Flux Decline in Microfiltration of Beer and Related Solutions of Model Foulants through Ceramic Membranes

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Abstract

Clarification and stabilization of beer as well as recovery of beer from surplus yeast are subjects of great interest. Microfiltration through ceramic membranes could address both these applications if the economy of this process is improved.

The aim of the present work was an experimental study of the flux decline in cross flow microfiltration of the filtered beer and aqueous solutions of model foulants. Ceramic membranes with two mean pore sizes of 200 and 500 nm were used. The used microfiltration stand enabled the cleaning of the membrane by back-flushing with the permeate. For better understanding of the fouling process and for identifying of the fouling capacity of individual foulants, the runs were conducted with aqueous solutions of selected model foulants as a- and β-amylase, catechin, commercial α-bitter acids, mixture of maltose and sucrose and washed beer yeast suspension. The concentration of the model foulants was similar as in beer. The suspension of the purified beer yeast (four times washed yeast with a physiological solution) was studied as well. A rapid flux decline was observed during the first two-three minutes. The membrane with larger pores, of 500 nm, exhibited lower steady flux than the more dense membrane with 200 nm pores. Repeated rinsing of the fouled membrane with water after microfiltration recovers only a small part of the initial flux. The order of model foulants with increasing flux decline capacity is:

mixture of maltose and sucrose < amylase < pure beer yeast < α-bitter acids < catechin.

Keywords: microfiltration, ceramic membranes, beer, back flushing, beer yeast, model solutions

Introduction

Beer filtration is one of the most important operations in the brewing process. Good filtration allows for a bright product, which is one of the main criteria for beer quality. Traditionally, beer is clarified by primary settlement of the yeast and larger solids, and then by filtration [1]. The purpose of this operation is to remove the remaining yeast and the colloidal precipitate together with any bacteria present. In order to facilitate this filtration, a number of additives must be added, such as diatomaceous earth or kieselguhr to flocculate, coalesce or aggregate the very finely dispersed substances in beer that would not normally settle out.

World beer production is considerable, approximately 1.5 billion hectolitres (1994). A typical figure is 0.1 kg of filter aid per hectolitre of beer [2]. It is natural that environmental concerns are forcing producers to seek alternative methods because disposal of spent media has been increasingly more restricted.

The installation of new technology in breweries has increased the amount of surplus yeast due to lower dry solids content when harvesting the yeast. Thus, beer losses are potentially higher and beer recovery should be taken into account [3, 4].

The potential of cross-flow microfiltration as a separation method for brewing is a subject of intensive study. Its possible application is either in the separation of the remaining yeast or for fining the final product. Another application using cross-flow microfiltration is the recovery of tank bottoms.

Studies have been carried out with organic and inor-

ganic microfiltration membranes [3, 5-8]. There are a few negative factors related to conventional polymeric membranes which have prevented their wide use in alcoholic beverage applications. These are: short membrane life time, limited temperature and chemical resistance, flavour changes caused by the extraction of polymers, and compressibility of the membrane structure. Ceramic membranes overcome all these problems. The most significant advantages of a ceramic microfiltration membrane are its extraordinary thermal resistance, enabling high temperature cleaning, robustness in respect to pressure and resistance against aggressive cleaning agents [9, 10].

Despite intensive research, membrane employment in breweries is tentative. It is interesting to note that, cross-flow microfiltration has enjoyed greater success in the wine industry [11]. Microfiltration of beer or reclaimed beer is generally only accepted as economically feasible at flow rates up to about 3,000 litres per hour [4]. The main reason for such a slow application of membrane separation is fouling of these membranes, which in beer filtration is severe and complicated. This phenomena has caused difficulties in obtaining an economical flux as well as good product quality [5-8]. To overcome this drawback many studies have dealt with possibilities to enhance the filtration flux. Fouling could be suppressed if the solute-membrane surface interactions are minimized. This could be done by controlling the hydrodynamic conditions of the feed with turbulent promoters [8], unsteady flows [12], rotating membranes [13] or injection of air into the feed stream [14], etc. From this point of view the concept of the sub-critical flux operation of microfiltration is promising very [15, 16].

Understanding the fouling process is complicated by the fact that the filtered beer is a mixture of many different components such as remaining yeast, high molecular compounds, e. g., proteins, and low molecular compounds, e. g., sugars, polyphenols, a-bitter acids, etc. In the filtration of beer the colloidal substances have considerable importance. The different kinds of beer contain considerably high quantities of especially polysaccharides. As it is known, when mashing and saccharifying, the malt starch is not fully converted to fermentable sugars [5, 7].

