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Desalination of soy sauce by nanofiltration

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ABSTRACT

Soy sauce is a traditional Chinese food condiment, normally containing a high concentration of sodium chloride (NaCl, 18–20%, w/v). To meet people's demand for healthy foods, part of NaCl needs to be removed from the raw soy sauce. In this study, nanofiltration was employed for the removal of salt and the recovery of nutritional components such as amino acid and fragrance from raw soy sauce, using four commercial NF membranes (NF270, NF-, NF90, Desal-5 DL). NF270 was found to be most suitable for the purpose. It was used to further study the effect of operation modes on desalination performance. The combination mode that concentration of the diluted soy sauce to its original volume, followed by diafiltration, was found to be most suitable one in terms of amino nitrogen (AN) and NaCl rejection, water consumption and operating pressure. Moreover, it was found that the rejection of AN was constant under the experimental conditions examined while NaCl rejection showed a linear relation with the concentration ratio of AN to NaCl. Based on mass balance and rejection equations, mathematical models were developed for predicting the concentration of solutes in retentate during desalination process, the simulation results agreed well with the experimental data.

1. Introduction

Soy sauce (Japanese shoyu) is a traditional condiment widely used in the Orient. In China, the annual production of soy sauce is around 5 million tons, with a sales value of around 20 billion Renmingbi (RMB, Chinese currency). It can be made from a mixture of soybeans and wheat using a well-established two-step fermentation process as it not only imparts a delicious flavor but also promotes digestion [1]. In order to avoid contamination by microbe during the fermentation, normally 18–20% NaCl is added. So the resulting broth contains a very high concentration of salt. However, according to recent medical studies, foods with high sodium content may cause many diseases such as high blood pressure and kidney problem [2], soy sauce with salt content not more than 130 g L^{-1} is currently preferred. Therefore, part of NaCl needs to be removed from the raw soy sauce to meet people's demand for healthy foods.

A number of technologies were used to eliminate NaCl from soy sauce, such as ion exchange [3], reverse osmosis [4,5], electrodialysis [5,6], freezing [7] and extraction [8]. However, these technologies suffer from their disadvantages such as adverse effect of taste and flavor, high capital and operation cost, etc. and thus are impractical in commercial use. In recent years, nanofiltration (NF) has appeared as a promising technique for desalination of industrial fluids due to its low rejection for monovalent salts [9–16]. Guu and Zall [17] reported that taste and flavor substance of soy sauce were mostly retained after 50% of the salt was removed by NF. Watanabe and Furukawa [18] applied two-step NF process to obtain light color, thick and low salt soy sauce. These reports suggest that NF could be feasible for desalination of soy sauce. Nevertheless, further studies on membrane selection and process optimization of soy sauce desalination have not been reported yet.

As the main applications of NF are water soften, desalination of dye as well as demineralization of whey and milk, most of research on NF-desalination was done with relatively dilute systems, where the salt concentration rarely exceeded 5% (w/v) [19–22]. Generally, the optimal operation mode in the NF-desalination consisted of three steps: pre-concentration, diafiltration and post-concentration [9,14]. In order to decrease water consumption, several studies on constant volume diafiltration (CVD), variable volume diafiltration (VVD) [23,24], counter-current diafiltration [25] and two-stage diafiltration [26] were also performed. However, in the present study, the soy sauce solution containing a high soluble solids (35–39%, w/v) was adopted in the experiments, a very high osmotic pressure would be expected due to the existing low molecular weight organic solutes (glucose, saccharides, amino acid, and peptide) and concentrated inorganic salt. On the other hand, concentration polarization would be severe in filtration operation due to the relatively high viscosity of soy sauce. Therefore, the osmotic pressure and the concentration polarization would be two impor-

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Nomenclature

C	solute concentration in retentate ($g\,L^{-1}$)
C_f	solute concentrations in feed ($g\,L^{-1}$)
C_i	solute concentration in the cell at the beginning of concentration step ($g\,L^{-1}$)
C_0	solute concentration in the cell at the end of the concentration step or the beginning of the diafiltration step ($g\,L^{-1}$)
C_p	solute concentrations in permeate ($g\,L^{-1}$)
$C_{R,av}$	average solute concentration in retentate ($g\,L^{-1}$)
M	regression constant, dimensionless
N	regression constant, dimensionless
R_{obs}	observed rejection (%)
V_C	feed volume or permeate volume in concentration step (mL)
V_d	volume of the diluted soy sauce (mL)
V_D	water consumption in diafiltration step (mL)
V_f	volume of feed (mL)
V_F	volume of the stocking soy sauce used for dilution (mL)
V_0	volume of cell (mL)
V_p	cumulative permeate volume (mL)

tant factors that must be considered, and the previous modes might not be appropriate for desalination of soy sauce.

Since the contents of amino nitrogen (AN) and soluble solids excluding sodium chloride (SSESC) are two key parameters in determining the quality of soy sauce products, and could be easily lost in desalination processes, the aims of this work were to examine the feasibility of desalination of soy sauce using nanofiltration and to develop a nanofiltration based process to remove NaCl efficiently but preserve the nutrients (e.g. AN and SSESC) as much as possible by selecting suitable membrane and operation mode. Several operation modes including diafiltration and concentration were applied to optimize the process in terms of the rejections of AN, NaCl, water consumption and TMP. A simple model was developed for predicting the concentration of solutes in retentate during nanofiltration.

