Utilization of membrane systems in beer processing

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ABSTRACT

Beer is the most consumed beverage after tea, carbonates, milk and coffee in the world and it continues to be a popular drink. One of the important reason for its popularity is that beer is a drink with a pleasant flavor, an attractive color and also because of its clarity. So, Membrane separation technology has become widely used in the food processing industryto attain these characteristics.As advantages of membrane filtration are included maintainingdissolved macromolecules that give the beer its flavor and functional properties while causes removal of yeast cells and turbidity colloids and also, reducing the components that cause turbidity of the bottled beer.Because of the potential of cross-flow microfiltration as a separation method for brewery, it has been investigated in the many of recent studies. Clarification of rough beer (RB) and pasteurization of clarified beer (CB) are as an application of cross-flow microfiltration (CFMF) in brewery. An important limitation in the performance of membrane processes is the fouling mechanism and the general effect of these phenomena, known as concentration polarization have described briefly in this review article. Moreover, the influence of important parameters in the filtration process such as temperature, pressure,type of membrane, pore size and the use of stamped membrane have been discussed.

Keywords: Flux; Fouling; Membrane; Microfiltration; Beer Processing.

INTRODUCTION

Beer is a beverage containing alcohol and carbon dioxide that can be produced in two ways. One way is through fermentation of an aqueous extract from malt, and the other one is by malt substitutes that have been treated with hops [1,2]. Beer is known to be the fifth most consumed beverage in the world after tea, carbonates, milk and coffee and it keeps its position as one of the most popular drinks with an average consumption of about 23 l/person each year [3]. And its popularity is mostly because of its pleasant flavor, attractive color and also its clarity foam [1].

The brewing industry is traced back into the ancient times and it has been an important and major tradition in many civilizations. And today it is still a dynamic segment that is open to modern technology and scientific progresses. Brewers are very much concerned with the finishing techniques, and they mostly use the best standards in terms of product quality as well as cost effectiveness [2].

Today membrane separation process (reverse osmosis, ultrafiltration and microfiltration) is widely and increasingly used in food industry in order to replace the traditional concentration, separation and clarification techniques [4].

Some of the properties of membranes are their stability at high temperatures, their efficient mechanical resistance, their resistance against organic solvents and only characteristics of the surface. In addition to that, they are also very resistant to the biological attacks and the sterilization to steam, so there is a less chance of its bacterial contamination[5,6]. Hence the final filtration process has to achieve a balance between allowing the passage of dissolved macromolecules that give the beer its flavor and functional its properties while removing particles such as yeast cells and turbidity colloids (coagulated protein-polyphenol complexes, proteins, protein tannins, hop resins) and also reducing the elements that would result

in turbidity of the final bottled beer (protein polyphenols and β-glucans) [7].
These items are the main advantages of using membranes in food industry: 1. Membranes helps separating molecules and microorganisms, 2. Thermal damage of products and microorganisms is minimized and 3. Using membranes requires quite moderate energy consumption [8]. Clarification is usually followed by pasteurization process (with plate heat exchanger). Pasteurization is a necessary stage in order to make sure about microbiological stability of the final product. When the retention of beer spoilage organisms (bacteria, yeast) is gained, a stability of 3–6 months could be ensured. Sterile filtration by crossflow microfiltration (CFMF) appears to be very interesting and allows elimination of the organoleptic problems induced by thermal processing. CFMF is tested in order to produce a microbial free beer without deterioration in beer quality by operating at low temperature (close to 0◦C), ensuring beer stability (biological, colloidal, color, aroma and flavor, foam stability), achieving economical flux; and indicating the viability of MF as a commercial alternative to pasteurization and dead-end filtration with cartridges[9]. Some advantages and disadvantages of the CFMF method in comparison with conventional pasteurization are briefly noted in **table 1**[2].
In the cross-flow microfiltration (CFMF) of fermented food products (beer, wine), the fouling mechanisms and local phenomenology associated with fouling are widely unknown but still unidentified. Consequently, industrial applications of CFMF encounter two main problems: 1. Controlling fouling mechanisms; and 2. Increasing permeate quality[10].

