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## Fouling and cleaning of membrane——a literature review

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**Abstract:** Membrane fouling curtails severely the economical and practical implementation of membrane process. The fundamental principles and mechanisms of membrane fouling as well as factors affecting fouling have been summarized in this paper. It also has covered three fouling resistance models and four kinds of approaches to improve membrane performance. Membrane cleaning methods are also discussed including physical, chemical, physico-chemical and biological methods. In the four groups of basic cleaning methods, biological cleaning has considerable advantages and potentials. Extensive research work should be carried out further to explore and develop new ideas and techniques in the field of membrane cleaning and restoration.

**Key words:** membrane; fouling; cleaning

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### 1 Introduction

During the past few years, membrane separations have become more widely used, and replaced some of the conventional concentration techniques because it does not require phase change and are energy-saving. The membrane separations are becoming an increasingly important tool for separation and concentration of a variety of materials ranging from oil/water emulsions to waste sludge. Unlike distillation and evaporation, membrane separation is a nonthermal technique and its separation efficiency is normally higher (Humphrey, 1992). Hence, its applications can be found in food and pharmaceutical industries as well. Retention of flavors and aromas in juices and maintaining enzyme or drug activity is possible by using membrane techniques (Jagannadh 1996).

Although there is considerable interest in the use of membrane technology, its efficient operation is hindered by two major factors, namely, concentration polarization and fouling.

#### 1.1 Concentration polarization

Concentration polarization has been defined to be an accumulation of solute species at upstream surface of the membrane (Delaney, 1977). Concentration polarization is considered to be a hydrodynamic/diffusion phenomenon (Glover, 1980). This can be alleviated by operating the system at a higher velocity (if the system can tolerate it) (Merin, 1980). Concentration polarization appears to be present to some degree in any membrane processing because of the fundamental limitations of mass transfer and the existence of a boundary layer.

#### 1.2 Membrane fouling and its mechanism

Fouling involves the adsorption or trapping of particles (foulants) that are present in the fluid being transported across the membrane and can be a physical and/or chemical phenomenon. Some typical foulants are proteins, lipids, bacteria and so on. The basic mechanisms of fouling have been studied by a number of researchers (Aimar, 1988; Howell, 1980; Matthiasson, 1983). The general consensus appears to be that fouling may be due to one or more of the following mechanisms: (1) Formation of a dynamic membrane (surface layer or filter cake) on the front face of the membrane. In ultrafiltration (UF), fouling occurs predominantly on the membrane surface where the dynamic membrane controls membrane behavior. (2) Fouling within the membrane structure; there is evidence (Labbe, 1990; Attia, 1991; Hanemaaijer, 1989) that protein deposits within the membrane pores as well as on the surface. In UF the amount of protein deposited within

the membrane pores is small compared with that on the membrane surface. However, in microfiltration (MF) there is greater deposition within the pores, and internal fouling appears to dominate within large pores. (3) Fouling at the pore entrance: a number of authors (Le, 1984; Weldring, 1988; Devereux, 1986) have considered that the deposition of materials on the surface of the membrane must have in some way obstructed the pore entrances. The loss of effective membrane surface porosity is dependent upon the size of the depositing molecules and the pore size.

A clear distinction must be made between concentration polarization and membrane fouling. Concentration polarization leads to gel formation when the concentration at the membrane surface reaches the solubility limits of the macrosolute. The main difference between gel formation and membrane fouling is that the gel layer is formed on the membrane surface, whereas the fouling layer is formed by solute-membrane interactions and is more closely bound to the membrane surface. Fouling is an irreversible adsorption of macromolecules whereas gel formation is reversible because of the low interactive forces between the macromolecules in the gel (Matthiason, 1980).

In this paper, the effects of the properties of the feed, membrane materials and operating parameters on membrane behavior and fouling have been discussed in some detail. Fouling resistance models and approaches to improve membrane performance are presented. Membrane cleaning methods including physical, chemical, physico-chemical and biological cleaning have also been reviewed.

## **2 Factors affecting or contributing to membrane fouling**

### **2.1 The effect of the feed properties**

#### **2.1.1 Concentration**

Summarizing many authors' work (Olson, 1977; Balmann Nobrega, 1989), we come to the conclusion that increasing concentration generally results in a decrease in the permeate flux but has little effect on the membrane retention characteristics, except when the component size changes with concentration. Where surface fouling occurs, increasing concentration has little effect on irreversible membrane fouling but causes an increase in reversible gel formation. When internal membrane fouling dominates, increasing concentration increases the rate of membrane fouling. At high concentrations, cake or surface fouling is likely to dominate.

