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Influence of proteins content in the feed on the course of membrane distillation

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ABSTRACT

The formation of deposit on the membrane surface (fouling) is one of the major operating problems of membrane processes. The influence of proteins on the course of membrane fouling was investigated during the whey concentration process. The Fourier transform infrared spectroscopy method was applied in order to determine the composition of the deposit precipitated from the feed as well as accumulated on the membrane surface on the feed side. The intensity of fouling can be limited by the pretreatment of feed and the selection of operating parameters of membrane distillation. The thermal and chemical pretreatment methods were used for whey deproteinization. The whey was subsequently concentrated by direct contact membrane distillation using polypropylene membranes at 323, 333, and 343 K. The concentrated whey contained all components of the feed.

Keywords: Whey; Polypropylene membrane; Membrane distillation

1. Introduction

Whey is a valuable by-product of milk processing industry, particularly the watery portion that is formed during the coagulation of milk casein in cheese making or in casein manufacture [1]. Whey is produced in large amounts and has a high polluting load, therefore poses significant environmental problems. On the other hand, whey contains much of the milk nutrients, including functional proteins and peptides which does not exceed 1%, fats at about 0.4–0.5%, lactic acid less than 1%, salts that may be in the range from 1% up to 3%, and all the water-soluble vitamins [2]. Whey contains also a significant amount of carbohydrates (typically 4–5%), mainly lactose, which consists of equal amounts of glucose [1,2]. These whey components are used in the industry to produce a variety of organic compounds. For example, the proteins are an ingredient to many food products, whereas the lactose is fermented to useful products, such as lactic acid or ethanol for fuel [1]. Therefore, whey has a huge potential as a source of added value compounds, challenging the industry to face whey surplus as a resource and not only as a waste problem.

The development of membrane processes based on new advanced separation techniques allows for environmentally friendly waste disposal. However, the major obstacle to realizing the widespread use of the membrane technologies is the problem of membrane fouling. Fouling results in a decrease of the permeate flux through a membrane due to a deposition of

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suspended or dissolved substances on the membrane surface and/or within its pores [3,4]. Several types of fouling can occur in the membrane systems, e.g. inorganic fouling or scaling, particulate and colloidal fouling, organic fouling, and biological fouling (biofouling) [3–6].

The membrane process, such as membrane distillation (MD), is well-known technique of separation [7] and is also a promising method, which can be applied for the concentration of whey components [8]. In the direct contact membrane distillation (DCMD), both warm feed and cold distillate are in a direct contact with a hydrophobic porous membrane. A thin air layer entrapped within the membrane pores comprises the gas membrane. The volatile components of the feed evaporate at the feed/membrane interface. These components subsequently diffuse through the air filling the membrane pores and condense in the cold distillate stream. The driving force for the mass transport is a difference of chemical potentials, mainly a vapor pressure difference which results from the temperature and composition of solutions in the layers adjacent to the membrane [9]. The retention of the gas phase in the membrane pores during the MD is an essential condition for a smooth operation of the process. However, a fouling layer formed on the membrane surface causes a progressive wettability of the membrane [10–12].

The membranes can be fouled by various constituents of the feed, such as polysaccharides, polyhydroxyaromatics, proteins, amino sugars, and humic substances [13,14]. Generally, a high amount of adsorbed whey protein on the hydrophobic membranes is reported [13]. The level of feed temperature significantly influences on the intensity of fouling. During the concentration via DCMD, it was found that fouling is practically negligible in the process occurring at lower temperatures (i.e. 293–311 K) [15]. On the contrary, a severe fouling by proteins was observed at higher feed temperatures [11,16,17].

The aim of the study was to examine the pretreatment of acidic whey to the fermentation process in a membrane bioreactor. The concentration of pretreated whey by thermal and chemical coagulation has been investigated using membrane distillation. The influence of proteins on the membrane fouling was also discussed.

2. Experimental

Scheme of the DCMD experimental setup is shown in Fig. 1. The details of its performance were presented in [18]. The experiments were carried out using a MD module with capillary membranes made from polypropylene (PP) (Membrana GmbH, Germany).

