ozone scrubbing was effective in extending the operational periods in membrane filtration before chemical cleaning. Ozone can kill microorganisms and they were supposed to be the primary reason for the decreased fouling.

4.2.2 Chemical pretreatment of the feed solution

Chemical pretreatment can, in many cases, improve flux. Many researchers have observed that the increase of feed solution pH improves the flux. Pretreatment with surfactants has been observed to improve retentions and that can be a reason to use micellar enhanced filtration. Flocculants are as well potential alternatives for pretreatment of the feed solution in order to improve the flux or the retentions of various species.

4.2.2.1 Adjustment of pH

In filtration of ampholytes, pH is of great importance. It is well known that e.g. proteins foul less if they are charged in the same way as the membrane. They can be both positively and negatively charged depending on pH. At their isoelectric point (IP) proteins have equal amounts of positive and negative charge and thus seem to be neutral. At this point the proteins maintain their smallest volume and usually aggregate and foul the membrane the most. Also protein hydrophilicity, their conformational state and the ionic strength of the solution affect their fouling properties. There are many studies where the fouling of proteins has been reduced by changing the pH /Nyström 1992, Clark et al. 1991/. In addition the ampholytic properties of proteins make it possible to fractionate them utilising adjustment of pH /Ehsani 1996/.

Another example where pH adjustment is used to increase the filtration performance is in the prevention of scaling on RO membranes. Decreasing pH of the feed water reduces the scaling significantly. Furthermore, scale inhibitors can be used to prevent scaling /Al-Ahmad and Aleem 1994, Kronmiller 1994, Fane 1994/.

It is also well known that in some cases a high pH has a positive effect on the flux. /Nuortila-Jokinen 1997, Jönsson et al. 1988/. Particularly, the fluxes of dense ultrafiltration and nanofiltration membranes have increased as a result of increased pH. It is thought that the increase in flux is caused by a change in the hydrophobic/hydrophilic properties of the membrane material. Normally, membranes become more negatively charged at high pH and they also become more hydrophilic. The higher hydrophilicity of the membranes makes it possible for small pores to open up for water flow /Jönsson et al. 1988/. Sometimes again a higher pH has caused lower permeate fluxes. Sierka and Folster (1995) showed that lower fluxes were achieved in the filtration of alkaline filtrates from the bleach plant than when filtering acidic filtrates. The same effect was reported for both the microfilters and the nanofiltration membranes (TFC S from Fluid Systems).

4.2.2.2 Micellar enhanced filtration

In membrane filtration surfactants can be used to treat the membrane or the solution to be filtered before filtration. Dunn and Scamehorn (1985) proposed a process where surfactant is added to the water stream at a concentration well above the critical micelle concentration, Fig. 3. Above the critical micelle concentration surfactants self-aggregate to form micelles; roughly spherical aggregates containing generally 50-100 surfactant molecules. The micelles are highly charged and the ions of opposite charge to the surfactant adsorb or bind electrostatically onto the surface of the micelles. Nonionic organic solutes originally dissolved in the water will tend to solubilise in the interior of the micelles. Both the counter-ion binding and the organic solubilisation can occur simultaneously. The micellar solution is forced through an ultrafiltration membrane having pores small enough to retain the micelles in the feed solution. The described method is called micellar enhanced ultrafiltration (MEUF) and it is tested with many organic components as well as metals. With surfactants, rejections for divalent cations have been over 99% using UF membranes whose cut-off values have been from 1000 to 20000 MWCO. Organic molecules have been retained very well too /Dunn and Scamehorn 1985, Scamehorn et al. 1986, Kandori and Schechter 1990, Morel et al. 1991, Tabatabai et al. 1995, Nyström and Mänttäri 1993/.

The method is very suitable for treatment of polluted water streams or for concentration of valuable products for further downstream purification. Removal of metals by MEUF depends nearly only on the valence of the metal ions to be removed. This restricts the use of MEUF for treatment of wastewater, which contains many ions (toxic and nontoxic). Also monovalent salts compete for the binding site with the heavy metals and reduce the efficiency of the multivalent ions. The use of chelating or complexing agents makes it possible to remove selectively heavy metals from solution by normal MEUF.

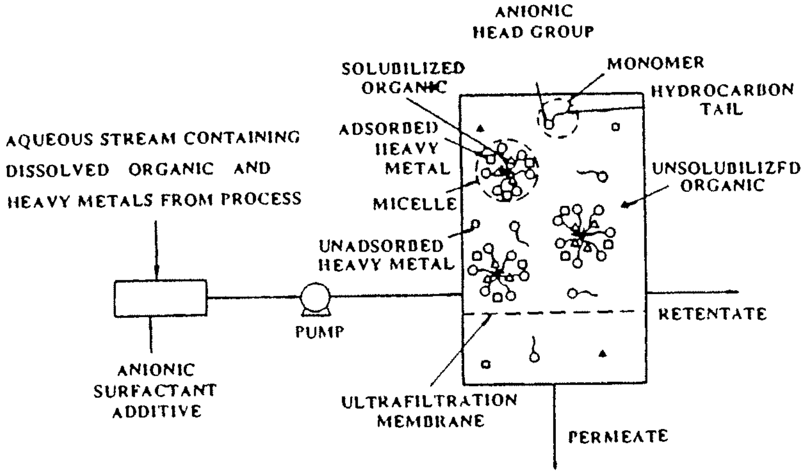


Figure 3. Schematic of micellar-enhanced ultrafiltration to remove dissolved heavy metal cations and organics from water /Scamehorn et al. 1989/.

One advantage of MEUF is the possibility to use the larger pore size membranes. The larger pores also mean higher flux and a more economic filtration process. Especially for lower molar mass compounds of value, MEUF may thus be economically superior to ordinary ultrafiltration.

4.2.2.3 Flocculation

Flocculants are not very widely used with membranes because they are rather expensive and they can also cause fouling of the membrane. Usually the filtrations are made using high shear rate, which means that flocs formed by flocculants may be destroyed during the filtration. However, flocculants are used successfully in mechanical pretreatment methods like sedimentation or flotation. They can improve the separation efficiency of these processes remarkably. Maleriat et al. (1996) used coagulation-flocculation pretreatment and cross-flow filtration for the processing of a landfill leachate. Pretreatment removed most of the suspended foulant materials. They showed that a combination of flocculation and membrane filtration could compete with usual biological treatment.

4.3 Modification of membranes

In order to get membranes with better properties for filtration of different types of solutes the membranes can be modified in different ways. The modification can be permanent or non-permanent and it can be carried out either before or after membrane preparation. The aim is to modify the surface chemistry of the membrane so that the attractive forces are reduced or the repulsive forces are increased between the solute and the membrane.

4.3.1 Permanent methods

In general, it is useful to increase the membrane hydrophilicity by introducing hydrophilic groups in the membrane material /Kulkarni et al. 1996/. These groups can be introduced through copolymerization or by grafting. The grafting can be done by using some kind of radical formation caused by irradiation (UV, gamma or plasma discharge). The membrane modification by grafting is permanent and the pores are also modified if it is made before the membrane is manufactured. The permanent grafting can also be made after casting, but then the pores are not altered as a consequence of modification. The modifying agents can be bound to the membrane by chemical reactions. In this case a permanent modification can be obtained, but often the modification agent in itself seems to plug part of the pores. Thus, the pure water flux of the membrane is decreased even though fouling is decreased.

Nyström and Järvinen (1991 a) have modified commercial polysulfone UF membranes using UV irradiation alone or together with different modification agents in liquid environment. The modifications were tested with protein solutions such as bovine serum albumin (BSA), lysozyme and whey protein. The contact angle and flux measurements proved that UV irradiation increased the hydrophilicity of the membranes and flux. The flux increase could be more than 400% compared to unmodified conditions without any loss in retention.

Recently Mukherjee et al. (1996) published a chemical treatment method, which causes a simultaneous improvement of flux and rejection of thin-film composite reverse osmosis membranes. They treated the membranes with acids such as hydrofluoric and fluosilicic acid and alcohols like isopropyl alcohol. In most cases permanent increases in both flux and rejection were observed. Even as high as 70% flux enhancement was obtained for the CPA2 and the SWC1 membranes (Fig. 4), which are commercially available aromatic polyamide based thin-film composite reverse osmosis membranes manufactured by Hydranautics. The reason for the improvement of the membrane performance of the barrier layer on treatment with HF has been explained to result from the partial fluoridation and the limited hydrolysis of the membrane skin.

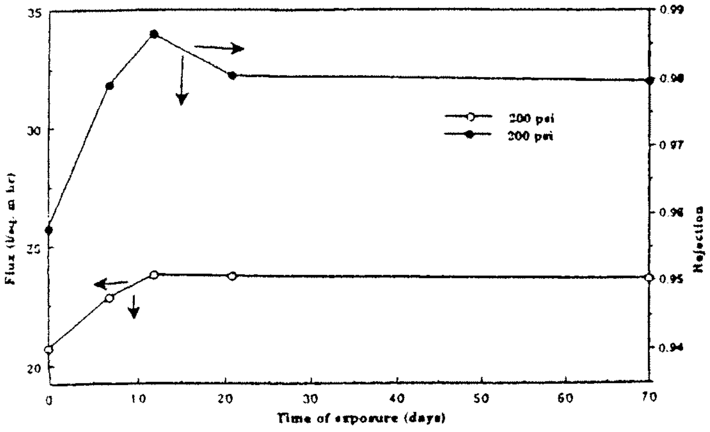


Figure 4. Variation of the flux and NaCl rejection for CPA2 membranes with time after treatment with 5 wt% HF. Note the increase in flux by 20% along with the increase in rejection /Mukherjee et al. 1996/.

4.3.2 Membrane pretreatment with surfactants and polyelectrolytes

Surfactants can be used to modify the membrane surface non-permanently. In many cases surfactants have shown to decrease the membrane flux. The flux reduction has been explained by concentration polarisation caused by retained micelles and also by preferential adsorption of surfactant molecules in the larger and internally more accessible pores. /Fane et al. 1985, Field et al. 1994/. Field et al. have studied surfactant effects on the water flux through microfiltration membranes. The reductions of flux were significantly larger for the hydrophobic membranes than for the hydrophilic membranes. In general, the larger the membrane pore size, the higher was the water flux decline after surfactant treatment. In larger membrane pores greater amounts of surfactants can be accumulated than in smaller size pores.

On the other hand, there is some evidence that cleaning with surfactant added in the cleaning solution may be considered as a temporary surface modification operation and may have a positive influence on membrane performance /Jönsson et al. 1988, Mänttäri et al. 1997/.

It has also been found that pretreatment of membranes with surfactants produces a significant improvement in membrane flux. Surfactant pretreatments can be carried out in two ways. The heterogeneous membrane surface can be covered by the charged or nonionic surfactants. Another way is to combine the effect of the extended hydrophilic steric barrier of long chain nonionic surfactants with the effect of the electrostatic repulsion that charged surfactants can provide. The concept is that the bulky nonionic surfactant prevents the protein from aggregating near the pore entrance while the small anionic surfactant reduces the fouling potential of those proteins, which penetrate the first surfactant layer (Fig. 5). The bulky nonionic surfactant keeps the protein away from the surface and the pores as both a hydrophilic and a steric barrier is formed and perhaps by reducing the solvent velocity towards the pores, thus causing less initial stress to the protein and less subsequent fouling. This technique has the added advantage of better coverage of adsorption sites since the surface may have areas of native charge as well as hydrophobic and hydrophilic patches. Chen et al. (1992) showed that the mixed surfactant treatments gave a better flux and less flux decline than the untreated membrane or membranes treated with either surfactant alone when bovine serum albumin (BSA) solution was ultrafiltered.

