ESPOO 2005 VTT PUBLICATIONS 576

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Electrically or ultrasonically enhanced membrane filtration of wastewater

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VTT Processes

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Dissertation for the degree of Doctor of Science in Technology to be presented with due permission for public examination and criticism in the Auditorium 1383 at Lappeenranta University of Technology, Lappeenranta, Finland, on the 11th of November, 2005, at 12 o'clock noon.

ISBN 951–38–6663–7 (soft back ed.)
ISSN 1235–0621 (soft back ed.)

ISBN 951–38–6664–5 (URL: http://www.vtt.fi/inf/pdf/)
ISSN 1455–0849 (URL: http://www.vtt.fi/inf/pdf/)

JULKAISIJA – UTGIVARE – PUBLISHER

VTT, Vuorimiehentie 5, PL 2000, 02044 VTT
puh. vaihde 020 722 111, faksi 020 722 4374

VTT, Bergsmansvägen 5, PB 2000, 02044 VTT
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Otamedia Oy, Espoo 2005

Kyllönen, Hanna. Electrically or ultrasonically enhanced membrane filtration of wastewater. Espoo 2005. VTT Publications 576. 79 p. + app. 54 p.

Keywords membrane filtration, fouling, electrofiltration, electric field, ultrasound, flux, transmembrane pressure, filters, wastewaters, wastewater purification

Abstract

Flux decline due to concentration polarisation and membrane fouling is a serious problem in membrane filtration. In this thesis the effect of an external DC electric or ultrasonic field separately on the flux in cross-flow membrane filtration of wastewater samples was studied.

Significant enhancement of the limiting flux compared with the flux with no electric field was achieved in the filtration of model wastewater. The most important parameters for the limiting flux enhancement were the electrophoretic mobility and the applied electric field strength. The electric field especially prevented the cake formation on the membrane surface. Its effect on other kinds of fouling was minor. The critical electric field strength was determined both theoretically and experimentally.

Electrofiltration was also studied in the industrial wastewater applications. The average electrophoretic mobility of the charged particles and colloids in the samples studied was usually only slightly negative. The best flux improvement in electrofiltration was achieved when filtering a sample with the highest electrophoretic mobility. In that case the limiting flux could be increased many-fold. Gas was produced on the electrodes in the filtration of the wastewater samples. The flux enhancement decreased significantly when the membrane worked as an electrode and gas was produced on the membrane. The problem did not exist when a non-conductive ceramic membrane was used and an electric field was applied across the membrane. However, the high conductivity caused high energy consumption, which is a problem in electrofiltration of industrial wastewater.

Ultrasound irradiation also provided enhancement in cross-flow membrane filtration. It increased the flux primarily by breaking the cake layer at the

membrane surface. Liquid jets produced by cavitation served as a basis for ultrasonic membrane cleaning. There are several factors, which affect the cavitation and thus influence the effectiveness of ultrasound in membrane fouling prevention. In this thesis important factors were studied from the literature and from experimental investigations. The experimental part was focused on the suitable ultrasound propagation direction and the effect of the transmembrane pressure, which previously have got little attention in the research of ultrasound assisted membrane filtration. Also some aspects of the effects of ultrasound frequency, particle size and cross-flow were studied experimentally. According to these studies a low frequency ultrasound irradiation during a short pause in filtration from the permeate side of the tight membrane, an ultrafiltration membrane, is efficient and, at the same time, a gentle method in membrane cleaning. For open membranes the ultrasound propagation direction should be different or the irradiation from the feed side should be combined with other cleaning techniques like backflushing.

Electrofiltration is not a universal method for the filtration of industrial wastewater. It is a competitive method, when the average electrophoretic mobility in the sample is high and the conductivity is low. Ultrasound assisted filtration is less dependent on the feed properties and could be more useful in the cleaning of membranes in industry. However, there are some factors, especially the development of transducer technology for membrane filtration applications and the control of membrane erosion caused by cavitation, which need further development.

Doctoral thesis

Lappeenranta University of Technology, Department of Chemical Technology, Lappeenranta, 2005

Supervisor

Prof. Marianne Nyström, Department of Chemical Technology, Lappeenranta University of Technology, Lappeenranta, Finland

Examiners

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Prof. Gustavo Capannelli, Department of Chemistry and Industrial Chemistry, Genova University, Genova, Italy

Preface

This study was carried out in the Laboratory of Membrane Technology and Technical Polymer Chemistry at Lappeenranta University of Technology. The experimental part of the work was carried out mainly during 1996–2000 at VTT Processes, Jyväskylä, and in the Department of Food Engineering at Lund University.

First of all, I wish to express my sincere gratitude to Professor Marianne Nyström, Head of the Laboratory of Membrane Technology and Technical Polymer Chemistry at Lappeenranta University of Technology for her support and guidance during this work. I also want to thank Docent Jutta Nuortila-Jokinen for giving the possibility to do part of my doctoral thesis in her project.

I am very grateful to VTT Processes for giving me the opportunity to do this long-lasting work. I want to thank my colleagues at VTT Processes for their great help especially with my technical problems. I wish to express my special thanks to Lic. Tech. Pentti Pirkonen for support, encouragement and valuable comments throughout my research work. The experimental part of the work has partly been done with assistance by Jorma Ihalainen, Toni Seppänen and Vesa Siltala. I want to express sincere thanks to all of them.

I am also grateful to the Department of Food Engineering at Lund University for giving me the opportunity to work there. I want to express my warmest appreciation to Professor Gun Trägårdh for guidance when- and whatever needed during my visits at Lund. I owe special thanks to Ph.D. Ingmar Huisman for his valuable advice during the work. I also want to mention Dan Johansson and his help with experiments.

I want to express my special thanks to my official pre-examiners Professor Timothy Mason, Coventry University, and Professor Gustavo Capannelli, Genova University.

VTT Processes, The Academy of Finland, NorFA, Tekes and Maa ja vesitekniikan tuki r.y. are gratefully acknowledged for financial support. I am also grateful to Aquaflow Ltd., Ekokem Oy, Filtermat Oy, Kemira Chemicals

Oyj, Larox Corporation, Lassila & Tikanoja Oyj, Outokumpu Oyj, Raisio Oyj and Rautaruukki Oyj for their co-operation.

Finally, I want to thank Antti for patience and support in every field needed during this work.

Jyväskylä, October 2005 Hanna Kyllönen

List of publications

This doctoral thesis is based on the following articles, which will be referred to in the text by the Roman numerals given below:

I Huotari (born Kyllönen), H. M., Trägårdh, G. and Huisman, I. H., Cross-flow membrane filtration enhanced by an external DC electric field: a review, *Trans. IChemE*, **77** A (1999) 461–468.

II Huotari, H. M., Huisman, I. H. and Trägårdh, G., Electrically enhanced cross-flow membrane filtration of oily waste water using the membrane as a cathode, *J. Membrane Sci.*, **156** (1999) 49–60.

III Huotari, H. M. and Nyström, M., Electrofiltration in industrial wastewater applications, *Trans. Filt. Soc.* (originally published in FILTRATION), **1** (2000) 17–22.

IV Kyllönen, H., Pirkonen, P. and Nyström, M., Membrane filtration enhanced by ultrasound: a review, *Desalination,* **181**:3 319–335.

V Kyllönen, H., Pirkonen, P., Nyström, M., Nuortila-Jokinen, J. and Grönroos, A., Experimental aspects of ultrasonically enhanced cross-flow membrane filtration of industrial wastewater, accepted to *Ultrason. Sonochem.*, 27.4.2005.

VI Huotari, H., Ultrasonically enhanced microfiltration of oily waste water, *Proceedings of 3rd Nordic Filtration Symposium*, Copenhagen, 1997.

The author Hanna Kyllönen (former Huotari) was the main researcher and the author of the articles mentioned above. Some of the measurements were done by technicians at VTT.

Other publications related to the subject by the author of the thesis:

Huotari, H., Ceramic membrane filtration for oily waters and emulsions, Confidential report, VTT Energy, Jyväskylä, 1995, 13 p. (in Finnish)

Huotari, H., Ihalainen, J. and Tuori, T., Water reduction in debarking plant by electroacustic filtration – preliminary study, Report ENE23/T0112/96, VTT Energy, Jyväskylä, 1996, 21 p. + app. 1. (in Finnish)

Huotari, H., Väärämäki, T. and Ihalainen, J., Ultrasonically and electrically enhanced ultrafiltration of oily wastewaters, Confidental report ENE23/T0111/96, VTT Energy, Jyväskylä, 1996, 28 p. + app. 3. (in Finnish)

Sabri, N., Tuori, T. and Huotari, H., Ultrasonically enhanced ultrafiltration of wastewaters from the pulp and paper industries. Poster presentation in Euromembrane ´97,The Netherlands, 1997.

Bowen, R., Hilal, N., Lovitt, R., Wright, C., Williams, P., Sabri, N., Tuori, T. and Huotari, H., Membrane fouling in pulp and paper industries – an atomic force microscope study. Poster presentation in Euromembrane ´97, The Netherlands, 1997.

Väisänen, P., Huuhilo, T., Puro, T., Nissén, M., Laari, A., Huotari, H., Buchert, J., Suvilampi, J., Nuortila-Jokinen, J. and Nyström, M., Effect of pretreatments on membrane filtration in the paper making process, in CACTUS Technology Programme – Yearbook 1999, Eds. E. Alakangas and K. Edelmann, VTT Energy, Jyväskylä, 1999, pp. 23–34.

Huotari, H. and Talja, R., Electroconductive heating, Confidential report, VTT Energy, Jyväskylä, 2000, 25 p.

Huotari, H., Siltala, V., Mursunen, H. and Suur-Askola, J., Electroflocculation basin for phosphorous removal from household wastewater in the sparsely populated area, Confidential report, VTT Energy, Jyväskylä, 2000, 18 p. (in Finnish)

Huotari, H., Trägårdh, G. and Nyström, M., Electrically enhanced membrane filtration of wastewater, Proceedings of 8th World Filtration Congress, Brighton, 2000, pp. 1197–1200.

Huotari, H., Platt. S. and Nyström M., MBR experiments in Finnish wastewater treatment plant, Poster presentation in ICOM, Toulouse, 2002.

Kyllönen, H., Pirkonen, P., Hintikka V., Parviainen, P., Grönroos, A. and Sekki, H., Ultrasonically aided mineral processing technique for remediation of soil contaminated by heavy metals, Ultrason. Sonochem., **11** (2004) 211–216.

Grönroos, A., Kyllönen, H., Korpijärvi, K., Pirkonen P., Paavola, T., Jokela, J. and Rintala, J., Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion, Ultrason. Sonochem., **12** (2005) 115–120.

Kyllönen, H., Pirkonen, P. and Nyström, M., Aspects in ultrasonically enhanced cross-flow membrane filtration of wastewater, Proceedings of 3rd Ultrasound in Environmental Applications Symposium (Ultraschall in der Umwelttechnik III), Hamburg, 2005, pp. 29–38.

Contents

Appendices of this publication are not included in the PDF version.
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Nomenclature

a	Particle radius	(m)
D_{50}	Average diameter	(m)
E	Electric field strength	(V/m)
I	Current density	(A/m^2)
J	Flux	(L/(m^{2}h) or m/s)
J_{lim}	Limiting flux	(L/(m^{2}h) or m/s)
L	Distance between electrodes	(m)
r	Radial coordinate	(m)
r_o	Radius of outer electrode	(m)
r_i	Radius of inner electrode	(m)
Δp	Transmembrane pressure	(Pa)
R_m	Resistance of membrane	(m^{-1})
u_e	Electrophoretic mobility of a particle	((m/s)/(V/m))
v_e	Electrophoretic velocity of a particle	(m/s)
v_p	Velocity of a particle	(m/s)
Q_p	Particle charge	(N/(V/m))
δ	Thickness of gel/cake layer	(m)
ε	Electrolyte permittivity	(C^2/(Jm))
ϕ	Electric potential at the electrode	(V)
ϕ_0	Electric potential at the outer electrode	(V)
ϕ_i	Electric potential at the inner electrode	(V)
η	Viscosity	(Pa s)
λ_0	Conductivity	(A/Vm, S/m)
ζ	Zeta potential	(V)

1. Introduction

In membrane processes the separation between two streams is always achieved via a permselective barrier, a membrane. Transport through the membrane takes place when the driving force is applied across the membrane. In most of the filtration processes the driving force is a pressure difference across the membrane. In this case the flux (*J*) can be calculated according to Darcy´s law:

$$J = \frac{\Delta p}{\eta R_m} \tag{1}$$

where Δp is the pressure difference across the membrane (transmembrane pressure), η is the viscosity of the permeate and R_m is the resistance of the filter medium.

During filtration the flux can decrease substantially with time. The flux decrease occurs mainly due to concentration polarisation, *i.e.* the build-up of a concentration boundary layer near the membrane, and membrane fouling. The fouling includes many processes, such as blocking the pores by particles; adsorption of substances on the filter medium surface and within the pores; and the formation of a cake layer of particles or colloids on the top of the filter medium. Many flux models have been developed, where fouling and concentration polarisation have been taken into account. For example, in the resistance in series approach, Eq. (1) is modified by replacing the resistance of the filter medium with the total resistance.

Flux decline due to concentration polarisation and membrane fouling is a serious problem in membrane filtration. New solutions for fouling prevention are needed. It is well known that electrochemical effects are important in conventional membrane filtration [Bowen 1993, Elzo *et al*. 1998, Huisman *et al*. 1998]. In general, both the membranes and the substances in the feed suspension are electrically charged. Interactions between the surface charges have been shown to influence membrane fouling. These results inspired researchers and engineers to use an external electric field to improve the efficiency of conventional membrane filtration. The application of an electric field to improve the cross-flow membrane filtration, called electrically enhanced membrane filtration or electrofiltration, has been investigated from the seventies [Henry *et al*. 1977]. In some of the reported results the electric field strength has improved the performance of membrane filtration but often the improvement has been minor. The theory of electrofiltration is complicated and there is still uncertainty about which factors are important for successful electrofiltration. The technique is not to my knowledge used in fouling prevention in industry, although there have been some commercial attempts and solutions patented by companies [Muralidhara 1990, Turner *et al*. 1996, Quigley and Wakeman 1998].

Another possibility to improve the performance of conventional membrane filtration is to use ultrasound. Although ultrasound applications can be found in several areas of industrial process engineering, e.g. in extraction processes, cleaning, emulsification, cell disruption, and degassing, ultrasonically assisted filters are still rare. However, some examples exist, e.g. Larox Corporation manufactures industrial ceramic microfilters (CERAMEC) for cake filtration of suspensions in the mining industry. Ultrasonic cleaning of the filter elements is carried out periodically in a separate cleaning sequence. The development of the ultrasonic treatment during filtration and cake dewatering has also been carried out at pilot scale [Heikkinen *et al*. 2000, Pirkonen 2001]. Filtermat Oy has developed an ultrasound assisted cross-flow microfilter (CERTUS) that has been tested in industrial pilot scale runs [Rantala and Kuula-Väisänen 1999].

In this thesis important parameters in DC (direct current) electric field or ultrasound assisted micro- and ultrafiltration have been studied from the literature and from experimental investigations. The potential of these techniques in industrial wastewater applications has been discussed with respect to these parameters. It is also possible to improve conventional micro- and ultrafiltration with a combined electric and ultrasonic field. The combined technique is not used in industry but some studies exist. In this thesis some thoughts have been presented about the potential of combined field for industrial wastewater applications from the basis of the literature and the experimental studies with individual fields.

2. Theory of electrofiltration

The theoretical treatment of cross-flow electrofiltration is a subject of considerable complexity. It may be treated theoretically as cross-flow membrane filtration with a superimposed electric field [Bowen 1993, Bowen and Sabuni 1992]. The factors, which influence the cross-flow electrofiltration flux, are the same as those that influence the flux in normal cross-flow filtration but, in this case, the external electric field also causes electrical effects. The electrical effects include electrokinetic phenomena, which in this case are electrophoresis and electro-osmosis. The electrokinetic behaviour is based on the surface charges as will be explained below. Other important electrical effects are the occurrence of electrochemical reactions at the electrodes and Joule heating [Jagannadh and Muralidhara 1996].

2.1 Origin of surface charge

Most substances acquire a surface electrical charge when brought into contact with a polar medium such as water. Surface charge may originate typically from ion adsorption, ionisation or ion dissolution [Bowen 1993, Shaw 1991]. Surfaces in contact with an aqueous medium are more often negatively charged (negative zeta potential in a liquid) than positively charged. This is because cations are usually more hydrated than anions, and thus they have a greater tendency to stay in the bulk medium, whereas the smaller, less hydrated and more polarising anions have a greater tendency to be specifically adsorbed [Shaw 1991]. Hydrocarbon oil droplets and even air bubbles suspended in water have negative zeta potentials due to adsorption of negative ions. Many solid substances contain functional groups, which are readily ionizable, such as -OH, -COOH and $-PO_4H_2$. For example, proteins have a charge mainly through the ionisation of carboxyl and amine groups to give $-COO^-$ and $-NH_3^+$ ions. A third way of acquiring surface charge is by unequal dissolution of the oppositely charged ions of which the molecules are composed. For example, silver iodide particles are negatively charged with an excess of I^- ions, and with a sufficient excess of Ag^+ ions, they are positively charged.

The surface charge affects the distribution of nearby ions in the medium. Ions of opposite charge are attracted towards the surface and ions of like charge are repelled from the surface. This leads to the formation of the electrical double layer. The electrical double layer consists of two regions. An inner region includes firmly adsorbed ions and is called the Stern layer (Fig. 1). In an outer region called the diffuse layer or the Gouy layer, ions are not bound to the surface but distributed according to the influence of electrical forces and random thermal motion. Ions in the Stern layer move with the particle, while ions in the diffuse layer are constantly changing as the particle moves through the continuous phase. The potential decreases from the surface potential to the Stern potential, and decays to zero in the diffuse layer. The electrical double layer theory has been developed in many different directions but the principle as stated by Shaw [1991] is still more or less the same today.

