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Development and applications of very high flux microfiltration membranes

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Abstract

Inorganic microfiltration membranes with a pore size down to 0.1 μm have been made using laser interference lithography and silicon micro machining technology. The membranes have an extremely small flow resistance due to a thickness smaller than the pore size, a high porosity and a very narrow pore size distribution. They are relatively insensible to fouling, because they have a smooth surface, short pore channels and because they can be operated in cross flow configuration at very low transmembrane pressures. Experiments with yeast cell filtration of beer show a minimal fouling tendency and a flux that is about 40 times higher than in conventional diatomaceous earth filtration. The uniform pore distribution makes the membranes suitable for many other applications like critical cell to cell separation, particle analysis systems, absolute filtrations and model experiments.

Keywords: Microfiltration; Inorganic membrane; High flux; Fouling; Yeast cells

1. Introduction

In cross flow microfiltration one of the major problems is membrane fouling. The use of lower transmembrane pressures is known to diminish this problem. However, filtrating at lower pressures generally gives lower fluxes due to the flow resistance of the membrane itself. To compensate for this flux decline, a larger membrane area is necessary. Replacing the membrane by one with a smaller flow resistance might be a good alternative.

The most important features that determine the resistance of a membrane with a certain maximum pore size are its thickness, porosity and pore size distribution. A very small resistance membrane should have a thickness smaller than the pore size, so that the pores are in the shape of holes instead of channels. The porosity should be as high as possible without weakening the membrane too much and the pore sizes should deviate as little as possible from the size of the largest pore, because unnecessarily small pores give a lower flux.

Keeping in mind the features above, we developed a very low resistance microfiltration membrane. In this report we describe its design, fabrication and performance and we will give some of the first test results.

2. Design and fabrication

As a thin microporous membrane is very vulnerable it should be reinforced by attaching it to a macroporous

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support. For this construction we use silicon micro machining technology because of its possibilities to make thin layers and to etch very small structures.

2.1. Pore size >1 μm: standard mask lithography

For the membrane we choose low stress silicon nitride that is deposited on a 380 μm thick polished silicon wafer by means of LPCVD (low pressure chemical vapour deposition). On this 1 μm thin silicon nitride layer a photosensitive lacquer layer is formed by spincoating. This layer is patterned with small holes (>1 μm) by exposing it to UV light through a photo mask and subsequently developing it. The pattern in the photosensitive layer is transferred into the silicon nitride membrane by means of RIE (reactive ion etching) with a CHF_3/O_2-plasma. Now the silicon underneath the membrane is partially etched away with a KOH-solution (25%, 70°C) in such a way that support bars arise. The fabrication process is schematically given in Fig. 1. Because the result (Fig. 2) looks more like a sieve than a filtration membrane, we will call it a microsieve.

2.2. Pore size <1 μm: laser interference lithography

In standard mask lithography the smallest possible dimensions are about 1 μm because of dispersion of the 400 nm UV light at the holes in the photo mask. Smaller holes are possible using a wafer stepper and deep UV light, but for large surfaces interference lithography [1] is an economically more interesting alternative. Fig. 3 gives a schematic representation of a typical exposure set-up, known as "Lloyd's mirror configuration". Part of an incoming plane wave will be reflected by the mirror and interferes with the undisturbed part of the wave to form an interference pattern (grating) on the substrate surface. To produce the plane wave, TE polarized light of an argon laser with a wavelength λ=351.1 nm is spatially filtered and expanded by focusing it onto a pinhole. The period Λ of the generated grating is defined by the relation

$$\Lambda = \frac{\lambda}{2 \sin \theta}, \tag{1}$$

where θ is the angle of incidence of the waves. The minimum period that can be fabricated with our configuration is $\Lambda=\lambda/2=175$ nm.