Furthermore, Fane et al. (1985) have studied the effect of surfactant on the ultrafiltration of proteins. They concluded that surfactant pretreatment increased the initial ultrafiltration flux and reduced the subsequent flux decline and the rate of protein deposition. The surfactant appears to render the surface of the membranes more homogeneously permeable, reduce the surface rugosity and increase hydrophilicity. These characteristics reduce locally high levels of polarisation around pores as well as the availability of hydrophobic sites for adhesion. The membranes most likely to be improved are those which are more hydrophilic in character and which have sparse surface porosity. The pretreated membranes have usually an improved response to cleaning. Without pretreatment the protein adsorption could be irreversible.

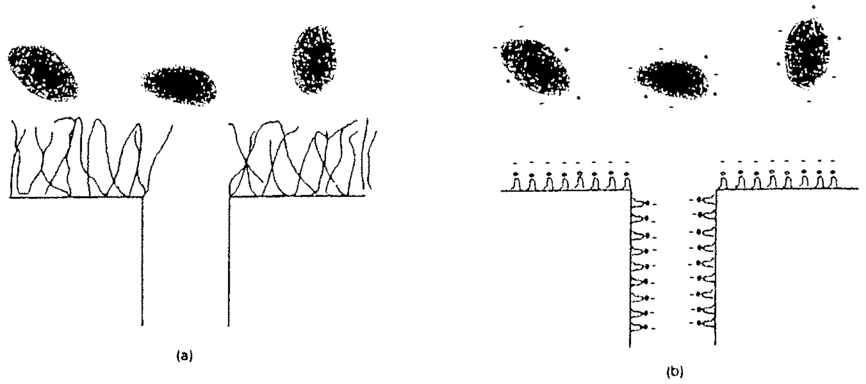


Figure 5. Schematic of surfactant pretreatment: (a) long nonionic surfactants provide a hydrophilic barrier against protein adsorption and (b) small anionic surfactants with charges repel proteins from the membrane surface /Chen et al. 1992/.

4.3.3 Dynamic modification

Membranes can be non-permanently pretreated with various polymers or inorganic components. Pretreatment with adsorbing polymers can be made by passive adsorption of the polymer from a solution onto the membrane surface or by convective adsorption during filtration of the adsorbent. This kind of modification layer can often be washed away with time. This is the situation especially if the modification layer has been made by passive adsorption of small molecules. During the convective adsorption process a certain amount of adsorption inside the pores also occurs. Thus, the pores are blocked to some extent and flux decreases. To minimise the pore blocking the high molar mass polymers are normally used to modify the membrane surface by convective adsorption. Membrane pretreatment with absorbed polymers and the effect of pretreatments on protein fouling have been studied rather widely during the last decade / Kim et al. 1988, Fane et al. 1985, Tripodi et al. 1988, Kimura et al. 1985, Nyström et al. 1991 b, Brink and Romijn 1990. /

In some cases it has been seen that the roughness of the membrane is one reason for fouling. In order to prevent this Langmuir-Blodgett layers can be applied on the membrane. This layer is so loose that it does not affect flux. The layer has a smoothening effect on the membrane surface and as a result it prevents fouling /Kim et al. 1989/.

4.4 Hydrodynamic methods

Chemical methods to improve the filtration performance change the properties of the membrane surface or change the solution conditions in a such a direction, that the membrane properties match the solution to be filtered so that fouling is not favoured. The mechanical or hydrodynamical methods increase the filtration performance through the control of mass transfer between the process fluid and the membrane. In membrane processes the retained solutes can accumulate at the membrane surface where their concentration will gradually increase. Such a concentration build-up will generate a diffusive flow back to the bulk of the feed, but after a given period of time steady-state conditions will be established. The higher solute concentration at the surface increases the osmotic pressure, thereby reducing the effective driving force and in addition making possible the interaction between the foulants and the membrane. The concentration profile in the boundary layer is shown in Fig. 6.

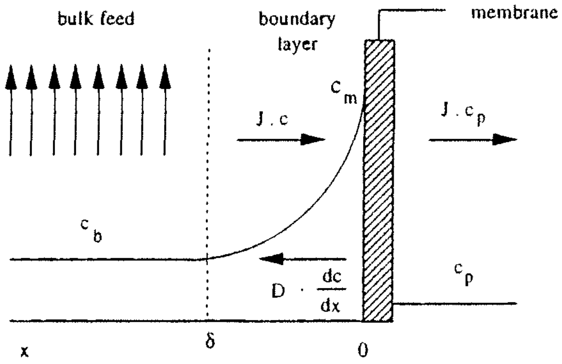


Figure 6. Concentration profile in the boundary layer under steady-state conditions /Mulder 1996/.

The solute flow to the membrane surface due to convective flow will be balanced by the solute flux through the membrane plus the diffusive flow from the membrane surface to the bulk Eq. (1). This is the case when fouling is excluded and only concentration polarisation phenomena are considered.

$$Jc + D\frac{dc}{dx} = Jc_p \tag{1}$$

where c concentration, kg/m^3

c_p concentration in the permeate, kg/m^3

D diffusion coefficient, m^2/s

J flux, m^3/m^{2}s

x coordinate perpendicular to membrane surface, m

The integration of Eq. (1) using the boundary conditions ($x=0 \rightarrow c=c_m$, $x=\delta \rightarrow c=c_b$) results in the 'film-model' relationship.

$$\frac{c_m - c_p}{c_b - c_p} = \exp\left(\frac{J\delta}{D}\right) \tag{2}$$

The mass-transfer coefficient (k) is the ratio of the diffusion coefficient (D) and the thickness of the boundary layer (δ).

$$k = \frac{D}{\delta} \tag{3}$$

When the solute is completely retained by the membrane ($C_p=0$) Eq.(2) becomes

$$\frac{c_m}{c_b} = \exp\left(\frac{J}{k}\right) \tag{4}$$

Eq.(4) is the basic equation for concentration polarisation. It shows that the flux (J) and the mass-transfer coefficient (k) and their origins (membrane part and hydrodynamics) are responsible for concentration polarisation. The mass-transfer coefficient is often presented using the Sherwood number (Sh) as shown below

$$Sh = \frac{kd_h}{D} = a\,\mathrm{Re}^b\,Sc^c \tag{5}$$

where a a,b,c adjustable parameters

Sc Schmidt number

Re Reynolds number

Equations (6) and (7) define the Reynolds number and Schmidt number respectively.

$$\mathrm{Re} = \frac{\rho v d_h}{\eta} \tag{6}$$

where ρ density, kg/m^3

v kinematic viscosity,

d_h hydraulic diameter, m

η bulk viscosity, Pa s

$$Sc = \frac{v}{D} \tag{7}$$

As the previous equations show, the extent of concentration polarisation can be reduced by manipulating the flux and the mass-transfer coefficient. The flux can be reduced by decreasing the driving force (pressure) but this is not a very attractive method to reduce concentration polarisation because the productivity decreases too and more membrane area is needed to get the same amount of permeate. However, it has been proved that in filtrations made below the critical flux fouling has been negligible and the cleaning frequency can be lowered.

A better way to reduce concentration polarisation is to manipulate the mass transfer coefficient. The mass-transfer coefficient depends strongly on the hydrodynamics of the system (flow velocity). This means that it is possible to modify and minimise the mass-transfer coefficient. Also the diffusion coefficient affects the mass transfer. The increase of temperature increases the diffusion of the solutes because the viscosity of the feed will decrease, which will also generally reduce concentration polarisation. However, an increase in feed temperature also causes an increase in the flux, which opposes the effect of the improved mass transfer. Another and better way to reduce concentration polarisation is to increase the feed velocity along the membrane and to change the membrane module shape and dimensions (decreasing the module length, changing the module design or increasing the hydraulic diameter) /Mulder 1995, Winzeler and Belfort 1993/.

In microfiltration and ultrafiltration the effect of concentration polarisation is usually high because the fluxes are high and the mass-transfer coefficients are low as a result of the low diffusion coefficient of macromolecular solutes and of small particles, colloids and emulsion droplets. The diffusion coefficients (D) of macromolecules are of the order of 10^{-10} to 10^{-11} m^2/s or less and for low molar mass solutes D is roughly of the order of 10^{-9} m^2/s. Thus, the effect of concentration polarisation is less severe in reverse osmosis both because the flux is lower and because the mass-transfer coefficients are higher /Mulder 1995/.

The hydrodynamic changes can increase mass transfer from the surface and thus reduce the dwelling time and the concentration of potential foulants in the vicinity of the membrane surface. Conventionally, the modification of mass transfer has been achieved by several standard methods. The simplest way is to increase the cross-flow velocity. However, with increase in the velocity the energy consumption increases as well. The energy consumption is related to the third power of the velocity. As a result other energy efficiency methods are developed for improving mass transfer. Different kinds of turbulence promoters into the fluid channels have been tried. Various ways of introducing secondary flow across the membrane surface have been developed over the last few years. These methods include the methods, where the membrane is moved, those where the fluid flow is dynamic and those, where the membrane is stationary and where the fluid flow is steady. /Howell 1996/.

4.4.1 Cross-flow velocity

Although the increase of cross-flow velocity is not an energy efficient method to increase mass transfer, it has been the most widely used method. A lot of research works have been done to find out the effect of cross-flow velocity on the filtration performance. At low pressure, flux is proportional to pressure, although the proportionality constant is commonly smaller than for the pure water case. As pressure increases a limiting case develops, where a further increase in pressure produces no further increase in flux. Therefore, concentrate flow velocity should be increased as a function of the transmembrane pressure to compensate the forces due to convective flux /Crozes et al. 1997, Dal-Cin et al. 1996, Jönsson and Trägårdh 1990, Jönsson 1993 and 1995/. For instance Nuortila-Jokinen (1997) showed in her Ph.D thesis how dramatically the permeate flux can change as a result of increased flow velocity (Fig 7).

Generally a higher cross-flow velocity also means a higher permeate flux. However, it has been proved, that when the suspension contains a greater portion of larger, unground, particles, the filtration rate in microfiltration decreases with increasing cross-flow velocity. The phenomenon is assumed to be caused by a particle classification near the filtering surface. The cross-flow velocity affects the larger particles more and they thus remain in the feed. The finer particles which are not so much affected by cross-flow velocity, are deposited at or near the membrane surface and they form a higher resistance cake and cause lower filtration rates /Tarleton and Wakeman 1994/.