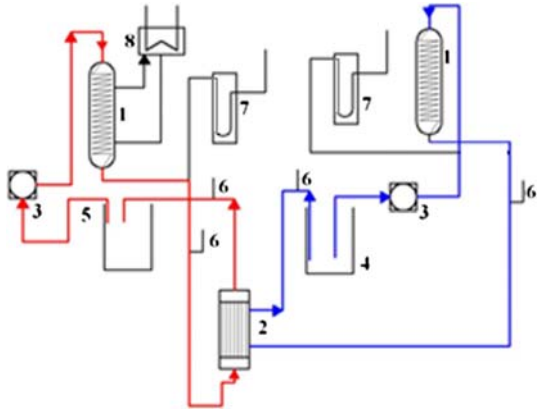

Fig. 1. Scheme of the MD experimental setup: (1) cooling system, (2) capillary module, (3) pump, (4) distillate tank, (5) feed tank, (6) thermometers, (7) manometers, and (8) thermostat.

The outside and inside diameters of the capillary membranes were 2.6 and 1.8 mm, respectively. The effective area of mass transfer is around 0.0122 m^2.

The studies were performed using acid raw whey as a feed. Raw acidic whey collected from a local dairy was characterized by the following parameters: proteins concentration range within 11–12 g/dm^3, chlorides concentration was 2–3 g/dm^3, and reducing sugars (lactose) was 30–40 g/dm^3. The pH was in the range of 3.6–4.2. Different concentrations depended on the whey supplies. A preliminary treatment of whey consisted of deproteinization by thermal (at 365 K) and chemical coagulation (NaOH addition to pH 6.2). The precipitated proteins were separated from the whey by centrifugation at 9,000 rpm for 10 min at 293 K. After this procedure, the pH of whey increased from 3.6 to 6.0 and 4.2 to 6.6. The deproteinized whey contained proteins with concentration from 6 to 8 g/dm^3, chlorides with concentration from 0.8 to 1.6 g/dm^3, lactose with concentration from 34 to 40 g/dm^3, and pH was from 6.0 to 6.6.

After pretreatment, the whey was concentrated by DCMD. The MD experiments were carried out at the inlet feed temperatures of 323, 333, and 343 K. The inlet temperature of the cold distillate was kept at 293 K for all the experiments. The cold system was initially supplied by distilled water. The flow rate was 350 cm^3/min for the feed and 430 cm^3/min for the distillate. The MD process was run for 6 h every day. After each experiment, the MD installation was rinsed by water. The membrane module was replaced by a new module after 160 h of MD process because of partial wettability. The temperature and mass of the feed and distillate were measured every two hour and the permeate flux was calculated.

The protein concentration in the feed was determined by the Sörensen method, the chloride concentration by the Mohr method, and the directly reducing sugars (lactose) by the Bertrand's method. The content of organic compounds both in the feed and the distillate was determined as the total organic carbon (TOC) using the TOC-Analyzer multi N/C (Analytic Jena, Germany). The calibration was carried out by using standard calibration solutions of $KHC_8H_4O_4$ (organic carbon) and Na_2CO_3 and $NaHCO_3$ (inorganic carbon).

The Fourier transform infrared spectroscopy (FT-IR) method was used for the analyses of the precipitate which was formed on the membrane surface on the feed side as a result of the whey concentration in MD process (Thermo Scientific Nicolet 380 FT-IR Spectrometer).

3. Results and discussion

Fig. 2 shows the changes of permeate flux during the MD process carried out at 323, 333, and 343 K. The permeate flux was slightly decreased at 323 and 333 K, but at 343 K its decrease was faster and was very unstable. The changes of the permeate flux after the feed supplementation by fresh whey at different temperatures are rather small. It could be affected by the influence of the fouling on the membrane surface and concentration polarization phenomenon. A phenomenon of the temperature polarization causes the temperatures at the membrane surfaces are different from the bulk temperatures measured in the feed and in the distillate. This phenomenon is present even when the feed is water and it causes a significant loss in the driving force [19]. Moreover, along with the increase of components concentration in the feed the properties of solution varies significantly (e.g. increase of viscosity and density), thereby, the concentration polarization phenomenon additionally influences on the permeate flux [19]. The permeate flux was decreased from 6.6 to 4.8 $kg/m^2 h$ at 323 K and from 7.0 to 3.9 $kg/m^2 h$ at 333 K during 84 h. The permeate flux varied from 11.3 to 1.5 $kg/m^2 h$ after 60 h at 343 K (Fig. 2). The flux decline during the process was caused probably by a deposit of the whey proteins on the membrane surface. The proteins were even partially precipitated from the whey during concentration at 343 K causing turbidity of the feed. The whey proteins were mainly responsible for fouling of the membrane surface and decrease of the permeate flux. Similar results were observed in [8]. An increase of proteins concentration in the layer adjacent to the membrane and even their partial deposition on the membrane surface reduced the permeate flux.