The flux decline is then the result of superposition of various mechanisms of membrane fouling. The nature of foulants in beer microfiltration has been studied by Gan et al. [7]. Pentosans have been determined as major contributors to fouling.

The difficulty in identifying the key foulant is the reason why membrane fouling remains a poorly understood phenomenon.

The aim of this work was to study the permeate flux decline due to fouling in microfiltration of less complex solutions as filtered beer, pure yeast suspension, and aqueous solutions of selected model foulants.

Experimental

Commercial beer of pilsner type after kieselguhr filtration was obtained from the local brewery Codecon.

The model yeast *Saccharomyces uvarum* was prepared by cultivation in a glucose medium. Yeast was separated from broth by centrifuge and washed one to three times by a physiological solution (8.5 kg•m^{-3} of NaCl). The concentration of the yeast suspended in the physiological solution used was the same as that in the surplus yeast, i.e. 10 wt.% (dry weight). The density and the dynamic viscosity of the yeast suspension at 12°C were 1100 kg • m^3 and 5 mPa-s, respectively.

For better understanding of the fouling process and for identifying foulants the runs were performed with aqueous solutions of selected potential foulants α - and β-amylase (as representants of proteins, 750 mg/1), catechin (as representant of polyphenols, 150 mg/1), commercial α-bitter acids (hop extract, which is an important component of beer, 60 mg/1) and mixture of maltotriose (1 g/1) and sucrose (1.5 g/1). The concentration of foulants was similar as in beer. Solutions of α - and β-amylase and bitter acids were, prior to microfiltration, boiled for 1.5 h to simulate the brewing process.

The tubular membrane used was an asymmetric α-Al$_2$O$_3$ ceramic microfiltration membrane supplied by SCT (F), which was 25 cm long, and had an inner diameter of 7 mm and a surface area of 50 cm^2. The nominal mean pore sizes of the used membranes were 200 and 500 nm. Characteristics of the membranes are in Table 1.

Table 1. Fluxes through the clean membranes at 12°C and 150 kPa.

Membrane	J, [l·m^{-2}·h^{-1}]	
	Destilled water	Physiological solution
200 nm	2300	850
500 nm	10200	3500

The microfiltration stand used in trials was described in previous work [17].

After each run the membrane was regenerated (cleaned) in the following cleaning sequence:

a) washing with a 2 wt.% solution of NaOH at 70°C and Δp = 20 kPa for 20 min, then at 100 kPa for 10 min,

b) rinsing with distilled water at room temperature,

c) washing with a 2 wt.% solution of HNO$_3$ at 70°C and Δp = 20 kPa for 20 min, then at 100 kPa for 10 min,

d) rinsing several times with distilled water at 12°C until the initial water or physiological solution flux through the membrane was obtained (Table 1).

The volumetric flow rate of the suspension was kept at 5 1 • min^{-1} with an average linear velocity of the feed in the module 2.2 m^{-1}. The flow conditions were turbulent, Re = 3400. The temperature of the feed (12°C) was kept by heat exchangers and cooling water. The operating transmembrane pressure for all trials was 150 kPa.

The typical flux profile in the back-flushing regime contains periods with peaks, (immediately after the back-flushing impulse) and base levels at the end of the period. The representative value of the permeate flux was calculated from the experimental data as an average flux by integration:

$$J = \frac{1}{\Delta t} \int_{\Delta t} J(t)\,dt$$

where dt was selected in a quasi steady state region.

Results and Discussion

The effect of the membrane pore size and operating conditions on the permeate flux in microfiltration of filtered beer (Figs. 1 to 3), pure yeast suspensions (Figs. 4 to 6), and aqueous solutions of model foulants (Figs. 7 and 8), has been studied.

Effect of Membrane Pore Size

Experiments were performed with two pore sizes of the membrane. Fig. 1 shows the flux decline data obtained in microfiltration of beer. It is evident that better filtration performance was achieved for the membrane with a pore size of 200 nm, and the steady flux approximately 17.5 $l \cdot m^{-2} \cdot h^{-1}$ while for the 500 nm membrane it was only 13.2 $l \cdot m^{-2} \cdot h^{-1}$. The lower performance for a membrane with the mean pore size 500 nm can be explained by particles and foulants accumulation within the pores of the membrane. To examine the fouling layer, after microfiltration the feed was removed and the unit was gently rinsed by water at low pressure. Then, the unit was filled with the physiological solution, to avoid osmolysis of cells, and the flux through the fouled membrane was measured at the same conditions as for beer with the results shown in Fig. 2. The steady permeate flux of the physiological solution through the fouled membrane rinsed with water is approximately three times higher than steady flux of beer but there is not a great difference between the first and the second rinsing. These results indicate strong adsorption of foulants probably also inside the pore structure of the membrane. It can be supposed that during the first rinsing an essential part of species, which are less strongly adsorbed on or in the membrane, was desorbed. Quite the same value of the permeate flux after the second rinsing indicates that most foulants are strongly adsorbed, and fouling inside of the pore structure occurs. For the more opened membrane with a pore size of 500 nm are the fluxes after rinsing lower than for a 200 nm pore size membrane. This suggests that inner blocking of larger pores occurs, which leads to a lower flux through the 500 nm membrane. On the other hand, the quality of beer recovered from surplus yeast was better for the membrane with a pore size of 500 nm as shown in paper [17].