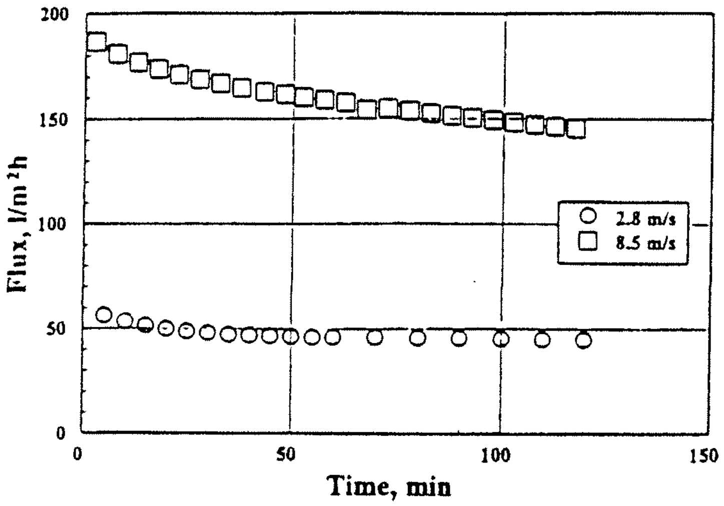


Figure 7. The effect of flow velocity in nanofiltration of neutral clear filtrate (tubular compact module, membrane WFN-4505 (Stork Friesland), 9 bar, 40 °C) /Nuortila-Jokinen 1997/.

4.4.1.1 Critical flux

The critical flux phenomenon has been studied particularly with microfiltration membranes. Field et al. (1995) defined the critical flux hypothesis for MF so that on start-up there exists a flux below which a decline of flux with time does not occur; above it fouling is observed. This flux is the critical flux and its value depends on the hydrodynamics in the system and probably also on other variables. This concept has been of interest for many researchers during the last years. It has been observed that an operating tactic for the commencement of filtration is very important in order to avoid fouling. A constant flux, rather than a constant pressure, operating mode should be preferred. If the flux is maintained constant during filtration, the transmembrane pressure then becomes a dependent variable. In such a way the convective flow of solutes towards the membrane is constant throughout a run. The critical flux is assumed to occur when convection towards the membrane is just balanced by back transport. The mechanisms of back transport, such as lateral migration and shear-enhanced diffusion are greater at higher cross-flow. Therefore, a higher critical flux with increased cross-flow is expected. /Field et al. 1995, Madaeni et al. 1996, Kwon et al. 1996/. It has been proven that filtration at a fixed permeate flux decreases membrane fouling. The obtained flux can be higher than the maximum flux obtained by keeping the pressure constant /Defrance et al. 1996/.

Benkahla et al. (1995) have observed that as transmembrane pressure is increased the flux increases linearly if a critical value of flux is not exceeded. Below this critical value the behaviour is reversible i.e. pressure can be reduced and the same fluxes are again obtained. However, if the critical flux value is exceeded then reducing pressure does not restore the original flux.

Another way to study critical flux is to measure the pressure needed to provide the flux. Then the flux is increased and the pressure is measured. The original flux is restored and the new pressure needed to maintain this flux is measured. If the pressure needed to maintain the restored flux is higher than the original pressure, the flux has been over the critical value. The flux-pressure profiles for operations below the critical flux showed little (for MF) or negligible (for UF) hysteresis. Chen et al. (1997) supposed that once the critical flux is exceeded, colloids in the polarised layer form a consolidated cake structure that is slow to depolarise, and which reduces the flux.

Madaeni et al. (1996) studied critical flux measuring the transmembrane pressure as a function of flux. They suggested, that the critical flux is the flux after which the transmembrane pressure increases dramatically as shown in Fig. 8.

One advantage in operating below the critical flux value is that cleaning in minimised and as a consequence fouling is reduced or even excluded.

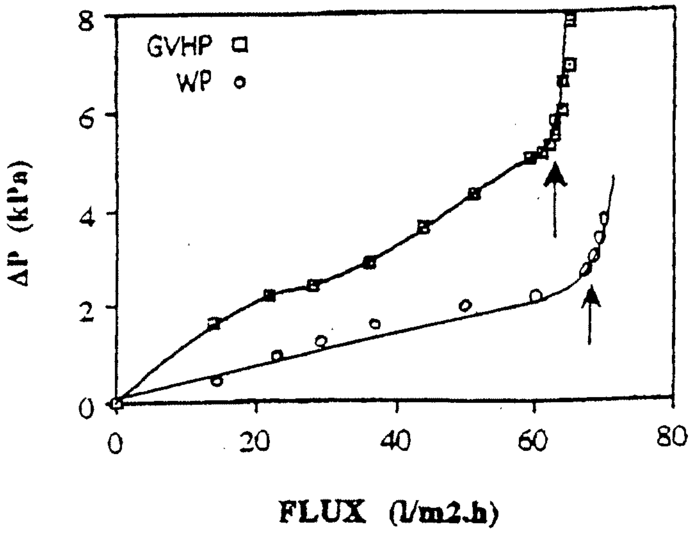


Figure 8. Transmembrane pressure versus flux for 0.22 μm membranes; GVHP is hydrophobic, WP is hydrophilic /Madaeni et al. 1996/.

4.4.2 Moving membrane filters

The dynamic membranes include vibrating and rotating systems. Commercially available dynamic membrane modules are for instance the Cross rotational filter (CR filter) and New Logics VSEP. They are rather complex systems but are capable of very high fluxes.

4.4.2.1 Rotating modules

The major advantage of a rotating unit is that the permeate flux becomes independent of the circulation flow, as the shear rate at the membrane surface is controlled by the rotational velocity. Thus more viscose or concentrated feeds can be treated in single pass flow, which means, that circulation pumping costs are reduced /Howell 1994, Howell 1996, Finnigan and Howell 1989/. The rotating module consists of two coaxial cylinders in which the inner cylinder, which contains the membrane, is rotating. A commercially available rotating module (Sulzer / Switzerland and Membrex / USA) is shown in Fig. 9 /Mulder 1995/.

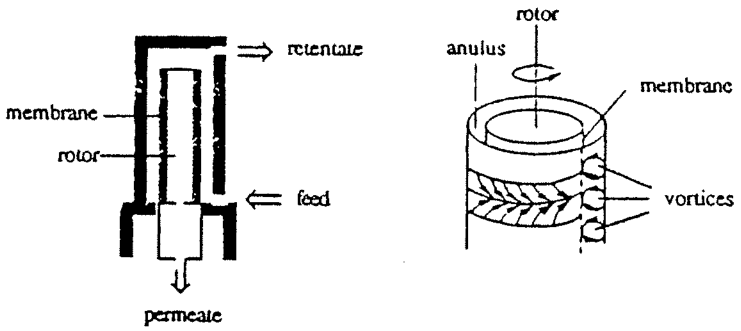


Figure 9. A rotating module (Sulzer / Switzerland and Membrex / USA) /Mulder 1995/.

4.4.2.2 CR filters

The CR filter is built up from stacked circular discs with membranes on both sides (Fig. 10). Between the discs, wings rotate at a distance of 5-10 mm from the membrane surfaces. The feed is put into rotation by the wings. The wings minimise the thickness of the filter cake or concentration polarisation on the membrane surface and throw the accumulated retentate off the membrane surface and thus maintain the high capacity of the filter. The cross-flow velocity on the surface of the membrane is typically over 10 m/s. A filter can contain up to 60 discs with diameters of 1 m and a total membrane surface area of 80 m^2.

Nanofiltration or reverse osmosis membranes can mostly not be used in CR filters because the maximum pressure is about 3 bar. However, the filter works very well in many applications, where ultrafiltration or microfiltration are used to treat waste water in order to get clean enough water for reuse.

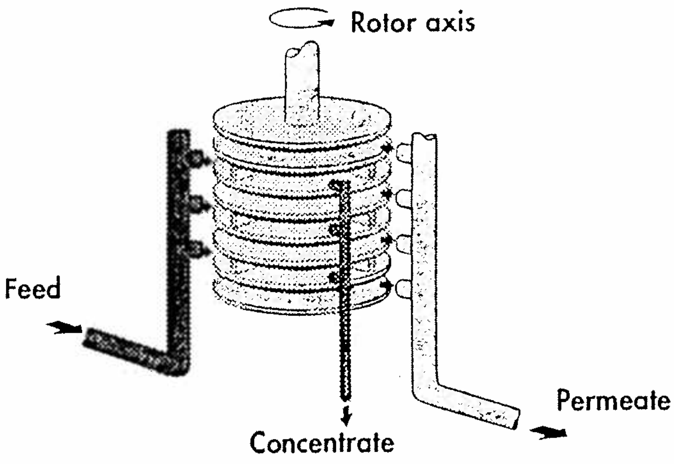


Figure 10. Principle construction of the CR filter /Raisio Flootek Ltd/.

Board mill white waters were treated successfully with a CR filter in Poland at the Czarnkow mill and in Sweden at the Svanboard mill. Both mills produce hard and porous board, and the white water contains many different substances as e.g. organic and inorganic subtances from bark, reused paper, asphalt, resins, phenols, pine tree oils, waxes and other additives. These effluents are very difficult to handle by biological treatment, due to the high content of organic matter, which is relatively difficult to degrade. Generally, board machines can withstand and live with rather dirty circulation waters. When this kind of white water systems are closed, the white water should be cleaned but there is no need to purify the white water completely. Thus, ultrafiltration membranes are proved to be tight enough to remove the colloidal and high molar mass substances from the system. It is enough to remove 10-20 kg colloidal and dissolved matter per produced ton board to be able to close this kind of white water systems. The

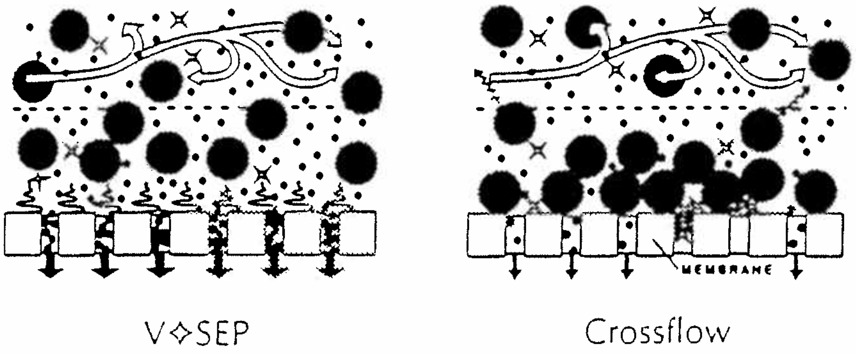
UF permeate is used as sealing water, cutting water, make up water and water to defibrators /Teppler et al. 1996/.

In paper mills the white waters should be cleaner than the board mill white waters. At Kirkniemi mill in Finland CR filters are used to treat paper mill white water, coating colour effluent and waters containing pigments. The total number of CR filters at Kirkniemi mill is 16. Thus, it is today the biggest membrane plant in the pulp and paper industry. CR filters are used very successfully at Frövifors board mill, where two CR filters treat the waste water from the coating process in order to recover coating colour. At Frövifors one part of their coating pigments is titanium dioxide, which is a very expensive pigment. The permeate of the CR filters does not contain colour and it is used for dilution of coating colour and for level control in tanks. The concentrate recovered corresponds to 5-7 tons of coating colour per day at a value of some 6000 US dollars /Teppler et al. 1996/.