After exposure the substrate is rotated over 90° and exposed again. Now the gratings cross each other and after development a square array of lacquer dots remains (see Fig. 4). These dots are transferred into holes by evaporating 15 nm of chromium onto the substrate and removing the dots in an ultrasonic acetone bath (lift off method). The pattern in the

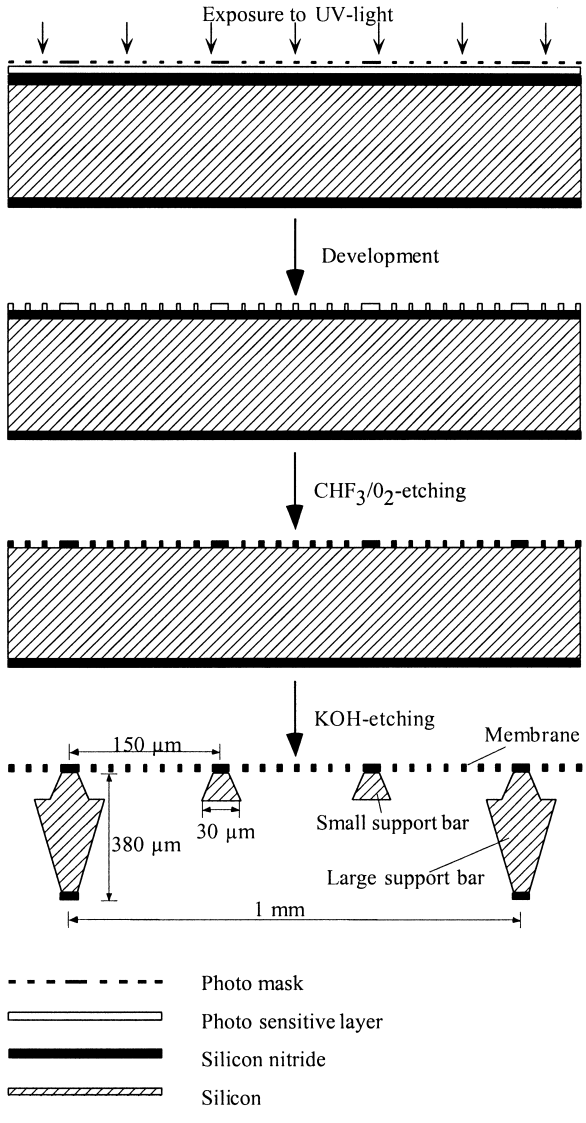

Fig. 1. Fabrication process of a microsieve with pores larger than 1 μm.

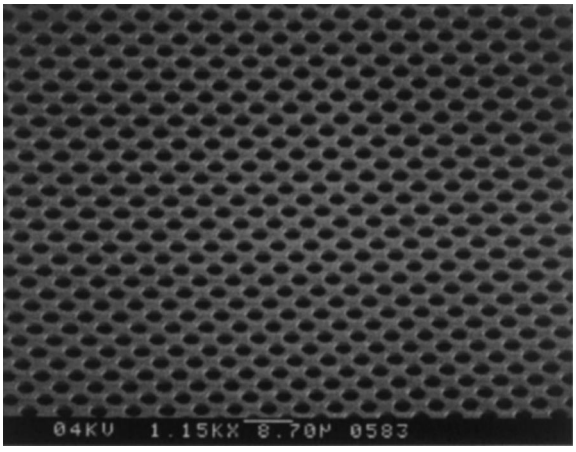

Fig. 2. SEM photo of the surface of a microsieve.

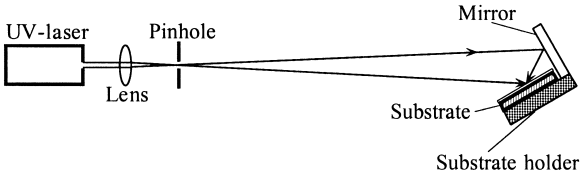

Fig. 3. Interference lithography set up used to produce submicron gratings.

created chromium layer is transferred into the 0.1–1 μm thin silicon nitride layer by means of RIE. With this method pores down to 0.1 μm can be produced. Interference lithography is applicable for large areas as Pallas et al. [2] reported the fabrication of uniform photoresist pedestals on a 50×50 cm^2 glass substrate.

The second problem in making pores smaller than 1 μm is the etching of the silicon underneath the membrane with a KOH solution. To make the support bars we have to etch the silicon through the pores while the hydrogen bubbles that are formed escape through the pores. However, to escape through a pore the hydrogen pressure has to exceed the bubble point pressure, which will be around a few bar for a pore size of 1 μm. For pore sizes below 1 μm the pressure gets so high that the membrane might break during etching. To solve this problem we etch the support bars partly from the front side of the wafer through the pores using an SF_6/O_2-plasma (see Fig. 5) and then we finish etching the support bars with a KOH-solution from the back side of the wafer. The process of making sieves

