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Recovery of volatile fatty acids via membrane contactor using flat membranes: Experimental and theoretical analysis

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ABSTRACT

Volatile fatty acid (VFA) separation from synthetic VFA solutions and leachate was investigated via the use of a membrane contactor. NaOH was used as a stripping solution to provide constant concentration gradient of VFAs in both sides of a membrane. Mass flux (12.23 g/m^2 h) and selectivity (1.599) observed for acetic acid were significantly higher than those reported in the literature and were observed at feed pH of 3.0, flow rate of 31.5 ± 0.9 mL/min, and stripping solution concentration of 1.0 N. This study revealed that the flow rate, stripping solution strength, and feed pH affect the mass transfer of VFAs through the PTFE membrane. Acetic and propionic acid separation performances observed in the present study provided a cost effective and environmental alternative due to elimination of the use of extractants.

1. Introduction

Organic fraction of municipal solid waste (OFMSW) creates environmental and economical problems throughout the world. OFMSWs can be conveniently treated via anaerobic digestion process to reduce their environmental impact, to recover energy and/or material, and to reduce operational cost while the massive disposal methods such as incineration and landfill are avoided (Thongsukmak and Sirkar, 2007). Anaerobic digestion processes involve the conversion of complex organic matter to methane gas through a multistep process involving the production of soluble compounds, organic acids, acetate, and hydrogen (Batstone et al., 2002).

Commodity chemicals are currently derived from fossil fuels (Eggeman and Verser, 2005). However, there is a recent interest in using organic acids such as volatile fatty acids (VFAs) as intermediates for the production of alcohols, aldehydes, ketones, and olefin via combined fermentation and chemical synthesis, which may eventually displace existing synthetic routes and reduce the fossil fuel use (Eggeman and Verser, 2005). Anaerobic digestion/fermentation of organic-rich wastes can be used for the natural production of organic acids such as VFAs by eliminating the methane forming phase (Diltz et al., 2007; Gryta and Barancewicz, 2011; Lee et al., 2001; Thongsukmak and Sirkar, 2007; Wodzki et al., 2000). Elimination of methane forming phase in anaerobic digestion processes to produce VFAs can be difficult, as the undissociated VFAs can freely permeate the cell membrane lowering pH within the cell (Zoetemeyer et al., 1982). In addition, accumulation of certain VFAs may alter the anaerobic fermentation process, causing reactions to became thermodynamically unfavorable, which may result in changes of the pathway of certain reactions (Pind et al., 2003). Therefore, VFAs should be removed from the anaerobic fermentation process in order to optimize the VFA production and possibly recover VFAs as valuable commodity chemicals. Separated VFAs from fermentation broths/leachate can be used as a raw material in industrial processes, carbon source in biological nitrogen/phosphorus removal processes (Thongsukmak and Sirkar, 2007), carbon source in bio-electrochemical or bio-H_2 processes (Keshav et al., 2009), and intermediates in production of commodity chemicals (Eggeman and Verser, 2005).

Studies have shown that volatile species such as ammonia and hydrogen cyanide in water can be separated via hydrophobic gas-filled membranes with the use of either acidic or alkaline reactive stripping solutions on one side of a membrane contactor (Ahn et al., 2011; Han et al., 2005; Hasanoglu et al., 2010; Kenfield et al., 1988; Lauterböck et al., 2012; Rothrock et al., 2013). Volatile characteristics of VFAs will also allow them to diffuse across the gas-filled pores of a hydrophobic membrane into an alkaline reactive stripping solution (e.g. NaOH), where it will react with NaOH to form ions. In case of acetic acid as a model VFA, the following reaction will occur on the stripping side of the membrane contactor:

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Nomenclature

A	membrane surface area
A_C	cross sectional area perpendicular to flow
K_E	experimental overall mass transfer coefficient
K_C	calculated overall mass transfer coefficient
K_F	individual feed side mass transfer coefficient
K_M	individual membrane mass transfer coefficient
K_S	individual stripping side mass transfer coefficient
m	mass of VFA
t	time
J	flux
D_H	hydraulic diameter
$D_{A,W}$	diffusion coefficient of VFAs in water
D_{AB}	diffusion coefficient of VFAs in air
W_P	wetted perimeter
Sh	Sherwood number
Sc	Schmidt number, $\mu/(\rho D_{A,W})$
Re	Reynolds number
V	volume
V_A	molar volume of VFA
V_B	molar volume of air
m_A	molar mass of VFA
m_B	molar mass of air
T	temperature
P	pressure

Greek letters

α	membrane selectivity
ρ	density of fluid
μ	dynamic viscosity
υ	kinematic viscosity, $\upsilon = \mu/\rho$
ε	membrane porosity
τ	tortuosity factor
δ	wall thickness of the membrane

$$CH_3COOH + NaOH \rightarrow NaCH_3COO + H_2O \quad (1)$$

Acetic acid is a weak acid and NaOH is a strong base, therefore reaction (1) will occur rapidly causing acetic acid concentration in the stripping solution to be negligible. As a result of constant concentration gradient, acetic acid will continue to transfer from feed solution to stripping solution. Therefore, separation of acetic acid or other VFAs will be achievable via the use of gas-filled membranes and a reactive alkaline solution.

In recent years, research has been conducted to investigate separation/recovery of fatty acids such as acetic, propionic, and valeric acids via membrane processes. However, this is the first study conducting experimental and theoretical analysis for the separation acetic acid and VFA mixture from synthetic solution and leachate of an anaerobically fermented OFMSW. In this study, separation of VFAs from synthetic VFA solution or leachate of fermented OFMSW via the use of gas-filled hydrophobic PTFE membranes was investigated. The objectives of the work presented here were to (a) investigate the mechanism of acetic acid separation from synthetic acetic acid solution and (b) investigate VFA separation from synthetic VFA mixture and leachate of fermented organic solid waste using a counter–current flow liquid–liquid contactor.

2. Materials and methods

2.1. Membrane contactor

Membrane contactor was made of four acrylic plates, which were adjoined using Teflon wrapped stainless-steel bolts. Two of these plates were placed on the outer surfaces of the contactor and these plates only contained the inlet and the outlet ports. Two inner plates (hereafter called liquid compartments) separated by a membrane, were placed inside of the contactor and contained liquid-flow channels (width, 5 mm; depth, 3 mm). The membrane was in contact with the feed and reactive alkaline stripping solutions (pH > 12). Contactors were operated in counter-current flow mode. The liquid volume of the compartments containing feed or alkaline stripping solutions was 6.4 cm^3 each and the cross-sectional area perpendicular to liquid flow was 0.15 cm^2. Total channel length on both sides of the contactor was 35.5 cm and the surface area of the membrane in contact with liquid was 19.25 cm^2. A flat hydrophobic PTFE (Emflon PTFE membrane, Pall Co.) membrane with pore size of 0.45 μm, porosity of 77.3%, and thickness of 75 μm was used in the assays.

2.2. Experimental

Three types of feed solutions were used in the experiments; (a) 0.1 M (6000 mg/L) acetic acid, (b) VFA mixture (0.1 M acetic, 0.08 M (6000 mg/L) propionic, 0.06 M (5500 mg/L) butyric, and 0.01 M (1021 mg/L) valeric acid), and (c) leachate of a fermented organic solid waste collected from an anaerobic leach-bed reactor. Concentration of acetic acid in synthetic acetic acid solution was selected according to the observed average acetic acid concentrations in leachate of a fermented organic solid waste reported in a previous study (Cavdar et al., 2011). Similarly, types and concentrations of VFAs in the synthetic VFA mixture was selected to approximately represent the VFA types and concentrations in the leachate of the fermented organic solid waste (Cavdar et al., 2011). Three different concentrations of NaOH (0.1 N, 0.5 N, or 1.0 N) was used as a reactive alkaline stripping solution to; (a) stabilize acetic acid as sodium acetate salt to prevent the back diffusion of acetic acid to the feed side and (b) provide constant gradient among the two sides of the contactor to maintain a constant flux of VFAs. Feed and stripping solutions were introduced to two sides of the membrane contactor module from 150 mL reservoirs using a peristaltic pump (Watson Marlow 323 Du/D) at a constant flow rate. A dual head pump was used to provide and maintain identical flow rates in each side of the membrane contactor. Feed and stripping solutions in reservoirs were continuously mixed at 400 rpm in order to quickly equilibrate the solutions before being pumped into the contactor. Liquid volumes in the feed and stripping solution reservoirs were measured at the beginning and end of each assay to determine the degree of liquid transfer.

Assays were conducted in six sets; A, B, C, D, E, and F. In assays A to D, 0.1 M synthetic acetic acid solution was used as a feed solution. In assay A, the aim was to determine the effect of NaOH concentration on the flux, selectivity, and overall mass transfer coefficient of acetic acid; therefore, three different NaOH concentrations were tested as a stripping solution. In assay A, flow rate of the feed and the stripping solutions was 31.5 ± 0.9 mL/min, and the pH of the feed solution was around 3 in all the experiments (Table 1). In assay B, pH of the feed solution was adjusted to 5.45 with the intention of determining the effect of feed pH on the acetic acid separation efficiency (Table 1). In assay B, 0.5 N NaOH was