4.4.2.3 Vibrating membrane

New Logic has developed the *Vibratory Shear Enhanced Processing* membrane module (VSEP module), which uses vibrational energy to increase the shear rate at the membrane/liquid interface. In a VSEP system the feed slurry remains nearly stationary, moving in a leisurely meandering flow between parallel membrane leaf elements. The leaf elements move in a vigorous vibratory motion tangential to the face of the membranes. Frequent differences in momentum between the membrane and the solution above the membrane result in very high wall shear rates (values as high as 150 000 s^{-1} is claimed) and effective depolarisation. This is about ten times the shear rate obtainable in cross-flow modules. The shear waves produced by the vibration of the membrane cause solids and foulants to be repelled and liquid to flow to the membrane pores unhindered. As a result, higher permeate fluxes can also be obtained and feed slurries of higher viscosity can be handled. The difference between traditional cross-flow and vibratory shear enhanced processing membrane modules is shown in Fig. 11 /Howell 1996, Shelley 1997, Buisson et al. 1994, Culkin 1991, Anonymous 1992/.

Nearly 99% of the total energy is claimed to be converted to shear at the membrane surface by the VSEP module and only 10% by conventional cross-flow modules. Because the shear forces are not produced by the bulk flow, the feed slurry can become viscous and still be successfully dewatered. An abrasion on the membrane surface can cause problems when particle size extends above 50 microns. Thus, prefilters are used to prevent the effect of abrasion. The membranes normally used in VSEP modules are made of organic materials, which limits their thermal stability. Another limit is the slurry viscosity. VSEP will not provide good filtration rates with extremely viscous streams.



V◇SEP

Crossflow

Figure 11 The working principle of a traditional cross-flow module and a vibratory shear enhanced processing module. In traditional cross-flow modules very high flow velocity is needed to remove retained particulates within the boundary layer. In VSEP modules the vibrational energy focuses shear waves at the membrane surface repelling solids and foulants while allowing for permeate rates up to ten times higher than conventional cross-flow /Anonymous 1992/.

VSEP membrane separators can be used in a wide variety of industrial applications. Membranes from reverse osmosis to microfiltration can perform separations from low molar mass solutes through particles with diameters of 30 μm. Current uses of VSEP modules include: latex dewatering, catalyst recovery, waste stream treatment (for instance white water treatment), sugar processing and many other separation processes.

This kind of module is developed at the beginning of the 90's. Thus, the technology is rather new and the mechanism how it works is not completely understood yet. No adequate theory is available to explain mass transfer in vibrating membrane systems /Eykamp 1995/.

4.4.3 Dynamic fluid flow

In membrane filtrations constant flows often require cross-flow velocities in the turbulent regime in order to manage concentration polarisation and fouling, while unsteady flows can be effective in both the laminar and in the turbulent regimes.

Dynamic fluid flow can be performed by using *pulsating flow* with or without inserts or baffles. Another approach is to use *backpulsing* from the permeate side thus directly moving the fluid and colloids from the membrane surface. The use of dynamic fluid flows requires careful optimisation of amplitude and frequency for either of the options chosen. Methods to induce the dynamic fluid flow on the membrane surface include designing membrane surfaces with organised roughness, pulsation of axial and lateral flow, and the use of curvilinear flow under conditions that promote instabilities or vortices. Fig. 12 summarises various approaches to induce instabilities in bulk flow across a membrane surface /Winzeler and Belfort 1993, Belfort et al. 1994/.

Secondary flows like Taylor and Dean vortex flows have been used to help depolarise the solute build-up on membranes. Taylor vortex filtration is attained by rotating the cylinder membrane device or using a rotor, which rotates on the surface of the membrane. The advantages of this type of device are excellent bulk fluid mixing, high wall shear rates, and weakly decoupled cross-flow with transmembrane flux. The limitations are high energy consumption to rotate the equipment, difficulty to repair, possible sealing and membrane replacement difficulties and most importantly, difficulties in scaling up the capacity of the module. The use of Dean vortices overcome the limitations associated with Taylor vortex filter devices. The Dean vortices are developed, when a fluid is forced to flow in a curved channel at high enough flow rates. The developed secondary vortex flow centrifugally sweeps the membrane surface depolarising the solute build-up /Winzeler and Belfort 1993/.

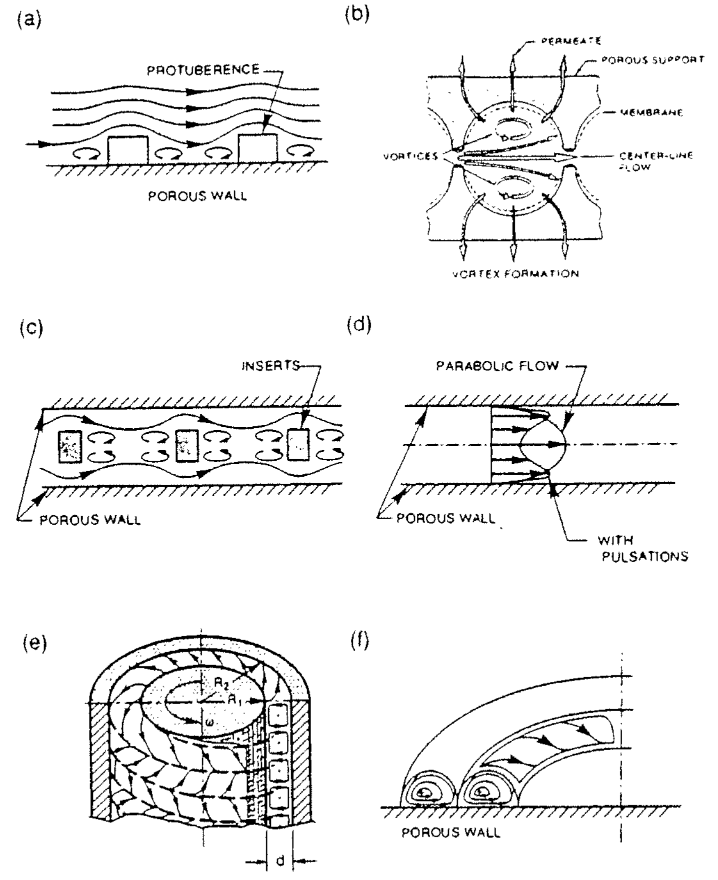


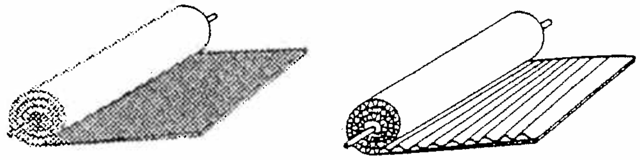
Figure 12. Methods to induce instabilities include: (a) placing protuberances on the membrane, (b) using a corrugated membrane surface, (c) placing inserts within the flow channel, (d) superimposing pulsations on the axial or permeate flows, (e) rotating a cylinder within a stationary outer cylinder to form Taylor vortices, and (f) flow in a curved channel to produce Dean vortices /Winzeler and Belford 1993/.

Placing *protuberances or corrugations* directly onto the membrane surface at defined separation distances induces periodic unsteady flows in the mass transfer boundary layer. Instabilities are produced to the solution-membrane interface region, and they depolarise the solute build-up. In this interfacial region the axial flow is smallest and the intensity of the vortices is relative low too. The protuberances can be extended further into the faster flowing regions of the fluid to increase the intensity and size of the vortices. This usually means that the axial pressure drop increases. Also, the presence of the protuberances results in a diminished active membrane area. The flat uniform membrane profile can be replaced with a well-defined rough surface such as a *furrowed profile*. Bulk flow enters each furrow and is swirled around at high speeds forming ball-bearing-like vortices. Thus the back-migration of polarised solutes increases and as a consequence the permeate flux increases. *Reversing bulk flow* several times per second has also been observed to increase the membrane permeation rates. These techniques are difficult to scale-up to intermediate or large size modules and are often limited by their high axial pressure drop. Only the *spacer* materials (mesh screens) are commonly used in spiral wound modules and plate-and-frame modules /Winzeler and Belford 1993/.

4.4.3.1 Spacers

The spacers are an essential component in spiral wound elements. The net-like spacer keeps adjacent membranes apart to form a feed channel as well as promotes the mass transfer. The spacer also presents an obstacle to axial flow and increases pressure losses. The optimal design of spacers has been studied by Da Costa et al. (1991). According to their studies the most effective spacer has a characteristics angle of about 80° for the range of conditions they considered. Later, Da Costa and Fane (1994) showed that also the size and location of filaments positioned transverse to flow are as important to flux enhancement as the hydrodynamic angle, which describes the change in direction of the fluid as it flows in the channel. Furthermore, a comparison of processing costs reveals that spacers, which induce no directional flow changes and with transverse filaments perpendicular to flow, close to the membrane, are economically better, than spacers characterized by zigzag flow path.

A conventional spiral wound module will be plugged by suspended solids. The main reason for the plugging of the module is the structure of the mesh type spacer. Using the spacer, which has a zigzag structure with a wide open channel, sufficient turbulence can be promoted (cross-flow velocity over 0.5 m/s) to prevent suspended solids deposition. A schematic illustration of three types of spacers is shown in Fig. 13 /Oinuma et al. 1993/.



(A) Mesh spacer (B) Conventional corrugated spacer

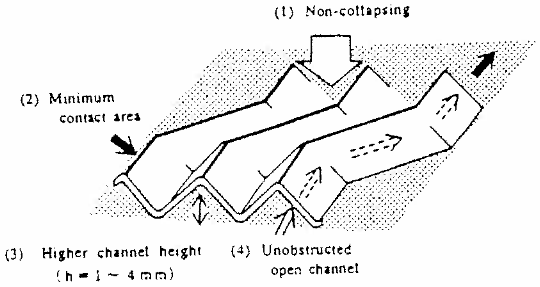


Figure 13. Various kinds of spacers in spiral wound modules /Oinuma et al. 1993/.

Conventional spiral wound elements are limited to cross-flow velocities of 0.3 to 0.6 m/s because of the hydraulic resistance of the flow paths in the elements. Schneider and Riddle (1990) introduced a spiral wound membrane element, where the hydraulic resistance is reduced by removing most of the mesh from the flow path and forming the feed flow path into an "M" shape of the membrane surface. They claimed that the new design results in an improvement in the feed velocity by a factor of five. This minimises the deposition of suspended solids on the surface of the membrane and increases the flux /Schneider and Riddle 1990/.

4.4.3.2 Crossing streams

Kaminski and Stawczyk (1996) proposed a new membrane module for reduction of the concentration polarisation layer. The main aim of the proposed method is to form two layers of the solution flowing over the membrane, which cross tangentially. The *crossing streams* cause that the momentum and the moments of the momentum are transferred to each other, and as a consequence, complex flows are formed. It was expected that the additional vortex motion of the liquid in the channel should reduce significantly the thickness of the concentration polarisation level. The idea is illustrated schematically in Fig 14.

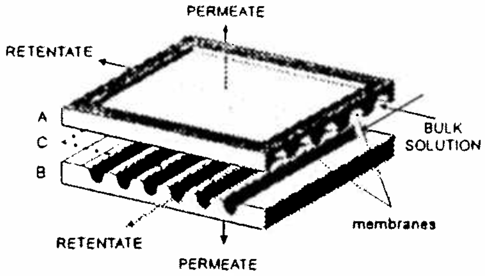


Figure 14. Schematic of the location of support plates in the module with tangentially crossed liquid streams / Kaminski and Stawczyk 1996/.