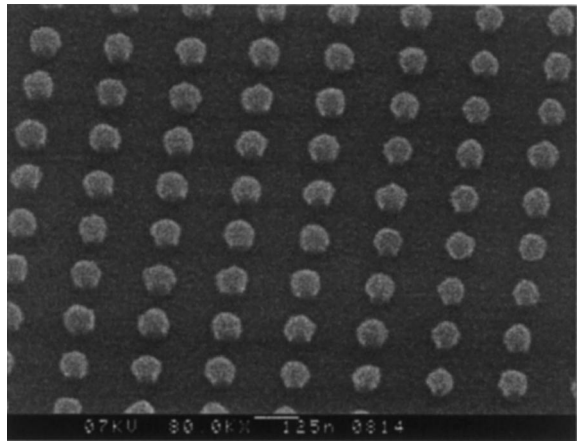

Fig. 4. SEM photo of lacquer dots that remain after a double exposure in the laser interference set up.

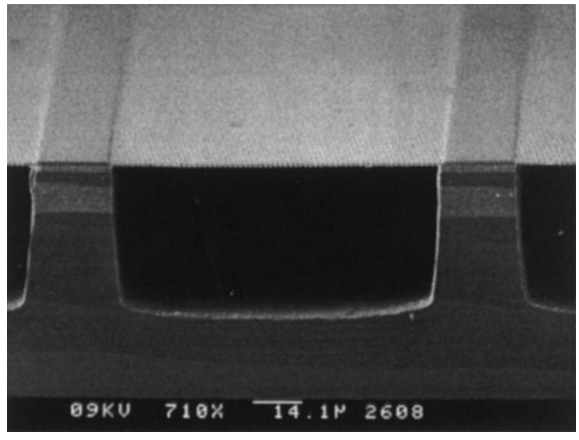

Fig. 5. SEM photo of a microsieve after etching with an SF_6/O_2-plasma through the pores. The photo shows a free hanging perforated membrane supported by vertical walls.

with pores smaller than 1 μm is given in Fig. 6. Fig. 7 shows a SEM photo of the resulting membrane.

3. Properties of the microsieve

3.1. Shape and distribution of the pores

When using a photo mask the pores can be given almost any shape, size and distribution. In the case of circular pores that are distributed in a square array

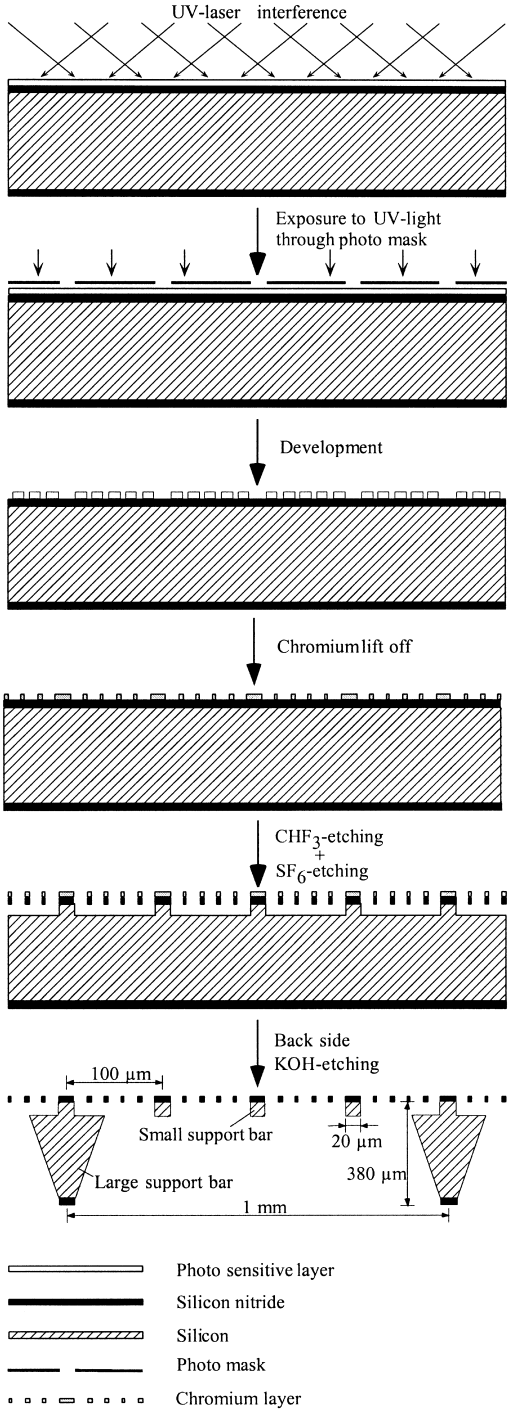

Fig. 6. Fabrication process of a microsieve with holes smaller than 1 µm. The third step is shown on a SEM photo in Fig. 4 and the fifth step in Fig. 5