Effect of Back-Flushing

To increase the permeate flux a back-flushing with permeate was employed. Fig. 3 shows the effect of an applied frequency of back-flushing on the permeate flux in microfiltration of beer. This illustrates the favourable effect of back-flushing with the permeate which can increase the average flux by 50 to 100%. From Fig. 3 it is evident that the frequency of back-flushing has to be chosen carefully, because for high frequencies the flux can decrease and eventually reach a zero value as it was for the 200 nm membrane.

Because of possible recovery of beer from surplus yeast, experiments with pure yeast were performed. To find the contribution of yeast to the membrane fouling,
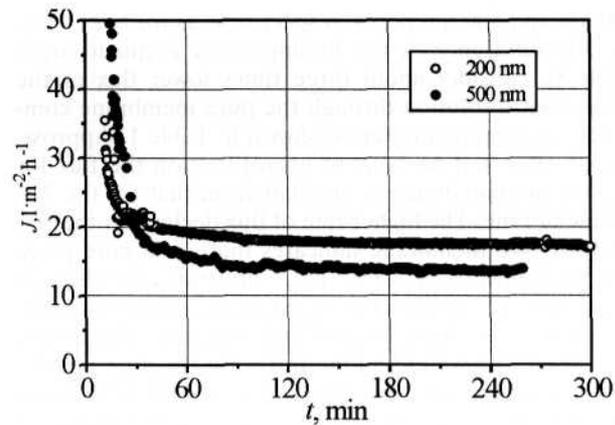
Fig. 1. Permeate flux vs. time in microfiltration of beer through different membranes. No back-flushing.
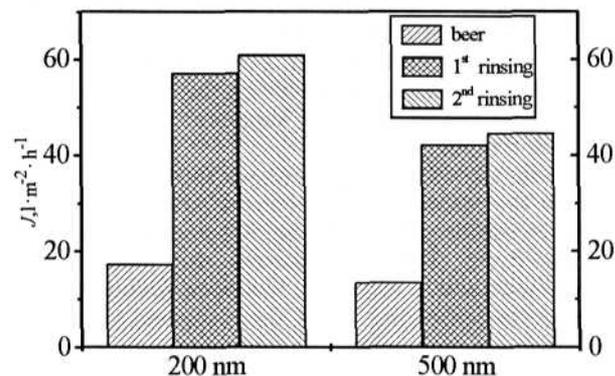
Fig. 2. Comparison of steady permeate flux in microfiltration of beer with steady flux of the physiological solution through a membrane fouled with beer after the first and the second rinsings of membrane with water. No back-flushing.
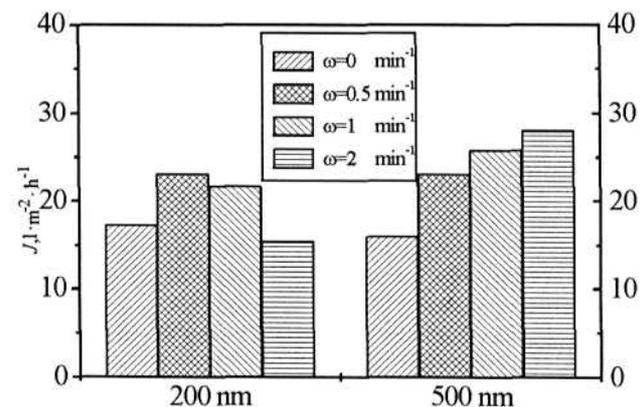
Fig. 3. Effect of frequency of back-flushing on steady permeate flux of beer for different membranes.

pure yeast suspensions were microfiltered. The yeast suspension from cultivation was three times centrifuged and washed with a physiological solution to remove other substances including low molecular foulants. Physiological solution was used to avoid osmolysis of cells. Fig. 4 shows that the flux for purified yeast suspensions is much higher, 54 and 34 $l \cdot m^{-2} \cdot h^{-1}$ for the membranes with