The changes of concentration for each component of the feed and distillate during MD operation were also studied. The whey has not contained any volatile compounds besides water. Therefore, during MD experiments all whey components were retained in the feed. As can be seen from Fig. 3, the protein concentration in the feed increased from 6.34 to 26.50 at 323 K and from 3.46 to 17.28 g/dm^3 at 333 K during 84 h of processing and from 6.14 to 18.05 at 343 K after 60 h. The feed was periodically supplemented by a new portion of pretreated whey and then was further concentrated. The aim of this procedure was obtaining the appropriate concentrations of lactose in whey, suitable to planned further fermentation process. The whey (feed) was concentrated to achieve the minimum volume needed to conduct the process (filling the pipes of the installation). Frequency of

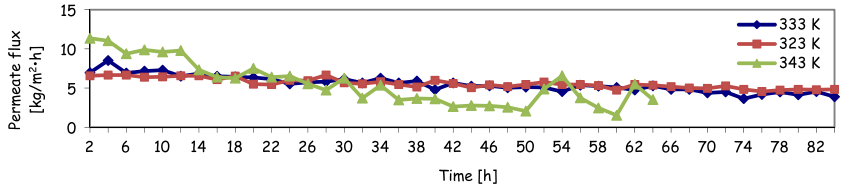

Fig. 2. Changes of permeate flux as a function of time of the MD.

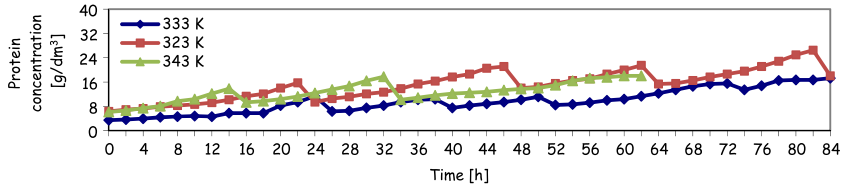

Fig. 3. Changes of protein concentration in the feed as a function of time of the MD at 323, 333, and 343 K.

supplementation was dependent on the value of permeate flux and was a little different at different feed temperatures. The addition of fresh, deproteinized whey, (which has a lower concentration than concentrated whey) in the meantime, resulted in a reduction of the protein concentration in the feed. After the subsequent supplementation and MD concentration, the whey contained higher protein concentration (Fig. 3). The protein concentration in the feed increased faster at 323 K. The lowest changes in the whey concentration were observed at 333 K. The tendency is similar to results described in [11,16,17]. Lowest concentration at higher feed temperature was probably caused by the precipitation of protein on the membrane surface. When the feed temperature was higher then higher proteins precipitation from a whey solution was observed. The proteins were not found in the MD permeate, but the permeate become slightly turbid, especially at 343 K. The same tendency was observed after the distillate replacement by distilled water after a few hours of processing. This was caused probably by partial wetting of the membrane with the temperature increase. Whey was previously thermally and chemically deproteinized. Therefore, at lower feed temperature no turbidity was observed. However, the precipitation of protein was occurred at 343 K. The membrane module was replaced by a new one after 160 h of MD process duration.

Simultaneously, the concentration of lactose was analyzed. Its concentration in the feed increased gradually in the same way, as in the case of protein. The curves in Fig. 4 indicate the periodic decrease in the lactose concentration after the addition of fresh, deproteinized whey. The highest increase of lactose concentration in the feed was obtained at 323 K (more than six times). The higher value of lactose concentration was obtained at 333 K, but starting concentration of lactose in the feed was higher than that at 323 K and increased from 21.55 to 142.98 g/dm^3 at 323 K and from 33.37 to 193.89 g/dm^3 at 333 K after 84 h of process and from 36.97 to 127.18 g/dm^3 at 343 K after 60 h of the process (Fig. 4). The final concentration of lactose was sufficient for the fermentation process.

