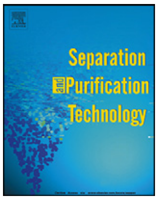
Separation and Purification Technology 69 (2009) 48–56

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Phenol recovery with tributyl phosphate in a hollow fiber membrane contactor: Experimental and model analysis

S.F. Shen[a], K.H. Smith[a], S. Cook[a], S.E. Kentish[a], J.M. Perera[a], T. Bowser[b], G.W. Stevens[a,*]

[a] *The Particulate Fluids Processing Centre, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia*
[b] *GlaxoSmithKline, Princes Highway, Port Fairy 3284, Australia*

ARTICLE INFO

Article history:
Received 11 March 2009
Received in revised form 25 June 2009
Accepted 25 June 2009

Keywords:
Membrane contractor
Hollow fiber membrane
Mass transfer coefficient
Phenol
Tributyl phosphate

ABSTRACT

The extraction and stripping of phenol using a solution of tributyl phosphate in kerosene in a hydrophobic polypropylene hollow fiber membrane contactor has been studied. The effect of the aqueous and the organic phase flow rates on the overall mass transfer coefficient for both extraction and stripping steps was investigated. Experimental values of the overall mass transfer coefficient were determined and compared with predicted values from the resistance in series model. Results showed that the overall mass transfer coefficients for extraction were about one order of magnitude greater than those measured during the stripping process. The experimental values were in good agreement with the predicted values for the extraction module. However, the predicted values were slightly overestimated for the stripping module. The individual mass transfer resistances were analyzed and the rate-controlling steps of mass transfer were also identified in both extraction and stripping modules. The major resistance in extraction and stripping was in the aqueous phase and in the membrane phase, respectively.

1. Introduction

Phenol and its derivatives are often present in the wastewater discharged of manufacturing processes such as in the petrochemical and agrochemical industries and in coal gasification wastewaters. Due to their potential harm to human health, most are listed as priority pollutants by the US Environmental Protection Agency [1]. Therefore, treatment processes must often be implemented before the waste streams can be safely discharged.

One of the most widely used methods of removing phenol is liquid–liquid extraction using esters, alcohols [1,2], alkylamines [3] and trialkylphosphine oxides [4] as extractant solvents. The use of tributyl phosphate (TBP) as an extractant is the focus of the present work. Compared to other solvents, TBP shows good extraction performance, has low solubility in water, a high flash point which lowers the flammability potential and is relatively inexpensive [5,6]. Phenol forms a complex with TBP as a solvating reagent as follows [6]:

$$C_6H_5OH + TBP = C_6H_5OH{\cdot}TBP \qquad (1)$$

Solvent extraction is conventionally conducted in devices such as mixer-settlers and pulsed plate columns. However, these devices exhibit important drawbacks associated with the dispersion of the two phases, such as emulsion formation and organic phase carryover. As a result, the wastewater streams can become contaminated by these organic chemicals, which are often equally as polluting. These problems can be substantially eliminated using membrane contactors [7].

The use of hollow fiber membrane contactors for non-dispersive solvent extraction has been extensively studied for many applications [7–11]. In this case, the interface between the aqueous and the organic phases is stabilized within the pores of the polymer membrane. There are many advantages associated with this non-dispersive configuration: they are highly compact devices with large specific surface area; the dispersion-free operation eliminates emulsion formation, phase entrainment and downstream phase separation; there is no limitation on the phase flow rate ratio; no need for density differences between the extractant and stripping phases; and there is greater flexibility in equipment configuration. Compared to dispersive extraction devices, the main drawback is the additional membrane resistance which lowers the overall mass transfer rate. However, this can be successfully offset by the greater interfacial mass transfer area found within a hollow fiber membrane unit [7].

In the literature, many researchers have studied solvent-based phenol recovery within hollow fiber membrane contactors [11–21]. However, the use of tributyl phosphate (TBP) as a phenol carrier in such a configuration has not been investigated. Further, there are conflicting reports on the use of empirical correlations for estimating the shell side mass transfer coefficient within such a hollow

---

[*] Corresponding author. Tel.: +61 3 83446621; fax: +61 3 8344 8824.
E-mail address: gstevens@unimelb.edu.au (G.W. Stevens).

1383-5866/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2009.06.024

fiber contactor [11,16,18,20,21]. The aim of this study is to identify the rate-limiting step for phenol extraction with TBP and to develop a reliable model for predicting the extraction and stripping performance in a hydrophobic hollow fiber membrane contactor. In order to do this, distribution ratios were determined for a system with 10% (v/v) TBP/Shellsol2046 as the extractant and sodium hydroxide (NaOH) as the stripping agent. The effect of phase flow rates on the overall mass transfer coefficient for both the extraction and stripping steps were studied and compared with predicted values obtained from the mass transfer model.

