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Permeation characteristics of volatile fatty acids solution by forward osmosis

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ABSTRACT

Permeation characteristics were investigated using forward osmosis for the dewatering of VFAs solution. A solution of VFAs produced by anaerobic mixed-culture fermentation can be used as a raw material to produce mixed alcohol and microbial biodiesel. A 35 g/L surrogate solution of 6:1:3 ratio (acetic, propionic, and butyric acids) was prepared. Under membrane orientation, the water flux, reverse salt flux, and rejection of VFAs in the FO mode were higher than those in the PRO mode. Both the flux and rejection rate were pH-dependent for the VFA solution. The flux increased at a lower pH, while the rejection increased at a higher pH. At pH 8, an optimum performance of 97% rejection and a 11.10 L/m^2 h water flux was obtained. The water flux was also influenced by the temperature, concentration of the draw solution, and type of draw solute, but the rejection of VFAs remained nearly constant. In a fermentation broth, the flux behaviors were different from those in a chemical solution because the remaining nutrients and by-products increased the osmotic pressure in the feed solution. The flux behavior findings obtained under various experimental conditions provide clues to the mechanisms and parameters for the dewatering of VFAs solution.

1. Introduction

Volatile fatty acids (VFAs) are receiving considerable attention as one of the most promising raw materials for making biofuels and chemicals based on carboxylic acids. VFAs are short chain fatty acids derived from the anaerobic digestion of living or dead biomass of plant, animal, and even microbial biomass sources by mixed cultures [1]. VFAs are mainly composed of acetic, propionic, and butyric acids with various ratios of 6:1:3, 5:1:5 or 8:1:1 [2]. VFAs can be converted into mixed alcohols or chemicals by hydrogenation (MixAlco process), which has been extensively studied by Holtzapple et al. (Fig. 1), while Chang and his associates have studied the use of VFAs for microbial biodiesels [3–5]. For VFAs to be utilized as a raw material for microbial biodiesel and mixed alcohols, they need to be produced in high concentrations with high productivity. The currently published concentration and productivity of VFAs are around 3.5 wt% and 7 g/L/d, respectively [6,7]; thus, they cannot be used directly as a raw material and require a dewatering process.

Membrane separation has an advantage over other separation processes, including distillation, evaporation, and extraction, among others, in terms of energy consumption because of its mild and non-phase changing conditions [8]. A variety of membrane processes are available depending on the size and nature of the separating components [9].

Forward osmosis (FO) has recently become increasingly popular. FO is an osmotic membrane process whereby the driving force for this separation is an osmotic pressure gradient between the feed and draw solutions. A draw solution having a high osmotic pressure (relative to that of the feed solution) is used to induce a net flow of water through the membrane [10]. FO has a lower energy consumption, a lower fouling propensity [11], and higher water recovery [12], unlike the pressure-driven membrane process. After pressure-retarded osmosis (PRO) was invented [13,14], little attention was paid to forward osmosis until Elimelech et al. [15,16] proposed a lab-scale FO system and performed desalination experiments using ammonium bicarbonate. Previous studies have extensively reviewed the detailed mechanism and properties of the forward osmosis system [10,17,18]. Thus, FO has been mainly used in water treatment applications, such as water purification and brackish

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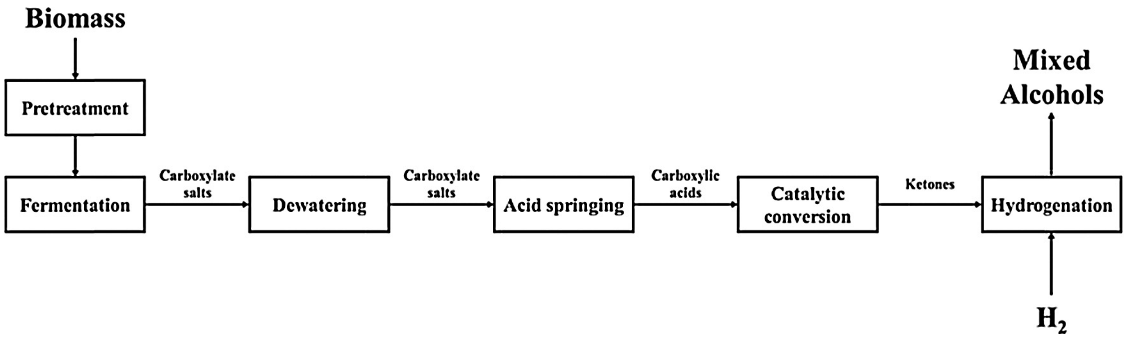

Fig. 1. Overview of the MixAlco process for production and application of VFAs.

water desalination. Recently, further studies have investigated the treatment of industrial wastewaters [10], treatment of liquid foods [19], algae biomass separation [20], and sludge dewatering [21].

