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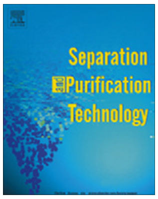

Ultrafiltration of orange press liquor: Optimization for permeate flux and fouling index by response surface methodology

René Andrés Ruby Figueroa, Alfredo Cassano *, Enrico Drioli

Institute on Membrane Technology, ITM-CNR, c/o University of Calabria, via P. Bucci, cubo 17/C, I-87030 Rende (CS), Italy

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ABSTRACT

A Box-Behnken design of response surface methodology (RSM) was used to analyze the performance of polysulphone ultrafiltration (UF) hollow fiber membranes in the clarification of orange press liquors. A regression model was developed for permeate flux, fouling index and blocking index as a function of transmembrane pressure (TMP), temperature and feed flow-rate.

The experimental operating conditions were selected within the following ranges: TMP 0.2–1.4 bar, temperature 15–35 °C, and feed flow-rate 85–245 L/h. A total of 30 experiments was performed according to the total recycle configuration. Based on the lack-of-fit test, the analysis of variance (ANOVA) showed the regression model to be adequate. From the regression analysis, the permeate flux, fouling index and blocking index were expressed with quadratic equations of TMP, temperature and feed flow-rate.

Quadratic terms of TMP, temperature and feed flow-rate showed a significant influence on the performance of the UF membrane.

A strong interaction effect of temperature and feed flow-rate was observed on the permeate flux while interactions TMP-temperature and TMP-feed flow-rate were found to be less significant. In the case of fouling index, interactions TMP-temperature and TMP-feed flow-rate produced a significant effect.

In order to maximize the permeate flux and minimize the fouling index, the desirability function approach was applied to analyze the regression model equations. The optimized operating variables were found to be 1.4 bar, 15 °C and 167.7 L/h for a maximum desirability of 0.76.

Experimental data of permeate flux and fouling index, obtained in optimized operating conditions, resulted in a good agreement with the predicted values of the regression model.

1. Introduction

Membrane processes are today consolidated systems in various productive sectors, since the separation process is athermal and involves no phase change or chemical agents. The introduction of these technologies in the industrial transformation cycle of the fruit juices represents one of the technological answers to the problem of the production of juices with high quality, natural fresh taste and additive-free. Juice clarification, stabilization, depectinization and concentration are typical steps where membrane processes as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been successfully utilized [1]. UF has been also developed for the treatment of wastewater and sewage in order to remove particulate and macromolecular materials [2–4].

The critical issue in a membrane-based separation process is the decline in permeate flux during its operation. Membrane fouling in crossflow ultrafiltration is a key factor affecting the economic and technological viability of the processes, which essentially depends on the permeate fluxes obtained and their stability with time [4]. Consequently, the identification and quantification of the prevalent fouling mechanism and efforts to minimize its effects during a continuous filtration process are extremely important [5].

The term *membrane fouling* is often used to describe a long term flux decline caused by accumulation of certain materials at the membrane surface [6]. It may occur due to a concentration polarization layer development over the membrane surface, the formation of a cake layer and/or a blockage of the membrane pores. The pore blocking can be further characterized by complete, intermediate and standard pore blocking [5].

Several studies are reported in literature about the membrane fouling. Some examples include concentration polarization [7], cake filtration [8–9] and blocking models [10]. In all of these models, the particle size or the ratio of the particle size to the membrane pores is the key parameter for choosing a suitable membrane. Concentration polarization occurs only when the particle diffusion flux is dominant, while the cake filtration model is used when particles

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* Corresponding author. Tel.: +39 0984 492067; fax: +39 0984 402103.
E-mail address: a.cassano@itm.cnr.it (A. Cassano).

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have accumulated on the membrane surface. When the particle size is smaller than or comparable to the membrane pores, particles have the opportunity to penetrate and block the pores. In this case, the membrane blocking model may be the appropriate method to relate the received filtrate volume, v, to filtration time, t [11].

Basically, researchers study the membrane separation performance by using the "one-factor-at-a-time" approach. However, the effect of operating variables such as transmembrane pressure, temperature, feed flow-rate and solute concentration on membrane fouling may not be independent of each other and it is necessary to consider their interactions. A possible solution is to use the response surface methodology (RSM) approach that is widely used to analyze the effects of multiple factors and their interactions [12].

RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes in which a response of interest is influenced by several variables and the objective is to optimize this response. RSM has important applications in the design, development and formulation of new products, as well as in the improvement of existing product design. It defines the effect of the independent variables, alone or in combination, on the process. In addition, in order to analyze the effects of the independent variables, this experimental methodology generates a mathematical model which describes the chemical or biochemical processes [13–15].