Table 1. Comparison of cross flow microfiltration and thermal Pasteurization

Process	Quality of product	Temperature of process	Stability of product
Cross flow microfiltration	-Remove microorganisms -Desirable organoleptic properties -Pleasant nutritional properties	Low (close to 0 ◦C)	Biology, colloidal, color, aroma, flavor and foam stability
Pasteurization	-Remove microorganisms - Organoleptic problems - Weak nutritional properties	High	Weak stability

MEMBRANE FILTRATION OF BEER

Evolution process of membrane

Studies have been shown many centuries ago Egyptian people used a specific type of ceramic clay mesh for clarifying wine. These ceramic filters might be considered as the first membranes used in food processing [11]. Commercialization of membrane preparation and membrane processing started in early 20th century, when Germany started to produce micro filters[12]. Then, filters were merely used in laboratory-scale sterility trials rather than in industrial filtering devices. However, the introduction of the micro filter marked the origination of one of the largest modem membrane applications, i.e. the cold sterilization of numerous kinds of food. When asymmetric membrane was first used in late 1950s, Membranes were developed to be used in large-scale commercial processes[13]. Using this this type of membrane, the high fluxes across the membrane that are necessary for commercial applications were gained. The first advantages in food industry appeared quickly when reverse osmosis membranes were developed for the purpose of purifying (desalting) water[14]. From that time membranes were introduced into several traditional processes (e.g. concentration by ultrafiltration instead of evaporation) [8].
In the beginning of the 20th century, it was observed that a membrane could efficiently separate two liquid chemicals that were blended together by applying a vacuum on the other side of the membrane that would result in a gradient of chemical potential. So, as a reaction to this gradient, the components of the mixture started to penetrate into the membrane and evaporate on the other side. This process is called "pervaporation". Separation process is ensured by differences in solvents sorption affinity and diffusion coefficients in the membrane. Industrially, pervaporation is specifically useful in separating mixtures which were difficult to separate by traditional techniques, such as distillation or extraction. Examples include azeotropic mixtures, such as alcohol/water, or some chemical products with close boiling points, such as acetic acid/water [15, 16].

The selection of membrane

The selectivity and performance of the membrane is determined by some notable properties such as thickness, porous or dense nature of the top layer, the size of its pores and geometry, and also its porosity. Furthermore, less obvious material properties such as glass transition temperature, composition, and hydrophobicity/hydrophilicity and membrane surface charge are considered very important [16].

For each membrane process, some visible membrane properties are determined separately in terms of structure and material. Rather thick membranes with a dense nature are applied in pervaporation process for their chemical stability. Contrary to that, nanofiltration membranes can be dense or nanoporous and are as thin as possible [16-20].

Membrane types could be classified based on the (molecular) size of the product that is to be separated[8]. Nanofiltration, ultrafiltration and microfiltration processes involve separation mechanisms in porous membranes, while reverse osmosis and pervaporation mostly use tight and dense membranes. Ultrafiltration and microfiltration membranes do the separation act on the basis of a simple sieving mechanism; i.e. the particle dimensions in relation to the pore size distribution of the membrane determine whether or not a particle can pass through the membrane. Reverse osmosis and pervaporation processes would able to separate species that have comparable sizes, such as sodium chloride and water. In such cases, the affinity between the membrane and the target component is considered to be important, as well as the velocity of the component permeating the membrane [21]. Differences in the diffusion coefficients of the components across the membrane are what cause separation. According to the theory of 'solution-diffusion', solubility and diffusivity together determine the membrane selectivity [8, 20]. Using diatomaceous earth (Keiselghur) filtration is known to be the standard operation in brewing industry for the final filtration of beer [3]. This process was challenged in the last several years because of some serious environmental, sanitary and economic considerations. Crossflow microfiltration (CMF) was promoted as an alternative process. Microfiltration shows several advantages over DE filtration including improvement in beer quality and flavor, guaranteed sterility of product, continuous operation and full plant automation [7].