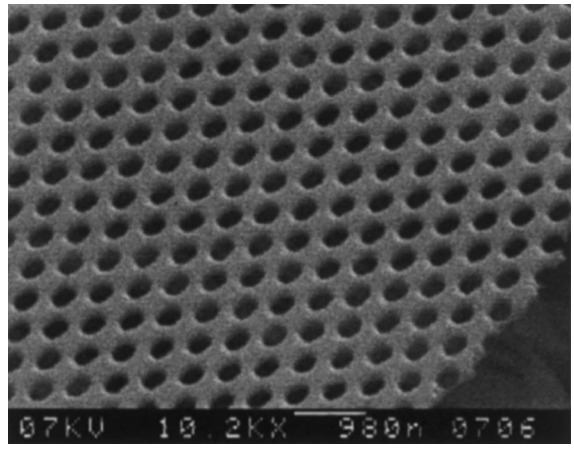

Fig. 7. SEM photo of the perforated membrane of a microsieve made with interference lithography.

with a pore size of half the pore period the porosity of the membrane can be calculated at 20%. After subtracting the dead area of the support bars (about one quarter), the porosity of the entire sieve will be 15%. If the ratio of the pore size and the pore period is increased, the porosity will also increase. However, an enlargement of the porosity will cause a decrease in the strength of the membrane. Therefore the applied pressure during filtration will be an important factor in determining the maximum allowable porosity.

The pattern definition with a photo mask is very accurate. The standard deviation in pore size is less than 1% for holes larger than 10 microns but rises to about 5% for 1 µm holes. The pattern definition of the interference method is less accurate (about 20% deviation), because the light intensity during the exposure varies over the substrate as a result of the Gaussian distribution in the intensity of the laser beam. This accuracy can easily be improved by increasing the distance between the pinhole and the substrate or by expanding the beam over a larger angle. However, these adjustments would lead to longer exposure times, which are already in the order of minutes for our 30 mW laser.

If the sieve is used to retain nondeformable spherical particles, an interesting option would be to create pores in the shape of slits. A slit with a width of the same size as the diameter of a circular pore should have an equal particle retention capability, but has a much smaller flow resistance. As we have not yet

tested membranes with slit shaped perforations, we will discuss this type of membranes in a next report.

3.2. Strength

The strength of the sieve is determined by the strength of the membrane and the support bars together. If the sieve is attached to a macro perforated stainless steel support, the strength of the sieve will be limited by the strength of the membrane. This strength is mainly dependent on the physical material properties, the thickness, the intrinsic tensile stress, the shape and distribution of the pores and the distance between the silicon support bars. If the intrinsic tensile stress is much smaller than the yield stress σ_{yield} the pressure $p_{\max}$ above which an unperforated membrane breaks can be estimated with [2]:

$$p_{\max} = 0.58 \frac{h\sigma_{\text{yield}}^{3/2}}{lE^{1/2}}, \tag{2}$$

where h is the thickness of the membrane, l the distance between the support bars and E Young's modulus. If some typical values for an unperforated low stress silicon nitride membrane are substituted in Eq. (2) (h=1.0 μm, l=1.0 mm, $\sigma_{\text{yield}}=4.0\times10^9$ MPa and $E=2.9\times10^{11}$ Pa), the calculated pressure above which the membrane breaks is 2.7 bar. Destructive tests with the microsieve show a value of 2.5 bar [5]. If a fraction κ of the membrane is perforated with a square array of square pores, the maximum pressure should decrease with $\kappa^{1/2}$. This is in agreement with test results which show that for a perforated area (porosity) of 25% the membrane breaks at half the pressure of an unperforated membrane. This pressure is still more than enough for the low pressure applications that the sieve has been designed for. However, to prevent the membrane from breaking by the bubble point pressure during etching, we etch small additional support bars underneath the membrane which increases the maximum allowable pressure up to 5 bar.