A similar character of changes for chlorides concentration in the feed was observed. The chloride concentrations increased from 0.58 to 2.81 g/dm^3 at 323 K and from 1.44 to 4.80 g/dm^3 at 333 K after 84 h of process and 1.10 to 3.56 g/dm^3 at 343 K after 60 h of the process (Fig. 5). The chlorides were not detected in the permeate by the analytical procedure. The retention coefficient of chlorides was 100% during MD at applied feed temperature.

The TOC value in the feed and permeate was also monitored. The retention coefficient of organic substances during MD was stable in the range 99.8–100% at 323, 333, and 343 K (Fig. 6).

As can be seen from Figs. 4 and 5, the character of the curves for lactose and chlorides concentration in the feed was similar. Both lactose and chlorides concentrations at the first 14 h of MD concentration increased 2.5 times at feed temperature of 343 K. It was caused by higher permeate flux in this period, whereas at temperature equal to 333 K the increase was close to 1.5. Different courses of the curves for protein concentrations should be explained by the fouling of the MD membrane. This phenomenon was caused by a deposit of the whey proteins which have a high affinity for hydrophobic membranes. Thus,

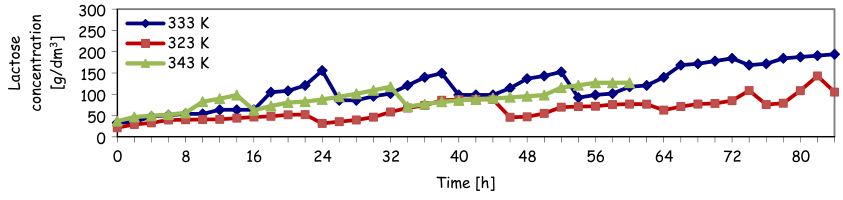

Fig. 4. Changes of lactose concentration in the feed as a function of time of the MD at 323, 333, and 343 K.

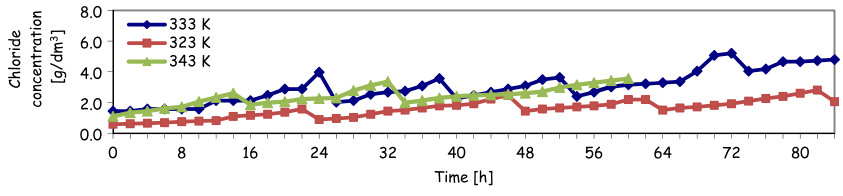

Fig. 5. Changes of chloride concentration in the feed as a function of time of the MD at 323, 333, and 343 K.

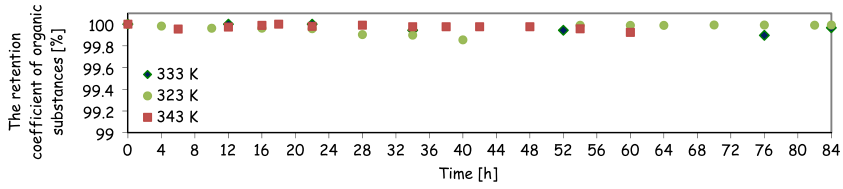

Fig. 6. Changes of organic substances concentration as a function of time of the MD at 323, 333, and 343 K.