#### **2.1.2 pH and ionic strength**

In this aspect, many researchers have ever reported their study (Muller, 1973; Hayes, 1974; Attia, 1988). For protein fouling, proteins are complex molecules and their aggregation or interaction with the membrane surface, which is influenced by the pH and ionic strength, is not clearly understood. The three most common explanations for the observed membrane behavior with pH and ionic strength are: that changes in protein conformation and stability affect the tendency of the protein to deposit on the membrane; that changes in the protein's effective size alter the porosity of the dynamic membrane; that changes in the charge difference between the protein and the membrane surface affect protein adsorption or deposition. It is likely that all three explanations have some validity. The contribution from each is dependent upon the protein type, conformation and pretreatment, and the type of membrane material used.

#### **2.1.3 Component interactions**

The presence of larger molecules in the feed solution causes a steric hinderance to the passage of smaller molecules through the membrane. This may occur because the larger component forms a dynamic membrane that has a smaller porosity than the original membrane, or because the larger component interacts within the membrane pores. In some cases, specific component interactions in the feed solution may also affect the retention of different components (Blatt, 1970; Porter, 1988; Wahlgren, 1989).

#### **2.1.4 Prefiltration and the removal of aggregates**

A series of studies (Tanny, 1982; Merin, 1983; Kelly, 1992) showed that the removal of large molecular weight compounds, by prefiltration or other means, results in an improvement in

the permeate flux in both UF and MF. Protein aggregates may potentially block the larger membrane pores, resulting in a disproportionate loss of flux, and may act as seeds or catalysts for the formation of a protein fouling layer on the membrane surface.

## **2.2 The effect of the membrane material and its physico-chemical properties**

Two characteristics of membrane appear to influence fouling, viz: (a) the pore size, porosity and the morphology of the membrane surface, and (b) the physico-chemical properties of the membrane.

### **2.2.1 Pore size**

Numerous examples (Gatenholm, 1988; Nobrega, 1989) showed that membrane fouling is more severe with increasing pore size. There appears to be an optimum pore size, below which the membrane resistance restricts permeate flow and above which severe membrane fouling reduces the flux. Increases in membrane retention are generally more severe as the pore size increases.

### **2.2.2 Porosity and pore size distribution**

Most UF and MF membranes have a wide pore size distribution. The flow through the largest pores dominates the total permeate flow, and, as a consequence, the permeate flux is very sensitive to fouling or plugging of the larger pores by, for example, protein aggregates. Membrane selectivity is poor with membranes of a wide pore size distribution. Membrane fouling changes the pore size distribution and pore density of the membrane. Thus, the permeate flow, component retentions and membrane selectivity change as the membrane fouls with time.

### **2.2.3 Physico-chemical properties**

Many situations arise where physico-chemical interactions occur between solution species and membrane materials. For example macrosolutes, such as proteins, can bind to polymer surfaces by a variety of mechanisms (Hofstee, 1982) including electrostatic interaction, hydrophobic effects, charge transfer (e. g. hydrogen bonding and  $\pi$ - $\pi$  bonding) or through combinations of these. Physico-chemical properties include charge effects and hydrophobicity.

(1) Charge effects: The charges on a membrane are strongly dependent upon the membrane material, the pH and the ionic strength of the feed solution (Heinemann, 1988; Brink, 1990; Casiraghi, 1983). A study carried out by Nakao *et al.* (Nakao, 1988) show that operation with a membrane of similar charge to the protein can enhance the permeate flux if concentration polarization is minimized. With membranes of a large pore size, greater protein selectivity may be possible.

(2) Hydrophobicity: A series of investigations (Fane, 1985; 1987; Stengard 1988) prove that proteins are generally less easily adsorbed to hydrophilic membranes than to hydrophobic membranes, and that there is the potential for permeate flux improvement for hydrophilic membranes. However, where concentration polarization and total protein deposition are high, the effect of hydrophobicity is masked by the effects of concentration polarization. The work of Sheldon *et al.* (Sheldon, 1991) suggests that the increase in protein adsorption on hydrophobic membranes may be due to increased protein denaturation at the surface of the membrane.