3.3. Flow rate

The resistance R_c of a circular pore in a membrane with a finite thickness h is given by [6]:

$$R_c = \left\{\frac{24\eta}{d^3}\right\}\left\{1+\frac{16h}{3\pi d}\right\}\{1-f(\kappa)\}, \tag{3}$$

with η the viscosity of the liquid and

$$f(\kappa) = \sum_{i=1} a_i \kappa^{i+1/2},$$

with a_1=0.894, a_2=0.111 and a_3=0.066.

The first term in Eq. (3) denotes the resistance of the pore in an infinitely thin membrane [3], the second term is a correction for a finite wall thickness [7] and the third term corrects for the synergetic effect of pores lying in a square array on a membrane with porosity κ [4].

If we take κ=0.20, h=d, $\eta=1.0\times10^{-3}$ Pa s and $N=4\kappa/\pi d^2$ the number of pores per m^2, the clean water flux is given by

$$Q = \frac{N\Delta p}{R_c} = 4.3 d\Delta p, \tag{4}$$

where Q is the flow rate in m^3/s and Δp the pressure difference over the membrane in Pa. If we calculate the flow rate in l/bar m^2 h, we get the graph in Fig. 8. For pores with a diameter of 1 μm, the clean water flux of 1.5×10^6 l/bar m^2 h is about a factor of 30 higher than for the best polymeric asymmetric membranes.

3.4. Other properties

Silicon nitride is one of the hardest materials known and is therefore well resistant against wear. The

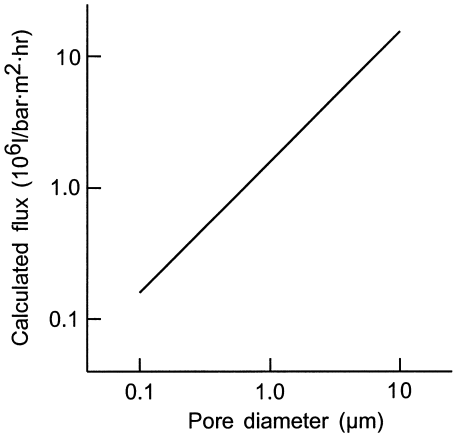

Fig. 8. Calculated clean water flux for circularly perforated microsieves with a porosity of 20% and a membrane thickness equal to the pore diameter.

material is biocompatible, hydrophilic, inert to almost all chemicals and can withstand temperatures upto 800°C. The membrane is optically flat with a surface roughness smaller than 10 nm.

4. Applications

4.1. Yeast cell filtration of beer

Common yeast cell filtration systems are still based on diatomaceous earth, although the exploitation costs of these systems are rather high. Tubular ceramic and polymeric membrane systems are being developed as an alternative for diatomaceous earth filtration. Complications in using these types of filtration membranes are yeast cell clogging and protein adsorption leading to a fast flux decline and subsequent elaborate in-line cleaning procedures.

The combination of a very smooth surface and low transmembrane pressures make the microsieve less sensible to these fouling problems. Experiments at the Grolsch breweries in which a microsieve was used for the filtration of beer [8,9] show a permeate flux of 4000 l/m^2 h during a period of at least 5 h without any increase in transmembrane pressure (see Fig. 9). This flux is about 40 times higher than typical fluxes obtained with diatomaceous earth or other membranes. In the experiments the formation of a cake layer was diminished by using a cross flow configuration in combination with backshocking techniques and a transmembrane pressure of only 20 cm H_2O (0.02 bar). As the sieve is made of an inert material it can be cleaned with aggressive chemicals or by steam sterilization. After cleaning the new permeate still has the tendency to foam. Many other membranes may give problems on this point, as it is difficult to remove cleaning agents from the large inner surface and from dead end pores. An additional advantage is the absoluteness of the filtration: the uniform pores permit not a single yeast cell to pass through the sieve.

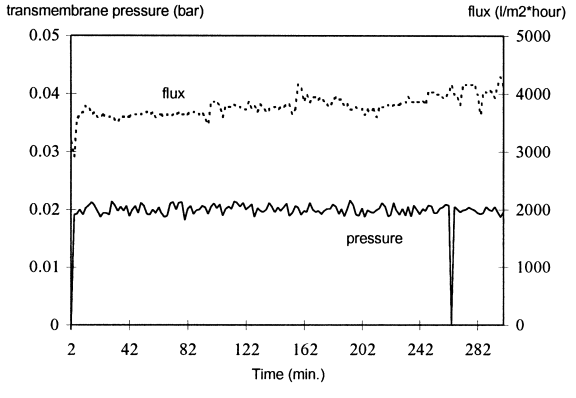

Fig. 9. Behaviour of flux and pressure in yeast cell filtration of larger beer with a microsieve.