The permeate flux with this new module was twice that obtained with a classical plate and frame module in the filtration of dextran solutions. This kind of arrangement can be used for a spiral-wound module too.

4.4.3.3 Transversal flow module

A *transversal flow* module using hollow fibers or capillary membranes with the top layer outside is a rather promising design to improve mass transfer. The feed is flowing perpendicular to the fibers, as indicated schematically in Fig. 15. The fibers act as turbulence promoters, which enhance the mass transfer clearly /Mulder 1995/. Knops et al. 1992 pointed out the benefits of a transversal flow module. They compared it with a tube-side fed longitudinal flow module. The experiments were carried out with polystyrene globules, which have no interactions with the membrane material (polyethersulphone, 0.2 μm). The permeate flux of a transversal module increased much more when the Reynolds number was increased than the flux of a longitudinal flow module did. The measured fluxes for a transversal flow module were twice as high as those measured for a longitudinal flow module. Thus, they concluded that a transversal flow microfiltration module requires less membrane area and/or less energy than longitudinal flow modules to produce the same amount of permeate /Knops et al. 1992/.

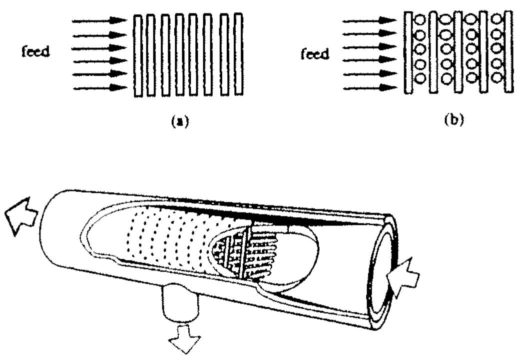


Figure 15 Schematic drawing of a transversal flow module with fibers arranged (a) parallel-in-line and (b) crossed-in-line /Mulder 1995/ and sketch of a transversal flow microfiltration module /Knops et al. 1992/.

4.4.3.4 Pulsation

An oscillating pressure gradient onto bulk axial flow in a tube produces a velocity profile with two equal maxima nearer the wall than the center-line (Fig 12 d). This increases the wall shear rate substantially and should increase back-diffusion of solute to the bulk flow region and improve the performance. The *pulsating flow* has been studied since the 1970's rather widely. Many researchers have pointed out that pulsatile flow increases significantly the permeate fluxes and this effect can be increased more using pulsatile flow with baffles. /Boothanon et al. 1991, Finnigan and Howell 1989 and 1990, Rodgers and Sparks 1992, Sais et al. 1997/.

In cross-flow ultrafiltration of a 1% albumin solution at pH 7.4, it was shown, that transmembrane pressure pulsing improved permeate flux for low cross-flow velocities, and the permeate flux values were twice the limiting flux values for nonpulsed cases, and that pressure dependency extended to higher pressures than in conventional ultrafiltration. However, pulsing did not improve flux values for turbulent flow cases. The frequency of the pulse was observed to be the dominant factor, and the increase of pulse amplitude did not affect the permeate flux. Rodgers and Sparks (1992) also observed that the transmembrane pressure should be negative during the pulse cycle in order to achieve improvement of the permeate flux.

Spiazzi et al. (1993) presented a tubular membrane module in which a rotating distributor disc was used to promote pulsatile flow only in the membranes. The rotative distributor disc had been perforated and placed in the front of the entrance plane of a tubular membrane bundle as Fig. 16 shows. The construction of the rotative distributor disc is simple, and the use of such a system can reduce the filtration costs because the recirculating flow velocity is half of that required by steady cross-flow filtration. The device was patented by Tech-Sep.

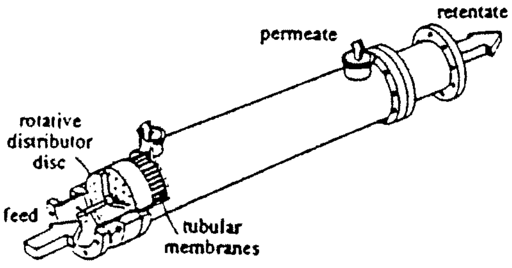


Figure 16. A tubular membrane module with the rotative distributor disc /Spiazzi 1993/.

The flow unsteadyness can be attained by using an intermittent jet located upstream of the filtration tube. The aim is to generate periodically large vortices, which can sweep the surface of the membrane when moving downstream. A circular nozzle is coaxially located upstream of the filtration tube (Fig. 17). The flow passes periodically either through the entire section of the tube (annulus part and jet nozzle) or only through the nozzle. Maranges and Fonade (1997) have shown that a flux enhancement obtained by this method could be higher than two-fold.

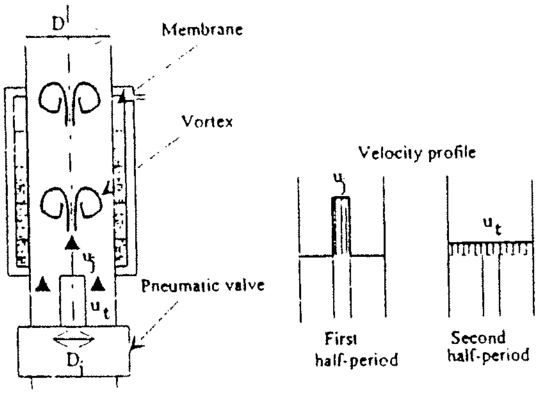


Figure 17. Generation of vortices in a tubular membrane by means of an intermittent jet /Maranges and Fonade 1997/.

4.4.3.5 Slug flow / air injection

Gas sparging, by injecting air into the liquid feed stream, to create a two-phase flow stream has proved to be an effective and simple technique for enhancing ultrafiltration and microfiltration processes /Cui and Wright 1994 and 1996, Cui et al. 1997, Cabassud et al. 1997, Mercier et al. 1997/. The enhancement of cross-flow ultrafiltration has been studied by Cui and Wright (1994). They injected air in the concentrate inside a tubular membrane. The injected air could reduce the concentration polarisation layer during ultrafiltration of macromolecules with tubular 100 kD PVDF membrane. Up to a 91% increase in permeate flux was achieved in the ultrafiltration of bovine serum albumin (BSA) solution at a concentration of 2.5 g/l and up to a 320% increase has been achieved in the downward co-current ultrafiltration of a 260 kD dextran solution. In this method the hydrodynamic disturbances result in an increase in both wall shear stresses and superficial liquid velocities and then lead to a significant enhancement in the permeate flux. The gas-liquid two-phase flow can have different flow patterns, including bubble flow, slug flow, churn flow, annular flow etc., depending on the gas and liquid velocities and the way that the two phases are mixed. In most applications using low rates of gas, the sparger type will determine whether the flow pattern is bubble flow or slug flow. A slug flow pattern has been observed to be the most efficient flow pattern in the filtration of bentonite and yeast suspension /Mercier et al. 1997/. A gas sparging like other hydrodynamic techniques to enhance membrane performance is efficient to enhance the permeate flux when the limiting phenomenon is the external fouling. In other words, it is very efficient in controlling concentration polarisation. However, the cleaning effect of gas sparging to remove absorbed macromolecules or microparticles, which are stuck onto the membrane surface and blocking the pores, is limited. The energy consumption of this process is much lower than that under steady conditions for the same filtration performance (reduction in the energy consumed by a factor of 3).

A novel membrane process named as airlift cross-flow filtration was developed on the basis of the theory of the airlift pump and the technique of gas sparged membrane filtration. In this process the airlift effect is used to drive liquid flow tangentially across the membrane surface and thus generate a gas-liquid two-phase cross-flow filtration. The new device possesses the advantages of enhanced cross-flow filtration without the need for a recirculating pump. The process is evaluated to be a low energy cost process compared to conventional single phase cross-flow operation and also process capital costs are diminished due to the elimination of a recirculating pump. The airlift cross-flow filtration can be operated at high transmembrane pressures and any type of membrane module can be integrated into the system. Fig. 18 presents the diagram of the experimental apparatus used in the airlift cross-flow filtration experiments /Cui et al. 1997/.

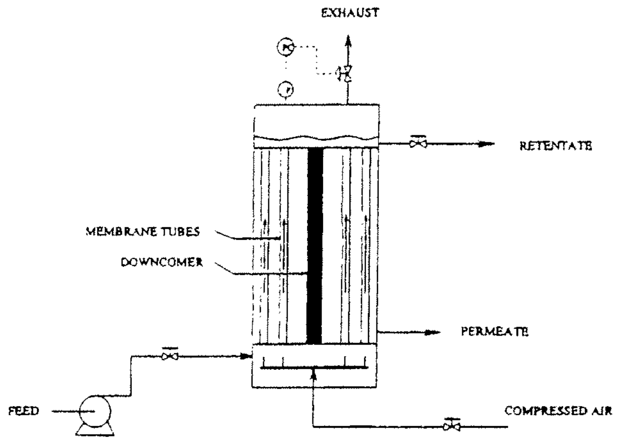


Figure 18. Diagram of airlift cross-flow filtration device /Cui et al. 1997/.

4.5 External fields

External fields (electric, ultrasonic and magnetic fields) are studied as methods to reduce fouling and improve the filtration performance. They can also be used to increase the cleaning efficiency.

4.5.1 Electric and ultrasonic field

Electric fields have been used to improve the efficiency of cross-flow membrane filtration for a long time. They can be used to clean the membrane and to prevent the deposition of charged particles onto a membrane surface. The DC field is applied either continuously or intermittently. The field strength, electrode placement and design, and the distance between the electrodes all depend on the electrical properties of the feed material. If the conductivity and zeta potential values of feed materials are low, the electric field may not improve the membrane performance. The conditions, which lead to an enhanced permeate flux are a high surface charge (zeta potential) at the particle surface, a particle size smaller than 5 μm, and suspension conductivities in the range from about 10 mS/m to 1 S/m. In general, increasing the electric field strength will cause less membrane fouling and a theoretical field strength exists, where the rate of particle migration is equal in magnitude but opposite in direction to the linear velocity of permeate through the filter medium /Jagannadh and Muralidhara1996, Wakeman and Sabri 1995, Tarleton 1988, 1992, Wakeman and Tarleton 1987/.

Different electrokinetic phenomena (Fig. 19) produce the improvements of membrane filtration when electric fields are applied. An electric field on the membrane surface would potentially lift the particles from the membrane surface and allow for the bulk flow to carry them away. This particle motion due to the action of an electric field is called electrophoresis. Simultaneously, an electrokinetic phenomenon called electroosmosis would allow for more fluid to flow across the membrane. These two phenomena are believed to improve membrane performance. The other mechanisms that can be suggested are caused by hydrodynamics, electrolysis, and/or electrocoagulation of the foulants. During the electrolysis process the gases are generated and they may have a sweeping action on the membrane surface, thus keeping the membrane surface clean.

This effect of gases on the improvement of membrane filtration is utilised in gas sparging filtrations.