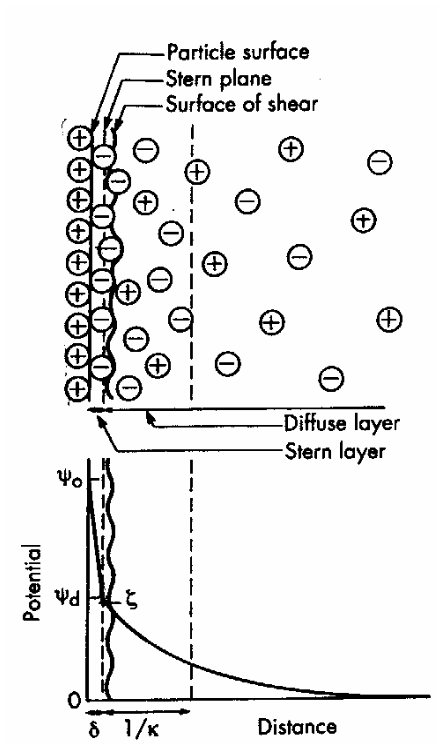

Figure 1. Schematic representation of the structure of the electric double layer according to Stern's theory [Shaw 1991].

The electrokinetic behaviour depends on the potential at the surface of shear between the charged surface and the electrolyte solution. This potential is called the zeta potential *(ζ)* (Fig. 1). The exact location of the shear plane is unknown, but with sufficient accuracy it is supposed to be located at a small distance further out from the Stern plane. The zeta potential is thus a bit smaller in magnitude than the Stern potential.

Electrokinetic measurements, such as electrophoresis, electro-osmosis and streaming potential measurements, are often used when the zeta potential is determined experimentally. The movement of charged surfaces, like particles or colloids, plus attached material relative to the stationary liquid by an electric field is called electrophoresis [Bowen 1993, Shaw 1991]. Electro-osmosis is the movement of a liquid by an applied electric field relative to a stationary charged surface, as a porous membrane. The electric field, which is created when liquid is forced with hydrostatic pressure to flow through a charged porous membrane, is referred to as the streaming potential. For electrofiltration the electrophoresis measurement is the most important. The method is explained in Chapter 4.

2.2 Variation in zeta potential

The zeta potential is considered in this study only from the electrofiltration point of view. Interactions between two particles, like attraction and repulsion, were not examined.

The zeta potential is often strongly dependent on the pH of the electrolyte solution. H^+ and OH^- are called ”potential-determining ions”, since the charge of the particles is determined by these ions. Some substances change the sign of the charge and thus the zeta potential from positive to negative, when pH is increasing. The zeta potential is zero at the isoelectric point. Proteins have a pH-dependent zeta potential (Fig. 2). At low pH a protein molecule is positively charged, while at high pH it is negatively charged [Shaw 1991]. Also the amphoteric groups of oxides, like titanium dioxide, are either negatively or positively charged depending on the pH [Elzo *et al.* 1998]. Oil droplets have negative zeta potentials at every measured pH but the magnitude is dependent on the pH [Shaw 1991, Vergouw *et al.* 1998]. Some particles, as latex, have the same zeta potential independently of the pH.

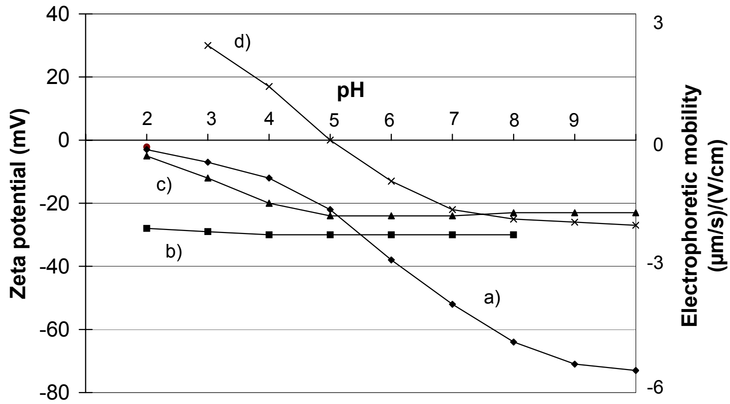

Figure 2. Zeta potentials as a function of pH in acetate-veronal buffer at a constant ionic strength of 0.05 mol/L. a) Hydrocarbon oil droplets. b) Sulphonated polystyrene latex particles. c) Arabic acid (carboxylated polymer) adsorbed on to oil droplets. d) Serum albumin adsorbed on to oil droplets [Shaw 1991].

With surface-active counter-ions the charge of the Stern layer can be reversed. It is as an example possible to generate a strong cationic charge on the surface of negatively charged silicate particles by using nonstoichiometric polyelectrolyte complexes [Vergouw *et al*. 1998]. Adsorption of surface-active co-ions can create a situation in which the zeta potential increases. With surface-active agents it is thus possible to strengthen the negative zeta potential.

Many authors have confirmed the effect of multivalent ions and ion concentration on the zeta potential [Huisman *et al*. 1998, Shaw 1991, Rios *et al*. 1998]. Multivalent ions are the most efficient. They compress the double layer with their greater charge concentration and decrease the zeta potential. For example the specific adsorption of Ca^{2+} cations on silica or α-alumina particle surfaces causes a significantly less negative zeta potential at a salt concentration of 10^{-3} M than when particles are suspended in NaCl solutions of the same strength [Elzo *et al*. 1998]. The zeta potential of these particles is slightly less negative when the ion concentration increases from 10^{-3} M to 10^{-1} M. The same effect is seen with the zeta potential of oil in water emulsions of commercial cutting oils [Rios *et al*. 1998]. The most significant effect on the zeta potentials is achieved with $AlCl_3$ salt having the highest valency. $AlCl_3$ decreases the negative zeta potential values (-60 - -80 mV) to close to zero. With $MgCl_2$ and $CaCl_2$ salts the decrease of the absolute value of the zeta potential is clear but not as significant as with $AlCl_3$. A minor effect is achieved with NaCl. Increasing the salt concentration from 10^{-4} mol/L to 10^{-1} mol/L decreases the negative zeta potential except with NaCl. With NaCl, slightly larger negative values can be obtained due to the preferential adsorption of chloride ions on the surface of oil droplets.

Oxidation and thus ageing can have a significant effect on zeta potentials of metal concentrates. It decreases the absolute value of the negative zeta potential. For example, a six-month storage of a Swedish copper concentrate can change the isoelectric point from pH 3.5 to pH 7.6 [Kramer *et al*. 1997]. The variation in isoelectric point of sphalerite is related to the sample origin, but the extent of surface oxidation, *i.e.* the presence of ionic metal and sulphur-oxygen species, is probably the key factor, which determines the isoelectric point [Mänttäri *et al*. 1996].

Microbial cells exhibit negative zeta potentials, but show significant differences regarding to the type of organism and growth conditions [Bros and Kroner 1990]. E.g. cells of the yeast *Saccharomyces cerevisiae* have a high negative charge under normal fermentation conditions due to the high phosphomannan content of the outer layer of the yeast cell wall [Bowen 1993].

2.3 Electrokinetic behaviour

The charged particles move by an applied electric field. An external electric field affects the trajectories of charged particles and colloids and can thus prevent them from being deposited on the membrane. This is called electrophoresis. If the membrane has charged pore walls, there will be an excess of counter-ions within the pore. These counter-ions will move in an applied electric field and drag the solvent (water) with them. The resulting water flux is called the electro-osmotic flow. The electrokinetic behaviour depends on the potential at the surface of shear between the charged surface and the electrolyte solution as told earlier.

The effect of an electric field on the flux in membrane filtration is mainly based on electrophoresis [Henry *et al.* 1977, Rios *et al.* 1988]. The electrophoretic mobility, u_e, describes the capability of particles to move in an electric field:

$$u_e = \frac{v_e}{E} \tag{2}$$

where v_e is the electrophoretic velocity and E is the electric field strength. In order to achieve improvements in the performance of membrane filtration, the sign of the charge of all those particles or colloids, required to be kept away from the membrane, must be same as that applied at the membrane.

If the active layer of the membrane is one of the electrodes, there is no net electric voltage across the membrane pores. There is therefore no electro-osmotic flow. However, if the support of the membrane is one of the electrodes or if an external electrode is used, there is an electric voltage across the membrane pores and electro-osmosis can be expected. The highest reported values of flux enhancement due to electro-osmosis are 15 % of the flux [Radovich and Behnam 1983] and 19 % of the flux [Radovich and Chao 1982]. In order for the flux to increase as a result of electro-osmosis the membrane zeta potential must have the same sign as the particles (negatively charged in most cases, which is true for most polymeric and ceramic membranes at high pH). If a cake layer forms on the membrane, this cake may induce an electro-osmotic flow, even if the membrane does not.

Many models have been published for the prediction of fluxes in electrofiltration [Bowen 1993, Henry *et al.* 1977, Bowen and Sabuni 1992, Rios *et al.* 1988, Radovich *et al*. 1985] as explained in more detail in App. I. These models can be roughly divided into resistance-in-series models and film theory models. In the resistance-in-series models the filtration flux is predicted at any stage using Darcy´s law (Eq. 1). The limiting flux (J_{lim}), *i.e.* the maximum steady-state flux achieved by increasing the pressure in electrofiltration can be predicted using the film theory.

In this study neither of the models is used directly, but a simple approach is employed and the forces acting on one particle are considered. In cross-flow filtration with an external electric field, there is a balance between the electrical force and the hydrodynamic force due to the permeate flow. Equating both forces on the particle using the frictional resistance in the medium according to Stokes´ law, the following equation is obtained:

$$Q_p \cdot E = 6 \cdot \pi \cdot \eta \cdot a \cdot v_e = 6 \cdot \pi \cdot \eta \cdot a \cdot \left(J - v_p \right) \qquad (3)$$

where Q_p is the net charge on the particle, E is the electric field strength, η is the viscosity of the medium, a is the radius of the particle, v_e is the electrophoretic velocity of the particle, which can be calculated according to Eq. (2), J is the flux and v_p is the net particle velocity towards the membrane. The critical electric field strength ($E_{critical}$) is defined as the electric field strength at which the net particle migration towards the membrane is zero [Bowen 1993, Henry *et al.* 1977] (see App. I). Combining Eqs (2) and (3) gives the critical electric field strength:

$$E_{critical} = \frac{J}{u_e} \qquad (4)$$

Eq. (4) can be used for the calculation of the limiting fluxes in an applied electric field, when the electrical force determines the particle transport. In a real system, there are also other mechanisms, such as Brownian diffusion, which determine the limiting flux. Many equations are available for the calculation of the limiting flux, when an electric field is not applied [Huisman 1998]. The flux enhancement due to the electrical force is additional to the flux obtained without an electric field [Radovich *et al.* 1985, Yukawa *et al.* 1983] and therefore:

$$J_{\lim} = J_{\lim}(E = 0) + E_{applied} \cdot u_e \qquad (5)$$

According to Eq. (5) the limiting flux enhancement is dependent on the electrophoretic mobility of the particles in the feed solution and the applied electric field strength. Eq. (5) is similar to the one obtained from film theory. When the limiting flux is estimated using these approaches, electro-osmosis is not taken into account.

2.4 Electrochemical reactions

Apart from electrophoresis and electro-osmosis, other effects occur in electrofiltration, such as electrochemical reactions. An electrochemical reaction is a chemical process involving the transfer of charge to or from an electrode. At the cathode, otherwise stable species, are reduced by the transfer of electrons from the electrode. Three additional types of basic reactions may occur: chemical reactions, adsorption and phase formation [Pletcher and Walsh 1990]. The type of reaction is dependent on the circumstances and the substances in the feed. A typical cathodic process in aqueous systems without noble metal ions is the formation of hydrogen gas:

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \text{ (cathode, -0.83 V)} \qquad (6)$$

Conversely, at the anode, an otherwise stable substance is oxidised by the removal of electrons from the substance to the electrode. A relevant example could be:

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \text{ (anode, +0.40 V)} \qquad (7)$$

A high current density indicates a high degree of simultaneous oxidation and reduction. The amount of gases produced can be calculated from Faraday's law. If the conductivity of the liquid increases, the current density increases causing more electrochemical reactions to take place at the electrodes. Gas formation influences the performance of membrane filtration. This is studied in the experimental part of this work.

3. Theory of ultrasound assisted membrane filtration

3.1 Origin of ultrasonically induced effects

In general, power ultrasound is characterised by an ability to transmit substantial amounts of mechanical energy through small mechanical movements. The passing of ultrasonic waves of a suitably high intensity through liquid and gaseous media is accomplished by primary phenomena such as cavitation, radiation pressure, acoustic streaming, and secondary phenomena of a physicochemical nature such as: dispersion, coagulation, and change in liquid properties [Ensminger 1988, Tuori 1998]. In many cases the effect of ultrasound is due to a combination of many effects acting synergistically [Pirkonen 2001].

As with any sound wave, ultrasound is propagated via a series of compression and rarefaction (decompression) waves induced in the molecules of the medium through which it passes. At a sufficiently high power, the rarefaction cycle may exceed the attractive forces of the liquid molecules, and cavitation bubbles (empty, gas- and/or vapor-filled bubbles) will form. Cavitation occurs at frequencies of roughly 20–1000 kHz. In aqueous systems, the collapse of the cavitation bubble will have significant mechanical and chemical effects. Each bubble acts as a localised `hot spot´ generating temperatures of about 4000–6000 K and pressures of 100–200 MPa. The implosions occur with lifetimes of < 10 µs [Mason and Cordemans 1996, Price 1992]. The bubble size can be as large as 100–200 µm prior to implosion [Price 1992], but the most effective bubble collapse occurs at a bubble size of several micrometers [Mettin *et al.* 1999]. The level of energy required to achieve cavitation is called the cavitation threshold.

3.2 Effects in micro/ultrafiltration

The exact mechanism for particle detachment with ultrasound from fouled membranes is still an open question. In a heterogeneous solid-liquid situation, a collapse of cavitation bubbles near a surface produces a nonsymmetrical inrush of fluid to fill the void, with the result that a liquid jet (microjet in Fig. 3) with a speed of the order of 110 m/s is formed and targeted at the surface [Mason and Cordemans 1996, Abramov 1998]. It is generally considered the collapse of cavitation bubbles and the following liquid jets serve as a basis for membrane cleaning like other ultrasound cleaning processes. The collapse produces sufficient energy to overcome the interaction between the foulant and the membrane [Juang and Lin 2004, Li *et al*. 2002]. Apart from the liquid jets there are other mechanisms, which can lead to particle release from a fouled surface. Microstreaming and microstreamers (bubble chains), which are cavitational mechanisms without a collapse of bubbles, have been found significant in detaching particles from the membrane surface in dead-end filtration with model particles [Lamminen *et al.* 2004]. Acoustic streaming, i.e. an acoustical streaming effect without cavitation, has also appeared as an important addition in the transport of particles away from the surface [Kobayashi *et al*. 2003, Lamminen *et al*. 2004, Simon *et al*. 2000].

Ultrasound irradiation does not influence the intrinsic permeability of the membranes [Lamminen *et al*. 2004, Muthukumaran *et al*. 2004]. There is no ultrasound effect for clean water and only a small effect for low particle sized colloids with insignificant rejection by the membrane, *i.e*. when there is no concentration polarisation or cake near the membrane. On the other hand, ultrasound seems to increase the flux of the colloids containing suspensions, which are highly rejected by the membrane [Chai *et al*. 1998]. This indicates that when using ultrasound there is bulk mass transfer in the concentration polarisation or cake layer near the membrane. Thus it is reasonable with ultrasound to operate above critical flux, *i.e.* the lowest flux without ultrasound that creates concentration polarisation. Ultrasound can break the cake layer and decrease the solute concentration near the membrane, and as a consequence of that the flux increases [Lamminen *et al*. 2004, Muthukumaran *et al*. 2004, Kobayashi *et al*. 1999]. It has been suggested that ultrasound is not effective in removing particles trapped in a membrane [Kokugan *et al*. 1995].

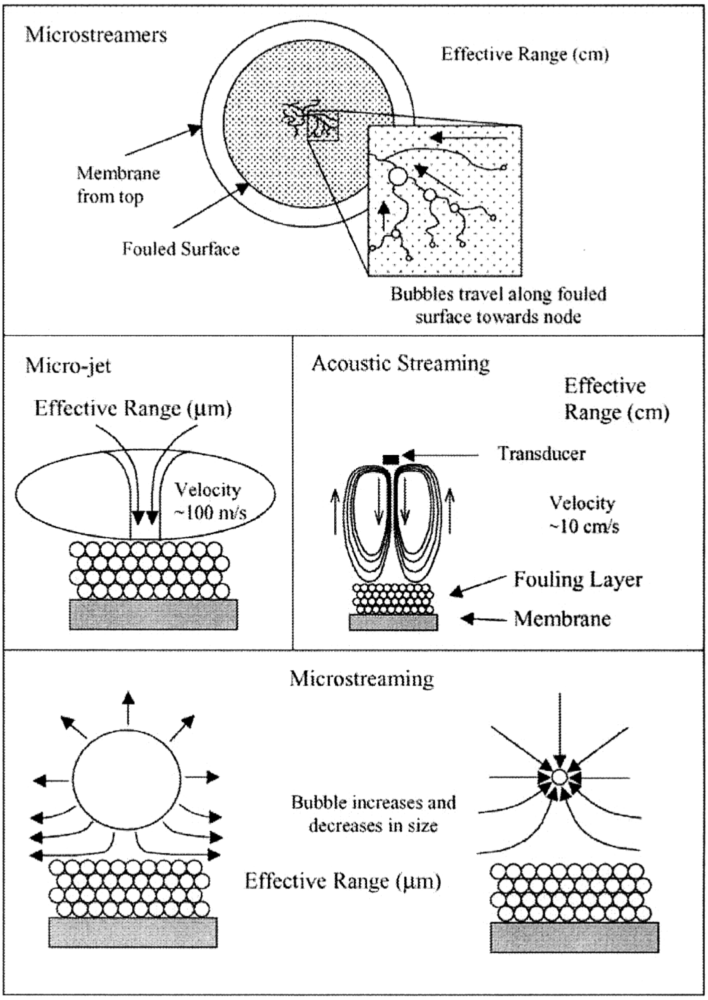

Figure 3. Possible mechanisms for particle removal/detachment observed with ultrasonic cleaning [Lamminen et al. 2004].