during the concentration of whey by MD process, proteins were adsorbed partially on the surface of the hydrophobic membrane and blocking it easily. Moreover, a slight turbidity of the feed and permeate was observed and was the highest at 343 K. It was suggested that in the MD process, a small part of proteins can penetrate the membrane pores resulting in a partial wetting of MD membrane. Infrared spectroscopy is based on the absorption of radiation due to vibrations between atoms in a molecule and, therefore, provides information about the chemical composition and conformational structure of whey components. The FT-IR method was used in order to determine the composition of the deposit precipitated from the feed as well as accumulated on the membrane surface on the feed side. The studies were performed with two and three membrane samples collected from the module, which was replaced after 160 h of MD operation by a new membrane module. The FT-IR spectra of clean and fouled polypropylene membranes are shown in Fig. 7. The spectrum of dried protein (from whey) is also shown in this figure. The fingerprint region of whey protein IR spectrum is the region from 1,800 to 800 cm^{-1}. In this range, the bonds forming the amide group (C=O, N–H, and C–N) exhibit absorption. The spectrum of fouled membrane prepared from PP exhibits IR peaks, i.e. broad band in the region of 3,000–3,700 and 1,500–1,800 cm^{-1}, which are absent for a clean membrane. These peaks are characteristic for proteins [20]. The two most important vibrational modes of amides are the amide I vibration, caused primarily by the stretching of the C=O bonds and the amide II vibration, caused by deformation of the N–H bonds and stretching of the C–N bonds. The amide I vibration is measured in the range from 1,700 to 1,600 cm^{-1} and the amide II region from 1,600 to 1,500 cm^{-1}. The exact frequencies at which these bonds absorb depend on the secondary structure of the proteins or peptides [21,22]. A very broad peak in the region between 3,000 and 3,700 cm^{-1} indicates the presence of exchangeable protons, typically from amine, amide, or carboxylic acid groups present in the proteins. The FT-IR analysis confirmed the presence of proteins in the membrane structure in the examined module on the feed side (Fig. 7). It can be seen in Fig. 7 that the intensity of the peaks characteristic for PP undergo a significant reduction in the case of fouled membranes, due to the coating of the membrane surface with foulants. The spectrum of less fouled membrane exhibits peaks with a high intensity characteristic of PP and a lesser intensity derived from protein. In the case of membrane

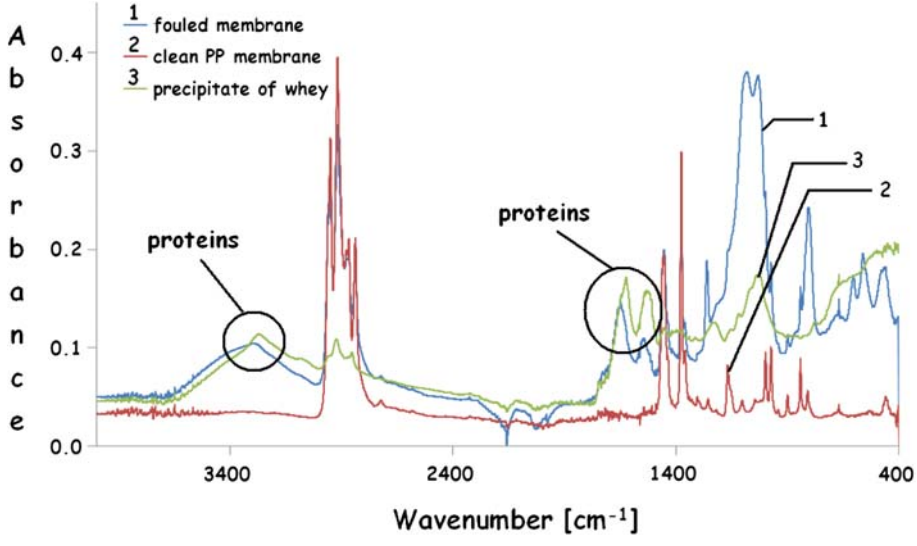

Fig. 7. FT-IR spectra of clean polypropylene membrane, fouled membrane after MD process, and dry whey protein.

being more fouled, this relationship is reversed. It was found that the chemical and thermal pretreatment of the whey for its deproteinization was insufficient for MD operation. Moreover, the proteins present in the whey caused the fouling of the MD membrane and subsequently wetting of the membrane.

4. Conclusions

(1) The permeate flux decreased faster at higher temperature, despite of frequent cleaning of the module during MD. The proteins adsorption on the membrane surface is the major factor to cause fouling in the MD process.
(2) Most of the whey components were retained in the feed in the MD experiments. During MD, the retention coefficient of chlorides was 100%, whereas for organic substances it was in the range of 99.8–100%.
(3) The concentration of proteins and lactose in the feed increased faster at lower temperature.
(4) During the concentration of whey by MD, a slight turbidity of the feed and permeate was observed and it was the largest at 343 K. The membrane module had to be replaced after 160 h, due to a partial wetting.
(5) The FT-IR studies confirmed that a part of proteins also penetrated the membrane pores.
(6) The chemical and thermal pretreatment of the whey for its deproteinization was insufficient for the MD operation.

Acknowledgements

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