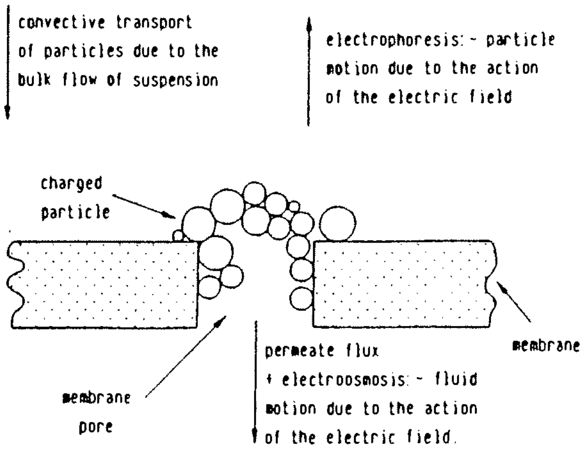


Figure 19. Some of the mechanisms involved in electrofiltration /Tarleton 1988/.

Most of the work on electromembranes was conducted using tubular membranes. One electrode (normally cathode) is located in the center of the tube and the other electrode away from the membrane. The centrally placed electrode attracts particles from the feed stream and keeps them away from the membrane surface. Because such an arrangement will be ineffective when the distance between the electrodes and the membrane surface is large, the electrodes are also placed directly over the membrane surface. In this case, the purpose of the electrode is to repel the particles away from the membrane surface.

Wakeman and Sabri (1995) showed that both constant and pulsed potential fields can reduce fouling in microfiltration. They concluded that maximum permeate flux and power consumption both occur when a constant potential field is applied to the filter. The flux increase also seemed to be disproportionately greater when extra power was applied to the system. This leads to a more effective utilisation of energy by the filter system, when the power is applied continuously, and to a smaller filter design.

The uneconomic power levels and as a result the high energy costs are the biggest limitations of the electric field enhanced filtration. Another limitation is the cost of the electrodes /Jagannadh and Muralidhara 1996/.

Combined ultrasonic and electric fields have been studied by Wakeman and Tarleton (1991) and Tarleton (1988, 1992). Both ultrasonic and electric fields can reduce membrane fouling caused by deposition of particulate colloidal material. Wakeman and Tarleton (1991) observed synergistic effects when electric and acoustic fields were applied simultaneously during microfiltration. Fig. 20 shows the synergy between electric and ultrasonic fields during the filtration of china clay suspension.

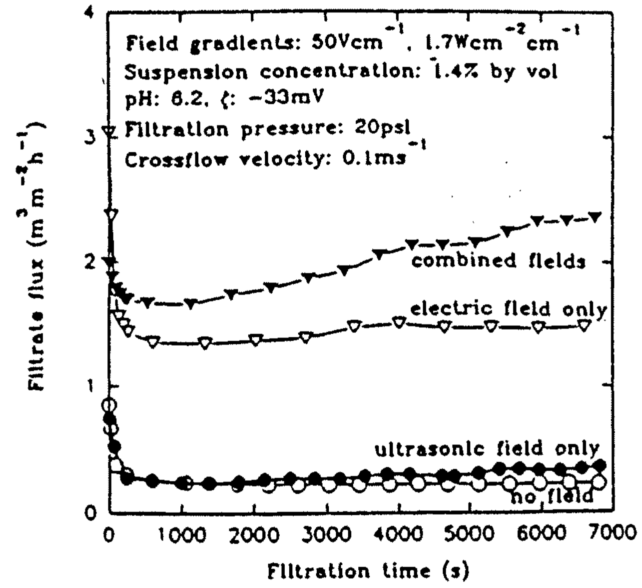


Figure 20. Synergy between electric and ultrasonic fields during the filtration of china clay suspension / Wakeman and Tarleton 1991/.

When ultrasonic waves are applied to a suspension (at frequencies in the range of 20 kHz to 100 kHz) the waves permeate through the mixture in the form of mechanical vibratory energy. High inertial forces are generated at the solid/liquid phase boundaries. These forces may be of sufficient magnitude to cause effects such as particulate dispersion, viscosity reduction, charges in the surface properties of the particles in suspension and cavitation. The cavitation process contains the rapid formation, oscillation, growth and subsequent violent destruction of gaseous microbubbles at nucleation sites. These sites occur on vessel walls, suspended particulates, existing air bubbles in the fluid medium, particles forming fouling layers and membrane pores. It is assumed that the agitation induced by cavitation close to the membrane is largely responsible for the effect observed when ultrasound is used to aid microfiltration. Ultrasound was utilised to enhance settling by causing agglomeration of particles and also to increase liquid flow rates through filters. Also ultrasound fields to enhance dewatering rates of fine slurries sludges during filtration have been studied. Ultrasound helps to reorientate the particles into their most stable position and thereby consolidate the structure of the cake /Tarleton 1992, Tarleton and Wakeman 1992, Muralidhara et al. 1986/.

External fields have also been observed to be effective during the cleaning cycle of the membrane. The cleaning with ultrasound dislodges the fouling layers formed on the membrane sufficiently to allow the cross-flowing streams to remove them. Thus, ultrasonic fields can be utilised not only during the filtration to enhance the permeate flow but also to improve the cleaning efficiency. External fields have also been tried out to improve the dewatering of fine slurries and sludges during filtration.

4.6 Abrasives and filtration aids

Abrasives and filtration aids can be used to prevent the particles to reach the membrane or to flush them out. Abrasives destroy the filtration cake by scouring it. It is not a good method because it may impair the filtration abilities of the membrane and can even destroy the membrane surface, and cause the process equipment to deteriorate. Thus, it can only be used when the membrane is hard enough. Other similar methods such as the use of soft, flexible foam balls can be successfully used in some cases. Filtration aids can be applied either as a precoat or as a mixture in the feed stream. The precoat method is very efficient in operating reverse osmosis, with high foulant concentration, to increase the permeate flux /Belfort 1980/. In the mixing method the filtration aid is mixed into the feed stream in order to get a higher cake permeability. However, the required concentration of filter aid can amount to four times as much as the foulant concentration and the filter aid needs to be constantly fed to the process /Milisic and Bersillon 1986/.

4.7 Cleaning

Although a suitable membrane has been chosen, an effective pretreatment method has been used and the filtration conditions have been adjusted in such a way that fouling of the membrane should be minimised there is always fouling in the filtration process. This means that effective cleaning methods are crucial for maintaining adequate long-term operation of all pressure-driven membrane processes. The filtration period should not be too long in order to avoid the permanent fouling of the membrane. On the other hand too frequent cleaning wears the membrane and increases the cleaning costs. The frequency with which membranes need to be cleaned should be estimated from process optimisation /Mulder 1995, Deqian 1987, Trägårdh 1989, Jönsson and Trägårdh 1990, Bartlett et al. 1995/. Maartens et al. (1996) used enzymes to clean the membranes fouled by biological waste waters. In enzymatic cleaning it is important to determine the nature of the foulants in order to the choose enzymes for the specific hydrolysis of these foulants. Enzymes have advantages over conventional cleaning agents such as biodegradability, and enzymes do not cause damage to the membranes.

4.7.1 Chemical cleaning

Chemical cleaning is the most important method for reducing fouling. The nature and concentration of chemicals as well as the cleaning time can be optimised. Chemical cleaning can be tailored according to the foulants. Generally, it can be said that acids are used to dissolve the precipitates of inorganic salts or oxide films and alkalies to solubilise organic foulants.

The cleaning process must remove deposits and restore the normal capacity and separation characteristics of the equipment. The chemicals should not only loosen and dissolve the foulants but they should also keep the foulants in dispersion or solution and avoid them to attach to the membrane surface again. Chemicals should not attack the membrane or other parts of the system and sometimes disinfecting of membrane is wanted too. The high demands for cleaning chemicals have forced the chemical manufacturers to develop different cleaning solutions to various membranes and processes. The cleaning solutions are often a mixture of chemicals. Alkaline cleaning solutions usually contain sodium hydroxide, phosphate, sequestering agents and surface active agents. The choice of surface active agents is very important, since some types may be adsorbed onto the membrane surface, resulting in a flux reduction. On the other hand, with a suitable choice of surfactant in the cleaning solution remarkable enhanced fluxes may be obtained. Thus, the cleaning can also be considered as an in situ surface modification operation /Ebrahim 1994, Trägårdh 1989, Jönsson and Trägårdh 1990, Mulder 1995, Deqian 1987/.

4.7.2 Mechanical cleaning

Many methods used during the filtration period to prevent concentration polarisation and fouling can be utilised in the cleaning cycle to improve the chemical cleaning efficiency. For instance back-flushing is used with chemical cleaning for microfiltration and ultrafiltration membranes. A pulsed electric field may drive particles and molecules away from the membrane surface. This method can be carried out without interrupting the process. In tubular systems also mechanical cleaning with oversized sponge balls is possible /Trägårdh 1989, Mulder 1995, Deqian 1987/.

5. Acknowledgement

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6. References

Al-Ahmad, M., Aleem, F.A., (1994). Scale formation and fouling problems and their predicted reflection on the performance of desalination plants in Saudi Arabia, *Desalination*, **96**(1-3), pp. 409-419.

Amirtharajah, A., (1990). Coagulation: Rejuvenation for a classical process, *Water E & M*, Dec. 1990, pp. 25-27, 32.

Anonymous (1992). New separation system extends the use of membranes, *Filtration & Separation*, **29**(5), pp. 376-378.

Attia, Y.A., Yu, S., (1991). Flocculation and filtration dewatering of coal slurries aided by a hydrophobic polymeric flocculant, *Sep. Sci. Techn.*, **26**(6), pp. 803-818.

Barlett, M., Bird, M.R., Howell, J.A., (1995). An experimental study for the development of a qualitative membrane cleaning model, *J. Membrane Sci.*, **105**, pp. 147-157.

Belfort, G., (1980). Artificial particulate fouling of hyperfiltration membranes IV. Dynamic protection from fouling. *Desalination*, **34**, pp. 159-169.

Belfort, G., Davis, R.H., Zydney, A.L., (1994). The behavior of suspension and macromolecular solutions in crossflow microfiltration, *J. Membrane Sci.*, **96**, pp. 1-58.

Benkahla, Y.K., Ould-Dris, A., Jaffrin, M.Y., Si-Hassen, D., (1995). Cake growth mechanism in cross-flow microfiltration of mineral suspensions, *J. Membrane Sci.*, **98**, pp. 107-117.

Boonthanon, S., Hwan, L.S., Vigneswaran, S., Ben Aim, R., Mora, J.C., (1991). Application of pulsating cleaning technique in crossflow microfiltration, *Filtration & Separation*, **28**(3), pp. 199-201.

Bring, L.S.E., Romijn, D.J., (1990). Reducing the protein fouling of polysulfone surfaces and polysulfone ultrafiltration membranes: Optimization of the type of presorbed layer, *J. Membrane Sci*, **78**, pp. 209-233.

Buisson, H., Adiga, M., Zaidi, A., (1994). High-shear membrane modules and their applications to process water management and wastewater treatment, *Engineering of membrane processes II*, 26-28 April, Tuscany, Italy.

Cabassud, C., Laborie, S., Laine, J.M., (1997). How slug flow can improve ultrafiltration flux in organic hollow fibres, *J. Membrane Sci.*, **128**, pp. 93-101.

Chen, V., Fane, A.G., Fell, C.J.D., (1992). The use of anionic surfactant for reducing fouling of ultrafiltration membranes: their effects and optimization, *J. Membrane Sci.*, **67**, pp. 249-261.

Chen, V., Fane, A.G., Madaeni, S., Wenten, I.G., (1997). Particle deposition during membrane filtration of colloids: transition between concentration polarization and cake formation, *J. Membrane Sci.*, **125**, pp. 109-125.

Cheng, Y.S., Fang, S.R., Tierney, J.W., Chiang, S.H., (1988). Application of enhanced vacuum filtration to dewatering of fine coal refuse, *Sep. Sci. Techn.*, **23**(12&13), pp. 2113-2130.

Cheng, Y.S., Chiang, S.H., Morsi, B.I., (1991). Enhancement of filtration and dewatering of fine coal using flocculants, *Mines et Carrieres.*, **3**, pp. 39-43.

Clark, W.M., Bansal, A., Sontakke, M., Ma, Y.H., (1991). Protein adsorption and fouling in ceramic ultrafiltration membranes, *J. Membrane Sci.*, **55**, pp. 21-38.

Crozes, G.F., Jacangelo, J.G., Anselme, C., Laine, J.M., (1997). Impact of ultrafiltration operating conditions on membrane irreversible fouling, *J. Membrane Sci.*, **124**, pp. 63-76.

Cui, Z.F., Wright, K.I.T., (1994). Gas-Liquid two-phase crossflow ultrafiltration of BSA and dextran solutions, *J. Membrane Sci.*, **90**, pp. 183-189.

Cui, Z.F., Wright, K.I.T., (1996). Flux enhancement with gas sparging in downwards crossflow ultrafiltration: performance and mechanism, *J. Membrane Sci*, **117**, pp. 109.

Cui, Z.F., Bellara S.R., Homewood, P., (1997). Airlift crossflow membrane filtration - a feasibility study with dextran ultrafiltration, *J. Membrane Sci.*, **128**, pp. 83-91.

Culkin, B., (1991). Vibratory shear enhanced processing: An answer to membrane fouling? *Chem. processing.*, Jan 1991.

Da Costa, A.R., Fane, A.G., Fell, C.J.D., Franken, A.C.M., (1991). Optimal channel spacer design for ultrafiltration, *J. Membrane Sci.*, **62**(3), pp. 275-291.

Da Costa, A.R., Fane, A.G., (1994). Net-type spacers: Effect of configuration on fluid flow path and ultrafiltration flux, *Ind. Eng. Chem. Res.*, **33**(7), pp. 1845-1851.

Dal-Cin, M.M., Striez, C.N., Tweddle, T.A., McFellan, F., Ramamurthy, P., (1996). Membrane performance with plug screw feeder pressate: operation conditions and membrane properties, *Desalination*, **105**(3), pp. 229-244.

Defrance, L., Jaffrin, M.Y., Gupta, B.B., (1996). Membrane fouling in sludge water treatment with mineral membranes, *Proc. International Membrane Science and Technology Conference*, 12-14 November, Sydney, Australia, p. H8.

Deqian, R., (1987). Cleaning and regeneration of membranes, *Desalination*, **62**, pp. 363-371.

Dunn, R.O, Scamehorn, J.F., (1985). Use of micellar-enhanced ultrafiltration to remove dissolved organics from aqueous streams, *Sep. Sci. Techn.*, **20**(4), pp. 257-284.

Ebrahim, S., (1994). Cleaning and regeneration of membranes in desalination and wastewater applications: State-of-the-art, *Desalination*, **96**, pp. 225-238.

Ehsani, N., (1996). A study of fractionating and ultrafiltration of proteins with characterized modified and unmodified membranes, *Ph.D Thesis*, Research papers 51, Lappeenranta University of Technology, Lappeenranta, Finland.

Eriksson, B., Trägårdh, G., (1996). Treatment of surface water rich in humus - Membrane filtration vs. conventional treatment, *Desalination*, **108**, pp. 117-128.

Eykamp, B., (1995). Microfiltration and ultrafiltration, In: *Membrane Separation Technology, Principles and Applications*, Noble, R. D., Stern, S. A., (ed.), Chapter 1, Elsevier, The Netherlands, pp. 1-43.

Fane A.G., Fell C.J.D., Kim, K.J., (1985). The effect of surfactant pretreatment on the ultrafiltration of proteins, *Desalination*, **53**, pp. 37-55.

Fane A.G., (1994). Fouling definition and characterisation. *Seminar on Fouling in Pressure driven Membrane Processes*, 4-5 July, Lappeenranta, Finland.

Fang, S.R., Cheng, Y.S., Chiang, S.H., (1988). Use of flocculant for filtration and dewatering of fine coals, In: *Interfacial Phenomena in Biotechnology and Material Processing*, Attia, Y.A., Moudgil, B.M., Chander, S. (ed.), Elsevier Science Publishers B.V., Amsterdam, 1988, pp. 515-529.

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., (1995). Critical flux concept for microfiltration fouling, *Desalination*, **100**, pp. 259-272.

Field, R.W., Song, H., Arnot, T., (1994). The influence of surfactant on water flux through microfiltration membranes, *J. Membrane Sci.*, **86**, pp. 291-304.

Finnigan, S.M., Howell, J.A., (1989). The effect of pulsed flow on ultrafiltration fluxes in a baffled tubular membrane system, In: *Fouling and cleaning in food processing*, Kessler, H.G., Lund, D.B. (ed.), Prien, Bavaria, Germany, 1989, pp. 216- 238.

Finnigan, S.M., Howell, J.A., (1990). The effect of pulsed flow on ultrafilration fluxes in a baffled tubular mrmbrane system, *Desalination*, **79**, pp. 181-202.

Flemming, H.-C., (1993). Mechanistic aspects of reverse osmosis membrane biofouling and prevention, In: *Reverse Osmosis, Membrane Technology, Water Chemistry, and Industrial Applications*, Amjad, Z., (ed.), Van Nostrand Reinhold, New York, pp. 210-236.

Halverson, F., Panzer, H.P., (1980). Flocculating Agents, Kirk-Othmer: *Encyclopedia of Chemical Technology*, Vol. 10, 3rd edition, John Wiley & Sons, Inc., USA 1980, pp. 489-523.

Hogg, R., (1988). Design and control of flocculation processes for solid-liquid separation, *Proc. of the Int. Technical Conf. on Filtration and Separation*, American Filtration Society, March 1988, pp. 353-358.

Howell, J.A., (1996). Enhancing the performance of membrane processes, *Proc. International Membrane Science and Technology Conference*, 12-14 November, Sydney, Australia, p. PL.2.

Howell, J.A., (1994). Flux enhancement, *Seminar on Fouling in Pressure driven Membrane Processes*, 4-5 July, Lappeenranta, Finland, 31 pp.

Hughes, M.A., (1990). Coagulation and flocculation, Part I, In: *Solid-Liquid separation*, 3rd ed., Svarovsky, L. (ed.), Butterworth & Co. (Publishers) Ltd, pp. 74-96.

Ives, K.J., (1990). Coagulation and flocculation, Part II - Orthokinetic flocculation, In: *Solid-Liquid separation*, 3rd ed., Svarovsky, L. (ed.), Butterworth & Co. (Publishers) Ltd, pp. 98-131.

Jagannadh, S.N., Muralidhara, H.S., (1996). Electrokinetics methods to control membrane fouling, *Ind. Eng. Chem. Res.*, **35**, pp. 1133-1140.

Jönsson A.-S., Blomgren, Y., Petersson, E., (1988). Influence of pH and surfactants on ultrafiltration membranes during treatment of bleach plant effluent, *Nord. Pulp Pap. Res. J.*, **4**, 159-165.

Jönsson A.-S., Trägårdh, G., (1990). Fundamental pronciples of ultrafiltration, *Chem. Eng. Process.*, **27**, pp. 67-81.

Jönsson A.-S., (1993). Influence of shear rate on the flux during ultrafiltration of colloidal substances, *J. Membrane Sci.*, **79**, pp. 93-99.

Jönsson A.-S., (1995). Concentration polarization and fouling during ultrafiltration of colloidal suspensions and hydrophobic solutes, *Sep. Sci. Techn.*, **30**(2), pp. 301-312.

Kaminski, W., Stawczyk, J., (1996). The concentration polarization layer reduction in the new membrane module, *7th World Filtration Congress*, Volume I, Budapest, 20-23 May, pp.457-461.

Kandori, K., Schechter, R.S., (1990). Selection of surfactant for micellar-enhanced ultrafiltration, *Sep. Sci. Techn.*, **25**(1&2), pp. 83-108.

Kim, K.J., Fane, A.G., Fell, C.J.D., (1988). The performance of ultrafiltration membranes pretreated by polymers, *Desalination*, **70**, pp. 229-249.

Kim, K.J., Fane, A.G., Fell, C.J.D., (1989). The effect of Langmuir-Blodgett layer pretreatment on the performance of ultrafiltration membranes, *J. Membrane Sci.*, **43**, pp. 187-204.

Kimura, S., Ohtani, T., Watanabe, A., (1985). Nature of dynamically formed ultrafiltration membranes, In: Reverse osmosis and ultrafiltration, Sourirajan, S., Matsuura, T., (Ed.), *ACS Symp. Ser.*, **281**, American Chemical Society, Washington, D.C., pp. 35-46.

Knops, F.N.M., Futselaar, H., Racz, I.G., (1992). The transversal flow microfiltration module. Theory, design, realization and experiments, *J. Membrane Sci.*, **73** pp. 153-161.

Koren, J.P.F., Syversen, U., (1995). State-of-the-art electroflocculation, *Filtration & Separation*, **32**(2), pp. 153-156.

Kronmiller, D.L., (1994). What every reverse osmosis water system manager should know, *Desalination*, **98**(1-3), pp. 401-411.

Kulkarni, A., Mukherjee, D., Gill, W.N., (1996). Flux enhancement by hydrophilization of thin film composite reverse osmosis membranes, *J. Membrane Sci.*, **114**, pp. 39-50.

Kwon, D.Y., Vigneswaran, S., Ngo, H.H., Ben Aim, R., Fane, A.G., Shin, H.S., (1996). Experimental study on critical flux in crossflow microfiltration, *Proc. International Membrane Science and Technology Conference*, 12-14 November, Sydney, Australia, p. PD.3.

Köster, R., Burg, B., Kaiser, M., (1992). Tenside als Hilfsmittel zur Entwässerung feinkörniger Feststoffe, *Aufbereitungs-Techn.*, **33**(5), pp. 267-273.

Leja, J., (1982). Surface Chemistry of Froth Flotation, Plenum Press, New York, p. 400.

Lu,S., Song, S., (1991). Hydrophobic interaction in flocculation and flotation , 1. Hydrophobic flocculation of fine mineral particles in aqueous solution, *Colloids Surf.*, **57**, pp. 49-60.

Luttinger, L.B., (1981). The use of polyelectrolytes in filtration processes, In: *Polyelectrolytes for water and wastewater treatment*, Schwoyer, W.K., (ed.), CRC Press, Inc. 1981, Boca Raton, Florida, USA, pp.211-242.

Maartens, A., Swart, P., Jacobs, E.P., (1996). Characterization and enzymatic cleaning of ultrafiltration membranes fouled during the treatment of biological waste waters, *Proc. International Membrane Science and Technology Conference*, 12-14 November, Sydney, Australia, p. H.9, pp. 283-285.