3.3 Important parameters in ultrasound assisted filtration

There are several factors, which influence the effectiveness of the ultrasound treatment in membrane cleaning. The examination of these factors leads almost always to examination of the build-up of cavitation, which indicates its importance in membrane cleaning. Ultrasound frequency and power intensity are the parameters characterising the ultrasound irradiation. Other parameters shown here are important also in conventional membrane filtration, but ultrasound produces some special features to the effects of these parameters in filtration. The effects of the pore size of membranes, the particle size, the transmembrane pressure and the cross-flow are presented in the experimental part of this study.

3.3.1 Ultrasound frequency

Ultrasound is transmitted into suspension at different frequencies. Frequencies from 25 kHz up to 1 MHz have been used in membrane filtration experiments. Lower ultrasound frequencies have had higher cleaning efficiencies than higher frequencies [Lamminen *et al*. 2004, Kobayashi *et al*. 2003, Kobayashi *et al*. 1999]. Although higher frequencies may cause more cavitation bubbles collapsing with time, the bubbles are smaller in size and collapse less energetically. They may not be capable of detaching particles from the cake layer as readily as bubbles formed at lower frequencies. At very high frequency the rarefaction (and compression) cycles are too short to permit a bubble to grow to a size sufficient to cause disruption of the liquid. Even if a bubble is to be produced during rarefaction, the time required to collapse that bubble may be longer than the time available in the compression half-cycle. The resultant cavitational effects will, therefore, be less at the higher frequencies [Mason and Lorimer 1988]. The efficiency of different ultrasound frequencies in membrane cleaning is also dependent on the circumstances during membrane fouling as will be seen in the experimental part of this work.

3.3.2 Ultrasonic power intensity

Power intensity is a measure of the sound energy the wave produces. The power intensity used in cleaning varies between 0.5 and 6 W/cm^2 [Ensminger 1988]. In general an increase in power intensity will provide an increase in the ultrasonic effects. Increasing the power intensity to the system increases the number of cavitation bubbles formed and increases the size of the cavitating zone due to the higher pressure amplitude of the sound wave with an increased power intensity [Lamminen *et al*. 2004]. Also, the hydrodynamic turbulence increases with increased power intensity. The higher the power intensity during ultrasonic irradiation the better the membrane cleaning and the greater the flux obtained [Kobayashi *et al*. 1999, Lamminen *et al*. 2004, Matsumoto *et al*. 1996, Muthukumaran *et al*. 2004]. This is true both for cleaning of fouled membranes and for on-line ultrasound treatment during filtration. Also, when the transducer is brought closer to the membrane at constant power intensity the effect of the ultrasound on improving filtration rates increases considerably [Wakeman and Tarleton 1991]. However, the relationship between flux and power may not be linear in the high power range. It is considered that the effect of ultrasonic cavitation is limited and that part of the ultrasonic power is converted to heat [Matsumoto *et al*. 1996].

At the higher frequencies cavitation bubbles, initially difficult to create (see 3.3.1), will develop by increasing the power intensity [Mason and Lorimer 1988]. The power intensity needed is also dependent on other operation circumstances. A flux increase is possible in cleaning of latex particles fouled ceramic membranes for all the frequencies from 70 to 1062 kHz, when increasing the power intensity from 0.21 to 2.1 W/cm^2 [Lamminen *et al*. 2004]. On the other hand, a power intensity increase from 2.6 W/cm^2 to 3.4 W/cm^2 was not sufficient for cleaning in dextran-UF at a frequency of 100 kHz [Kobayashi *et al*. 1999].

3.3.3 Feed properties

The flux varies when filtering at different feed concentrations both in ultrasound assisted membrane filtration and in conventional filtration. As the feed concentration is high, the flux can be very small in the case with no ultrasound, but the flux can be increased significantly with ultrasound. However, ultrasound has less effect on flux at a very high concentration of feed than at a lower concentration [Wakeman and Tarleton 1991, Kobayashi *et al*. 1999]. It must be noted that a higher particle concentration produces a greater attenuation of the sound waves as they pass through the cross-flow suspension due to an increased acoustic impedance. The degree of attenuation varies with different feed solids and experimental conditions, and it is considered to be an important parameter controlling the efficiency of the ultrasonic field [Wakeman and Tarleton 1991].

The formation of voids or vapour-filled microbubbles (cavities) in a liquid requires that the negative pressure in the rarefaction region must overcome the natural cohesive forces acting within the liquid. It follows therefore that cavitation should be more difficult to produce in viscous liquids, or liquids with high surface tensions [Mason and Lorimer 1988]. When studying the percentage gain in filtrate flux with ultrasound, the gain decreased rapidly when the suspension viscosity increased from 1 cP to 4 cP [Wakeman and Tarleton 1991]. Thus the effect of ultrasound on flux would be reduced when the viscosity is increased.

The effect of temperature in ultrasound assisted membrane filtration is not straight-forward. According to Mason and Lorimer [1988] temperature is known to affect the cavitation threshold. In general, the threshold limit has been found to increase with a decrease in temperature. This may in part be due to increases in either the surface tension or the viscosity of the liquid as the temperature decreases, or it may be due to decreases in the liquid vapour pressure. On the other hand, the effects resulting from cavitational collapse are reduced as the temperature is increased. From the filtration point of view, an increase in temperature increases the flux due to the decrease in viscosity. In cleaning processes the maximum cavitation is reported to occur at about 60–70°C falling to about the half when temperature is either lowered to 40°C or raised to 85°C [Quartly-Watson 1998]. In cleaning processes higher temperatures also produce improved diffusion, higher solubility, increased chemical splitting of soil, and increased Reynolds numbers due to the decreased viscosity [Muthukumaran *et al*. 2005].

In the study by Li *et al*. [2002] on ultrasound cleaning of nylon membranes fouled by Kraft mill effluent, the authors observed that the flux decreases when the cleaning temperature increases from 23 to 40°C. This was caused by a change in the ultrasonic cavitation intensity as the temperature increased. Ultrasonic cleaning of a microfilter is mainly caused by ultrasonic cavitation and the acoustically excited bubble break-ups on the membrane surface. An increase in solution temperature gives rise to an increase in the vapor saturation pressure in the bubble so that the shock-wave intensity during the bubble break-ups decreases. Also different results have been achieved in membrane cleaning. Chai *et al*. [1999] studied permeate flux recovery of peptone fouled polysulphone membrane at temperatures of 20, 30 and 40°C. They observed that ultrasonic water cleaning was the fastest at the highest temperature. Muthukumaran *et al*.

[2005] obtained similar results when cleaning polymeric ultrafiltration membranes fouled by whey. A higher cleaning efficiency was obtained when using a temperature of 55°C than when using 25°C. The optimum temperature in ultrasound assisted membrane cleaning is dependent on many factors and thus it must be determined case by case.

3.4 Models for predicting flux

Analogous to electrofiltration the cross-flow filtration enhanced by ultrasound may be treated theoretically as cross-flow filtration with a superimposed ultrasonic field, which causes acoustical effects. From the above it is clear that the acoustical effects are the combination of many effects, such as cavitation and acoustic streaming. Thus ultrasonically assisted membrane filtration is complicated and affected by many parameters. There is still no generally usable model available. Apart from that a lot of empirical work is still required for predicting fluxes using these models. From the models for conventional membrane filtration the resistance-in-series model [Li *et al*. 2002, Matsumoto *et al*. 1996, Juang and Lin 2004] and the film theory [Kobayashi *et al*. 1999, Simon *et al*. 2000] have been modified for ultrasonically enhanced membrane filtration by some researchers. The models are explained in more detail in App. IV.

3.5 Membrane erosion

When considering ultrasound as a cleaning technique the lifetime of the membranes has to be taken into account. Various results have been achieved when studying the influence of ultrasound irradiation on the membrane. Damage on the membrane surface has been discovered in some studies [Masselin *et al*. 2001, Sabri *et al*. 1997, Juang and Lin 2004] whereas in others a frequent use of ultrasound did not affect the membranes [Lamminen *et al.* 2004, Muthukumaran *et al*. 2004].

It is quite obvious that the influence of ultrasound irradiation on membranes is dependent on the membrane material itself. Masselin *et al*. [2001] studied the effect of ultrasound irradiation at a frequency of 45 kHz on different polymeric membrane materials for two hours. They observed that polyethersulphone (PES) was affected by irradiation over its entire surface but the polyvinylidenefluoride (PVDF) and the hydrophilic polyacrylonitrile (PAN) membranes showed no significant changes. The power was not reported but was presumably the same for all the membranes.

The power affecting at the membrane also naturally influences the erosion of membranes. Juang and Lin [2004] observed a slightly destroyed structure of regenerated cellulose membranes (Amicon YM10) when using a horn transducer with a tip distance of 10 mm and with more than 80 W power. When using a larger tip distance (> 20 mm) even a power of 240 W could be used without destroying the membrane structure.

There are also other factors affecting the erosion of membranes in an ultrasonic field. In a stagnant environment it is possible for a cavitation bubble to become trapped at a certain point on the membrane surface and physically erode the surface by repeated oscillations at this point. The presence of cross-flow during ultrasonic irradiation reduces the likelihood of such an event occurring [Muthukumaran *et al*. 2004]. In the studies by Muthukumaran *et al*. [2004] lasting over a month with repetitive use of ultrasonic cleaning in a cross-flow membrane module, which was immersed in an ultrasonic water bath, no significant change in the clean water flux of the polysulphone (PS) membrane was noticed, indicating that the ultrasonic treatment did not appear to damage the membrane structure itself.

4. Materials and methods

The materials and methods used in this study are described in detail in Appendices II and III for electric field assisted filtration, and respectively in V and VI for ultrasound assisted filtration. Below are only the materials and methods mentioned, which are characteristic for electrofiltration or ultrasound assisted membrane filtration.

4.1 Electrofiltration

4.1.1 Electrophoretic mobility measurements

The average electrophoretic mobility of particles or colloids in a feed was determined for electrofiltration studies. The electrophoretic mobility (u_e) can be determined by measuring the velocity of the particles (v_e) in an applied electric field using a known electric field strength (E). The zeta potential (ζ) is transformed according to the so-called Smoluchowski equation. This equation is valid when the particle size is large compared to the double layer thickness, thus in most cases for particles in aqueous media [Bowen 1993, Shaw 1991]:

$$u_e = \frac{v_e}{E} = \frac{\varepsilon \cdot \zeta}{\eta} \tag{8}$$

where ε is the electrolyte permittivity and η is the viscosity.

Such devices as Coulter Delsa 440 series instruments and the Malvern ZetaSizer were used for measuring the electrophoretic velocity of the particles. With the development of lasers, light scattering methods exploiting the Doppler effect have become available to assess very accurately the speed of particles in suspension [Langley Ford Instruments 1988]. The measurements were carried out using a procedure of its own for each device. There are still some common rules for electrophoretic measurements generally. First, the substances in the electrolyte solution influence the zeta potential. A sample dilution without changing the electrolyte is important and thus the dilution of industrial wastewater samples was somewhat difficult. It was normally done by the centrifuged particle free wastewater. Due to the viscosity-temperature relationship, also temperature is an important parameter affecting the zeta potential. The temperature of a sample was adjusted during measurements to the same 25°C as used in the filtration. Also, at the point where the electrophoretic velocity was measured, i.e. the location of the laser beam, the electro-osmotic velocity must be zero. The measured electrophoretic mobility (u_e) and the zeta potential (ζ) as well as three other important parameters, pH, conductivity (λ_0) and average particle size (D_{50}), of the samples studied here are shown in Table 1.

Table 1. Wastewater samples used in the electrofiltration experiments.

Wastewater (industry)	pH	λ_0 (mS/cm)	D_{50} (µm)	ζ** (mV)	u_e** (µm/s)/(V/cm)
Model wastewater, oil emulsion	7.2	0.007	0.3	-55	-4.1
Model wastewater, cleaning agent	9.2	0.04	0.02	negative	negative
Model wastewater, mixture (150 g/l oil and 0.1% cleaning agent)	8.8	0.04	0.3	-67	-5.0
Wastewater from grinding (metal)	8.7	1.8	22	-14	-1.1
	8.8	0.8	22	-10	-0.8
	8.6	2.2	55	-19	-1.5
Wastewater from DUO-grinding (metal)	9.5	3.0	7	-15	-1.2
Oily wastewater (metal)	3.1	5.1	5	-7	-0.5
Soot-like wastewater (chemical)	9.4	1.7	36	-45	-3.5
Potassium formiate (chemical)	10.0	174			
Ferric sulphate (chemical)	1.4	20*	1.5	-17 and 9	-1.3 and 0.7
Ferric chloride sulphate (chemical)	0.6	20*	7		
Vegetable oil in water (food)	2.0	7.0		+20	1.6
Coating wastewater (paper)	7.5	0.5	8	-27	-2.1
Filtrate of thermo mechanical pulp (paper)	4.1	0.7	47	-21	-1.6

* Very viscotic liquid, conductivity increased when diluted with distilled water.
** Complex industrial wastewater samples caused uncertainty to results.

4.1.2 Electric field strength

In a flat sheet system the electric field strength, E, is easily calculated according to its definition:

$$E = \frac{\phi}{L} \tag{9}$$

where ϕ is the electric potential (voltage) and L is the distance between the electrodes. However, in a tubular system Eq. (9) must be modified. The electric field strength distributions between two concentric cylinders can be calculated according to Eq. (10) [Wakeman and Tarleton 1987]:

$$E = \frac{(\phi_0 - \phi_i)}{r \log_e (r_0 / r_i)} \tag{10}$$

where ϕ_0 is the electric potential at the outer electrode, ϕ_i is the electric potential at the inner electrode, r is the radial coordinate, r_o is the radius of the outer electrode and r_i is the radius of the inner electrode. According to some authors [Bowen and Sabuni 1992, Bowen and Ahmad 1997], the electric field strength may not be calculated from the overall applied voltage, since the drop in voltage at the electrode-solution interfaces (overpotential) is unknown. Hence, E is calculated according to Ohm´s law from the unambiguous values of the current density (I), the cell dimensions, and the known conductivity of the bulk solution (λ_0):

$$E = \frac{I}{\lambda_0} \tag{11}$$

In this study primarily Eq. (11) was used.

4.1.3 Electric field assisted membrane module

Two different configurations have been reported for electrofiltration, as explained with more details in App. I. An electric field can be applied across the membrane with one electrode on either side of the membrane, which is the most common way, or the electric field may be applied between the membrane and another electrode. When an electric field is applied across the membrane [Henry *et al*. 1977, Bros and Kroner 1990, Rios *et al*. 1988, Radovich and Behnam 1983, Radovich and Chao 1982, Wakeman and Tarleton 1987, Bowen and Ahmad 1997], the cathode is usually on the permeate side and the anode is on the feed side. The cathode is often made of stainless steel. According to Bowen [1993], one of the best anode materials is made of titanium, coated with a thin layer of a noble metal such as platinum. The membrane material can either be electrically conductive or non-conductive. When the membrane is made of metal, carbon or another conductive material, it is possible to use the membrane as an electrode [Turner *et al*. 1996, Bowen *et al*. 1989, Guizard *et al*. 1989]. The electric field can be applied in tubular, flat sheet or spiral wound modules.

In this study the suitable tubular module configuration for industrial wastewater samples was studied. First the conductive CFCC (carbon fibre carbon composite) membranes (Carbonne Lorraine, France) with pore sizes of 0.05 and 0.1 μm were used as cathodes (Fig 4a). The CFCC-membrane is composed of a thin carbon filtration layer, which constitutes the inside surface of a fine asymmetrical support tube, made of carbon fiber. Then an electric field was applied across the CFCC-membrane (Fig. 4b). The electrodes used here were made of stainless steel. An electric field was also applied across the α-alumina ceramic Membralox^R membranes (USF SCT, France), with a pore size of 0.1 μm. (Fig. 4c).

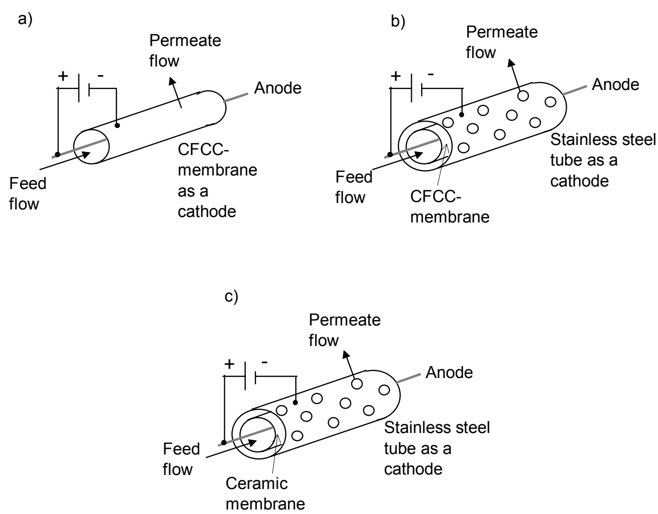

Figure 4. Schematic illustration of the module configurations used in this study [III].

