Isopropanol Removal from Pharmaceutical Process Wastewater with Combination of Distillation and Pervaporation

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Abstract
The research is motivated by an industrial problem, that is isopropanol (IPA) removal from pharmaceutical process wastewater. To complete the target hybrid treatment is investigated. Isopropanol dehydration with combination of distillation and hydrophilic pervaporation (PV) is used. The goal of this research is to rigorously model and optimize this hybrid treatment in professional flowsheet simulator environment. The number of minimal theoretical stages of distillation column and minimal membrane transfer area are determined. Considering the results, it can be concluded that, the distillation and pervaporation methods are suitable for separation isopropanol and water in min. 99.5 weight percent purity (m/m%).

Keywords
Isopropanol removal; modelling; mrocess wastewater; mydrophilic pervaporation; distillation

INTRODUCTION

The industrial application of pervaporation separation has been increasing in recent decades, thanks to traditional separation techniques (distillation, absorption, etc.), while ensuring lower energy consumption and high selectivity. One of the main areas of application of liquid mixtures is the dehydration of the various aqueous azeotropic solvent mixtures. Separation can be carried out without the addition of an extra component, the recovered solvent and process wastewater can be recycled, so that pervaporation is an environmentally friendly process (Toth, 2018; Toth et al., 2018).

Alcohol and water separation is a well-known method of pervaporation method in chemical and environmental sector. It can be mentioned isopropanol forms minimal boiling azeotropic mixture with water, which means separation problem. Isopropanol (IPA) content above ~88 m/m% can not be achieved with conventional distillation processes (Marsden, 1954; Gmehling et al., 1978). If the azeotropic composition can be approached with distillation, then the distillate product (D) can be further purified using pervaporation dehydration (Szabados et al., 2018; Toth, 2019).

e 1 (NRTL model).

Pervaporation can be characterized by certain quantities and factors. The flux is calculated using the following equation (Huang et al., 2014):

$$J_i = \frac{P_i}{\Delta t \cdot A}, \quad (1)$$

where P_i is the partial weight of component i in the permeate, t is the time of duration of experiment and A is the membrane area. Separation factor is calculated by the following equation:

$$\alpha = \frac{y_i(1-x_i)}{x_i(1-y_i)}, \quad (2)$$

where α is separation factor (dimensionless), x_i is weight fraction of ethyl acetate in feed and y_i is weight fraction of ethyl acetate of permeate (Toth et al., 2015).

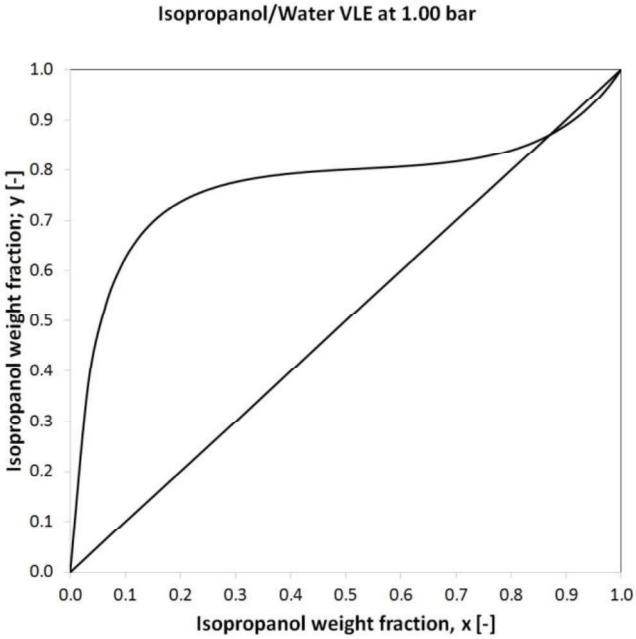

Figure 1. Vapour-liquid equilibrium of IPA-Water mixture

An essential tool for designing and optimizing separation processes is the appropriate computer modelling, which as accurate as possible model is needed (Rautenbach et al., 1990; Wijmans and Baker, 1995; Baker, 2012; Luis and Van der Bruggen, 2015; Csizmadia and Till, 2018). Model parameter estimation is achieved using laboratory experiments (Toth et al., 2018).