## **2.3 The effect of the processing variables**

### **2.3.1 Transmembrane pressure**

Summarizing the studies carried out recently (Forman, 1990; Jonsson, 1986a; 1986a), we come to the conclusion that increasing the transmembrane pressure in the low pressure range (<4 bar) initially results in an increase in permeate flux but also an increase in the fouling rate. Initially, membrane retention can decrease due to increased concentration polarization, but after more time, in UF the increased rate of fouling results in an increase in the final component retention. In UF there is an overall increase in permeate throughput.

In MF the increase in fouling rate with pressure increasing is much higher than UF, and in some cases the permeate flux may decline to less than the flux at lower pressure. Membrane retention increases with the increase in membrane fouling and appears to remain constant only at very low pressures and low concentrations. To maximize the permeate flux there is an optimum pressure, below which the driving force is too low and above which increased fouling causes a large

reduction in flux. The optimum pressure decreases with the increasing of membrane pore size.

### 2.3.2 Temperature

Increasing the temperature generally results in an increase in the permeate flux due to the dual effect of lowering the permeate viscosity, which assists flow rate, and of increasing diffusivity, which assists the dispersion of the polarized layer both in UF and MF (Attia, 1991; Scott, 1988). Fouling on the membrane surface may be reduced due to the increase in diffusivity and a lessening of concentration polarization. On the other hand, the removal of the surface layer may lead to greater internal fouling (Attia, 1991; Piot, 1984).

### 2.3.3 Cross-flow velocity and turbulence promoters

Increasing the cross-flow velocity generally results in an improvement in permeate flux in both UF (Blatt, 1970; Nakanishi Kessler, 1985) and MF (Attia, 1991). Further evidence shows that membrane fouling decreases and the effective pore size increases with increasing velocity. However, where internal fouling rather than surface fouling occurs the cross-flow velocity has limited the effect (Bowen, 1991). Various means of creating greater turbulence at the membrane surface (Finnigan, 1989; Wyatt, 1986) generally result in an improvement in mass transfer and a higher membrane flux.

## 3 Fouling resistance model

In this section some fouling resistance models are summarized. Three general types of model have been proposed.

### 3.1 The cake layer model

A cake layer forms as foulant deposits on the surface of the membrane and effects the flux as a resistance in series with the membrane resistance. The resistance of the deposit may be calculated from the Carman-Kozeny equation as:

$$R_f = a \cdot \Gamma, \quad (1)$$

$$a = 180 \cdot (1 - \epsilon) / d_s^2 \cdot \epsilon^3 \cdot \rho. \quad (2)$$

The advantage of this model is the convenience it offers in obtaining an apparent value of macromolecular deposit resistance, such as  $R_f$  or a relative value such as  $RFR = R_f / R_m$ . It is probably more suited for particle deposition than macromolecular fouling.

The weakness of the cake layer model may be summarized as; (a) This model does not consider the blocking of pores by adsorbed solutes; (b) It is difficult to explain the formation of the cake layer by physico-chemical theory; (c) The "cake layer" resistance has been observed to depend on the membrane parameters such as hydraulic permeability.

### 3.2 Pore restriction model

The model assumes that flux decrease is due to the pore becoming thinner because of adsorption, i. e.,

$$J_1 / J_0 = (r - \Delta r)^4 / r^4, \quad (3)$$

which is based on the Hagen - Poiseuilles equation.

Pore restriction model has the advantages that it considers the deposit-membrane interaction, which makes it possible to connect the resistance model with retention models, such as those dependent on the Ferry equation (Ferry, 1936):

$$R = [\lambda(\lambda - 2)^2], \quad (4)$$

$$= r_{\text{solute}} / r_{\text{pore}}, \quad (5)$$

such as the experimental models of Hanemaaijer (Hanemaaijer, 1989).

Some of the objections against this model are: (a) Large amounts of protein deposits, i. e., about 1 g/m<sup>2</sup>, are found on, for example, polysulphone membranes at high solute concentrations, whereas the corresponding monolayer amount is about 5 mg/m<sup>2</sup>. It is difficult to assume all of or at least the great part of this deposit to be pore associated. (b) This approach most often assumes the pore radius to be sharply defined. However, a distribution in the pore radius in UF membranes has

been measured by Munari (Munari, 1987).