4.2 Ultrasound assisted filtration

4.2.1 Feeds

In ultrasound assisted filtration experiments only wastewaters from industry were used. Bark press filtrates (Table 2) from paper industry were filtered in most of the studies. Methods for characterising the feeds from paper industry are described in App. V.

Table 2. Characteristics of feeds from paper industry [V].

Feed	Type	D_{50} (µm)	Dry solids (g/L)	SS (g/L)	COD (mg/L)
1	Bark press filtrate	16	20	5.9	37 000
2	Bark press filtrate	9.0	18	5.7	38 000
3	Bark press filtrate	3.8	3.2	2.0	6 400
4	Bark press filtrate	6.4	14	4.8	31 000
5	Fabric press filtrate	24	5.0		4 800

Oil emulsion from a hazardous waste treatment plant was characterised measuring particle size, pH and oil contents (Table 3 and Fig. 5). The particle size of the oil emulsion was increased using an electroflocculation method (App. VI). The particle size distribution was determined using a Malvern 2600c equipment. The distribution was obtained as a cumulative accumulation of the volume share compared to the total volume. pH was measured using a Handylab 2 pH-meter. Oil contents were determined according to an SFS 3009 standard.

Table 3. Characteristics of oily wastewater samples.

Feed	D_{50} (µm)	pH	Oil content (mg/L)	Total oil and grease (mg/L)
Gravity separated emulsion	0.8	6.7	2140	3500
Electroflocculated emulsion	4.8	4.6	1340	1800

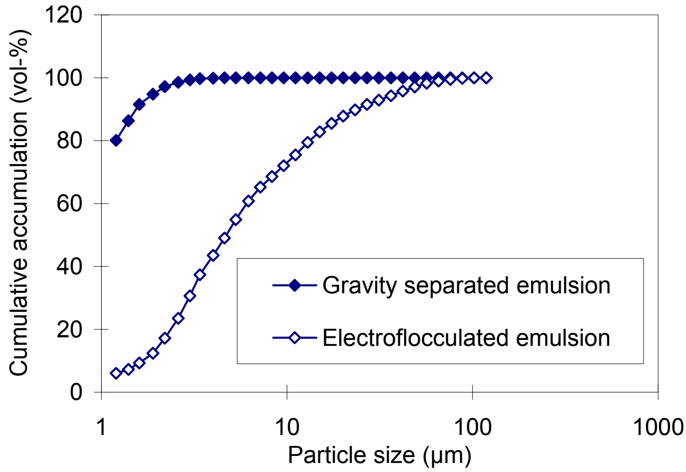

Figure 5. Particle size distributions of oily wastewater samples [VI].

4.2.2 Ultrasound equipment and frequencies

Ultrasonic transducers are designed to convert either mechanical or electrical energy into high frequency sound. Electromechanical transducers are by far the most versatile and widely used compared to mechanical transducers [Mason and Lorimer 1988]. The two main types of electromechanical transducers are based on either the piezoelectric or the magnetostrictive effect, the more commonly used of which are the piezoelectric transducers. Although development and optimisation of ultrasonic transducers has been done for ultrasound assisted cake filters [Heikkinen *et al*. 2000, Heikkola and Laitinen 2005], there is not much development of transducer technology for membrane filtration. This is one of the main reasons for preventing the break-through of ultrasound assisted membrane filters [Pirkonen 2001].

In this study the transducer elements were piezoelectric, wall-type made by Vibraclean Oy (Finland) or self-made by VTT Processes (Finland). The transducers operated with frequencies of 27, 40 or 200 kHz. 27 and 40 kHz piezoelectric transducer elements were built up using four Langevin type sandwich transducers side by side (Fig. 6). The transducer element of 200 kHz was made using ten small sandwich type transducers. The face area of all the transducers was 8 cm x 22 cm. A Martin Walter 1000 PCI ultrasonic generator containing a power adjuster was used for the transducers working at frequencies of 27 or 40 kHz. A Tabor Electronic 8553 function generator was used for adjusting the frequency of 200 kHz and in that case an ENI 1140LA power amplifier was used for power adjustment.

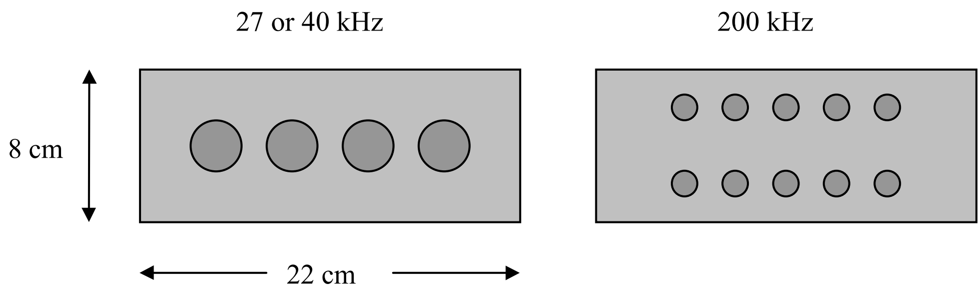

Figure 6. Schematic illustration of the transducers used in the study. The diameter of the transducers of 27 kHz was 5.9 cm, of 40 kHz 4.5 cm and of 200 kHz 2.5 cm [V].

4.2.3 Ultrasound assisted membrane modules

There is little research done about the behaviour of different membrane materials in ultrasonic field experiments except from the erosion point of view. Ultrasonic cleaning is effective on sound-reflecting materials [Bayevsky 2004]. Alumina is a good sound-reflecting material that offers the potential for facile cleaning by ultrasound [Lamminen *et al*. 2004].

Ultrasound can not keep the particles totally away from the membrane, like an electric field, but it cleans the membrane. Thus the membrane properties, as pore size, pore geometries, porosity and hydrophilicity, are important also from the ultrasound treatment point of view. In this study the experiments were mainly carried out using the same alumina-based membrane material with similar properties but a varying pore size.

The flat-sheet membranes used in ultrasound assisted membrane filtration experiments (Table 4) were alumina-based ceramic membranes with mean pore sizes of 0.12 µm (Tampere University of Technology, Finland), 0.19 µm

(Tampere University of Technology, Finland) and 0.25 µm (supplied by Larox corporation, Finland), and a commercial polymeric PES-50H membrane (Nadir-Filtration, Germany). Most of the studies were carried out using a 0.12 µm ceramic membrane with a porosity of approximately 45 % [Levänen 2004]. An alumina-based ceramic membrane (supplied by Larox Corporation, Finland) with a pore size of 0.75 µm and a porosity of 45 % [Smått 2001] was also used in preliminary dead-end filtration studies.

Table 4. Membranes used in the experiments [V].

Membrane	Pore size (µm)	Method for pore size Measurement	Pure water flux (L/(m^2h))
1	0.12	Mercury porosimetry	420–490 (0.9 bar, 22 °C)
2	0.19	Mercury porosimetry	600–700 (1 bar, 20 °C)
3	0.25	Capillary flow porosimetry	2000 (at 1 bar, 20°C)
4	0.75	Capillary flow porosimetry	6000 (at 1 bar, 20°C)
PES-50H	Cut off 50 000		550 (at 3 bar, 20 °C)

Conventional membrane modules are very compact and there is not enough space for transducers. In previous ultrasound assisted membrane filtration studies presented in literature either ultrasonic baths were used or the ultrasonic transducer element was integrated to the specially designed cross-flow membrane module. In ultrasonic baths transducers were attached to the outside surface of the water bath or a horn transducer was employed. In many studies the whole membrane module was immersed in an ultrasonic water bath. The ultrasound wave is able to pass through the membrane housing to the inside without changing its frequency [Kobayashi *et al.* 2003]. However, the ultrasound intensity of the sonic power decreases significantly by propagation through the housing. The ultrasound power decline is 1/10 for propagation [Kobayashi et al. 2003, Kobayashi *et al*. 1999]. An ultrasonic bath, where a whole membrane module is immersed, is only useful in laboratory studies because there is a high waste of acoustic energy in the bath during the cleaning process [Li *et al*. 2002, Muthukumaran *et al*. 2005].

In this study a special ultrasonically assisted cross-flow membrane filtration module was built to avoid the loss of ultrasonic efficiency to the surroundings. The transducer was assembled either on the feed or on the permeate side of the membrane in the dead-end membrane module (Fig. 7) used in preliminary experiments. The transducer was assembled on the feed flow side in the cross-flow membrane module at a distance of 1 cm from the membrane, which was not an optimised distance but proved to be efficient for membrane cleaning in cross-flow conditions (Fig. 8).

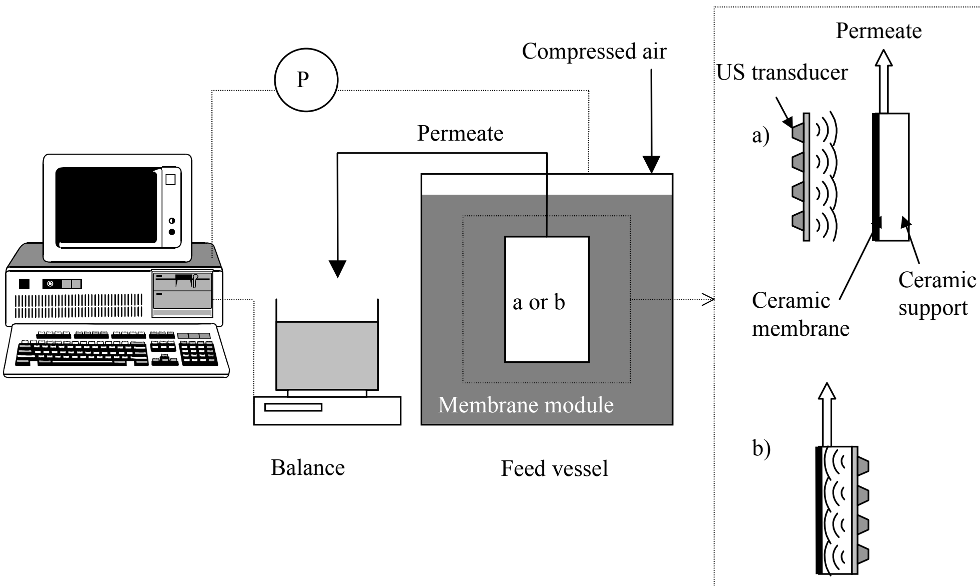

Figure 7. Schematic illustration of the dead-end filtration equipment and the membrane modules used in preliminary experiments. a) Ultrasound irradiation coming from the feed side of the membrane. b) Ultrasound irradiation coming from the permeate side of the membrane [V].

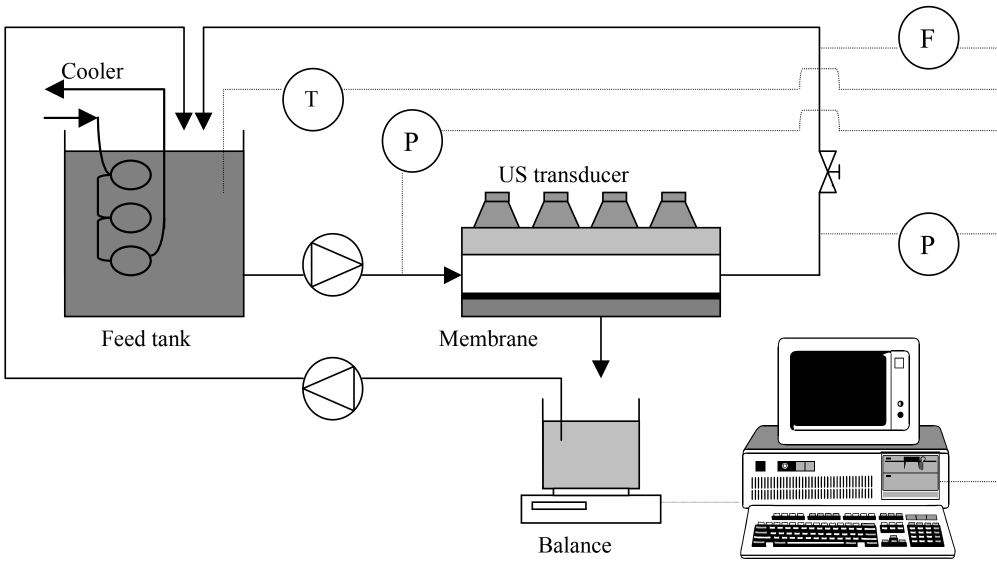

Figure 8. Schematic picture of the cross-flow membrane filtration equipment [V].

4.2.4 Power intensities

In the strictest sense the power intensity is the amount of energy carried per second per unit area by the wave [Mason and Lorimer 1988]. The usual unit of sound intensity is W/cm^2. The power intensity can be determined simply from the input or output power of the sonicator per unit area of the transducer surface [Kobayashi *et al*. 1999] or calorimetrically [Lamminen *et al*. 2004, Kobayashi *et al*. 2003, Raso *et al*. 1999]. The intensity of the ultrasound field can also be expressed as the ultrasonic power density gradient, Wcm^{-2}cm^{-1}. The gradient can be varied by using an ultrasonic source with a fixed power output and by changing its separation distance from the membrane surface [Wakeman and Tarleton 1991]. In this research the ultrasound power intensity was calculated using the input power values and the areas of four (or ten) sandwich transducers. The input power values and power intensities used in each experiment are told in Chapter 5.

A continuous use of ultrasonic waves from the start of filtration has been very effective in several studies [Matsumoto *et al*. 1996, Tarleton and Wakeman 1990]. In that case the cake layer formation on the membrane surface is prevented from the beginning. However, the continuous use of ultrasound is undesirable in term of energy consumption. The power intensity level affecting on the membrane surface also affects the erosion of membranes. Apart from that the intense continuous ultrasound treatment could decompose macromolecules in the feed [Chai *et al.* 1998, Grönroos *et al*. 2004]. A short burst of ultrasonic power or an intermittent ultrasonic field has been used in some studies as a cost-effective method of membrane cleaning [Muthukumaran *et al*. 2004, Sabri *et al*. 1997]. Intermittent ultrasound irradiation was more often used in this study than continuous irradiation. The flux obtained was the same in both cases but intermittent ultrasound prolonged the lifetime of the membranes used.

5. Results and discussion

5.1 Electrofiltration

5.1.1 Effect of an electric field on the limiting flux [II]

In this study the effect of an electric field on the flux at different pressures was studied in order to clarify the fouling prevention mechanism when using this technique. This is described in detail in App. II.

Fig. 9 shows the flux for a low flow rate with and without an electric field when increasing the pressure in steps. For the experiment without an electric field, the flux increased with increasing pressure until a cake started to form on the membrane surface and it was no longer possible to increase the flux by increasing the pressure. This pressure is called the critical pressure and the flux the limiting flux. A cake started to form already at a transmembrane pressure of 0.5 bar. However, using an electric field it was possible to avoid cake formation at the pressures studied. The flux-pressure curve bends slightly at low pressure, but a plateau was not seen even at 4 bar (see also App. II, Fig. 2). This means that the limiting flux increased from 75 to over 350 L/(m^2h), when an electric field strength of 2.4 kV/m was applied. The enhancement in the limiting flux can also be estimated by calculation. When calculated according to Eq. (5) generated in this thesis (using u_e = 5.0 (μm/s)/(V/cm), as the mean electrophoretic mobility) the limiting flux was 430 L/(m^2h). This is close to the value obtained experimentally. When the feed flow was high, the limiting flux could not be achieved for the 0.05 μm membrane due to the limitation in pressure of the equipment (App. II, Fig. 3).

When there was no cake on the membrane, the flux enhancement with an electric field was minor. This was the case when the membrane worked as a cathode. The flux could have been improved with an electric field also below the limiting flux due to electro-osmotic flow, if an electric field would have been applied across the membrane. However, the effect of electro-osmotic flow on the flux has been minor or even negligible in the studies of other authors [Rios *et al.* 1988, Radovich and Behnam 1983].

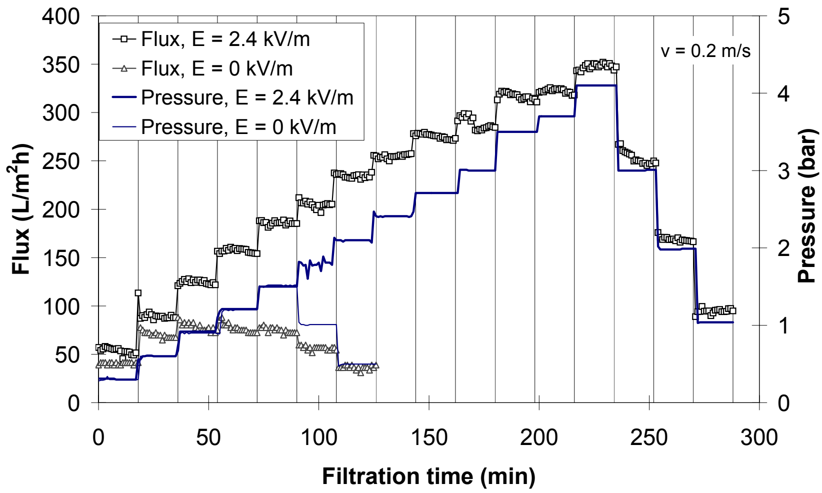

Figure 9. Fluxes at low flow rate in a constant pressure filtration of a mixture of oil emulsion and cleaning agent. The pressure was increased in steps and decreased again. The mixture was filtered using a 0.05 µm CFCC-membrane.