4.2. Leukocyte depletion of blood cell concentrates

Because of its smoothness and biocompatibility the microsieve might be used for the filtration of blood. Experiments show no activation of blood platelets. The narrow pore size distribution allows separation of cells that differ in size or deformability, for example erythrocytes and leukocytes. It is important that such a separation is done at very low transmembrane pressures, otherwise hemolysis will occur and leukocytes will be deformed and pushed through the pores. Using a sieve with 5 μm small pores in a cross flow configuration, we found a leukocyte depletion of more than 99% at a transmembrane pressure of only 3 cm H_2O [10].

4.3. Support for gas separation

The microsieve might be used as a support for a gas permeable layer. Before KOH-etching (see Fig. 1) a very thin layer of e.g. paladium can be sputtered onto the membrane. The result after KOH-etching will be a microsieve with a thin palladium layer in its pores. As this kind of sieve can resist very high temperatures, it might be used as a semi-permeable membrane in hydrogen separation.

4.4. Particle analysis system

In very dilute suspensions it might be important to have a fast determination of the kind and concentration of particles (e.g. liquid contaminated with bacteria). The small flow resistance of the microsieve allows a large amount of liquid to be concentrated on a very small surface, herewith simplifying the analysis of the suspended particles.

4.5. Model experiments

Verification of new theories in membrane research is often complicated by variations in membrane properties. For example, the formation of a cake layer depends on the size and distribution of the pores and the flatness and smoothness of the membrane. The verification of a model that predicts such a cake layer formation would be more accurate using a microsieve with its well-defined properties.

5. Discussion

The extremely low flow resistance of the microsieve can only be profited when the formation of a cake layer is avoided. For instance in the case of beer filtration a monolayer of yeast cells will already have a higher resistance than the sieve itself. Therefore it is important to choose the filtration conditions so that no cake layer can be formed. In order to be able to design a cross flow module in which the membrane surface is kept clean (a 'self cleaning' module), we developed a simple single particle model that predicts under which conditions the formation of a cake layer can be avoided. We verified the model with an adjustable test module and found that it gives a good prediction of the formation of a cake layer. Moreover, the experiments showed that it is possible to avoid a monolayer of yeast cells for realistic values of the cross flow parameters. They also showed that an *increase* of the transmembrane pressure beyond a certain critical pressure leads to a *decrease* of the permeate flow, herewith emphasizing the importance of filtrating without a cake layer. An attendant advantage of a clean membrane is that it is easier for small particles (like protein) to pass: they are not obstructed by smaller pores caused by yeast cells. This reduces the concentration polarization and thus the chance of formation of an irreversible gel layer. We are now building a self-cleaning module for the filtration of beer. We expect the permeate yield to be a lot higher than described in this report, for until now we could only diminish the cake layer with the help of backshocking. Moreover, we plan to do the future beer filtrations with slits instead of circular pores, which should increase the flux a few times more. The developed single particle model with experimental results will be presented in a next paper.

The microsieve has to be made in a cleanroom environment with expensive machinery. Therefore most of its applications will be in small scale systems and in the filtration of precious liquids. However, its long lifetime (in the order of years) and easy cleanability makes it also an interesting option for large scale applications where conventional filters have to be replaced very often, like in the beer industry. Calculations including investment and operational costs show that a lifetime of one year already makes it economically feasible to replace diatomaceous earth filtration by filtration with microsieves.

6. Conclusions

We developed a new microfiltration membrane (microsieve) that is relatively insensible to fouling. The extremely small flow resistance allows filtration at very low transmembrane pressures and the small and smooth inner surface of the membrane reduces the adsorption of protein. Moreover, the membrane is easy to clean as it is resistant to almost any chemical. The small flow resistance is obtained by making the membrane thinner than the pore size, the porosity as high as possible and by giving the pores a uniform size and distribution over the surface. Experiments with beer show a very high permeate flux of 4000 l/m^2 h without an increase in transmembrane pressure for at least 5 h.

The very well-defined surface of the microsieve makes it suitable for many other applications like critical cell to cell separation (e.g. in blood), particle analysis systems, absolute filtrations and model experiments.

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