### 3.3 Combination model

It is, of course, possible to combine both previous models, in which both cake-layer formation and deposit – membrane interactions occur. Nilsson (Nilsson, 1988) has suggested that a secondary deposit of the cake-layer type is formed above an adsorbed layer, the latter interacting with the membrane pore flow.

## 4 Approaches to improve membrane performance

The various approaches to minimize the effects of membrane fouling and concentration polarization on membrane performance can be grouped into four categories: boundary layer (or velocity) control; turbulence inducers/generators; membrane modification and materials; and combined (external) fields. The approaches in these categories are discussed in detail in the present paper. The first two approaches mainly address concentration polarization issues, while the other two mainly focus on membrane fouling.

### 4.1 Boundary layer (or velocity) control

This approach is based on the fact that by increasing the velocity of flow, one can decrease the boundary layer thickness or the resistance due to the boundary layer. Much of the definitive work in this area was in the mid and late 1960s (Brian, 1965; Michaels, 1968). One recent study utilized flow pulsation along with a periodic back washing from the permeate side to minimize concentration polarization (Gupta, 1991). Additional insight on the boundary layer control approach can be found in Belfort (1988) and Belfort *et al.* (Belfort, 1994).

### 4.2 Turbulence inducers/generators

Turbulence inducers/generators are an extension of boundary layer control approaches. Some specific examples of inducers/generators include ribbed spacers and channels, added particles or spheres of different densities, and ribbed or wavy membranes themselves. Some examples of turbulence inducers are discussed by Belfort (Belfort, 1988) and Rios (Rios, 1987).

### 4.3 Membrane modification and materials

Velocity or turbulence on the membrane surface minimizes the contact of fouling materials with membrane. However, ultimately, the foulant does react or interact with the membrane. If this interaction can be prevented by the membrane material itself, then fouling can be minimized. Thus the development of new membrane materials and surface modification thereof is another way to address the fouling problem.

For example, the ideal UF membrane for most applications would be hydrophilic and homogeneously permeable. Attempts have been made to achieve these characteristics by pretreating the membrane with hydrophilic surfactants and polymers (Michales, 1983; Fane, 1985). Kim *et al.* (Kim, 1988) reported that the fouling of UF membrane by protein has been reduced by surface pretreatment with various polymer such as methylcellulose (MC), polyvinylalcohol (PVA) and polyvinylpyrrolidone (PVP). In most cases the treatment provided an increase in initial UF flux and a slower flux decline. A paper by Light (Light, 1987) illustrates that changing membrane materials affects the surface charge, which results in reduced biological fouling. Stedronsky (Stedronsky, 1992) developed a surface modified support membrane which comprises a polymeric support membrane uniform monomolecular layer of modifying polymer irreversibly adsorbed onto surface. The membrane is resistant to cleaning agents such as ethanol, surfactants, solvents and caustic. It is useful as UF and MF membrane used in industry, particularly in the food processing industry and in environmental applications.

### 4.4 Combined (external) fields

The general approach of using external fields (e.g., electrical, magnetic) addresses most of the limitations of the other approaches discussed above. Some examples of the external fields approach are listed in Table 1. These examples clearly show the use of an external electrical field and other fields such as vibration and magnetic fields in a variety of areas such as colloids, proteins

and oil. Table 1 also indicates the general applicability of the external fields approach to UF, MF and RO.

**Table 1** Examples of external fields approach

Topic or area	References
Optimization of an electrical field for cross-flow MF	Wakeman, 1986
High-frequency vibration and excitation during RO	Henry, 1977
Prevention of protein and paint fouling using an electrical field	Mullon, 1985
Combination of membrane and an electrical field for colloids	Bier, 1959

## 5 Membrane cleaning

Cleaning methods used for membrane regeneration could be broadly categorized into four types: physical, chemical, physico-chemical and biological methods.