200 nm and 500 nm pores, respectively, as for beer, (Fig. 1). The difference in the fouling effect is much larger when we consider about three times lower flux of the physiological solution through the pure membrane compared with distilled water, as shown in Table 1. Approximately after half an hour of microfiltration the flux for the 500 nm membrane is one half from that for the 200 nm membrane. The higher rate of flux decline for the 500 nm pore size membrane indicates that an in-pore plugging mechanism is probable. Fig. 5 illustrates the effect of frequency of back-flushing on permeate in the microfiltration of yeast. After microfiltration of yeast the system was rinsed with water and the fluxes for the pure physiological solution were examined. The results from these experiments are shown in Fig. 6. It is visible that each rinsing of the membrane caused an increase of the permeate flux because of removing a part of foulants deposited on and in the membrane. From the comparison of analogical results for microfiltration of beer (Fig. 2) and yeast (Fig. 6) we can assume that for the washed yeast, foulants are less strongly adsorbed on the membrane comparing with foulants in beer. Foulants, mostly yeast, were probably accumulated mainly on the membrane surface. In-pore plugging can be supposed for the membrane with 500 nm pores.

The influence of frequency of back-flushing with permeate on the microfiltration of yeast, after a different number of washings through the 500 nm membrane is documented in Fig. 4. Whereas for once- and twice-washed yeast a maximum has been found on frequency dependences, for the 4 times washed yeast the permeate flux increased with the frequency of back-flushing.

Model Foulants

The initial study was focused on measuring the flux decline during microfiltration of aqueous solutions of selected model foulants. As model foulants were chosen: mixture of maltose and sucrose, mixture of α- and β-amylase, catechin (as representant of polyphenols), and α-bitter acids. From the analysis of the rates of flux decline of individual substances, the mechanism of membrane fouling during filtration could be determined. The effect of model foulant type on the flux decline for the 500 nm membrane is shown in Fig. 7.

