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Behavior and rejection mechanisms of fruit juice phenolic compounds in model solution during nanofiltration

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ABSTRACT

Behavior and rejection mechanisms of typical phenolic compounds in fruit juice during nanofiltration (NF) are not clear. Because the system of actual fruit juice is very complex, in this study, rejection mechanisms of six typical fruit juice phenolic compounds in model solutions with two NF membranes were investigated. Molecular structure parameters of these phenolics, such as hydrophobic properties, electrical parameters, and spatial parameters on the process were considered in a general quantitative structure activity relationship (QSAR) model. Principal component analysis and partial least square regression were used to find the relationships between rejection and molecular parameters. Results showed that NF performances of phenolics could be affected by filtration operating conditions, membrane properties and molecular parameters. In QSAR models, dipole moment, acidity coefficient, Octanol-water partition coefficient and fifth-order path cluster molecules connectivity index were the most important molecular parameters, and correlation coefficients for two membranes were 0.895 and 0.833, respectively. QSAR models can be successfully applied to predict the rejection for NF of fruit juice phenolics model solution.

1. Introduction

Fruit juices as a healthy drink become a focus of people's living and consumption in the new century. Currently, its manufacture process has been attracted more attention by consumers and researchers, and become a critical issue in the industry. Membrane technology has certain advantages such as no phase change and chemical change, low temperature, simple operation, energy-saving, environmental protection, etc. (Yazdanshenas et al., 2010). It has been used for clarification and concentration of fruit juice since the invention of asymmetric membranes by Loeb and Souriragan in the early 1960s (D'souza and Mawson, 2005). Nanofiltration (NF) is a pressure-driven separation process in which the filtration efficiency depends on steric (sieving) and charge (Donnan) effects (Echavarriá et al., 2011). It has been gradually applied to concentration of fruit juices because it can avoid nutrient losing and aromatic substances escaping (Salehi, 2014; Sotoft et al., 2012; Salgado et al., 2013). Because NF application in fruit juice processing is still in its infancy, there are many theoretical and technical problems. For example, membrane fouling which affects the product quality, operating costs and the plant maintenance, limits the widespread application in the field of fruit juice concentration processing (Bruggen et al., 2008).

Phenolic compounds are one of the main active ingredients in fruit juices, such as apple juice, pear juice, orange juice, grape juice, etc. It is a kind of important components with many types and complex structure including ferulic acid, chlorogenic acid, gallic acid, rutin, quercetin, etc. (Rinaldo et al., 2011). Some important beneficial features of these substances to human body have been

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reported, such as anti-microbial, antioxidant, eliminating free radicals, lowering blood pressure and lowering blood fat (Marquardt et al., 2014). Phenolic compounds are classified into some major groupings distinguished by the number of constitutive carbon atoms in conjunction with the structure of basic phenolic skeleton (Robards et al., 1999). To our knowledge, the behavior and rejection mechanisms of such phenolics in NF process have not been studied thoroughly.

In recent years, quantitative structure activity relationship (QSAR) in organics, which is a method related an activity of compounds quantitatively to chemicals descriptors (structure or property) (Sawyer et al., 2003), has been a hot focused field. QSAR has the objective of prediction but maintaining a relationship to mechanistic interpretation. Applications of QSAR for development of models to find relationships between permeability of membranes and organic compounds have been reported related to drug discovery and medicinal chemistry (Fujikawa et al., 2007). More recently, Yangali-Quintanillaa et al. (2010) uses the QSAR analysis to quantify the activity compounds and rejection of membrane, in terms of organic compound physicochemical properties, membrane characteristics and operating conditions. Therefore, phenolics are one of the key indicators in fruit juice processing. Therefore, it is necessary to establish a relatively reliable and accurate QSAR model, which can predict rejections of phenolic compounds during NF. It can further demonstrate rejection mechanism of fruit juice phenolic compounds during NF.

In this study, fruit juice phenolic compounds model solutions were used to investigate the effects of operating and molecular parameters on NF processes. Principal component analysis and partial least square regression were applied to develop a QSAR model, which would be demonstrated the relationship between rejection and molecular parameters.