The flux levels obtained when decreasing the pressure from the maximum value were always lower than those obtained earlier, when increasing the pressure. This indicates some degree of irreversible fouling (Fig. 9). The reversibility of fouling was similar for filtration with and without an electric field. Irreversible fouling was also seen as a decrease in the pure water flux after filtration, compared with values before filtration. All fluxes in the filtration of the mixture of oil emulsion and the cleaning agent were considerably lower than the pure water flux already at low pressures. Adsorption or other kinds of fouling occurred and it was not possible to prevent this decrease using an electric field. However, when only the oil droplets were filtered the fluxes followed the pure water flux curve up to 1 bar. The flux was then 750 L/(m^2h) (Fig. 10). The experimentally determined limiting flux increase was around 830 L/(m^2h). It is also close to the value, 880 L/(m^2h), calculated using Eq. (5).

The flux when an electric field was applied was not influenced significantly by an oil concentration in the feed in the range of 150 to 1660 mg/L (see App. II, Fig. 8). The same flux decrease, when increasing the concentration, was seen in the filtration without an electric field. Thus, the flux enhancement with an electric field was not influenced by the studied oil concentrations.

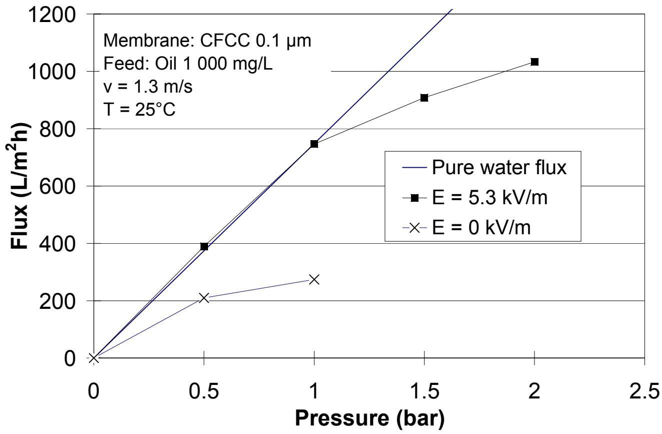

Figure 10. Limiting flux when only oil emulsion was filtered. The pore size of the CFCC-membrane used was 0.1 µm.

5.1.2 Critical electric field strength [I, II]

In electrofiltration a sufficiently high electric field strength should be used in order to prevent particle deposition on the membrane and to get flux increase as shown above. The minimum value is the critical electric field strength (see Theory of electrofiltration) which can be determined by calculation or experimentally as will be shown next.

Eq. (4) generated in this study for the critical electric field strength was achieved when the forces acting on one particle were considered. According to Eq. (4) the calculated critical electric field strength for the mixture of the oil emulsion and the cleaning agent is 1.1 kV/m at 2 bar when using the 0.05 µm CFCC-membrane and 0.6 kV/m at 1 bar. The critical electric field strength can be determined experimentally by increasing the electric field strength at different cross-flow velocities [Radovich *et al*. 1985]. At the critical electric field strength the flux starts to be independent of the cross-flow velocity. In this study the value is determined experimentally by measuring the flux at different electric field strengths. The flux increase changes clearly at the critical electric field strength when the particles are not depositing any more on the membrane. At 2 bar, the experimental critical electric field strength was high enough to be estimated from the curve shown in Fig. 11. It was found to be in the range

0.6–2.4 kV/m, which is in agreement with the calculated value. When the electric field strength was higher than the critical, a further increase in the electric field strength did not significantly influence the flux. Thus in the case of a cathodic membrane the electric field strength should not be much higher than the critical electric field strength in order to minimise the energy consumption. When the electric field is applied across the membrane the increasing electric field strength can linearly increase the flux also above the critical electric field strength. It is, however, not economical to run electrofiltration above the critical pressure.

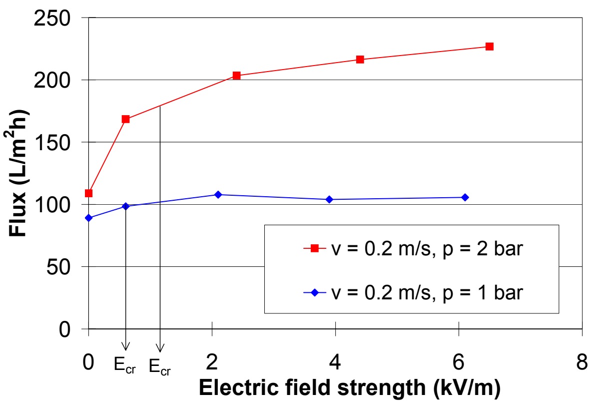

Figure 11. Critical electric field strength as a function of flux in the filtration of a mixture of oil emulsion and a cleaning agent using 0.05 μm membrane [II].

When an 850 mg/L oil emulsion was filtered using a 0.1 μm CFCC-membrane, the experimentally determined critical electric field strength was around 5 kV/m. This is close to the calculated value 4.5 kV/m. If pressure or membrane pore size were increased in an attempt to increase the flux, the critical electric field strength increased and a higher voltage was needed. This can also be seen theoretically from Eq. (4).

5.1.3 Cross-flow velocity [II]

High cross-flow velocities are used in conventional membrane filtration in order to minimise fouling and achieve higher fluxes. However, a high cross-flow velocity increases the axial pressure drop, which can cause problems on an industrial scale. In this study the possibilities to use low cross-flow velocities in electrofiltration are studied.

The effect of cross-flow velocity on flux was examined in the case, when the feed consisted only of oil emulsion and when the feed was a mixture of an oil emulsion and a cleaning agent. In both cases high fluxes compared to the fluxes without an electric field were achieved at low cross-flow velocity (see App. II). When the oil emulsion particles in the feed were larger than 100 nm, the flux increased from 460 L/(m^{2}h) to 530 L/(m^{2}h) when the cross-flow velocity was decreased from 2.8 m/s to 0.2 m/s (Fig. 12). This is because above the critical electric field strength, the particles were drawn towards the central electrode. This resulted in a high particle concentration in the centre of the membrane tube. Increasing the cross-flow velocity led to an increase in diffusive transport of the particles towards the membrane and to lower fluxes. When filtering a mixture of small cleaning agent particles together with large oil particles the cross-flow velocity had no effect on the flux in electrofiltration. For the small particles, diffusion was high already at low cross-flow velocities due to Brownian motion. Diffusion caused by the concentration gradient is important for particles smaller than 50 nm but not for particles larger than 100 nm in diameter [Huisman 1998].

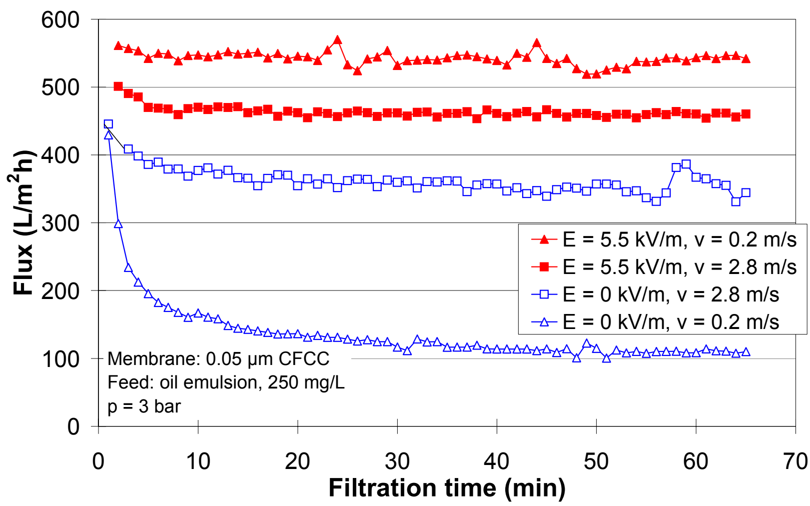

Figure 12. Steady-state fluxes at low and high flow velocity with and without an applied electric field, when the feed consisted of only large oil emulsion droplets. The pure water flux at 3 bar was 560 L/(m^{2}h) [II].

The use of high flow rate and an electric field are optional methods, which both move particles away from the membrane surface. There was no need to use high flow velocity in electrofiltration. Very low cross-flow velocity could be used when an electric field was applied.

5.1.4 Membrane selectivity [II]

The charged particles or molecular aggregates, which one wants to retain, migrate away from the membrane independently of the pore size, if the electric field strength is higher than the critical value. Thus, the membrane selectivity should be improved using an electric field. However, the membrane pore size is usually smaller than the size of the charged substances, and therefore the solute retention is usually not affected significantly by the application of an electric field, although the permeate flux is significantly enhanced [Akay and Wakeman 1997]. In this study the same phenomenon occurred with the CFCC-membrane and the model wastewater as will be seen below.

When a CFCC-membrane with a pore size of 0.1 μm was used, the application of an electric field improved the permeate quality when the wastewater contained only oil emulsion. Oil and COD retentions after a 3 h filtration were 85% without an electric field at 2.8 m/s and 1 bar, and 98% with an electric field at 0.2 m/s and 1 bar. After a 5 h filtration the flux was 350 L/(m^2h) without an electric field and 620 L/(m^2h) with an electric field. When treating the oil emulsion without an electric field above the critical pressure with the 0.1 μm membrane, the permeate quality was significantly worse when a velocity of 0.2 m/s was used instead of 2.8 m/s. This was not the case when an electric field was applied. The permeate quality was improved when the cross-flow velocity decreased because more diffusion towards the membrane occurred due to turbulence.

When only the oil emulsion was filtered with a 0.05 μm membrane, the COD retention was 94% even without an electric field, and no significant improvement was achieved by applying an electric field. When the feed consisted of both small cleaning agent particles and large oil emulsion droplets the permeate quality with the 0.05 μm membrane was slightly better with an electric field than without. The oil retention increased from 90 to 94% and the COD retention from 70 to 78%. (see also App. II).

5.1.5 Intermittent electric field [II]

For the purpose of reducing the power consumption, some studies about pulsed electric fields are seen in literature [Bowen *et al.* 1989, Wakeman and Sabri 1995]. According to Wakeman and Sabri [1995] both continuous and pulsed fields reduce fouling in membrane filtration, but a continuously applied electric field leads to a more effective utilisation of energy. In electrofiltration usually the limiting flux is increased with an electric field. This means, that particles above the critical pressure start to deposit on the membrane immediately after switching off the electric field. The higher the pressure and the electric field strength the faster the flux decreases. The question is, if the flux recovery (reversibility) is achieved at high pressure when switching on the electric field. The flux recovery should be close to hundred percent in order not to loose flux efficiency. In this study the effect of an intermittent electric field on the flux recovery was studied in the case of three different model wastewater samples.

Upon switching off the electrical field, and restoring it after half an hour, the flux recovery was rather poor for both the oil emulsion and the mixture of oil emulsion and the cleaning agent (Fig. 13). The higher the pressure above the critical pressure, the lower the flux after restoring the electric field. In the case of the mixture it was possible to recover 90% of the original flux at 1 bar but only 55% at 3 bar. Thus, when a high pressure was used and the effect of the electric field was substantial, it was not possible to use an intermittent electric field without losing efficiency. The best flux recovery was achieved when only colloids consisting of cleaning agent were filtered. In this case, 98% of the original flux was recovered at 2 bar but at 3 bar the flux recovery was 93%.

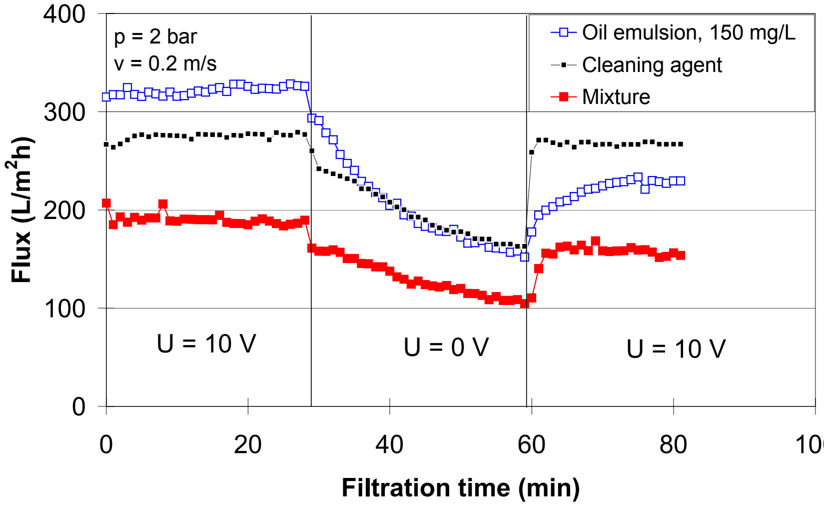

Figure 13. The flux recovery in the filtration of three different kinds of oily wastewater with a 0.05 µm CFCC-membrane. The electric field strengths were 3.5 kV/m for the oil emulsion, 3.4 kV/m for the cleaning agent and 2.4 kV/m for the mixture. The pure water flux at 2 bar was 406 L/(m^{2}h) [II].

When using a pulsed electric field there is every likelihood to foul the membrane irreversibly during switching off the electric field, because the pressures used in electrofiltration are high. Thus it is probable that the pulsation leads to a less effective energy consumption.

5.1.6 Effect of conductivity on process design [III]

In a typical industrial wastewater the conductivity is higher (> 500 µS/cm) than in the model wastewater samples studied (7–32 µS/cm). According to some authors [Bowen *et al.* 1989, Wakeman and Sabri 1995], the effective operation of electrofiltration is limited to the same conductivity range as for electro-osmotic dewatering, which is from 0.10 to 10 mS/cm. However, it is possible to achieve many-fold flux enhancements at very low conductivity values, < 10 µS/cm, as seen above. The high conductivity, actually, caused problems in electrofiltration and inspired to find a suitable module configuration for the industrial wastewater samples. In this study the effect of conductivity on flux in three different module configurations (Fig. 4) was studied (see also App. III).

First the conductivity of the model wastewater was increased in the simplest electrofiltration module, where the conductive CFCC-membrane worked as the cathode (Fig. 4a). The increased conductivity affected the flux negatively. The flux in the model wastewater electrofiltration decreased from 740 to 220 L/(m^2h), when the conductivity of the oil emulsion increased by NaOH to a more realistic value of 800 µS/cm (Fig. 14). Conversely, the flux decreased when a conductive membrane was used and the conductivity of the model wastewater was increased by NaCl. A low flux was detected also, when an industrial wastewater was filtered using this module configuration.

The decreased electrophoretic mobility could not be the reason for the decreased flux. Emulsified oil has a pH-dependent charge and increasing the conductivity with NaOH the mean absolute electrophoretic mobility increased from -4.1 to -5.8 (µm/s)/(V/cm) due to the changed pH (see also Fig. 2). According to Eq. (5), a higher electrophoretic mobility increases the flux. The increased conductivity increased the current density causing more electrochemical reactions to take place at the electrodes. Thus more hydrogen gas (Eq. 6) was produced at the membrane. This could have influenced the electric field strength. When increasing the conductivity the decrease of the electric field strength was, however, minor calculated using the conductivity of the bulk and the current density measured during filtration (App. III). The flux was thus most likely not decreased because of the decreased electric field strength, but because of the space taken by the hydrogen gas in the pores of the membrane. Hydrogen bubbles at the electrodes could also be regarded as foulants in the system. Bubbles, when formed, might have been stuck in the membrane, and therefore fouled the membrane temporarily. The pressure needed to push the bubbles through the membrane is dependent on their size. The diameter of hydrogen gas bubbles, for instance, is dependent on factors such as cathode surface morphology, current density and temperature [Koren and Syversen 1995]. Reported bubble diameters at constant current density at atmospheric pressure are 20 µm. To get an idea of the pressure needed it is about 7 bar according to the bubble point method for a membrane pore diameter of 0.1µm.

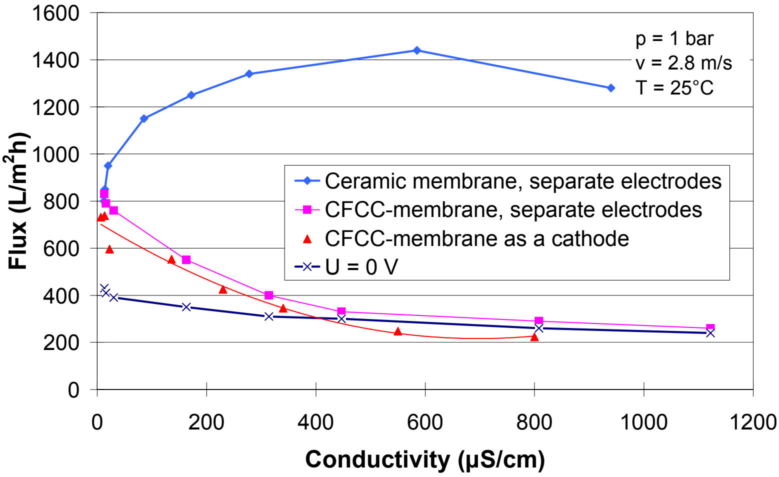

Figure 14. Effect of conductivity on flux in electrofiltration when using different module configurations. The electric field strength was 4–6 kV/m except when U = 0 V [III].

An attempt to solve the gas production problem on the membrane was made by using a separate cathode around the CFCC-membrane (Fig. 4b). However, the flux decreased exactly in the same way as it did when the membrane worked as a cathode (Fig. 14). The conductive membrane seemed to work as part of the cathode in an aqueous system, although the electrode did not touch it. The gas formed on the membrane caused the decreased flux. The distance between the membrane and the electrodes was short. Increasing the distances, however, would most likely not have reduced the problem. The membrane would still work as part of one of the electrodes.

Next the membrane material was changed to a non-conductive ceramic and an electric field was applied across the membrane with one electrode on either side of the membrane (Fig. 4c). The flux did not decrease by increasing the conductivity (Fig. 14) in this module configuration. The flux increased instead. When the pH of the feed was increased the electrophoretic mobility of the oil droplets increased. This gave a higher flux at the same electric field strength due to an otherwise too low electric field strength for keeping the particles away from the membrane. The fluxes achieved, 1 400 L/(m^2h), were even a bit higher than the pure water fluxes when electro-osmosis occurred. The electric potential across the membrane was not zero in this module configuration as it was when the CFCC-membrane worked as a cathode.