Nomenclature

A	membrane area of mass transfer (m^2)
c	phenol concentration ($g\,L^{-1}$)
D	distribution ratio
d_{in}	inner diameter of hollow fiber membrane (m)
d_h	the hydraulic diameter of shell side (m)
d_{lm}	logarithmic mean diameter of hollow fiber (m)
d_{out}	outer diameter of hollow fiber membrane (m)
D_{aq}	diffusivity of phenol in the aqueous phase ($m^2\,s^{-1}$)
D_{org}	diffusivity of the organic phase ($m^2\,s^{-1}$)
F_i	fractional resistance (%)
J_{sol}	phenol mass transfer flux ($g\,s^{-1}$)
k	local mass transfer coefficient ($m\,s^{-1}$)
K	overall mass transfer coefficient ($m\,s^{-1}$)
K_{eq}	the equilibrium constant of chemical reaction (Eq. (6))
l	length of hollow fiber (m)
M	molar concentration ($kmol\,m^{-3}$)
Q	defined in Eq. (5)
Q_{aq}	flow rate of the aqueous phase ($m^3\,s^{-1}$)
Q_{org}	flow rate of the organic phase ($m^3\,s^{-1}$)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
t	time (s)
V	defined in Eq. (4)
V_{aq}	volume of the aqueous phase (m^3)
V_{org}	volume of the organic phase (m^3)
Greek letters	
δ	membrane thickness (m)
ε	membrane porosity
μ	viscosity ($kg\,m^{-1}\,s^{-1}$)
ρ	density ($kg\,m^{-3}$)
τ	tortuosity of membrane pores
σ	interfacial tension ($N\,m^{-1}$)
θ	the contact angle
Φ	the packing fraction of membrane contactor
β	the constant, defined in Eq. (15)
γ	defined in Eq. (2)
Subscripts	
aq	aqueous
m	membrane
org	organic
s	shell
t	tube
Superscripts	
*	the equilibrium concentration between two phases
0	the initial concentration

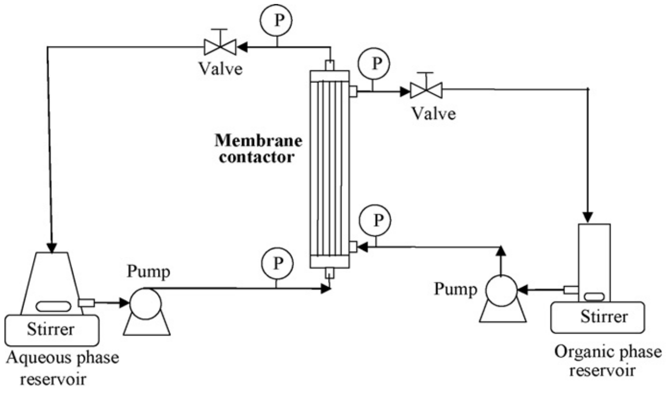


Fig. 1. Schematic diagram of experimental set-up for phenol extraction and stripping.

2. Theory

2.1. Overall mass transfer coefficient calculation

The transfer of phenol from the aqueous phase to the organic phase during the extraction process can be described in terms of the overall mass transfer coefficient, K_{aq}, which is defined by

$$J_{sol} = K_{aq}A(c_{aq} - c^*_{aq}) \tag{2}$$

where J_{sol} is the phenol flux, A is the effective interfacial area, c_{aq} is the concentration of phenol in the aqueous solution at time t, and c^*_{aq} is the equilibrium concentration of phenol in the aqueous phase.

By making an unsteady state mass balance and assuming a constant distribution ratio, K_{aq} can be determined from concentration of phenol in the aqueous phase with time [12,22,23]. The equations for recirculating co-current flow as shown in Fig. 1 are

$$c_{aq} = \frac{Vc^0_{aq}}{1+V} + \frac{c^0_{aq}}{1+V}\exp(-\gamma t) \tag{3}$$

$$K_{aq} = \frac{-Q_{aq}}{(1+Q)A_m}\ln\left[1-\gamma\left(\frac{V_{aq}}{Q_{aq}}\right)\left(\frac{1+Q}{1+V}\right)\right] \tag{4}$$

$$V = \frac{V_{aq}}{V_{org}\times D} \tag{5}$$

$$Q = \frac{Q_{aq}}{Q_{org}\times D} \tag{6}$$

c^0_{aq} is the initial concentration in the aqueous feed solution. Q_{aq} and Q_{org} are the aqueous and organic phase flow rates, respectively. V_{aq} and V_{org} are the volumes of the aqueous and organic phases. A_m is the effective interfacial area, γ is the fitting coefficient, that is a function of flowrate, volume of solvent and mass transfer coefficient, and D is the distribution ratio.

In the stripping process, the transfer of phenol from the organic phase back to the aqueous phase involves the following chemical reaction [16,19]

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O \tag{7}$$

The phenol flux for stripping can be expressed based on the permeation model of such a stripping process as follows [8,11,16]:

$$J_{sol} = K_{org}A(c_{org} - c^*_{org}) \tag{8}$$

where J_{sol}, $mol\,s^{-1}$, can be calculated from the slope of the linear part of the stripping curves multiplied by the volume of the organic phase. K_{org} is the overall mass transfer coefficient. A is the effective area of mass transfer based on the inside diameter of hollow fiber membrane and c_{org} is the bulk concentration of phenol in the organic phase at time t and c^*_{org} is the concentration of phenol in