Crossflow microfiltration provides an attractive substitute for fluid clarification/ pasteurization/sterilization in beverage, brewing, and dairy industries. In beer and wine industry, because it eliminates the residues generated by this kind of treatment and the need for filter aids, microfiltration process is known to be an efficient alternative for traditional clarification processes such as diatomaceous earth filtration[22].

Fouling mechanism

An important limitation in the performance of membrane processes is that the permeate flux is adversely affected by the transient build-up of a layer of rejected particles on the membrane upstream interface that makes controlling clarification process very difficult. The general effect of these phenomena, which are known as concentration polarization, is a rapid permeate flux decay during the primary stage of filtration process, followed by a long and gradual decline in flux towards a steady, or nearly-steady-state limit value. However, another and even more important aspect of concentration polarization phenomena that should be considered is related to the physicochemical interactions of the accumulated material with the membrane. Here, a fouling mechanism, such as adsorption on the membrane pore walls and pore plugging by the solute penetration takes place rather than the build-up of a particle cake layer at the interface [23-25]. The direct consequence of this fully reversible concentration polarization is a resistance arising from the osmotic pressure, resulting in a decline in the driving force. However, the solute concentration, especially proteins, near the membrane interface can reach such high values that gel layer formation occurs. Gel layer formation is usually referred to as 'membrane fouling' and is in most cases irreversible or only partly reversible. Thus, a reversible and direct decrease in flux through the membrane is known as "concentration polarization", while an irreversible and long-term decrease in flux is defined as "membrane fouling". Generally, they both take place in every membrane process, but the influences are most presiding in microfiltration, ultrafiltration and reverse osmosis and in some cases in pervaporation[8, 25-27].

The various modes of pore blocking are as a function of the solid/solute size and shape in relation to the membrane pore size distribution: complete pore blocking (the pore entrance is sealed); pore bridging (partial obstruction of the entrance) and internal pore blinding (material not rejected by the pore entrance is adsorbed or trapped in the pore wall or in the membrane support) [28].

It might be useful for process engineers designing systems to categorize the fouling based on the following model [2, 24, 25]:

Complete Pore Blocking

In case that particles are larger than pore size, the membrane portion of the filtration area reached by the particles is blocked as a result of a complete pore obstruction by means of sealing (blocking). The complete pore blocking reduces the membrane surface. Depending on the cross-flow velocity, permeate flux may grow by increasing the applied transmembrane pressure .

Partial Pore Blocking

Like the previous section**,** solid particles or macromolecules that reach an open pore at any time might sell it. However, a dynamic situation of blocking/unblocking can occur. Particles may also bridge a pore by obstructing the entrance and without completely blocking it.

Cake Formation

Particles or macromolecules that do not enter the pores form a cake on the membrane surface. The overall resistance is formed by the cake resistance and the membrane resistance, which is supposed to remain stable.

Internal Pore Blocking

The particles that enter pores are either deposited or adsorbed, thus reducing the pore volume. The irregularity of the pore passages makes the particles become tightly fixed by blinding to the pore. Here, membrane resistance would increases as a result of pore size reduction. In addition to that, in case internal pore blocking takes place, fouling becomes independent of crossflow velocity and no limiting values would be gained for the flux.

The nature of particles in the rough beer has a notable influence on the fouling of the membrane. Besides, the chemical diversity and large size range of particle responsible for beer haze make the clarification difficult to achieve with membrane processes. The contribution of colloidal haze components in membrane fouling is a close relationship between particle size distribution, physicochemical interactions and membrane structures [2].

This phenomenon has caused some problems in achieving an economical flux and also a good product quality. Many studies have dealt with possibilities to develop the filtration flux in order to overcome this drawback. Fouling could be suppressed if the solute-membrane surface interactions are minimized. This could be carried out through monitoring the hydrodynamic conditions of the feed with turbulent promoters, unstable flows, rotating membranes or injection of air into the feed stream, and etc. [29].