2. Material and methods

2.1. Membrane and raw soy sauce

Four commercial NF membranes, NF270, NF-, NF90 (Filmtec/DOW), Desal-5 DL (GE Osmonics), were tested in the present work. Based on the manufacturers' data sheets and literatures [27,28], the properties of these NF membranes are shown in Table 1. Raw soy sauce was kindly provided by a food plant in China. Characteristics of this industrial fluid are presented as follows: soluble solid, $360\,g\,L^{-1}$; NaCl, $177\,g\,L^{-1}$; amino nitrogen, $11.2\,g\,L^{-1}$; pH 5.1; viscosity, 2.7 mPa S (20 °C).

2.2. Pretreatment of raw soy sauce

The raw soy sauce from the manufacturer normally contained a lot of visible suspended solids and microbes (>5000 cfu mL^{-1}). All these may constitute major foulants in membrane filtration and should be removed before desalination operation. As applied in industry, the pretreatment consisted of sedimentation, centrifugation and microfiltration, that is, after sedimentation for at least 7 days in a fridge, raw soy sauce of the upper layer was collected and centrifuged by J6-MC high capacity refrigerated centrifuge (BECKMAN, USA) for 30 min (4000 rpm, $4600 \times g$), then the supernatant was filtrated by the module of hollow fiber microfiltration membrane with pore size 0.1 μm (MIF-503, Tianjin Motimo Membrane Technology Ltd., China) at a pressure of 0.05–0.07 MPa. Table 2 shows the analytical results of the raw soy sauce with and without pretreatment. As can be seen, the nutrients in the soy sauce were not affected after the pretreatment. The microbial counts and absorbency at 530 nm indicated that most of the microbes and suspended solids were removed after the pretreatment, and the viable microbes in the resulting soy sauce were only 80 cfu mL^{-1}, much lower than its initial 6300 cfu mL^{-1}, while the absorbency decreased to 0.100 from its initial 0.594. In the following sections, the raw soy sauce with pretreatment is referred to as stocking soy sauce or undiluted soy sauce.

All deionized water and feed were filtered through 0.22 μm microporous filters (MEMBRANA, Germany) before use.

2.3. Experimental set-up and procedure

Fig. 1 illustrates the schematic diagram of set-up for nanofiltration desalination experiment. The dead-end filtration experiments were conducted in a homemade magnetic stirred cell in concentration or diafiltration mode. The working volume of the cell was 12.8 mL, which could be fitted with a membrane disc having an effective diameter of 24 mm within the module, and the effective membrane surface area was $4.52 \times 10^{-4}\,m^2$. All the experiments were performed at room temperature (22 °C) and a constant permeate flux. Feed or deionized water was pumped into the filtration cell through a switching valve (V-7, Pharmacia, Sweden) using a high performance positive displacement pump (P-500, Pharmacia, Sweden). In diafiltration mode, diluent (e.g. deionized water) was pumped into the cell directly, while in concentration mode, the diluent was diverted into an injection column (Superloop 50 mL, Pharmacia, Sweden) through a by-pass of the switching valve, where a given volume of the diluted soy sauce was pre-filled. The fluid pumped continuously into the column would push the soy sauce into the cell until no soy sauce was left in the column, while in the cell, the diluted soy sauce would be concentrated to its original volume of the undiluted soy sauce used. The transmembrane pressure (TMP) was continuously monitored by a pressure sensor (MLH040BSB09A, Honeywell, USA) and the data were collected automatically by a computer.

A fresh membrane was used for each experiment. The membrane was soaked in the deionized water for at least 48 h prior to use. Additionally, the membranes were pre-pressured with deionized water until a constant pressure (e.g. 35 bar) was obtained. Before desalination experiments started, the cell was full of soy sauce sample (12.8 mL). In order to decrease operation pressure, the stocking soy sauce was diluted by deionized water into different degree for subsequent concentration or diafiltration operation. In concentration step, all the diluted soy sauce was concentrated to its original volume. In diafiltration step, the constant volume diafiltration mode (CVD) was employed and deionized water was used as the diluent, as described elsewhere [23]. And these experiments ran at a constant flux of $6.64\,L\,m^{-2}\,h^{-1}$ except elsewhere stated. The permeate was collected in vials for analysis and the vials were replaced manually when 1 or 2 mL permeate in each vial was collected until a total volume of 10–12 mL of permeate was pooled. To normalize all experiments, the volume of stocking soy sauce used for desalination was 12.8 mL, which was exactly the same as the cell volume. After desalination operation, the final volume of the soy sauce obtained was also 12.8 mL.

2.4. Analytical methods

The pH values and NaCl content of the solutions were measured using an ion meter equipped with pH and Cl^- electrodes (PXSJ-216, Shanghai, China). Amino nitrogen (AN) and soluble solids were