Madaeni, S.S., Fane, A.G., Wiley, D.E., (1996). Factors influencing critical flux in membrane filtration of biomass, *Proc. International Membrane Science and Technology Conference*, 12-14 November, Sydney, Australia, p. D.10.

Maleriat, J.P., Trebouet, D., Jaouen, P., Quemeneur, F., (1996). Study of a combined process using natural flocculating agents and crossflow filtration for the processing of an aged landfill leachate, *7th World Filtration Congress*, Volume II, Budapest, 20-23 May, pp. 507-511.

Maranges,C., Fonade, C., (1997). Flux enhancement in crossflow filtration using an unsteady jet, *J. Membrane Sci.*, **123**, pp. 1-8.

Mehrotra, V.P., Wakeman, R.J., Sastry, K.V.S., (1982). Dewatering flocculated coal fines, *Filtration & Separation*, **19**(3), pp. 197-201.

Mercier, M., Fonade, C., Lafforgue-Delorme, C., (1997). How slug flow can enhance the ultrafiltration flux in mineral tubular membranes, *J. Membrane Sci.*, **128**, pp. 103-113.

Milisic, V., Bersillon, J.L., (1986). Anti-fouling techniques in cross-flow microfiltration, *Filtration & Separation*, **23**(6), pp. 347-349.

Morel, G., Graciaa, A., Lachaise, J., (1991). Enhanced nitrate ultrafiltration by cationic surfactant, *J. Membrane Sci.*, **56**, pp. 1-12.

Mukherjee, D., Kulkarni, A., Gill, W.N., (1996). Chemical treatment for improving performance of reverse osmosis membranes, *Desalination*, **104**, pp. 239-249.

Mulder, M.H.V., (1995). Polarization phenomena and membrane fouling, *In: Membrane Separation Technology, Principles and Applications*, Noble, R. D., Stern, S. A., (ed.), Chapter 2, Elsevier, The Netherlands, pp. 45-84.

Mulder, M., (1996). Basic principles of membrane technology, Kluwer Akademic Publishers, The Netherland, p. 419.

Muralidhara, H.S., Senapati, N., Ensminger, D., Chauhan, P., (1986). Electro-aqoustic separation process for fine particle suspension, *Filtration & Separation*, **23**(6), pp. 351-353.

Murkes, J., (1986). Low-shear and high-shear cross-flow filtration, *Filtration & Separation*, **23**(6), pp. 364-365.

Mänttäri, M., Nuortila-Jokinen, J., Nyström, M., (1997). Evaluation of nanofiltration membranes for filtration of paper mill total effluent, *Filtration & Separation*, **34**(3), pp.275-280.

Nuortila-Jokinen, J., (1997). Choice of optimal membrane processes for economical treatment of paper machine clear filtrate, *Ph.D Thesis*, Lappeenranta University of Technology, Research papers 58, Lappeenranta , Finland.

Nyström, M., Järvinen, P., (1991 a). Modification of polysulfone ultrafiltration membranes with UV irradiation and hydrophilicity increasing agents, *J. Membrane Sci.*, **60**, pp. 275-296.

Nyström, M., Ehsani, N., Ojamo, H., (1991 b). Separation of lignocellulosics hydrolyzing enzymes with modified ultrafiltration membranes, *Biosep.*, 2, pp. 187-196.

Nyström, M., (1992). Interaction of model proteins with characterized modified and unmodified polysulfone ultrafiltration membranes, *Ph.D Thesis*, Dept. Phys. Chem., Åbo Akademi, Turku, Finland.

Nyström M., Mänttäri M., (1993). Micellar enhanced ultrafiltration, MEUF, as a tool to concentrate metals or hydrophobic pollutants from wastewater, *Proceedings of the 6th World Filtration Congress*, 18-21 May, 1993, Nagoya, Japan, pp. 722-725.

Nyström, M., Ruohomäki, K., Kaipia, L., (1996). Humic acid as a fouling agent in filtration, *Desalination*, **106**, pp. 79-87.

Oinuma, M., Mizuniva, T., Sawada, S., Yabe, K., (1993). A new suspended solid separation system using spiral wound ultrafiltration membrane, *12 th Semicond. Pure Water Chem. Conf.*, pp. 180-195.

Pearse, M.J., Allen, A.P., (1983). The Use of Flocculants and Surfactants in the Filtration of Mineral Slurries, *Filtration & Separation*, **20**(1), pp. 22-27.

Penniman, J.G., (1981). Electrokinetics, In: *Polyelectrolytes for water and wastewater treatment*, Schwoyer, W.K., (ed.), CRC Press, Inc. 1981, Boca Raton, Florida, USA, pp. 61-90.

Raisio Flootek Ltd., CR-filter - Membrane filter for purification and recycling of industrial waste water, Finland.

Ramamurthy, P., Poole, R., Dorica, J.G., (1993). Fouling of ultrafiltration membranes during treatment of CTMP screw press filtrates, *Proc. 1993 Environmental Conf.*, 26-28 October, Thunder Bay, Canada, pp. 67-71

Reuter, J.M., Hartan, H.G., (1986). Structure and reaction kinetics of polyelectrolytes and their use in solid-liquid-processing, *Aufbereitungs-Tech.*, **11**, pp. 598-606.

Rodgers, V.G.J., Sparks, R.E., (1992). Effect of transmembrane pressure pulsing on concentration polarization, *J. Membrane Sci.*, **68**, pp. 149-168.

Sais, H., Ben Aim, R., Gupta, B.B., Jaffrin, M.Y., (1997). Cross flow filtration with pulsation means energy saving, *7th Word Filtration Congress*, 20-23 May, Budapest, Hungary, pp. 442-446.

Scamehorn, J.F., Ellington, R.T., Christian, S.D., Penney, B.W., Dunn, R.O., Bhat, S.N., (1986). Removal of multivalent metal cations from water using micellar-enhanced ultrafiltration, *AICHE Symp. Ser.*, **250**(82), pp.48-58.

Scamehorn, J.F., Christian, S.D.,Ellington, R.T., (1989). Use of Micellar-Enhanced Ultrafitration to remove multivalent metal ions from aqueous streams, In: *Surfactant-based separation processes*, Scamehorn, J.F., Harwell, J.H. (ed.), Surfactant Science Series, vol 33, Marcel Dekker, New York, pp. 29-51.

Schneider, B.M., Riddle, R.A., (1990). New high velocity spiral wound MF-UF-RO elements design constructed with an "M" path open channel, feed separator, *The International Water Conf.*, **51**st Annual meeting, 22-24 October, Pittsburgh, USA. pp. 382-395.

Schulze, S., Stahl, W., (1996). Improvement of the filtration and sedimentation behaviour using micro-organisms as natural flocculants, *Proc. 7th World Filtration Congress*, 20-23 May, Budapest, Hungary, pp. 162-166.

Shelley, S., (1997). Membrane-based separation, with a twist, *Chem. Eng.*, **104**(2), p. 107.

Sierka, R.A., Folster, H.G., (1995). Membrane treatment of bleach plant filtrates, *Proc. in 1995 Topical Conference, Recent developments and future opportunities in separation technology*, Vol 1, 12-17 November, Miami Beach, Florida, USA.

Smith, G.R.S., (1990). Filter aids, In: *Solid-Liquid separation*, Svarovsky, L. (ed.), 3rd edition, Butterworth & Co. (Publishers) Ltd, pp. 338-357.

Song, S., Lu, S, (1994). Hydrophobic flocculation of fine hematite, siderite, and rhodochrosite particles in aqueous solution, *J. Colloid Interface Sci.*, **166**, pp. 35-42.

Spiazzi, E., Lenoir, J., Grangeon, A., (1993). A new generation of insteady-state flow regime in tubular membranes as an anti-fouling technique: A hydradynamic approach, *J. Membrane Sci.*, **80**, pp. 49-57.

Stahl, W., Stroh, G., (1990). Influence of surfactant on filtration characteristics in vacuum and pressure filtration, *5th World Filtration Congress*, p. 161-167.

Stroh, G., Stahl, W., (1990). Effect of surfactants on the filtration properties of fine particles, *Filtration & Separation*, **27**(3), pp. 197-199.

Tabatabai, A., Scamehorn, J.F., Christian, S.D., (1995). Economic feasibility study of polyelectrolyte-enhanced ultrafiltration (PEUF) for water softening, *J. Membrane Sci.*, **100**, pp. 193-207.

Takizawa, S., Fujita, K., Soo, K.H., (1996). Membrane fouling decrease by microfiltration with ozone scrubbing, *Desalination*, **106**, pp. 423-426.

Tarleton, E.S., (1988). How electric and ultrasonic fields assist membrane filtration, *Filtration & Separation*, **25**(6), 402-406.

Tarleton, E.S., (1992). The role of field-assisted techniques in solid/liquid separation, *Filtration & Separation*, **29**(3), pp. 246-252.

Tarleton, E.S, Wakeman, R.J., (1992). Electro-acoustic crossflow microfiltration, *Filtration & Separation*, **29**(5), pp.425-432.

Tarleton, E.S, Wakeman, R.J., (1994). Understanding flux decline in crossflow microfiltration: Part II - Effect of process parameters, *Trans IChemE*, **72**(A), pp. 431-440.

Teppler, M., Paatero, J., Bergdahl, J., Damen, H, (1996). PM and BM white water treatment with membrane technology, *PST Symposium*, 28 November, Munchen, Germany, pp. 28.

Tripodi, M.K., Hassett, R.J., Shaffer, A.F., Stimpson, D.I., Burge, J.J., Stedronsky, E.R., Henis, J.M., (1988). Applications of surface modified membranes for protein purification, *Proc. IMSTEC'88 International Membrane Technology Conference*, 15-17 November, Sydney, A7-A10.

Trägårdh, G., (1989). Membrane cleaning, *Desalination*, **71**, pp. 325-335.

Wakeman, R.J., Tarleton, E.S., (1987). Membrane fouling prevention in crossflow microfiltration by the use of electrical fields, *Chem. Eng. Sci.*, **42**(4), pp. 829-842.

Wakeman, R.J., Thuraisingham, S.T., Tarleton, E.S., (1989). Colloid science in slid-liquid separation technology, Is it important?, *Filtration & Separation*, **26**(4), pp. 277-283.

Wakeman, R.J., Tarleton, E.S., (1991). An experimental study of electroacoustic crossflow microfiltration, *Chem. Eng. Res. Des.*, **69**(A), pp. 386-397.

Wakeman, R.J., Sabri, M.N., (1995). Utilizing pulsed electric fields in crossflow microfiltration of titania suspensions, *Chem. Eng. Res. Des.*, **73** (A), pp. 455-463.

Ward, A.S., (1996). Pretreatment techniques, In Solid-Liquid Filtration and Separation Technology, Rushton, A., Ward, A.S., Holdich, R.G. (eds), 1st edition, VCH Publishers, Inc., pp. 74-96.

Winzeler, H.B., Belfort, G., (1993). Enhanced performance for pressure-driven membrane processes: the argument for fluid instabilities, *J. Membrane Sci.*, **80**, pp. 35-47.

Zhu, X., Elimelech, M., (1995). Fouling of reverse osmosis membranes by aluminium oxide colloids, *J. Env. Eng.*, **121**(12), pp. 884-892.