Key membrane foulants

Several researchers have attempted to identify membrane fouling as the main factor in restricting the application of CMF. The issue is complex with the major foulants found to include protein, polyphenols, carbohydrates (β-glucans and pentosans), haze micro- and macro-colloids, high molecular weight nitrogenous compounds, yeast cells and oxalate salts and trace minerals [30,31]. Notwithstanding the fact that the size of the particular components is smaller than the average pore size of a microfiltration membrane, it is the macro-colloids produced by combinations of these components, complexes of protein, polyphenol, carbohydrate and metal ions, and high molecular weight polysaccharides that contribute to flux decrease and membrane fouling [16]. Trace minerals such as Ca^{2+} and Cu^{2+} serve an important function as 'bridging agents' between the key membrane foulants. Not all components cause a negative effect on fouling. The inclusion of yeast was discovered to enhance flux and the removal of yeast by centrifugation making a decrease in flux [31, 32]. Protein by itself was not found to have a part in membrane fouling process [33]. Its function as an organic solvent and a 'wetting' agent, ethanol was found to aid the passage of other solutes and thus increase the flux rate [31].

Comparison of dead- end and cross-flow systems

The first membrane filtration setups were used in the dead-end mode. This kind of classic filtration allows liquid to pass while retaining the target compounds.By applying this technique strict fouling and concentration polarization (sometimes accompanied by cake formation) can occur, and this would lead to an extremely large decline in flux as well as an inefficient processing. Despite the fact that dead-end filtration is considered to be a very simple operation, in practically all processes the cross-flow filtration principleare currently used. In this technique the feed is pumped parallel to the membrane surface, so diminishing the thickness of the hydraulic stagnant layer and decreasing the tendency towards concentration polarization and fouling. The cross-flow velocity, transmembrane pressure and back flush frequency are prominent process parameters that are normally tuned to the optimum for low fouling, high flux and also low energy costs[8, 34].

THE EFFECT OF IMPORTANT PARAMETERS ON FILTRATION

The effect of pressure on filtration

Traditional microbiology commonly relies on vacuum filtration which can achieve a maximum pressure differential to 1 bar across the membrane. Actually by using commercial filtration equipment, this degree of vacuum is not obtained in practice. It was possible to adopt the pressure over a wide range by applying the upmost pressure filtration cell. Experiments demonstrated that the filtration rate increased as the pressure was raised; nonetheless, the relationship between pressure and filtration was discovered to be non-linear [35].

The increase in transmembrane pressure causes an increase in both the initial and final flux values, even in the presence of fouling. Results showed that crossflow filtration of rough beer with a low transmembrane pressure would result in a low flux. Another consequence of the increase in transmembrane pressure is decreasing the concentrations of carbohydrates and proteins in the permeate, standing for the development of a fouling layer that restricts the passage of these components [33].

The effect of temperature on filtration

For the purpose of investigating the effects of temperature on filtration, some beer samples were filtered at different temperatures. Findings showed that filtration rate was fast at high temperatures and slow at low temperatures because of increasing in the amount of insoluble substances. Besides, it is also found that the filtration temperature can influence the volume, which is filtered [35, 36].

The effect of membrane type on filtration

There are a few negative factors related to traditional polymeric membranes, which have prevented their wide use in alcoholic beverage applications. These factors include: short membrane lifetime, limited temperature and chemical resistance, flavor changes caused by the extraction of polymers, and also the compressibility of the membrane structure. membranes are able to defeat all these problems. The most remarkable benefits of a ceramic microfiltration membrane are extraordinary thermal resistance that would enable high temperature cleaning, robustness in respect to pressure and also an effective resistance against aggressive cleaning agents [29].Ceramic membranes have an advantage over polymeric membranes regarding fouling, due to their ability to undergo severe cleaning methods. However, the resulted fluxes are usually notably lower. Ceramic membranes with a small flow resistance would, therefore, be considerably desirable for beer filtration [27, 37, 38]. Polymers are a widely used material for membranes. However, in case of wetting, they start to swell, leading to altered the structure of the membrane [26]. Swelling occurs because a solvent enters and passes through the membrane, because of a chemical potential gradient. This makes the permeability to increase, but on the other hand decreases selectivity, since another component in the feed mixture can benefit from the now available free volume inside the membrane, and permeate as well[20]. This property could be applied as an advantage. The swelling phenomenon can make the structure of a polymeric micro- or nanoporous nanofiltration membrane more dense [5].

The membranes tested included mixed esters of cellulose, cellulose acetate, PVDF, cellulose nitrate and nylon. For the range of beverages filtered, the mixed esters of cellulose or cellulose acetate membranes showed the fastest filtration rate, with cellulose nitrate a little slower, the nylon membranes being much poorer [35].

The effect of the stamped surface on membrane foulingis visible whenthe time course of the flux decreased.The rate of membrane fouling could be suppressed by The hydrodynamic instabilities produced in the stamped membrane. This turns to be evident in comparing the time course of flux for microfiltration of the yeast suspension. The steady flux of permeate was achieved later than the smooth membrane When undergoing microfiltration of a yeast suspension by the stamped membrane. Hence, in the following time interval the stamped membrane would work at much higher fluxes and also a higher final steady flux would be resulted. Increasing crossflow velocity could increase the permeate flux. High shear rates in the stamped membrane with a combination of the shaped membrane surfacewould slow down the accumulation of particles on the membrane surface[39].

The effect of Pore size on filtration

Comparing the steady-state resistances obtained during the MF of rough beer (RB) and clarified beer (CB) demonstrates that the fouling mechanism differs according to the mean membrane pore diameter [2].

With the 1.4µm membrane, yeast resistance was the leading fouling mechanism and was very sensitive to the cross-flow velocity. With the membranes of pore diameters inferior to 1 µm, the deposition or adsorption of CB compounds such as proteins, polyphenols and carbohydrates were the leading fouling mechanism. Moreover yeast cells may show opposite effect on membrane filtration performances.

The presence of yeast cells resulted in the decrease of the resistance to mass transfer and the increase of the permeate flux [39]. This can be explained by a less compact deposit in the presence of yeast cells and shows the impact of a secondary or dynamic membrane. We may suppose that if the mean pore diameter is superior or inferior to 1µm, the order of magnitude of the resistance due to yeast cells and colloids would differ to a much more extent. Potential applications of MF in beer industry are clarification (elimination of yeast cells and suspended matter) and cold-sterilization [40].

In case the main goal of the filtration is clarification, then large pore membranes (superior to 1 µm) should be used due to the higher permeate flow rates and the low retention of essential beer compounds. In case the objective of filtration would be pasteurization, here no membrane can satisfy the cold-sterilization and beer quality criteria at the same time. In addition to that, permeate flux obtained with these membranes is yet too low to make this technique economically applicable [2,41].

CONCLUSION

As a serious quality problemin bright beer is formation of permanent haze which causerestrictions on the product shelf- life. Application of cross-flow microfiltration (CFMF) for clarification of rough beer (RB) and pasteurization of clarified beer (CB) stand as a potential usages of membranes in the food industry.

Beer clarification by microfiltration requires a finely balanced retention of colloidal particulates (yeast cells, chill haze flocs, etc.) and the transmission of soluble macromolecules including carbohydrates, proteins, flavor, and color compounds which would result in the "whole some" quality of a beer. The required porous transmission of these macromolecular species led to complex,an unavoidable and dynamic in-pore membrane fouling in terms of fouling constituents, structure formation and kinetics, which are known to be the main barrier in obtaining an economically viable flux and consistency in permeate quality. The presence of yeast cells could be assumed to less compact proteins and polyphenols fouling.

Nowadayes, there areinvention concerns about application of a microporous membrane constructed of polyester with pore size between 0.1 and 1 micron for the filtration of beer. The membrane filter proved to be particularly suitable for microbiological stabilization of the beer and for the separation of the turbid substances.

The membrane makes possible the removal the germs which are considered hazardous to the beer and the harmful turbid substances, and to simultaneously filter the beer with a high throughput and therefore economically and at low costs.

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