The best fluxes were achieved using the non-conductive membrane with separate electrodes. According to Wakeman and Tarleton [1991] an electrode should be located downstream of the membrane support in order to carry the bubbles away with the permeate flow. The other electrode can not be placed closer than about 3 mm from the membrane surface. Gas evolving from this electrode is flushed out of the module by the cross-flow stream. In the module configuration studied the outer electrode was 2 mm from the outer diameter of the membrane. The inner electrode was 2.4 mm from the membrane surface. These distances seemed to be sufficient. The avoidance of the gas problem on the feed side is also a question of cross-flow velocity, which can not be too low.

5.1.7 Suitability of industrial wastewaters for electrofiltration [III]

More than ten industrial wastewater samples were studied for electrofiltration (Table 1). In a typical industrial wastewater the mean electrophoretic mobility was only slightly negative. The values were different from the values of the model wastewaters used. The electrophoretic mobility is the most important parameter, which affects the flux enhancement and thus characterises the suitability of a sample for electrofiltration. The conductivity of a sample is related to the electric field strength and the energy consumption and thus to the suitability of the sample for electrofiltration. The next chapter will deal with energy consumption.

The absolute electrophoretic mobility should be as high as possible. In one sample studied the electrophoretic mobility was clearly higher, -3.5 (µm/s)/(V/cm), than in other samples. In this case the flux increased significantly from 300 to 1200 L/(m^2h) when an electric field was applied (Fig. 15). The flux after three hours of filtration was 1070 L/(m^2h), and it showed a small decrease with time. This was because the pressure of 1.5 bar was too high for the electric field strength, 3.3 kV/m as calculated using Eq. (11). The permeate quality was the same with and without an electric field, because the pore size of the membrane was sufficiently small for particle retention. The electric field seemed to be very useful in the treatment of this wastewater, but the circumstances need to be optimised further.

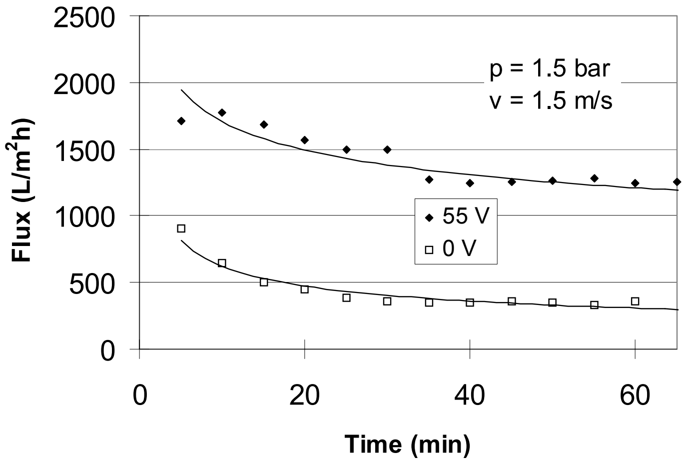

Figure 15. Filtration of an industrial wastewater with a high average electrophoretic mobility [III].

In other samples the average electrophoretic mobility was usually only slightly negative. When the average electrophoretic mobility is close to zero the sample can contain both negatively and positively charged particles or colloids. In the cases studied the flux was somewhat higher with an electric field than, when no electric field was applied or the flux had a clear decreasing trend and reached a lower level than with no electric field. The reason for the decreased flux can be the particles or colloids having no charge or a different sign than the average electrophoretic mobility. In this study sodium hydroxide or a commercial dispersing agent was used for increasing the negative electrophoretic mobility. The best result was achieved for particles from metal grinding. With dispersing agent the mobility could be changed from -1.5 to -2.1 (µm/s)/(V/cm). The electrophoretic mobility was still not very high, but the treatment increased the flux from 100 to 400 L/(m^{2}h). The flux increase was significant. However, the amount of dispersing agent needed, 0.2 % for the whole mass of wastewater, was much too high for industrial use. On the whole, the change of the electrophoretic mobility of an industrial wastewater, which contained a lot of different ions and particles, was not easy in practice.

Electrofiltration has the best possibility to be successful when the electrophoretic mobility in the feed is high without any modification. This, unfortunately, is seldom the case, which makes the electrofiltration technique less attractive for the equipment manufacturer.

5.1.8 Energy consumption in electrofiltration [I, III]

Apart from the electrophoretic mobility, the electric field strength plays a main role in flux enhancement. The electric field strength is inversely proportional to the conductivity of the sample (Eq. 11). If the conductivity increases, the current increases, when the same electric field strength is needed. This means higher energy consumption. The conductivity of the industrial wastewater samples studied varied from 0.5 up to 174 mS/cm. It was 1.7 mS/cm in the sample with which the best flux enhancement with an electric field was achieved. It is not very high and still when only the electric field was taken into account the energy consumption was 22 kWh/m^3. The continuous application of an electric field typically requires energy more than 10 kWh/m^3 of permeate [Bowen *et al.* 1989]. Thus 22 kWh/m^3 is normal in electrofiltration but, however, too high for industrial purposes.

Energy consumption can be decreased linearly by decreasing the electric field strength or the distance between the electrodes. If both of them can be decreased the effect is exponential. If the electric field strength could be decreased, in the case of the best flux enhancement, from 3.3 $\rightarrow$ 2.2 kV/m, and the distance between the electrodes could be halved, the energy consumption would then be 6.4 kWh/m^3. This is more realistic for industrial use. The higher energy consumption due to the longer distance in a non-conductive membrane filtration module is needed when the membrane works as an electrode. However, the conductivity of the industrial wastewater is hardly ever sufficiently low as would be needed for the conductive membrane filtration module.

In electrofiltration a clearly lower cross-flow velocity could be used compared to conventional microfiltration and thus less energy is consumed for pumping. The possibility of using larger pores would decrease the pressure needed and thus also the energy consumption due to pumping. However, the normal pumping energy for microfiltration is still low, 2 kWh/m^3 [Bowen *et al.* 1989], compared to the energy consumption shown above. In electrofiltration the running costs can thus be competitive only if the conductivity is low.

5.2 Ultrasound assisted filtration

5.2.1 Ultrasound propagation direction [V]

The suitable propagation direction of ultrasound was primarily studied using the dead end –filter module and bark press filtrate. The studies were carried out with ceramic membranes, the mean pore sizes of which were 0.12 µm (membrane 1 in Table 4) and 0.75 µm (membrane 4). The membranes are called correspondingly ultrafiltration and microfiltration membranes in the present study. The transmembrane pressure in the experiments was 0.9 bar. Ultrasound was focussed to the membrane from the permeate side or from the feed side of the membrane using a frequency of 40 kHz and an input power of 200 or 400 W. With the *ultrafiltration* membrane the highest flux was obtained with both input powers studied when the ultrasound propagation direction was from the feed side of the membrane (Fig. 16a). Ultrasound irradiation from the permeate side resulted in a slightly higher flux than without ultrasound. However, different results were achieved in dead-end filtration with the *microfiltration* membrane. Ultrasound propagation from the feed side of the membrane resulted in fouling of the membrane (Fig. 16b) and the flux decreased to the same level as without ultrasound (20 L/(m^2h)). Ultrasound propagation from the permeate side resulted in a steady state flux of 120 L/(m^2h).

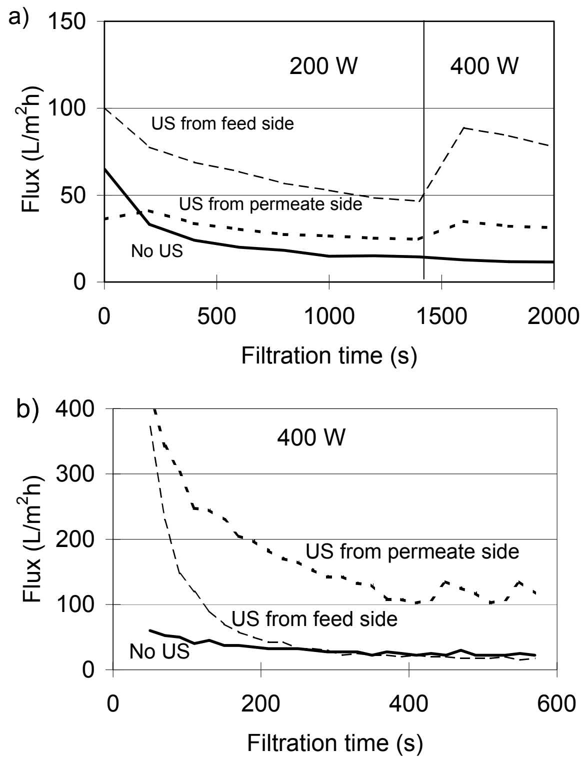

Figure 16. Flux as a function of filtration time when filtering bark press filtrate (feed 1) with different membranes and ultrasound propagation directions. a) Ultrafiltration membrane (membrane 1). b) Microfiltration membrane (membrane 4) [V].

A similar trend was also seen in cross-flow membrane filtration when applying ultrasound from the feed flow side of the membrane. The *microfiltration* membrane (membrane 3) was fouled readily with bark press filtrate when irradiating ultrasound with an input power of 400 W and a frequency of 40 kHz (Fig. 17). On the other hand, with the *ultrafiltration* membrane (membrane 1) a steady state flux was achieved with the same input power and frequency (Fig. 18). The flux with ultrasound was double compared to the flux without (35 compared to 70 L/(m^2h)). However, the fluxes with the membranes studied were far from the pure water fluxes of the membranes.

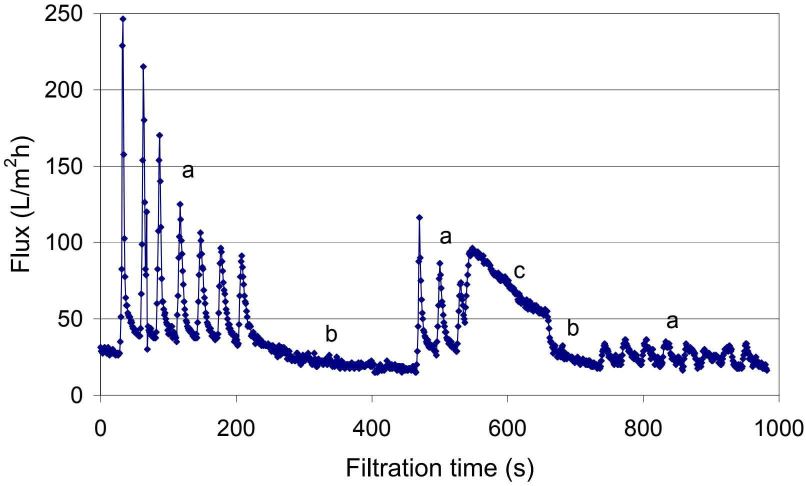

Figure 17. Ultrasound propagation from the feed flow side of the microfiltration membrane (membrane 3). Flux as a function of time when filtering bark press filtrate (feed 3) using a pressure of 1 bar and a cross-flow velocity of 0.45 m/s. a) Intermittent ultrasound (40 kHz, 400 W) was irradiated for 5 s every 30 s. b) No ultrasound. c) Continuous ultrasound (40 kHz and 400 W) [V].

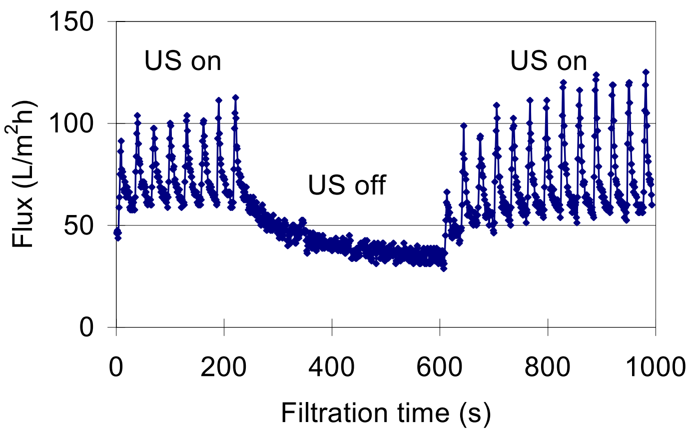

Figure 18. Ultrasound propagation from the feed flow side of the ultrafiltration membrane (membrane 1). Flux as a function of filtration time when filtering bark press filtrate (feed 3) using a pressure of 3 bar and a cross-flow velocity of 0.45 m/s. Intermittent ultrasound (40 kHz, 400 W) was irradiated for 5 s every 30 s [V].

According to these results cake formation could be prevented at the membrane surface when irradiating ultrasound from the feed flow side of the membrane if the membrane was tight enough, like ultrafiltration membranes, to prevent particles of the feed to penetrate inside the membrane. With more open membranes, like microfiltration membranes, ultrasound could not increase the flux at the pressure studied if ultrasound was irradiated from the feed flow side of the membrane. The results are in agreement with the studies of other researchers [Kobayashi *et al*. 1999, Matsumoto *et al*. 1996]. However, ultrasound irradiated from the feed flow side has been successfully used simultaneously with backflush pulsing during filtration in a CERTUS-microfilter [Rantala and Kuula-Väisänen 1999]. Thus, for open membranes the ultrasound propagation direction should be different or the irradiation from the feed side should be combined with other cleaning techniques. The effect of different membrane porosities with same pore size were not studied in this thesis but the ceramic membranes used had similar porosities, approximately 45 %.

5.2.2 Effect of particle size [IV, VI]

Having a smaller mean size the particle movement in the sound field follows more closely that of the suspending fluid than having a larger mean size [Tuori *et al*. 1993, Wakeman and Tarleton 1991]. In the case of small particles the ultrasonic field could possibly promote sufficient motion at or near the fouling layer surface to cause the particles to stay in suspension or to resuspend. Thus with a suspension containing smaller sized particles less fouling occurs at the membrane surface in ultrasound assisted membrane filtration than when containing larger sized particles. Alternatively smaller particles in suspension may cause less attenuation of the sound field. On the other hand, large particles follow better lower frequencies (1 kHz) than higher frequencies (100 kHz) and all sizes of particles (1–1000 µm) follow easily the ultrasonic vibration when the density is near to that of water [Tuori *et al*. 1993].

The experiments in this study, however, showed that there are more important feed properties than the particle size, which affect the efficiency of the ultrasonic treatment. The ultrasound irradiation was more effective in cross-flow membrane filtration of oily wastewater when the oil emulsion was pre-treated and significantly larger particles were formed. During pre-treatment the charges of the feed particles were reduced in order to make the flocculation possible. The flux increased only from 13 to 20 L/m^{2}h when using a very high input power (600 W) and decreased to the level of 4 L/m^{2}h during filtration. A higher permeate flux and an improved quality were achieved with electroflocculated particles. The flux increased from 20 to 50 L/m^{2}h (Fig. 19) when using ultrasound and only an input power of 230 W was required instead of 600 W. The effect of particle size was also affected by the relation of membrane pore size to particle size. When bigger particles were filtered they were not able to penetrate inside the pores and thus were easier to be taken away from the membrane surface using ultrasound than smaller particles from the pores. Also ultrasound was not able to push the particles inside the pores (see Chapter 5.2.1).

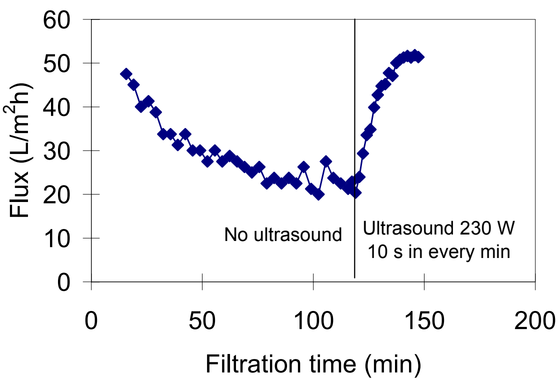

Figure 19. Flux as a function of filtration time when flocculated oily wastewater was filtered with and without ultrasound [VI].

5.2.3 Effect of pressure [V, VI]

A foulant containing feed (high COD) fouled the membranes severely in the study because of a strong compaction of the cake layer due to the high transmembrane pressure used. The cleaning of the membranes required an efficient ultrasonic treatment. One problem in ultrasound aided experiments was the wear of the membranes, which has also been seen by some other researchers (see Chapter 3). Membranes irradiated by ultrasound, using frequencies of 27 or 40 kHz, became damaged at some spots of the membrane surface (Fig. 20). The wear of the surface was especially seen with polymeric membranes but with the ceramic 0.12 μm membrane as well. This made us look for more gentle ultrasonic treatment conditions for membranes without loosing any efficiency of the treatment.

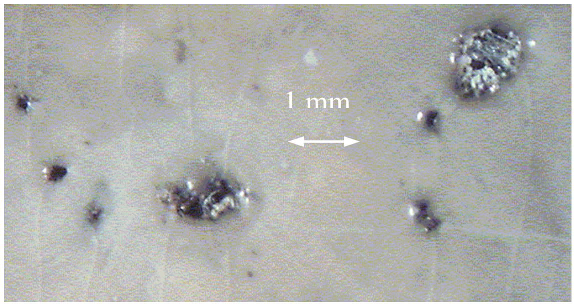

Figure 20. Damaged PES-50H polymeric membrane irradiated by ultrasound.

