Separation and Purification Technology 172 (2017) 277–284

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Continuous dialysis of mixture of inorganic acids

Zdeněk Palatý *, Helena Bendová

Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

ARTICLE INFO

Article history:
Received 14 July 2016
Received in revised form 16 August 2016
Accepted 16 August 2016
Available online 19 August 2016

Keywords:
Diffusion dialysis
Anion-exchange membrane
Sulphuric acid
Phosphoric acid
Continuous dialyzer

ABSTRACT

The simultaneous transport of sulphuric and phosphoric acids through a polymeric membrane was investigated at steady state in a two-compartment counter-current dialyzer. For this purpose, an anion-exchange membrane Neosepta-AFN (Astom Corporation, Tokyo, Japan) was used. This transport was quantified by four membrane mass transfer coefficients which are dependent upon the concentrations of both acids in the feed. These coefficients were determined by a two-step procedure. In the first step, the basic differential equations describing the dependences of the volumetric liquid flow rates and acid concentrations on the length coordinate in the individual compartments were numerically integrated. In the second step, an objective function was minimised to ensure the best coincidence between the experimental and calculated data.

1. Introduction

Diffusion dialysis, which belongs to a group of promising separation processes, is preferably used to recover inorganic acids from acid waste waters generated in steel, metal-refining and electroplating industries. Its main advantage is a high acid recovery yield, high rejection of metals, low environmental impact and low consumption of energy. The only energy is that ensuring the transport of liquid streams into a dialyzer. On the other hand, diffusion dialysis is a very slow process due to the fact that its controlling step is the transport of components through the membrane by diffusion.

In order to determine process characteristics, two types of equipment are used, i.e., a batch cell [1–10] and continuous dialyzer [11–20]. In the former case, the data on time dependences of the liquid volumes and component concentrations in the individual compartments are treated, while in the latter case, the characteristics are calculated from the volumetric liquid flow rates and concentrations of all streams at steady state.

The anion-exchange membranes Neosepta-AFN and Selemion DSV were used in the separation of acetic and propionic acids from their sodium salts by Narębska and Staniszewski [1]. Xu and Yang [2] prepared a series of anion-exchange membranes from poly(2,6-dimethyl-1,4-phenylene oxide) by bromination, chloromethylation and amination, which were used in the recovery of sulphuric acid from titanium white waste liquor. Palatý and Bendová [3] reported on the separation of aqueous solutions of $HCl + FeCl_2$ by an anion-exchange membrane Neosepta-AFN. The experiments revealed that this membrane is a good separator for $HCl + FeCl_2$ mixture—ferrous chloride was efficiently rejected while hydrochloric acid passed well through the membrane. Xu et al. [4] investigated the recovery of H_2SO_4 from waste anodic aluminium oxidation solutions using the diffusion dialysis process both in a batch and continuous dialyzer equipped with a commercial polymeric membrane DF-120. Recently [5], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-SiO_2 hybrid membranes were synthesised and successfully used in the recovery of hydrochloric acid from its mixture with ferrous chloride. The experiments in a batch cell proved that the separation factor of commercial polymeric membrane DF-120 was much lower than that of hybrid membrane. In literature [6], the same research group presented results on diffusion dialysis of different inorganic acids in the presence of their sodium salts, i.e., $HCl + NaCl$, $H_2SO_4 + Na_2SO_4$ and $H_3PO_4 + Na_3PO_4$ in a batch dialyzer. For this purpose, a novel organic/inorganic hybrid membrane was used. The simultaneous transport of nitric acid and sodium nitrate was investigated in a batch cell by Palatý and Bendová [7]. In this paper, the transport of the individual components was quantified by four concentration dependent phenomenological coefficients. Wang et al. [8] prepared and tested polyelectrolyte complexes/polyvinyl alcohol membranes. Authors proved that these membranes can be applied for both acid and alkali recovery through the diffusion dialysis process. Luo et al. [9] investigated diffusion dialysis of hydrochloric acid in the presence of their different metal salts (systems: $HCl + NaCl$, $HCl + FeCl_2$, $HCl + NiCl_2$, $HCl + CuCl_2$, $HCl + ZnCl_2$, and $HCl + AlCl_3$) using a novel organic/inorganic hybrid membrane. Errosion effects of $HCl + FeCl_2$ solutions on the membrane structure during the diffusion dialysis process were investigated by Mao et al. [10]. The tests were carried