Hydrophilic pervaporation is able to dehydrate alcohol compounds. The polyvinyl alcohol (PVA) is among the most interesting and promising membranes for hydrophilic pervaporation and it has been extensively investigated. Table 1 shows some PVA hydrophilic membranes for isopropanol-water separation.

Table 1. PVA membranes for isopropanol dehydration

PVA membrane type	x_{IPA} [m/m%]	J [g/m^{2}h]	α [-]	Ref.
1PVA/Silicalite-1 (5 wt.%)	90	38	11240	Adoor *et al.* 2007
2PVA/Silicalite-1 (10 wt.%)	90	26	17990	Adoor *et al.* 2007
3PVA/ZSM-5 zeolite (Si/Al = 25, 20 wt.%)	90	631	2014	Huang *et al.* 2019
4Hybrid PVA	90	18	1570	Sajjan *et al.* 2013
530 mass% GTMAC/PVA	90	190	1575	Sajjan *et al.* 2013
620 mass% GTMAC/PVA	90	165	1262	Sajjan *et al.* 2013
710 mass% GTMAC/PVA	90	132	1073	Sajjan *et al.* 2013
8PVA + TEOS	90	96	913	Sajjan *et al.* 2013
940 mass% GTMAC/PVA	90	325	417	Sajjan *et al.* 2013
10SA/PVA (50:50)	90	36	117	Kurkuri *et al.* 2002
11PVA with glutaraldehyde	90	191	115	Burshe *et al.* 1997
12Pervap 2201, PVA membrane	80	4	604	Molina 2003

MATERIAL AND METHODS

In the pharmaceutical sector it is an actual problem that IPA should be separated from an aqueous mixture (Nangare et al., 2017; Cheng et al., 2018). PWW from pharmaceutical industry has to be separated with the following initial composition: 5 m/m% IPA and 95 m/m% water. The product purity is 99.5 m/m% in both cases and 800 kg/h PWW must be treated. Before optimization, laboratory experiments have to be carried out.

The experimental set-up is a P-28 membrane unit from CM-Celfa Membrantechnik AG (see Figure 2 and Figure 3). The flat sheet membrane with 28 cm^2 effective area is placed on a sintered disc separating the feed and the permeate sides. Cross-flow circulation velocity is kept at a permanent value of ~182 l/h (Toth and Mizsey, 2015).

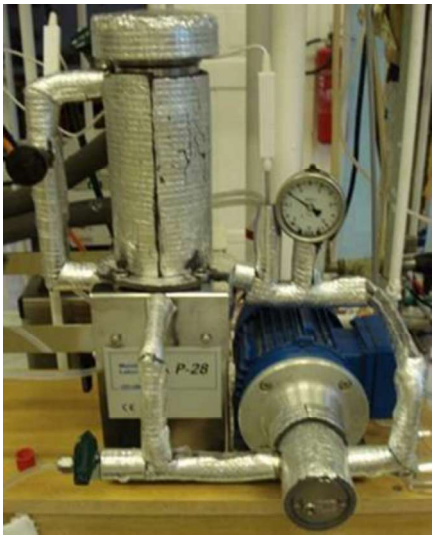

Figure 2. Photo of CM-Celfa Membrantechnik AG P-28 universal test membrane apparatus (Toth, 2015)