### 5.1 Physical cleaning methods

Physical cleaning methods depend on mechanical treatment to dislodge and remove foulants from membrane surfaces. Some of these mechanical treatments include:

Periodical backflushing, i. e. applying a pressure on the permeate side, thus pushing part of the permeate back through the membrane. It is used with some types of membrane modules. The efficiency of this type of cleaning not only depends strongly on the type of suspension to be treated and the type of fouling that it causes, but also on the frequency and amplitude of the pulses of reverse pressure (Galaj, 1984). Comstock and Durham (Comstock, 1993) ever reported that the optimum cleaning frequency could be determined for reverse osmosis membrane by providing range of samples of liquid containing antifoulant concentrations to be purified in reverse osmosis system. Periodical backflushing is the most widely used cleaning methods in industry. Large amounts of work (Jonsson, 1995; Fuji Photo Film Co. LTD, 1994) have showed its advantages.

Vibration, where mechanical energy is imparted to the permeator vessel by a pneumatic hammer device that is attached to the pressure vessel. While the hammer device is vibrating the permeator, a feed-to-brine flush is maintained to remove any shaken loose matter from the membrane.

Air sparge, where periodic bursts of air are injected into a forward permeate flush ahead of the permeator. The air disturbs the fibers, loosening foulant from the fiber walls (suitable for hollow fiber configuration). In a study conducted by Takizawa Satoshi *et al.* (Takizawa, 1996), a hollow fiber membrane module was scrubbed with ozone gas. In comparison with a control experiment, it was proved that membrane fouling could be significantly subdued by ozone scrubbing. Pre-ozonation of raw water also had the same effect of decreasing membrane fouling. Corsin P *et al.* (Corsin, 1993) used pressurized air and mixture that was pressured to 4—6 bar to clean membrane used in MF and UF. They also reported that ozone or chlorine compounds can be added to the mixtures. This mixture is able to unblock the membrane rapidly and efficiently.

Automatic sponge ball cleaning, where a sponge ball made of polyurethane or other materials is inserted into the permeator for a few seconds. This will scrub the foulants from the membrane surface, this technology is only applicable for tubular modules. Yanagi and Mori (Yanagi, 1980) evaluated the automatic sponge ball cleaning technique for tubular NTR RO modules using secondary effluent from municipal waste water treatment plants at Osaka, Japan. The experiments confirmed that sand filtration of the feed and the use of chemical cleaning reagents to restore the membranes were unnecessary when the sponge ball cleaning technique was used. Only pH adjustment and chlorination were needed as pretreatment. Furthermore, no damage to the membrane surface was recognized. Also, the product water flux and the salt rejection remained unchanged.

Ultrasonication: In the research of Matsumoto-Y *et al.* (Matsumoto, 1996), cross-flow MF with ultrasonic wave cleaning was carried out. The steady-state flux obtained in filtration with

ultrasonication was 4-to 6-fold greater than that without ultrasound, and a high flux was obtained even at low feed flow velocity. Ultrasonication was very effective for removing the cake layer deposited on the membrane surface, and preventing plugging of membrane pores.

## 5.2 Chemical cleaning methods

Some literature reviews of research works and experiences in membrane cleaning and restoration revealed that chemical methods are widely used for membrane cleaning and regeneration. The chemical cleaning methods depend purely on chemical reactions to remove foulants from membrane surfaces. Each type of foulants requires certain types of chemical agents.

Cleaning agents: The cleaning process must remove deposits and restore the normal capacity and separation characteristics of membrane. The chemicals used should (1) loosen and dissolve the fouling; (2) keep the foulant in dispersion and solution; (3) avoid new fouling; (4) not attack the membrane (and other parts of the system).

Not only is the cleaning ability of a detergent important, but also such factors as the ease with which it can be dispensed and rinsed away, its chemical stability during use and other factors such as cost and safety (Kane, 1985).

The following types of cleaning agents are often used for cleaning membrane plants: Alkalies: hydroxides, carbonates, and phosphates; acids: nitric and phosphoric; surface-active agents: anionic, cationic, and nonionic; sequestering agents: EDTA; formulated cleaning agents: often consist of a mixture of alkalies, phosphates, sequestering agents and wetting agents.

A large number of cleaning recommendations are reported in the literature. In a study of the cleaning of sintered stainless steel microfiltration membrane fouled using a solution of reconstituted whey protein concentrate powder, Bird and Bartlett (Bird, 1995) found that flux recovery of >97% was achieved by treating the membrane with 0.5 wt% sodium hydroxide solution at 50°C for 30 min, cross-flow velocity of 1.6 m/s and zero transmembrane pressure. In cleaning UF membranes used for the preparation of chymosin or prochymosin (Crawford, 1995), a chemical method using dilute NaOCl at moderate temperature was developed. 100% efficiency was obtained with 180–200ppm NaOCl at 20–60 min.