Pressure is known to affect the ultrasonic cavitation. The cavitation threshold rises with pressure. Once the threshold is exceeded at high pressure, the cavitation bubbles collapse more violently and rapidly but the number of bubbles decreases more than at low pressures [Mason and Lorimer 1988]. The effect of pressure was studied using copper plates painted with silver paint, which were directly irradiated by ultrasound in water with an input power of 400 W and a frequency of 40 kHz. The pressure varied from zero to three bars. At a pressure of zero bar the plate wore evenly (Fig. 21). The silver paint layer was not broken. Holes were already seen at one bar, and the higher the pressure the bigger the holes were in the silver paint layer. On the other hand, the unevenness of the ultrasonic field was clear at high pressure and the higher the pressure the larger the areas of intact regions. This indicated that cleaning of membranes using ultrasound would be more difficult at pressurised conditions than at atmospheric pressure. Same results were obtained using 27 kHz and 120 W.

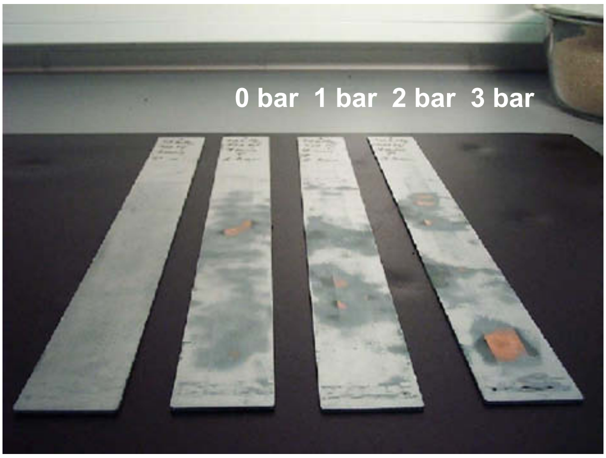

Figure 21. Erosion of silver paint when using ultrasound at pressures from zero to three bar. Copper plates painted with silver paint were directly irradiated for 4 min with 40 kHz ultrasound at an input power of 400 W [V].

The ultrasonic cleaning at atmospheric pressure succeeded in membrane filtration experiments when using 0.19 μm ceramic membranes (membrane 2), 27 kHz frequency and 120 W input power (power intensity of 1.1 W/cm^2). The ultrasonic treatment was carried out normally during filtration (1.9 bar and 0.6 m/s) of bark press filtrate and when the filtration system was on an intermission pause (0 bar and 0 m/s). When the membrane was treated for ten seconds with ultrasound during filtration the flux increased from 14 L/(m^{2}h) up to 30 L/(m^{2}h). The flux was 127 L/(m^{2}h) without an effect of intermittent pumping after ten seconds of ultrasound irradiation during a pause in filtration (Fig. 22). Even two seconds of irradiation was sufficient to clean the membrane surface. However, the irradiation should have been repeated every few minutes in order to keep the flux at a higher level than without any treatment. This was because the feed contained a lot of colloids (COD = 31 000 mg/L). The results were similar in the study of ultrasonically enhanced microfiltration of electroflocculated oily wastewater (App. VI) except for that the flux stayed much longer at a higher level after irradiation compared to the bark press effluent filtration.

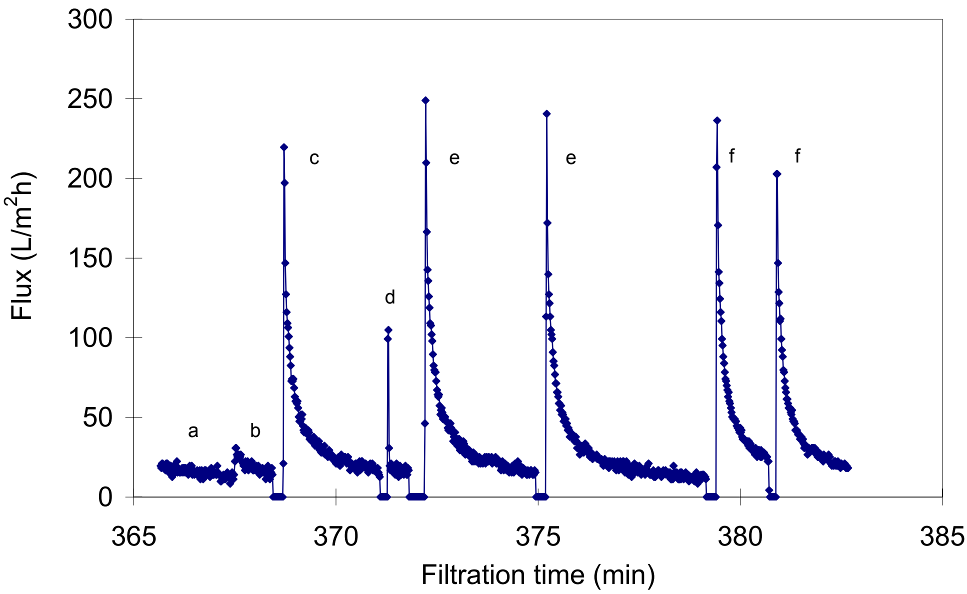

Figure 22. Flux when filtering bark press filtrate (feed 4) with a membrane of a pore size of 0.19 µm using a pressure of 1.9 bar and a cross-flow velocity of 0.6 m/s. a) No ultrasound. b) 10 s ultrasound (120 W) irradiation at the beginning of the filtration period. c) 10 s ultrasound (120 W) irradiation during a pause in filtration. d) Effect of intermittent pumping. e) 5 s irradiation during a pause. f) 2 s irradiation during a pause [V].

Matsumoto *et al*. [1996] studied a filtration method in which a feed pump and an ultrasonic generator were operated alternately. They found that intermittent driving of the feed pump alone greatly increased the rate of filtration compared to that obtained in continuous pumping operation. However, backwashing with ultrasound waves was more effective. In our studies, the peak of the flux due to intermittent pumping was of very short duration and lower compared to the flux increase obtained from ultrasound irradiation (Fig. 22).

The change of permeate quality due to the ultrasound irradiation was not systematically examined in this study. On the other hand, the ultrasound treatment during a pause in filtration could not affect the permeate quality. Table 5 shows the reductions of different parameters of bark press filter using a 0.19 µm membrane (membrane 2) without ultrasound (see also App.V).

Table 5. Feed and permeate qualities when using 0.19 µm membrane in the filtration of bark press filtrate [V].

	Feed (feed 4)	Permeate	Reduction (%)
Microbes (number/mg)	9×10^6	0.2×10^6	98
SS (mg/L)	4820	16.8	99
COD (mg/L)	31 100	16 900	46
Chloride (mg/L)	79.5	65.2	18
Total phosphorous (mg/L)	43.9	20.0	73
Total nitrogen (mg/L)	21.0	7.0	67

The ultrasonic irradiation during a short pause in filtration turned out to be an efficient and at the same time also a gentle method for membrane cleaning. There was a more even field at atmospheric pressure, which reduced the ultrasonic power intensity and the ultrasonic irradiation time (duration in seconds) needed. This method could work as an on-line cleaning method of membranes and lengthen chemical-cleaning intervals. However, a lot of development work, e.g. apparatus design, should be done until it is applicable on an industrial scale.

The effect of pressure in ultrasound assisted membrane filtration is not studied extensively. Bayevsky [2004] has developed a method in his patent, where an applied vacuum reduces a cavitation threshold avoiding damage to sensitive membrane filters. Moreover, vacuum may also reduce the energy consumption, and be used to provide some flow through the permeate channel to improve the cleaning of contaminants clogging the membrane pores. The fluxes obtained with this technique were not shown.

5.2.4 Effect of cross-flow [IV, V]

The feed concentration near the membrane is dependent on the cross-flow velocity of the feed solution. The flux increases in proportion to the feed flow velocity when ultrasonic waves are not used, but the flux can be high regardless of the feed flow velocity when ultrasonic waves are used [Muthukumaran *et al.*

2005, Matsumoto *et al*. 1996]. This is because the cake layer is removed by the shearing action of the ultrasonic waves and continually carried away from the membrane surface by the feed flow.

In this study the effect of cross-flow on cavitation effects on surfaces was briefly examined at 3 bar using the same silver paint coated plates as above. The presence of cross-flow during ultrasonic irradiation diminished the area of holes in the silver layer. Thus, the effects of cavitation on the membrane surface decreased due to cross-flow. The cross-flow velocity in the experiment was 0.2 m/s (Re 4 800). Muthukumaran *et al.* [2004] proposed that in a stagnant environment it is possible for a cavitation bubble to become trapped at a point on the membrane surface and physically erode the surface by repeated oscillations at this point. The presence of cross-flow during ultrasonic irradiation reduces the likelihood of such an event to occur. Thus, it could be suggested that a higher cross-flow velocity than the one used in the membrane filtration experiments (0.6 m/s, Re 12 000) could have reduced the damage on the membrane surface. However, increasing the cross-flow velocity might not be an energy saving method. On the other hand, there was no need to have cross-flow during ultrasonic irradiation under atmospheric pressure in the circumstances studied.

Divergent results on the effects of cross-flow have also been obtained. Kobayashi *et al.* [1999] studied the effect of cross-flow velocities of 0.2, 0.29 and 0.38 m/s on the flux in ultrasound (40 kHz) aided ultrafiltration. When no ultrasound was used the limiting flux was not influenced by the feed flow rate, but when ultrasound was irradiated the highest limiting flux was obtained with the highest cross-flow velocity. Li *et al*. [2002] obtained similar results when studying ultrasound assisted water cleaning of nylon membranes fouled by Kraft paper mill effluent. These studies indicate that the cleaning effects of ultrasound irradiation at the membrane are not decreased by a higher cross-flow velocity.

5.2.5 Effect of frequency [IV, V]

The effect of frequency on the efficiency of ultrasonic treatment during a short pause in filtration was examined by filtering the fabric press filtrate with a polymeric PES-50H ultrafiltration membrane. An ultrasound irradiation for five seconds was carried out using either a frequency of 27 or 200 kHz at an input power of 200 W (1.8 W/cm^2 or 4.1 W/cm^2). The influence of ultrasonic irradiation on the flux was minor when 200 kHz was used compared to 27 kHz (Fig. 23).

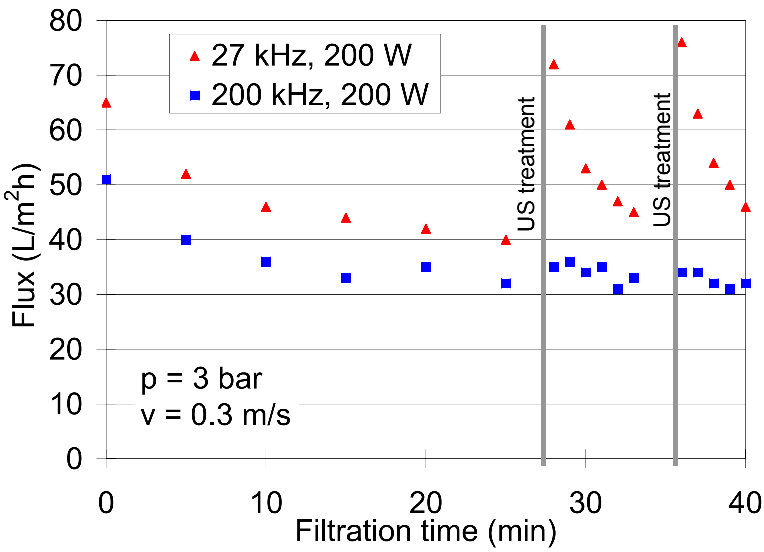

Figure 23. Flux as function of filtration time when filtering fabric press filtrate (feed 5) with a PES-50 membrane. Ultrasound was irradiated using different frequencies during a pause in filtration [V].

Kobayashi *et al.* [1999] got similar results when studying cross-flow filtration of dextran irradiating the membranes using 28, 45 and 100 kHz at a power intensity of 2.7 W/cm^2 (the output power of the sonicator per unit area of the transducer surface). They got minor effects when using a frequency of 100 kHz and significant effects when using frequencies of 28 or 45 kHz. Kobayashi *et al.* [2003] got nearly no effect on the flux in milk microfiltration with cellulose membrane and only a slight effect in peptone ultrafiltration with polysulphone membrane, when using a frequency of 100 kHz although the power intensity was 23 W/cm^2 (measured calorimetrically). Lamminen *et al*. [2004] studied the effect of frequency at a constant power intensity of 0.21 W/cm^2 (measured using calorimetry) when cleaning fouled membranes in a dead-end filtration system. In their study sulphate polystyrene latex particles with a diameter of 0.53 µm were removed well from the ceramic 0.2 µm membrane surface at a frequency of 200 kHz. This differs from the results obtained in the present study but also the filtration circumstances were different, e.g. the membranes were fouled with model particles which may have loosened easier from the membrane surface than the colloids in fabric press filtrate. Lamminen *et al*. [2004] obtained some effect on the flux even at a frequency of 1062 kHz.

In the present study the vibration of transducers was examined using a Polytec PSV-200 Scanning Laser Vibrometer when the transducer was working at 200 kHz or 27 kHz. The field produced by the transducer working at 200 kHz was even but the amplitude at the input power showing the intensity of an ultrasonic wave was many-fold less compared to the amplitude produced by a transducer of 27 kHz. Because the cavitation threshold is more difficult to obtain using a frequency of 200 kHz than 27 kHz [Mason and Lorimer 1988], it was very likely that there was poor cavitation at an input power of 200 W and a frequency of 200 kHz, and the minor increase of the flux was because of that. At high COD and at high transmembrane pressure cavitation would have been needed to reduce the fouling layer on the membrane.

5.2.6 Ultrasound combined with electric field

In this study some preliminary attempts of both ultrasound and electric field assisted membrane filtration were also carried out. The circumstances were not optimal for the combined technique and it should be studied more thoroughly. However, some thoughts have been put forth from the basis of the literature and the experimental studies with individual fields.

Wakeman and Tarleton [1991] examined the combined effects of ultrasonic and electric fields on microfiltration of china clay or anatase suspensions. The filter was specially designed to include mesh electrodes on both sides of the planar membrane and ultrasonic transducers in contact with the suspension on the upstream side of the microfiltration membrane. The effect of the electric field proved to be dominant compared to that of the ultrasonic field. When the two fields were applied simultaneously the flux was better than the additive effects of the individual effects. The synergism was greater with the more problematic suspensions and in particular at higher feed concentration. On the other hand, if an electric field operates well during membrane filtration, i.e. the formation of a cake layer and concentration polarisation are prevented on the membrane surface, there is no need to use an ultrasonic field. Ultrasound primarily breakes the cake or decreases the concentration on the membrane surface. A combined field could be useful if part of the colloids are not affected by the electric field but are able to be detached from the membrane surface by ultrasound. Thus in order to achieve improvements in the performance of membrane filtration, the combined technique, as also electrofiltration, requires suitable feed properties. They are, however, seldom realised in industry.

6. Conclusions

In this thesis was shown that an external DC electric field provides significant enhancement in cross-flow membrane filtration when the conditions are suitable for particle migration away from the membrane. The electric field was observed to influence especially the cake formation, and thus the limiting flux. In order to achieve improvements in the performance of membrane filtration, the electrofiltration technique requires suitable feed properties, which restrict the wider use of this technology. The sign of the charge of those particles or colloids, required to be kept away from the membrane must be the same and the same as that applied at the membrane. Limiting flux enhancement was shown both in theory and practice to be dependent on the electrophoretic mobility (or zeta potential) and the electric field strength applied. The electric field strength applied should be a little above the critical electric field strength in order to obtain the maximum benefit from the energy used.

According to this work, apart from the flux enhancement an electric field gives other benefits to the performance of membrane filtration. The quality of the permeate can be improved with an electric field, if the membrane pore size is too large to retain particles or colloids. However, if the membrane pore size is smaller than the size of the charged substances, the solute retention is not affected by the application of an electric field. Also, low cross-flow velocities are possible in electrofiltration. It was proven in this thesis that decreasing the cross-flow velocity above the critical electric field strength has no harmful effect on the flux or even increases it.

The conductivity was shown to be an important parameter in electrofiltration of industrial wastewaters. In these wastewaters the conductivity is often high, which increases the gas formation at the electrodes. This causes a negative effect on the flux, when conductive membranes are used. This problem was shown in this thesis to be overcome by using a non-conductive membrane. The high conductivity due to high salt concentration is one of the reasons for having low average electrophoretic mobility of particles, which can foul the membrane. The increase of the electrophoretic mobility of industrial wastewater samples is not easy in practice. The conductivity affects also the energy consumption in electrofiltration. If the conductivity is low, a sufficiently high electric field strength can be obtained with lower energy consumption than when the conductivity is high. The energy consumption can be decreased by shortening the distance between the electrodes, optimising the electric field strength applied, and pulsating the electric field. Unfortunately, these methods are often impractical.

Ultrasound irradiation was also shown to provide enhancement in cross-flow membrane filtration. It increases the flux primarily by breaking the cake layer at the membrane surface and decreasing the solute concentration near the membrane. Thus there is no need to use ultrasound in electrofiltration, where an electric field prevents the cake formation or concentration polarisation on the membrane surface. Cavitation produced liquid jets serve as a basis for ultrasonic cleaning processes. There are several factors, which affect the cavitation and thus influence the efficiency of ultrasound irradiation in fouling prevention.

From the ultrasound propagation point of view the pore size of the membrane is important. It was proven in this thesis that if the membranes are tight enough, like ultrafiltration membranes, ultrasound irradiated from the feed side of the membrane can increase the flux significantly. It was also shown that the more open the membrane the easier the membrane is fouled with wastewater particles when irradiating ultrasound from the feed flow side of the membrane. For open membranes, like microfiltration membranes, the ultrasound propagation direction should be different or ultrasound irradiation should be combined with other cleaning techniques like backflushing.

Although small particles follow the ultrasonic vibration more readily than large particles there are more important factors influencing the efficiency of ultrasound assisted membrane cleaning. It was observed in this work that ultrasonic irradiation can be more effective for pre-flocculated larger feed particles than for particles without pre-treatment. During pre-treatment the charge of the feed particles was reduced in order to make the flocculation possible. This makes the particle removal from the membrane surface easier during ultrasound irradiation, and the flocculated particles are removed from the membrane surface with less power intensity. Also, bigger particles were not able to penetrate inside the pores and thus were easier to be taken away using ultrasound.