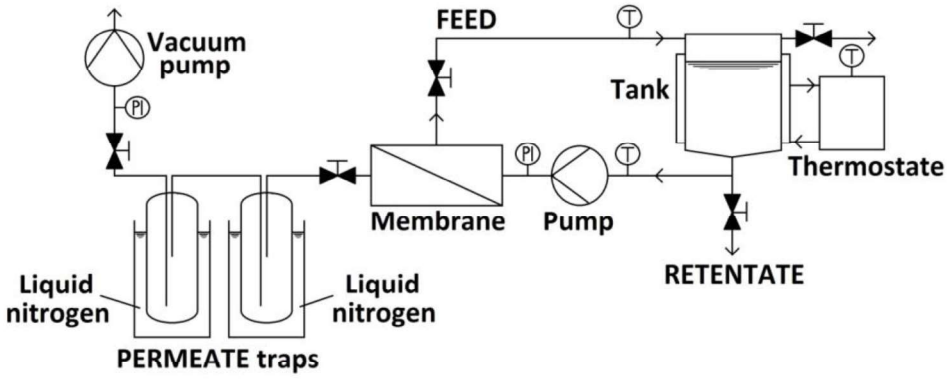

Figure 3. Schematic figure of CM-Celfa P-28 pervaporation unit (Toth and Mizsey, 2015)

The vacuum on the permeate side is maintained with VACUUMBRAND PC2003 VARIO vacuum pump and kept at 2 Torr (2.67 mbar). The isotherm conditions are assured with a thermostate and monitored with thermometers at the inlet and outlet of the unit. The permeate is collected in two traps connected in series and cooled with liquid nitrogen to prevent loss of the permeate. The ethyl

acetate content is measured with Shimadzu GC-14B gas chromatograph. The water content of organophilic experiments are measured with Hanna HI 904 coulometric Karl Fischer titrator (Toth et al., 2015).

According to the methodology of Valentínyi et al. (2013) the pervaporation can be described with the following semi-empirical model:

$$J_i = \frac{1}{1+\{[\bar{D}_i \cdot exp(B \cdot x_{i1})]/(Q_0 \cdot p_{i0} \cdot \bar{\gamma}_i)\}} \cdot \frac{[\bar{D}_i \cdot exp(B \cdot x_{i1})]}{\bar{\gamma}_i} \cdot \left(\frac{p_{i1} - p_{is}}{p_{i0}}\right) \qquad i = (1, \ldots, k) \quad (3)$$

The model is an improvement of Rautenbach's model (Rautenbach *et al.* 1990) and it considers the concentration dependencies of the transport coefficient. Four parameters of this model are estimated based on our measured data: transport coefficients (D_i), permeability coefficients (Q_0), activation energies (E_i) and B parameter. The estimations are completed with the STATISTICA® program environment (Andre et al., 2018; Haaz and Toth 2018).

Professional flowsheet simulator is applied for separation of isopropanol-water mixture. First step, PWW is pumped into the middle of the distillation column and pervaporation separates further the IPA-rich intermediate product. It can be determined the suitable water can be received as bottom product (W) of distillation. Actually it is the purified PWW. The isopropanol substance can be appropriate using this hybrid method as retentate (R) of pervaporation dehydration.

Additional apparatuses are also needed for PV process (Toth et al., 2015). The temperature and the pressure must be increased for the operational level prior to the first membrane unit, because the feed (F) has atmospheric conditions, 20 °C and 1 bar. Permeate (P) streams leaving the pervaporation units are collected, mixed, condensed with cooler and its pressure is increased again from vacuum with pump. The applied feed temperature in membrane modules is 70°C. Feed and permeate pressures are the following, 3 bar and 0.008 bar. UNIQUAC thermodynamic model is applied in the case of SCDS distillation column and exponential Rautenbach model (Valentínyi et al., 2013) for the pervaporation.

ChemCAD professional flowsheet simulator is used for the investigation of hybrid separation (see Figure 4).