In the study of cleaning ultrafiltration membrane used for the treatment of waste water soluble lubrication oil (Kurita Water Ind. Ltd., 1992), a kind of cleaning agent was developed which contains a saturated alcohol fatty group and an alkali or anion surfactant. It proves that the cleaner is successful in removing permeate oil completely and regenerating the filtering capacity of membrane. Darton and Turner (Darton, 1991), reported that a low temperature caustic detergent at pH 12, which was alternated with acid cleaning using peracetic acid and hydrogen peroxide at pH 2, had been successful in eliminating sulphate-reducing bacteria that occurred when the membranes were immersed for two weeks in bi-sulphite solution at the seawater reverse osmosis plant in Gibraltar (UK). Pervov (1991) showed that 2% ethylenediaminetetraacetic acid (EDTA) and citric acid stabilized by ammonia to pH 7 are excellent agents for CaSO<sub>4</sub> and CaCO<sub>3</sub> dissolution.

In the study of cleaning the reverse osmotic membrane module in concentration of milk, Nitto Denko Corp. (1995) reported that any capacity of the membrane module was recovered by cleaning the membrane with circulating nitric acid aqueous solution of pH 1.8 first and next with 0.5% peracetic acid solution.

## 5.3 Physico-chemical cleaning methods

The physico-chemical cleaning methods use physical cleaning methods with the addition of chemical agents to enhance cleaning effectiveness.

Kuiper *et al.* (Kuiper, 1974), operated a 16 m<sup>3</sup>/d RO plant for 19 months on a highly polluted source using turbulence cellulose acetate membranes. Mechanical cleaning (depressurising and flushing) with foam balls, supplemented by acid washing, proved to be the most effective cleaning method.

## 5.4 Biological cleaning methods

Biological cleaning can be broadly described as the use of cleaning mixtures which contain bioactive agents (micro-organisms or enzymes) to enhance the removal of foulants.

In recent years, substrate specificity and environmental friendly have lead to an increase in the use of enzymes and enzyme detergent mixtures in cleaning mixtures for household and industrial use. Detergent or cleaning mixtures that contain enzymes have, however, not previously been used on a large scale for the cleaning of membrane fouled by biological process effluents.

Enzymes are ideal cleaning agents for this purpose as they are highly specific for the reactions they catalyze and the substrates with which they interact. In addition, enzymes act under mild conditions of pH, temperature and ionic strength and will not damage the membrane surface, while mechanical and chemical removal of foulants usually lead to membrane damage and additional pollution. Extension of membrane technology to effluent treatment of biologically related processes, as well as the increasing pressure on the environment has, however, compelled researchers to re-examine enzymes as possible cleaning agents for fouled membranes (Jacobs, 1991; Coolbear, 1992; Chen, 1992) and for the prevention of fouling by the adsorption of enzymes onto membranes (Chen, 1992; Howell, 1982).

A Maartens *et al.* (Maartens, 1996) recently reported their research. Enzymes, specific for the degradation of protein and lipids, were tested as key components of biological cleaning regimes for polysulphone membrane fouled in abattoir effluent. These enzymes include Protease A, Lipase A, the commercial agents Alkazyme and Zymex (formulated cleaning agents). In this paper, optimal enzyme concentration and incubation times were determined for the different preparations. The ability of each cleaning agent to remove adsorbed protein and lipid material, as well as their ability to restore the water-contact angle and pure-water flux of the fouled membrane, were determined and compared. These variables were also used to compare the cleaning efficiency of enzymatic cleaning agents with conventional chemical agents (SDS and Triton X100) under optimal conditions. Experimental results obtained in this investigation showed that detergents such as SDS or Triton X100 used alone as cleaning agents also removed lipid material. The detergents alone, were, however, significantly less effective than when used in conjunction with enzymes. The enzymes and enzymes detergent mixtures were effective cleaning agents and the pure-water flux of statically fouled membrane could be restored by treatment with these agents.