Citrus fruits are widely used in the food industry for the production of fresh and concentrated juice, citrus-based drinks and cans. This process is accompanied by the production of large amounts of by-products such as peels and seed residues which may account for up to 50% of the total fruit weight. Most of the waste residue from commercial juice extractors is shredded, limed, cured and pressed into press liquors and press cakes which are then processed independently. Press liquors are enriched in bioactive compounds, such as flavonoids and phenolic acids, recognized for their beneficial implications in human health due to their antioxidant activity and free radical scavenging ability [16]. They are usually concentrated in multiple effect heat evaporators to yield citrus molasses, while d-limonene is obtained from the condensate.

The UF process can be considered a valid approach for separating and recovering valuable products from finely divided solid waste materials present in citrus press liquor. It separates the flow from the press liquor into a permeate having a total soluble solids content and an acidity level approximating those of the press liquor and a retentate containing the suspended solids such as proteins and fibers and high molecular weight carbohydrates such as pectins associated with cloud [17,18].

In this work the objective was to use the RSM approach for investigating the simple effect and the interaction of different operating conditions, such as transmembrane pressure (TMP), temperature and feed flow-rate, on permeate flux, membrane fouling and blocking index of UF polysulphone hollow fibers. From the regression model sets of operating variables were determined for optimizing the clarification of orange press liquors.

2. Theory

Hermia [2,5,19–21] developed four empirical models for dead-end filtration based on constant pressure filtration laws that correspond to four basic types of fouling: complete blocking, intermediate blocking, standard blocking and cake layer formation. The type of fouling considered depends on the value of the parameter i in the following equation:

$$\frac{\partial^2 t}{\partial v^2} = K\left(\frac{\partial t}{\partial v}\right)^i \qquad (1)$$

where the blocking index i and the resistance coefficient K are functions of the blocking models. The membrane blocking phenomena can be described by these parameters; for example, $i = 2$ is complete blocking, $i = 1.5$ is standard blocking, $i = 1$ is intermediate blocking, and $i = 0$ is cake filtration.

The blocking index and the resistance coefficient can be calculated by plotting d^2t/dv^2 versus dt/dv or solving Eq. (1) [11].

In this work a non-linear regression, based on the permeate flux experimental data, was used to obtain the blocking index i for each experimental run.

3. Materials and methods

3.1. Feed solution

Citrus press liquors, with a suspended solid content of 7.13 ± 1.41% (w/w), were supplied by Gioia Succhi Srl (Rosarno, Reggio Calabria, Italy). Liquors were left overnight at room temperature to let the majority of the cloud particles settle out. A partially clear liquor was recovered by decanting of the cloud layer. Liquors were then depectinized by adding 7 g/kg of pectinase (4 h at room temperature) from *Aspergillus aculeatus* (Sigma–Aldrich, Milan, Italy) and filtered with a nylon cloth. Final liquors (feed solution), depleted in suspended solids, had a pH of 3.6 and a total soluble solids content of 8.6 °Brix. They were stored at −17°C and defrosted at room temperature before use.

3.2. UF equipment and procedures

UF experiments were performed by using a laboratory unit (Fig. 1) equipped with a hollow fiber polysulphone membrane module supplied by China Blue Star Membrane Technology Co., Ltd (Beijing, China) with an effective membrane area of 0.16 m^2 and a nominal molecular weight cut-off (MWCO) of 100 kDa. A heat exchanger, placed into the feed tank, was used to keep the feed temperature constant.

Experimental runs were performed according to the total recycle configuration in which permeate and retentate streams were both continuously recycled back to the feed tank to ensure a steady state in the volume and composition of the feed. The operating conditions varied according to the experimental design described in the following. The mass of permeate collected was measured with an accuracy of ±0.1 g every 10 min for periods of 180 min.

3.3. Cleaning procedure

The initial hydraulic permeability of the membrane module was 191.22 L/m^2hbar at 20 °C. After each run, the membrane module was submitted to a cleaning procedure by using an enzymatic detergent (Ultrasil 50, Henkel Chemicals Ltd., Dussendorf) at a concentration of 1.0% (w/w) and at a temperature of 40 °C for 60 min. After a rinsing with distilled water for 15–20 min, the membrane module was cleaned with a 0.2% (w/w) NaOH solution at 40 °C for 60 min. A final rinsing with distilled water for 20 min was performed. After the cleaning step the hydraulic permeability of the membrane module, in fixed conditions (temperature 20 °C, feed flow-rate 245 L/h), was measured.

The recovery of the hydraulic permeability after the cleaning procedure was higher than 89.6%.

3.4. Fouling index

The fouling index was calculated by comparing the hydraulic permeability before and after the treatment of orange press liquor according to the following equation: