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Journal of Membrane Science 277 (2006) 129–136
journal of MEMBRANE SCIENCE
www.elsevier.com/locate/memsci

Membrane air-stripping of aroma compounds

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Received 18 July 2005; received in revised form 11 October 2005; accepted 17 October 2005
Available online 21 November 2005

Abstract

The selective extraction of aroma compounds from a highly diluted aqueous feed by membrane air-stripping (MAS) was studied. The pilot-scale apparatus used for this study was made of a hollow fiber membrane contactor coupled with a multi-step condensation unit. The aqueous feed model solution containing 10 aroma compounds (at $\sim 2 \times 10^{-2}$ kg m^{-3} each) cross-flowed on the shell side of the membrane and air flowed in the lumen of the hollow fibers. The impact of operating conditions (hydrodynamic conditions of aqueous feed and stripping air phases) on mass transfer was investigated and modeled. The limiting step of mass transfer was identified: the transfer in the gas boundary layer always represents the major resistance to mass transfer. However, its contribution depends on the volatility of the aroma compound (from 68% to 100% for dimethyldisulfide, where $H = 65.2 \times 10^{-3}$ at 298 K, and from 98% to 100% for hexanol, where $H = 1.15 \times 10^{-3}$ at 298 K, depending on the operating conditions). The global efficiency of the process was then evaluated. It showed that MAS coupled with multi-step condensation made it possible to extract aroma compounds of intermediate volatility (Henry's law constant, $H \sim 3 \times 10^{-2}$) with a high recovery yield (>90%) and a high selectivity over water (>1500). Moreover, molecules with lower volatilities ($H < 1 \times 10^{-3}$) are almost not ever extracted (recovery yield <5%), which makes this technology highly effective for the selective extraction of aroma compounds with intermediate volatility from aqueous streams.

Keywords: Membrane air-stripping; Hollow fiber membrane contactor; Multi-step condensation; Volatile organic compound; Mass transfer

1. Introduction

Aroma extracts are widely used in the food industry to improve the flavor of formulated foods or to compensate for the flavor losses of natural raw products during industrial processing. Food industries and aroma manufacturers are thus seeking technologies that allow the selective extraction of aroma compounds from odorous wastewater. Aroma compounds are small molecules (MW < 300 g mol^{-1}) with varying degrees of volatility and hydrophobicity. Distillation and liquid/liquid extraction, based on the volatility and hydrophobicity of the molecules to be extracted, respectively, cover the majority of industrial applications [1].

However, these techniques suffer from several limitations, which has led to the search for a highly efficient and low-cost alternative technology. This technology must be able to operate at moderate temperatures because of the heat-sensitivity of some of the aroma compounds, and the need for low-energy consumption. It must avoid the use of chemical products that can be harmful for the consumer. Moreover, this technology has to be compact in order to be easily integrated into existing process designs. Compactness and low-energy consumption are characteristic of membrane processes. Consequently, they have been investigated in this paper as a potentially promising technique. Concerning the extraction of volatile organic compounds (VOCs) or, more particularly, aroma compounds, recent studies show the advantages of using membrane contactors. According to Gabelman and Hwang [2], a membrane contactor is a device that achieves liquid/liquid or gas/liquid mass transfer without dispersion of one phase into another. As a consequence, the extracting phase can either be an organic solvent [3,4] (or edible oil [5]), vacuum [6], air [7,8] or even a dense gas [9–11].

The objective of this paper is based on the understanding of aroma compound transfer in a membrane air-stripping (MAS) pilot plant made up of a hollow fiber membrane contactor (HFC) coupled with a multi-step condensation system. Hollow fiber geometry was chosen because it offers a high degree of compactness and a large interfacial exchange area. The condensation system is known for its efficiency in recovering diluted aroma compounds in a gas [12,13] and adds selectivity to the global

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doi:10.1016/j.memsci.2005.10.023

separation. A highly diluted model solution made of 10 aroma compounds in water (cross-flowed on the shell side) was stripped by air (flowed in the lumen of the hollow fibers). The impact of operating conditions (aqueous feed temperature, aqueous feed and air-stripping hydrodynamic conditions) and the physico-chemical properties of the molecules on mass transfer were studied. Modeling of mass transfer has been proposed using a resistances-in-series approach. Finally, the efficiency of the MAS/multi-step condensation was discussed.

2. Theory

MAS is a concentration-driven operation. As a result, the mass transfer rate of a compound ($\dot{m}$, kg s^{-1}) can be defined by Eq. (1):

$$\dot{m} = K_f A_f (C_f - C_f^*) \tag{1}$$

where K_f is the overall mass transfer coefficient of the compound based on the aqueous feed phase concentration (m s^{-1}), A_f the outer surface area of the fibers (m^2) since the aqueous feed phase cross-flows on the shell side, C_f the concentration of the compound in the aqueous phase (kg m^{-3}) and C_f^* is the concentration at the air–liquid interface (kg m^{-3}). C_f^* is an equilibrium concentration in the liquid phase and can be expressed through the Henry's law constant, or the air–liquid partition coefficient, defined as:

$$H = \left[\frac{C_s}{C_f}\right]_{\text{at equilibrium}} \tag{2}$$

where H is the dimensionless (kg m^{-3}/kg m^{-3}) Henry's law constant and C_s^* is the equilibrium concentration (kg m^{-3}) of the compound in the gas.

Determining K_f leads to a quantification of the efficiency of the extraction process for each molecule, independently of the driving force. The method used to calculate K_f was previously described by Mahmud et al. [14].

According to Mahmud et al. [15], the change in aroma compound concentration of the solution in an ideal separator (completely mixed feed reservoir) of a batch MAS system as a function of time can be described by the following linear relationship:

$$\ln\left(\frac{C_f(t=0)}{C_f(t)}\right) = \alpha t \tag{3}$$

α is determined using Eq. (3) from the slope of the plot of $\ln[C_f(t=0)/C_f(t)]$ versus t. Substituting the value of α in the following equation (Eq. (4)) provides the overall aqueous feed phase-based mass transfer coefficient (K_f) for the system, when stripping air and aqueous feed streams are on the lumen and the shell side, respectively [15]:

$$K_f = \frac{\bar{u}_f}{aL}\left(\frac{Q_s'}{Q_s' - Q_f}\right)\ln\left[\left(\frac{Q_f}{Q_s'}\right)\left(\frac{Q_s' - V_f\alpha}{Q_f - V_f\alpha}\right)\right] \tag{4}$$

where $\bar{u}_f$ is the aqueous feed mean velocity on the shell side (m s^{-1}), a the specific surface corresponding to the surface to volume ratio (m^2 m^{-3}), L the hollow fiber length (m), Q_f the aqueous feed flow rate (m^3 s^{-1}), Q_s' (defined as the ratio Q_s/H) the stripping capacity (m^3 s^{-1}), Q_s the stripping air flow rate (m^3 s^{-1}) and V_f is the volume of the aqueous feed reservoir (m^3).

2.1. Mass transfer coefficient modeling

Mass transfer in MAS involves three sequential steps. First, molecules diffuse from the bulk of the liquid phase through the liquid boundary layer, and then into the air-filled pores (or, eventually, through partially liquid-filled pores [14]) and, finally, diffuse through the gas film. The overall mass transfer resistance is hence the combined effect of these three separate local mass transfer resistances. Since mass transfer resistances are considered to be proportional to the inverse of the corresponding mass transfer coefficients, the overall liquid phase-based mass transfer resistance ($1/K_f$) can be expressed as follows:

$$\frac{1}{K_f A_f} = \frac{1}{A_f k_f} + \frac{1}{\overline{A_m} k_m H} + \frac{1}{A_s k_s H} \tag{5}$$

where k_f, k_m and k_s are the local mass transfer coefficients (m s^{-1}) in the aqueous feed phase, in the membrane and in the stripping gas phase, respectively, A_s the inner membrane surface area (m^2) since air flows in the fibers and $\overline{A_m}$ is the mean surface area of the membrane (m^2). Local mass transfer coefficients can then be estimated using correlations based on dimensionless numbers.

When the aqueous feed flows on the shell side, a modified form of the Kreith and Black [16] correlation originally developed for heat transfer in cross-flow heat exchangers can be used to determine the local aqueous feed mass transfer coefficient:

$$k_f = 0.39 D_w^{0.67} \nu_w^{-0.26} \bar{u}_f^{0.59} d_h^{-0.41} \tag{6}$$

where D_w is the diffusion coefficient of the compounds in water (m^2 s^{-1}), ν_w the kinematic viscosity of water (m^2 s^{-1}) and d_h is the hydraulic diameter of the hollow fiber (m).

Considering the work of Kiani et al. [17] on membrane-based solvent extraction, the membrane mass transfer coefficient is predicted as:

$$k_m = \frac{D_a \varepsilon}{\tau e} \tag{7}$$

where D_a is the diffusion coefficient of the compound in air (m^2 s^{-1}) as it fills the pores of the membrane, ε and τ the membrane porosity (dimensionless) and tortuosity (dimensionless), respectively, and e is the membrane thickness (m). The diffusion mechanism of the aroma compounds in the membrane pores can be considered as molecular diffusion since Knudsen diffusion is negligible. Mahmud et al. [14] have proposed the introduction of a correction factor in the previous equation in order to take the presence of water in the pores of the membrane into account.

The local mass transfer coefficient in the fibers can be predicted using the Graetz solution, when $Gz \rightarrow 0$, which corresponds to the conditions of this study [18]:

$$k_s = 0.5 \frac{d_i u_s}{L} \tag{8}$$