A study carried out by M.J. Munoz-Aguado *et al.* (Munoz-Aguado, 1996) investigated the effect of enzyme and surfactants on a totally retentive polysulphone membrane fouled with a simple component, bovine serum albumin (BSA), and a complex mixture, reconstituted whey protein concentrate. In an effort to elucidate cleaning mechanisms, a commercial enzyme/surfactant cleaner, Terg-A-Zyme, had been compared with pure enzyme ( $\alpha$ -chymotrypsin) and pure surfactant (CTAB) combinations. The results showed that for foulants containing proteinaceous components enzymatic cleaners played a vital role in scissioning specific points in the protein strands while detergent cleaners also interact with the protein strands at specific points but in addition rapidly solubilize any small loose protein fragments. It is more effective to clean first with an enzyme ( $\alpha$ -chymotrypsin) and then with a detergent (CTAB) than a single step cleaning with either detergent or enzyme alone, or if both are present in the same cleaner it must be formulated in such a way that the action of each component does not interfere with any others.

An investigation of fouling and cleaning of membranes in the UF of the aqueous extract of soy flour was conducted by S.K. Sayed Razavi *et al.* (Sayed, 1996). The aqueous extract of soy flour is an emulsion/suspension of protein, lipids and carbohydrates. The effects of individual applications of rinse wash, 0.5 wt% hydrochloric acid, 0.5 wt% sodium hydroxide and 0.75 wt% protease detergent on the water flux recovery (WFR) were studied. Results showed that the rinse wash and the acid solution were almost ineffective in removing membrane fouling. Caustic cleaning was more effective than acidic washing, but only gave a WFR of 18%. Protease detergent was the most effective giving a WFR of 42%. The water flux, however, was not fully recovered by any of the cleaning agents acting separately. A sequential procedure comprising successive steps of rinsing with water, washing with sodium hydroxide, protease detergent and sodium hypochlorite solution followed by a final flushing step was successful in restoring the water flux of the membrane.



In the study carried out by Krack R and Manners H (Krack, 1996), the method used for cleaning beer filtration membranes comprises the following steps: (a) treatment the membranes with an aqueous enzyme solution of enzymes containing beta-glucanases, xylanases and cellulases; (b) cleaning with an acidic aqueous solution, and (c) cleaning with an alkaline peroxide solution. In this way, the primary and secondary blockage of the membrane by e. g. cloudy substances, yeast residue, glucanes and so on is eliminated, thereby preventing an increase in the darkness of the beer or a reduction in flavour.

## 6 Conclusions

Optimization of membrane cleaning protocols requires in depth understanding of the complex interactions between the foulant and the membrane. In addition it is important to consider the economic impact of cleaning procedures including the costs of the cleaning process itself together with the effect of the procedures on membrane lifetime and efficiency.

Cleaning studies so far performed are mainly trial-and-error ones, a better understanding of cleaning mechanism and of the effects of different cleaning agents on different foulants and different types of membrane is definitely needed.

The literature review reveals that chemical cleaning methods are widely implemented, even though results are not always encouraging. Extensive research work should be carried out to evaluate the effectiveness of the available chemical agents, including the commercially available cleaning agents, and to develop more technically and economically feasible cleaning procedures.

Physical and physico-chemical methods are not given enough attention, even though some of these methods, such as forward flushing and reverse flushing, seem to be economically very attractive.

Proteases have a long commercial history, with many early biotechnology patents dealing with protease applications. They are still the most widely used of any enzyme type. Judged from the enzyme cleaning mentioned above, proteases have tremendous potential in membrane cleaning. Extensive research work should be carried out to explore and develop the application of enzyme in these fields.

The importance of membrane cleaning should certainly be recognized and addressed, and more time and effort should be devoted to understand fouling mechanisms and to develop more feasible and cost-effective cleaning and restoration procedures for each type of fouling.

### Symbols:

$a$ —intrinsic resistance of cake layer (m/g)

$d_s$ —diameter of solute (m)

$\epsilon$ —porosity

$\Gamma$ —surface density of deposit (g/m<sup>2</sup>)

$J$ —flux (l/m<sup>2</sup>)

$\lambda$ — $\gamma_{\text{solute}}/\gamma_{\text{pore}}$

$r$ —radius (m)

$\Delta r$ —radius decrease (m)

$R_f$ —hydraulic resistance of the membrane fouling layer (l/m)

$R_m$ —hydraulic resistance of the membrane (l/m)

$\rho$ —density of solute (g/m<sup>3</sup>)

Subscripts

0—pure water flux of membrane before fouling

1—pure water flux of membrane after fouling

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