From comparison of the flux decline rates in Fig. 7 it is obvious that for catechin and bitter acids with the steady flux of about 178 and 55 $1 \cdot m^{-2} \cdot h^{-1}$, respectively, a rapid flux decline was observed. During the first three minutes the permeate flux falls quickly. These results could be surprising because as it is known bitter acids and catechin pass through the membrane. This can be explained by their adsorption on the pore walls causing reduction of the effective pore size. An interesting result is for amylase, for which the steady flux is 500 $1 \cdot m^{-2} \; \blacksquare \; h^{-1}$. This higher flux indicates that proteins are not the major foulants in beer. Pure yeast, after three or four washings, decreases substantially the permeate flux, see Figs. 4 and 5, but the steady flux can be substantially increased by back-flushing, as shown in Fig. 5 for 4-times washed yeast. It has to be considered that yeast is suspended in the physiological solution, whose flux through the mem-
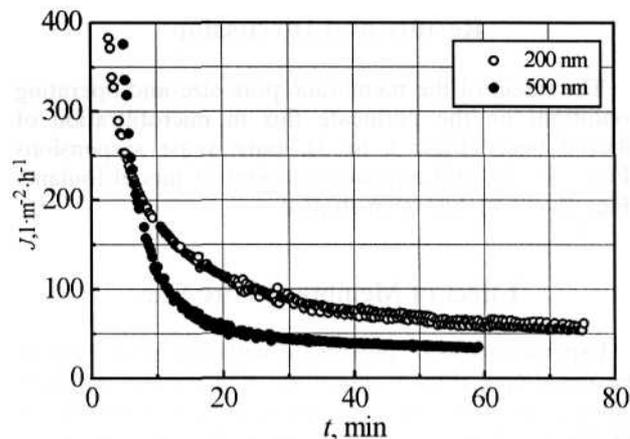
Fig. 4. Permeate flux vs. time in microfiltration of 3-times washed model yeast in the physiological solution for different membranes. No back-flushing.
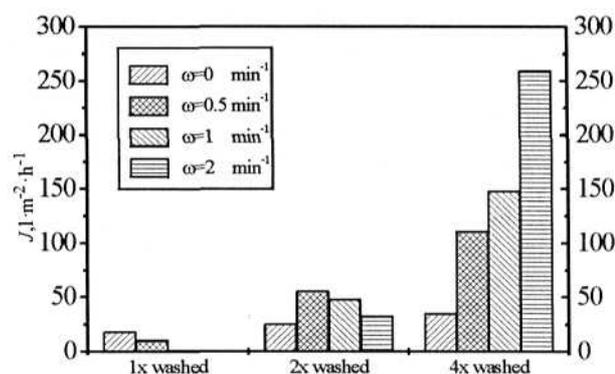
Fig. 5. Influence of the frequency of back-flushing on the steady permeate flux in the microfiltration of a suspension of pure yeast in the physiological solution. Yeast was washed from one to four times by the physiological solution. Membrane 500 nm.
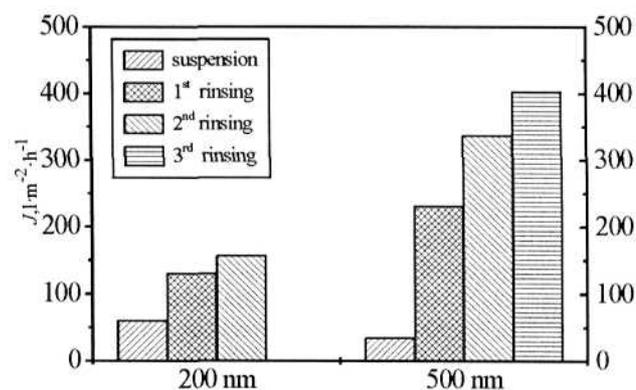
Fig. 6. Influence of rinsing of the fouled membrane on steady permeate flux in the microfiltration of a suspension of 3-times washed yeast in the physiological solution and the flux of the pure physiological solution through the membrane fouled with yeast after one, two or three rinsings of membrane. No back-flushing.
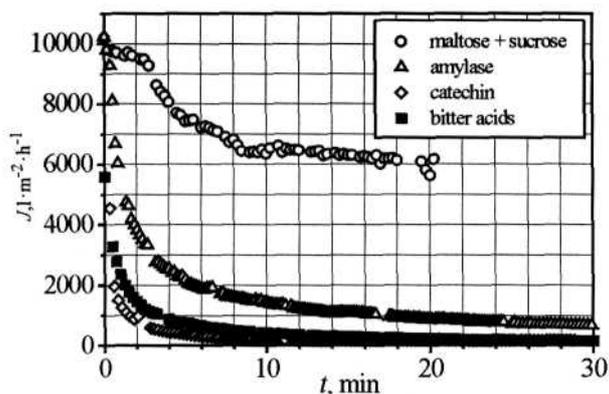
Fig. 7. Effect of model foulants on the permeate flux decline. No back-flushing. Feed: aqueous solutions of foulants, as defined in part 3. Membrane: 500 nm.
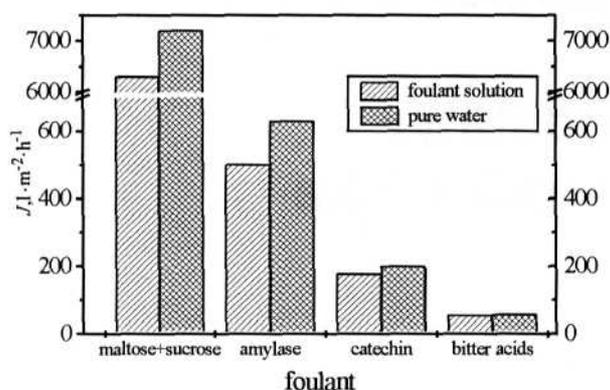
Fig. 8. Comparison of the steady permeate fluxes in the microfiltration of model foulant solutions and the fluxes of pure water through the fouled membranes rinsed with water. Membrane: 500 nm.

brane is about three times lower than for distilled water, as shown in Table 1.

Conclusions

The fouling of membrane in microfiltration of beer and solutions of model foulants is severe. A dramatic permeate flux decline has been observed. The membrane with larger pores, 500 nm, exhibited lower steady flux than the more dense membrane with 200 nm pores. Beer quality was better for the membrane with a pore size of 500 nm as shown in paper [17].

Repeated rinsing of the fouled membrane with water recovers only a small part of the initial flux. This manifests the strong affinity of foulants to the membrane.

Introduction of the mild back-flushing, frequency up to 2 min^{-1}, is very effective, especially in the case of a more opened membrane (500 nm), where the achieved flux of beer was improved by 60% and the steady flux was 27 l m^{-2}·h^{-1}.

The studied model foulants, which theirselves are not retained by the membrane (in steady flux conditions) and even low molecular ones, decrease greatly the permeate flux by two orders of magnitude. The order of foulants with increasing flux decline capacity is: mixture of maltose and sucrose < amylase < pure beer yeast < α-bitter acids < catechin.

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