This work confirmed that the lower ultrasound frequencies have higher cleaning efficiencies than higher frequencies. On the other hand, an increased power intensity provides an increase in ultrasound effects. In membrane cleaning at high COD and at high transmembrane pressure the power intensity needed during filtration was observed to be so high that the membranes became damaged. Increasing the pressure leads to an increase in the cavitation threshold, an increase in the intensity of bubble collapse and a decrease in the amount of collapsing bubbles. Thus at pressurised conditions the unevenness of the ultrasonic field is increased compared to the conditions at atmospheric pressure. It was shown in this thesis that increasing the pressure during irradiation leads to an increase in both the amount of damages and in untouched regions on the membrane surface. The more even ultrasonic field at atmospheric pressure reduces the ultrasonic power intensity and the irradiation time needed. Also, a high flux enhancement is obtained with an intermittent ultrasonic field. It was proven in this work that a low frequency ultrasound irradiation during a short pause in filtration is efficient and, at the same time, a gentle method in membrane cleaning. This method could lengthen the chemical cleaning intervals when filtering industrial wastewater.

In ultrasound aided filtration the flux can be high regardless of the cross-flow velocity. However, it was shown here that the effects of cavitation and thus the damage on the membrane surface may decrease due to cross-flow. Increasing the cross-flow velocity is, however, not an energy saving method. On the other hand, there is no need to have cross-flow during ultrasonic irradiation at atmospheric pressure.

The change of permeate quality due to the ultrasound irradiation is not systematically examined. The ultrasound treatment during a pause in filtration may not affect the permeate quality.

Electrofiltration is not a universal method for the filtration of industrial wastewater. It is a competitive method, when the average electrophoretic mobility in the sample is high and the conductivity is low. Ultrasound assisted filtration is less dependent on the feed properties and is a possible method for membrane cleaning in industry. However, there are some factors, especially the development of transducer technology for membrane filtration applications and the control of membrane erosion caused by cavitation, which need further development.

References

Abramov, O.V., *High-intensity Ultrasonics; Theory and Industrial Applications*, Gordon and Breach Science Publishers, London (1998) 692 p.

Akay, G. and Wakeman, R. J., Electric field enhanced cross-flow microfiltration of hydrophobically modified water soluble polymers, *J. Membrane Sci.*, **131** (1997) 229–236.

Bayevsky, M., Systems and methods for ultrasonic cleaning of cross-flow membrane filters, *US patent* 2004/0016699.

Bowen, W. R., Electrochemical aspects of microfiltration and ultrafiltration, in *Membranes in Bioprocessing*, ed. J. A. Howell, V. Sanchez and R. W. Field, Chapman & Hall, Cambridge (1993) 265–292.

Bowen, W. R. and Ahmad, A. L., Pulsed electrophoretic filter-cake release in dead-end membrane processes, *AIChE J.*, **43** (1997) 959–970.

Bowen, W. R. and Sabuni, H. A. M., Pulsed electrokinetic cleaning of cellulose nitrate microfiltration membranes, *Ind. Eng. Chem. Res.*, **31** (1992) 515–523.

Bowen, W. R., Kingdon, R. S. and Sabuni, H. A. M., Electrically enhanced separation processes: the basis of *in situ* intermittent electrolytic membrane cleaning (IIEMC) and *in situ* electrolytic membrane restoration (IEMR), *J. Membrane Sci.*, **40** (1989) 219–229.

Bros, A. and Kroner, K. H., Electro-cross-flow filtration of microbial suspensions, *Proceedings of ICOM´90*, Chicago (1990) 616–618.

Chai, X., Kobayashi, T. and Fujii, N., Ultrasound effect on cross-flow filtration of polyacrylonitrile ultrafiltration membranes, *J. Membrane Sci.*, **148** (1998) 129–135.

Chai, X., Kobayashi, T. and Fujii, N., Ultrasound-associated cleaning of polymeric membranes for water treatment, *Sep. Purif. Technol.*, **15** (1999) 139–146.

Elzo, D., Huisman, I. H., Middelink, E. and Gekas, V., Charge effects on inorganic membrane performance in a cross-flow microfiltration process, *Colloids Surf. A: Physicochem. Eng. Aspects*., **138** (1998) 145–156.

Ensminger, D., *Ultrasonics: Fundamentals, Technology and Applications*, 2nd Edition. Marcel Dekker Inc., New York (1988) 581.

Grönroos, A., Pirkonen, P., and Ruppert, O., Ultrasonic depolymerization of aqueous carboxymethylcellulose, *Ultrason. Sonochem*., **11** (2004) 9–12.

Guizard, C., Legault, F., Idrissi, N., Larbot, A., Cot, L. and Gavach, C., Electronically conductive mineral membranes designed for electro-ultrafiltration, *J. Membrane Sci*., **41** (1989) 127–142.

Heikkinen, J., Tuori, T., Wakeman, R.J., Juárez, J.A., Elvira, L., Rodriguez, G., Kaess, G., James, A. and Ekberg, B. Development of deliquoring method enhanced by electric and acoustic force fields, *Proceedings of World Filtration Congress 8*, Brighton (2000) 409–413.

Heikkola, E. and Laitinen, M., Model-based optimization of ultrasonic transducers, *Ultrason. Sonochem*., **12** (2005) 53–57.

Henry, J. D., Lawer, L. F. and Kuo, C. H. A., A solid/liquid separation process based on cross-flow and electrofiltration, *AIChE J.*, **23** (1977) 851–859.

Huisman, I. H., 1998, Cross-flow microfiltration of particle suspensions: The influence of hydrodynamics and physico-chemical interactions, *Thesis*, Department of Food Engineering, Lund University, Lund (1998) 15–84.

Huisman, I.H., Elzo, D., Middelink, E. and Trägårdh, C., Properties of the cake layer formed during cross-flow microfiltration, *Colloids Surf. A: Physicochem. Eng. Aspects*, **138** (1998) 265–281.

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

Juang, R.-S. and Lin, K.-H., Flux recovery in the ultrafiltration of suspended solutions with ultrasound, *J. Membrane Sci*., **243** (2004) 115–124.

Kobayashi, T., Chai, X. and Fujii, N., Ultrasound enhanced cross-flow membrane filtration, *Sep. Purif. Technol*., **17** (1999) 31–40.

Kobayashi, T., Kobayashi, T., Hosaka, Y. and Fujii, N., Ultrasound-enhanced membrane-cleaning processes applied water treatments: influence of sonic frequency on filtration treatments, *Ultrasonics*, **41** (2003) 185–190.

Kokugan, T., Kaseno, S., Fufiwara, S. and Shimizu, M., Ultrasonic effect on ultrafiltration properties of ceramic membrane, *Membrane,* **20** (1995) 213.

Koren, J. P. F. and Syversen, U., State-of-the-art electroflocculation, *Filtr. Sep.*, **32** (1995) (2) 153–156.

Kramer, G., Buchhammer, H.-M. and Lunkwitz, K. Surface modification by polyelectrolyte complexes: influence of modification procedure, polyelectrolyte components and substrates, *J. Appl. Polym. Sci.*, **65** (1997) 41–50.

Lamminen, M. O., Walker, H. W. and Weavers, L. K., Mechanisms and factors influencing the ultrasonic cleaning of particle-fouled ceramic membranes, *J. Membrane Sci.*, **237** (2004) 213–223.

Langley Ford Instruments, Product Reference Manual, *Coulter Delsa 440*, Division of Coulter Electronics of New England, Inc., U.S.A. (1988) 2:1–22.

Levänen, E., Alumina membranes – Colloidal processing and evolution of functional properties, *Thesis*, Tampere University of Tecnology, Finland (2004) 78.

Li, J., Sanderson, R.D. and Jacobs, E.P., Ultrasonic cleaning of nylon microfiltration membranes fouled by Kraft paper mill effluent, *J. Membrane Sci.*, **205** (2002) 247–257.

Mason, T. and Cordemans, D., Ultrasonic intensification of chemical processing and related processes, A review, *Trans IChemE* **74** (1996) 511–516.

Mason, T.J. and Lorimer, J.P., *Sonochemistry*, Ellis Horwood Limited, Great Britain (1988).

Masselin, I., Chasseray, X., Durand-Bourlier, L., Lainé, J.-M., Syzaref, P.-Y. and Laemordant, D., Effect of sonicationon polymeric membranes, *J. Membrane Sci*., **181** (2001) 213–220.

Matsumoto, Y., Miwa, T., Nakao, S.-I. and Kimura, S., Improvement of membrane permeation performance by ultrasonic microfiltration, *J. Chem. Eng. Jpn*., **29** (4) (1996) 561–567.

Mettin, R., Luther, S. and Lauterborn, W., Bubble size distributions and structures in acoustic cavitation, *Proceedings of 2nd Conference, Applications of Power Ultrasound in Physical and Chemical Processing*, Toulouse (1999) 125–129.

Muralidhara, H. S., Recent developments in solid-liquids separation including electrotechnologies, *Proceedings of Vth World Filtration Conference*, Nice (1990) 74–79.

Muthukumaran, S., Kentish, S., Lalchandani, S., Ashokkumar, M., Mawson, R., Stevens, G.W. and Grieser, F., The optimisation of ultrasonic cleaning procedures for dairy fouled ultrafiltration membranes, *Ultrason. Sonochem*., **12** (2005) 29–35.

Muthukumaran, S., Yang, K., Seuren, A., Kentish, S., Ashokkumar, M., Stevens, G.W. and Grieser, F., The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry, *Sep. Purif. Technol.*, **39** (2004) 99–107.

Mänttäri, M., Nyström, M. and Ekberg, B., Influence of flocculants on the performance of a ceramic capillary filter, *Filtr. Sep.*, **33** (1996) (1) 75–80.

Pirkonen, P., Ultrasound in filtration and sludge dewatering, *Advances in Sonochemistry,* ed. T. Mason and A. Tiehm, JAI Press Inc., **6** (2001) 221–246.

Pletcher, D. and Walsh, F. C., *Industrial Electrochemistry*, 2nd edition, Chapman and Hall, Great Britain (1990) 1–60.

Price, G.J., *Current Trends in Sonochemistry*, The Royal Society of Chemistry (1992).

Quartly-Watson, T., The importance of power ultrasound in cleaning and disinfection in the poultry industry – a case study, *Ultrasound in Food Processing*, ed. J. Povey and T. Mason, Thomas Science, UK (1998) 144–150.

Quigley, M. B. G. and Wakeman, R. J., Membrane filter with electrical and /or acoustic enhancement, *International Patent* WO 98/03245.

Radovich, J. M. and Behnam, B., Concentration ultrafiltration and diafiltration of albumin with an electric field, *Sep. Sci Technol*., **18** (1983) 215–222.

Radovich, J.M. and Chao, I.-M., Electroultrafiltration of a cationic electrodeposition paint, *J. Coatings Technol*., **54** (1982) 33–40.

Radovich, J.M., Behnam, B. and Mullon C., Steady-state modeling of electroultrafiltration at constant concentration, *Sep. Sci. Technol*., **20** (1985) 315–329.

Rantala, P. and Kuula-Väisänen, P., Filtration of paper mill process waters using a Certus-polishing filter with ceramic membrane, *Proceedings of 6th IAWQ Symposium on Forest Industry Wastewaters*, Tampere (1999) 239–244.

Raso, J., Mañas, P., Pagán, R. and Sala, F. J., Influence of different factors on the output power transferred into medium by ultrasound, *Ultrason. Sonochem*., **5** (1999) 157–162.

Rios, G., Pazos, C. and Coca J., Zeta potentials of cutting-oil water emulsions: influence of inorganic salts, *J. Disp. Sci. Technol*., **19** (1998) 661–678.

Rios, G.M., Rakotoarisoa, H. and Tarodo de la Fuente, B., Basic transport mechanism of ultrafiltration in the presence of an electric field, *J. Membrane Sci*., **38** (1988) 147–159.

Sabri, N., Pirkonen, P. and Sekki, H., Ultrasonically enhanced membrane filtration of paper mill effluent*, Proceedings of Applications of Power Ultrasound in Physical and Chemical Processing*, Toulouse (1997) 99–104.

Shaw, D. J., 1991, *Introduction to Colloid and Surface Chemistry*, Fourth edition, Butterworth-Heinemann Ltd., Great Britain (1991) 175–209.

Simon, A., Penpenic, L., Gondrexon, N., Taha, S. and Dorange, G., A comparative study between classical stirred and ultrasonically-assisted dead-end ultrafiltration, *Ultrason. Sonochem.*, **7** (2000) 183–186.

Smått, J.-H., Characterisation of ceramic filter media, *Confidential report*, Larox Corporation, Finland (2001) 10.

Tarleton, E. S. and Wakeman, R. J. Microfiltration enhanced by electrical and ultrasonic force fields, *Filtr. Sep.*, 27 (1990) 192–194.

Tuori, T., Enhancing filtration by electro-acoustic methods, *Thesis*, Lougborough University, UK (1998) 162.

Tuori, T., Martikainen, P. and Järvelä, E., Enhancement of Bio/fiber sludge filtration by electro-acoustic method, *Proceedings of 6th World Filtration Congress,* Nagoya (1993) 206–210.

Turner, A., Neville, M. and Fennell, P., Cleaner membranes, *The Chemical Engineer*, **11** (1996) 19–21.

Vergouw, J. M., Difeo, A., Xu, Z. and Finch, J. A., An agglomeration study of sulphide minerals using zeta potential and settling rate. Part II: sphalerite/pyrite and sphalerite/galena, *Minerals Eng.*, **II** (7) (1998) 605–614.

Wakeman, R. J. and Sabri, M.N., Utilizing pulsed electric fields in cross-flow microfiltration by the use of electric fields, *Trans. IChemE*, **73** Part A (1995) 455–463.

Wakeman, R. J. and Tarleton, E. S., 1987, Membrane fouling prevention in cross-flow microfiltration, *Chem. Eng. Sci*., **42** (4) (1987) 829–842.

Wakeman, R. J. and Tarleton, E. S., An experimental study of electroacoustic cross-flow microfiltration, *Trans. IChemE*, **69** Part A (1991) 386–397.

Yukawa, H., Shimura, K., Suda, A. and Maniwa, A., Cross-flow electro-ultrafiltration for colloidal solutions of protein, *J. Chem. Eng. Jpn*., **16** (4) (1983) 305–311.

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Title

Electrically or ultrasonically enhanced membrane filtration of wastewater

Abstract

Flux decline due to concentration polarisation and membrane fouling is a serious problem in membrane filtration. In this thesis the effect of an external DC electric or ultrasonic field separately on the flux in cross-flow membrane filtration of wastewater samples was studied.

Significant enhancement of the flux compared with the flux with no electric field was achieved in the filtration of model wastewater. The most important parameters for the flux enhancement were the electrophoretic mobility and the applied electric field strength. However, the average electrophoretic mobility of the charged particles in the industrial wastewater samples studied was usually only slightly negative. Thus enhancements when using appropriate electric field strengths were not good enough. Another problem with the industrial wastewater samples was the high conductivity, which caused high consumption of energy. Ultrasound irradiation also provided enhancement in membrane filtration of wastewaters. There are several factors, which affect the cavitation and thus influence the effectiveness of ultrasound in membrane fouling prevention. This thesis was focused on the suitable ultrasound propagation direction and the effect of the transmembrane pressure, which previously have got little attention in the research of ultrasound assisted membrane filtration. According to this study a low frequency ultrasound irradiation from the permeate side of the tight membrane at the transmembrane pressure of zero bar is efficient and, at the same time, a gentle method in membrane cleaning. For open membranes the ultrasound propagation direction should be different or the irradiation from the feed side should be combined with other cleaning techniques.

Electrofiltration is not a universal method for the filtration of industrial wastewater. It is a competitive method, when the average electrophoretic mobility in the sample is high and the conductivity is low. Ultrasound assisted filtration is less dependent on the feed properties and could be more useful in the cleaning of membranes in industry. However, there are some factors, especially the development of transducer technology for membrane filtration applications and the control of membrane erosion caused by cavitation, which need further development.

Keywords
membrane filtration, fouling, electrofiltration, electric field, ultrasound, flux, transmembrane pressure, filters, wastewaters, wastewater purification

Activity unit
VTT Processes, Koivurannantie 1, P.O.Box 1603, FI–40101 JYVÄSKYLÄ, Finland

ISBN			Project number
951–38–6663–7 (soft back ed.) 951–38–6664–5 (URL:http://www.vtt.fi/inf/pdf/)			
Date October 2005	Language English	Pages 79 p. + app. 54 p.	Price C
Name of project		Commissioned by	
Series title and ISSN VTT Publications 1235–0621 (soft back ed.) 1455–0849 (URL: http://www.vtt.fi/inf/pdf/)		Sold by VTT Information Service P.O.Box 2000, FI–02044 VTT, Finland Phone internat. +358 20 722 4404 Fax +358 20 722 4374	

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Tätä julkaisua myy	Denna publikation säljs av	This publication is available from
VTT TIETOPALVELU PL 2000 02044 VTT Puh. 020 722 4404 Faksi 020 722 4374	VTT INFORMATIONSTJÄNST PB 2000 02044 VTT Tel. 020 722 4404 Fax 020 722 4374	VTT INFORMATION SERVICE P.O.Box 2000 FI–02044 VTT, Finland Phone internat. +358 20 722 4404 Fax +358 20 722 4374

ISBN 951- 38- 6663- 7 (soft back ed.)
ISSN 1235- 0621 (soft back ed.)

ISBN 951- 38- 6664- 5 (URL: http://www.vtt.fi/inf/pdf/)
ISSN 1455- 0849 (URL: http://www.vtt.fi/inf/pdf/)