However, to date, few studies on the dewatering of biochemical and biofuel have been reported [22,23]. Moreover, as water permeates through the membrane to the draw solution, a small fraction of the feed solute is also transported, while the draw solute simultaneously permeates through the membrane to the feed solution. The regeneration of draw solutes from diluted draw solutions is required, thus hybrid systems including well-established low energy processes should be considered to recycle draw solute [24]. The concentrated feed solution including draw solute due to the occurrence of reverse draw solute flux can be recovered by the "acid springing" process [25], which can produce pure VFAs from this concentrated feed solution for conversion to ketone or mixed alcohol (Fig. 1) [5]. However, when employing the dewatering process through FO its usage becomes substantially more effective since the rejection of feed solute is higher. The rejection of feed solute close to 100% indicates that only water passes through the membrane from the feed to the draw solution, completely preventing any feed solutes from crossing over [10,26]. The rejection of feed solute is an important parameter in an FO system to obtain a high concentration of VFAs. Additionally, the dewatering of biochemical and biofuel by FO plays an important role in the economics of the products for low energy consumption compared to distillation [15].

In this study, to effectively dewater VFAs solution, permeation characteristics, including water flux, reverse salt flux, and rejection of VFAs in an FO system were investigated. We carried out the dewatering of VFAs solution with the FO system using an asymmetric semi-permeable membrane. In addition, to optimize and describe the effects of the parameters, we tested the effects of the temperature, concentration of the draw solution, and type of draw solutes on the water flux and rejection of VFAs. Moreover, the water flux and rejection of VFAs were examined in a pressure-assisted osmosis (PAO) system applying various hydraulic pressures against various neutralizing agents in the feed solution. Flux behavior of the FO system, under various experimental conditions, clarified the mechanisms and parameters for the dewatering process of VFAs solution.

2. Material and method

2.1. Membrane

The forward osmosis membrane is the cartridge membrane, which is made of cellulose triacetate with an embedded polyester screen mesh. This membrane was provided by Hydration Technologies, Inc. (Albany, OR, USA). According to the user manual, the suggested pH range of the membrane in this experiment was between 3 and 8. In addition, sodium chloride rejection was around 95% (93–95%). Other characteristics of this membrane were described elsewhere [27].

2.2. Feed and draw solutions

Feed solutions including VFAs, succinic acid, ethanol and ABE mixture (composed ofacetone, butanol and ethanol) (Junsei Chemical Co. Ltd., Japan) were prepared by diluting with distilled water. In a mass ratio, the VFAs from seaweeds were conventionally composed of acetic acid, propionic acid, and butyric acidin a ratio of 6:1:3, respectively. The ABE mixture was produced in a 3:6:1 mass ratio [28]. The pH of the solutions was adjusted with ammonia, NaOH, $Ca(OH)_2$ or HCl solution to a desired value. The draw solution used in this study was a 5 M or saturated NaCl solution (Junsei Chemical Co. Ltd., Japan). $CaCl_2$, $MgCl_2$, KCl, and $(NH_4)HCO_3$ (Junsei Chemical Co. Ltd., Japan) were used as additional draw solutions for comparative analysis with the NaCl solution.

In addition, a 35 g/L VFAs fermentation broth was prepared at 35 °C under pH 8 from anaerobic sludge obtained from Daejeon Metropolitan City Facilities Management Corporation. A 105 g/L succinic acid fermentation broth was also obtained at 39 °C and pH 6.5 by *Mannheimia succiniciproducens* [29]. The fermentation broth consisted of fermentation products and few carbon sources (glucose or glycerol): typically, 95% succinic acid and 5% other compounds (four parts pyruvic acid, one part acetic acid). The properties of the fermentation broth samples are presented in Table 1.

2.3. Forward osmosis experiments

The FO experiments were performed with a lab-scale flow circulating FO system as described in Fig. S1 [30]. The plate-and-frame membrane cell was a counter-current flow type with straight structured channels on both sides. The membrane cell was 10.0 cm in

Table 1
Characteristics of fermentation broths in this study.

Composition	Fermentation broth	
	Volatile fatty acids	Succinic acid
Concentration (g/L)	35.12	106.64
pH	7.98	6.51
COD_{cr} (g/L)	82.22	161.79
Cation (g/L)		
NH_4^+	12.45	7.05
Na^+	3.97	0.14
K^+	0.39	0.50
Mg^{2+}	0.01	8.32
Ca^{2+}	0.08	2.27
Anion (g/L)		
SO_4^{2-}	0.65	20.97
PO_4^{2-}	1.32	0.54

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