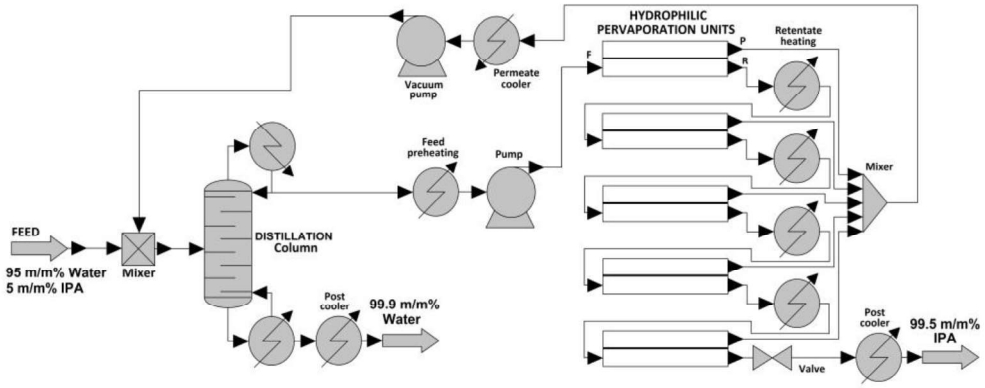

Figure 4. Flowsheet of isopropanol-water separation with distillation and hydrophilic pervaporation

RESULTS AND DISCUSSION

Results of simulations with distillation and hydrophilic PV process are listed in Table 2.

Table 2. Optimized results of ethanol-water separation

	Distillation			Pervaporation	
	F	W	D	P	R
IPA [m/m%]	5	0.1	86	1	99.5
Water [m/m%]	95	99.9	4	99	0.5

Figure 5 shows the isopropanol concentrations of retentate stream in the function of membrane module numbers.

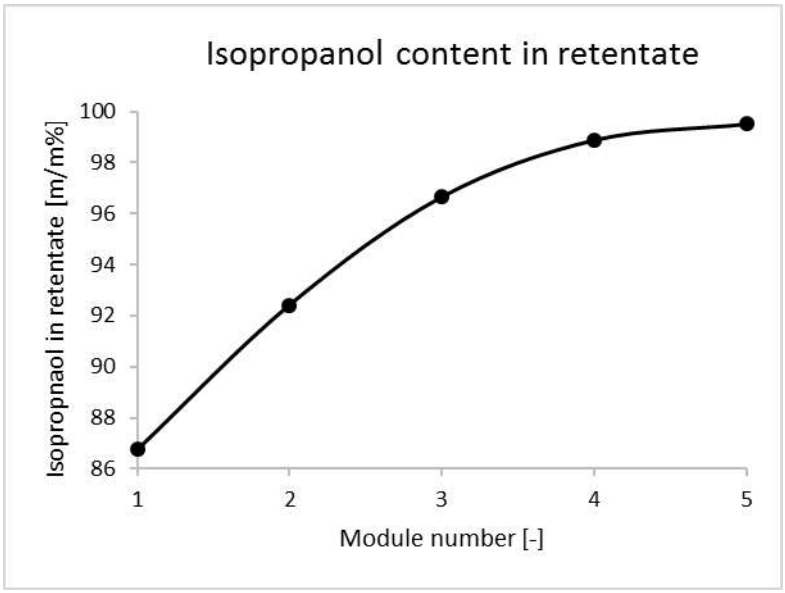

Figure 5.Isopropanol concentration in retentate stream

It can be seen 5 membrane module is sufficient for reach the enrichment limit, which is 99.5 m/m% isopropanol. The optimized column has 25 theoretical plates and the reflux ratio is 1 in the optimized case. 90 m^2 effective membrane transfer area is required for removal IPA from PWW.

SUMMARY

The combination of distillation and pervaporation dehydration is investigated in professional flowsheet environment. It can be concluded isopropanol-water mixture can be separated into pure components with this hybrid operation. The goal composition, which is 99.5 m/m% in both product case can be reached.

ACKNOWLEDGEMENT

This work was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences, ÚNKP-19-4-BME-416 New National Excellence Program of the Ministry for Innovation and Technology, OTKA 112699 and 128543. This research was supported by the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, aimed to promote the cooperation between the higher education and the industry. The research reported in this paper has been supported by the National Research, Development and Innovation Fund (TUDFO/51757/2019-ITM, Thematic Excellence Program). The authors thank the members of Environmental and Process Engineering Research Group (http://www.envproceng.eu/en/home-en/) for their help.

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