2. Materials and methods

2.1. Experimental apparatus

A laboratory bench scale cross-flow NF apparatus was used in all experiments, shown in Fig. 1. The feed solution was charged into a 5 L feed tank and re-circulated at a flow rate of 1.2 L/min using a diaphragm pump (DP-130, Shanghai new xishan, China). This pump also provided the required constant operating pressure to the feed. Two needle valves were installed on the feed and retentate lines respectively to adjust the fluid flow rate. A flowmeter (KOBOLD Instrument Company, Germany), calibrated for the present experiments, was utilized. Two pressure gauges (ACUTEK, USA) were used to determine the feed and retentate pressure, respectively. As the outlet for permeation was opened to the air, average value of these two pressure meters was assumed to be the transmembrane pressure (TMP). Sample solution was kept at 25 °C by a heat exchanger. The flow rate of permeate was measured by a digital balance (GE2120, Sartorius, Edgewood, NY) with an accuracy of 0.01 g. Permeate was collected and regularly returned to the storage tank to be a constant feed concentration.

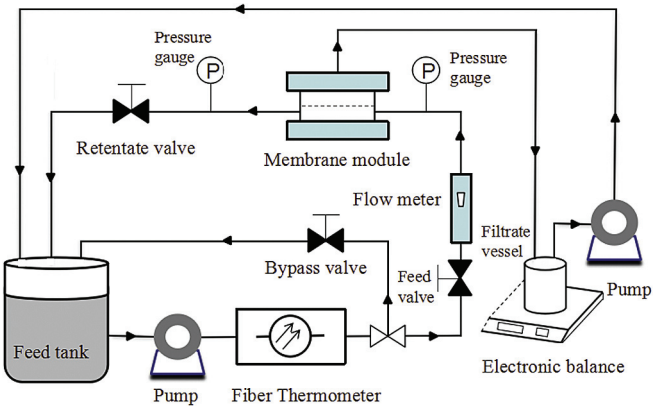

Fig. 1. Schematic diagram of the NF system. (1) feed tank; (2) pump; (3) bypass valve; (4) feed valve; (5) flow meter; (6,10) pressure gauge; (7) membrane module; (8) filtrate vessel; (9) electronic balance; (11) retentate valve.

2.2. Properties of NF membranes

The most important parameters that characterize a membrane are its permeability and its separation capability (Nagarale et al., 2006). Two commercially NF membranes (Vontron, China), VNF1 and VNF2, were used in this study. The properties of these two NF membranes are shown in Table 1.

Membrane separation capability is normally established by using the molecular weight cut-off (MWCO) concept, which corresponds to the size of particles that are rejected by the membrane 90% of the time (Atra et al., 2005). To determine the MWCO of a membrane, several organic compounds with different and narrow molecular weights including ethanol, isopropanol, n-butyl alcohol, glycerol, glucose, polyethylene glycol (peg) 200–600 and others are tested with the membranes under the same conditions. The operation pressure, flow velocity and inflow organic compounds concentration for two kinds NF membrane were 6.0 bar, 1.2 L/min and 1000 mg/L, respectively. Meanwhile, the rejections of these organic compounds were determined during NF process. Rejection curve of composite membrane against neutral organics was described with molecular weight (Mw) as the abscissa and the rejection as the ordinate. In the curve, the rejection reaches 90% corresponding Mw is the MWCO of this membrane.

In order to evaluate pore structure and electrical properties of NF membranes, most of the researchers used the fine mesh model and the surface charge model (Wang et al., 1995). Based on the fine pore model, the pore sizes of two NF membranes can be calculated using test results of ethanol, isopropanol, isobutanol, glycerol and other neutral solutes in NF permeability. Based on the surface charge model, the surface charge density of these two NF membranes can be calculated using the results of NaCl solution and Gouy-Chapman electric double layer theory (Peeters et al., 1999). The values of the surface charge density is calculated under the condition of 10 mmol/L NaCl solution.

2.3. NF processes

Performances of six typical fruit juice phenolic compounds, including gallic acid (GA), protocatechuate, caffeic acid, chlorogenic acid, ferulic acid and rutin during NF process were investigated. All solutions were prepared with deionized water. In order to analyze the effects of different factors in NF process, experiments were carried out at TMPs of 2, 4, 6, 8 bar and concentrations of 1, 2, 4 g/L. The flow rate was kept constant at 1.2 L/min. Before NF running, membranes should be pretreated with 70% ethanol, removing all residual protein or other impurities, and compacted with deionized water for 1 h. Each run was conducted as following: First, the permeate flux of intrinsic membrane was determined at the start with deionized water. Then the feed was pumped into the system and the permeate flux was measured in a same interval till it reached a constant value. After each experiment, the membranes were cleaned by backwashing for 0.5 h with deionized water, and followed by 0.1 M NaOH for 10 min.

The permeate flux was calculated according to the following equation (Toh et al., 2007; Mello et al., 2010):