* Corresponding author.
E-mail address: Zdenek.Palaty@upce.cz (Z. Palatý).

http://dx.doi.org/10.1016/j.seppur.2016.08.020
1383-5866/

Nomenclature

A	membrane area, m^2
A_{ik}	($i = A, B$; $k = 1, 2$) coefficients in Eq. (17), kmol m^{-3}
$A_{ij,k}$	($i = A, B$; $j = A, B$; $k = 1, 3$) constants in Eq. (15), m^3 $kmol^{-1}$
$A_{ij,k}$	($i = A, B$; $j = A, B$; $k = 2, 4$) constants in Eq. (15), m^6 $kmol^{-2}$
a_0	constant in Eq. (16)
a_1	constant in Eq. (16), m^3 $kmol^{-1}$
a_2	constant in Eq. (16), m^6 $kmol^{-2}$
b_{i1}	constants in Eq. (18), kmol m^{-3}
b_{i2}	constants in Eq. (18)
b_{i3}	constants in Eq. (18), m^3 $kmol^{-1}$
b_{i4}	constants in Eq. (19), kmol m^{-3}
b_{i5}	constants in Eq. (19)
b_{i6}	constants in Eq. (19), m^3 $kmol^{-1}$
b_{i7}	constants in Eq. (20)
b_{i8}	constants in Eq. (20), m^3 $kmol^{-1}$
b_{i9}	constants in Eq. (20), m^6 $kmol^{-2}$
C	constant in Eq. (12)
c	molar concentration, kmol m^{-3}
D	diffusion coefficient, m^2 s^{-1}
d	width of compartment, m
d_e	$(= 2d\delta(d + \delta))$ equivalent diameter, m
F	objective function
f	general function
J	flux, kmol m^{-2} s^{-1}
k_{ij}	($i = A, B$; $j = A, B$) membrane mass transfer coefficients, m s^{-1}
$k_{ij,0}$	($i = A, B$; $j = A, B$) constants in Eq. (15), m s^{-1}
k_L	liquid mass transfer coefficient, m s^{-1}
M	molar mass, kg $kmol^{-1}$
n	number of experiments
p_i	($i = A, B$) coefficients in Eq. (17)
Re	$(= ud_e/\nu)$ Reynolds number
Sc	(νD) Schmidt number
Sh	$(= k_L d_e/D)$ Sherwood number
u	liquid flow rate, m s^{-1}
$\dot{V}$	volumetric liquid flow rate, m^3 s^{-1}
x_{i0}	($i = A, B$) coefficients in Eq. (17), kmol m^{-3}
z	length coordinate, m
z_T	total height of compartment, m
δ	thickness, m
ν	kinematic viscosity, m^2 s^{-1}
ρ	density, kg m^{-3}
Ψ	partition coefficient

Superscripts and subscripts

A	referred to component A, i.e., H_2SO_4
B	referred to component B, i.e., H_3PO_4
$calc$	calculated
exp	experimental
f	solution/membrane interface
in	inlet
M	referred to membrane
out	outlet
w	referred to solvent
I	referred to compartment I
II	referred to compartment II

out with commercial membranes DF-120 and 9010, and the membranes based on quartenised poly(2,6-dimethyl-1,4-phenylene oxide and polyvinyl alcohol. Oh et al. [11] experimentally studied diffusion dialysis to investigate the effect of metal ions on its performance for recovery of acids. It was found that formation of complexes affected the selectivity of this separation due to the existence of complexes bearing negative charges. Xu and Yang [12] experimentally proved that mixed acid (HNO_3 + HF) can selectively be separated from the spent liquor containing mainly HNO_3, HF and titanium ions by diffusion dialysis. The results showed that this separation is strongly affected by the membrane water content and ion-exchange capacity. Another experiments with surface cross-linked PPO anion-exchange membranes used in the recovery of sulphuric acid and nickel from electrolysis spent liquor proved that nickel leakage can be controlled within 4%, whereas the recovery of acid can reach 66–72% [13]. Literature [14] presents the results on the recovery of hydrochloric acid from HCl + $FeCl_2$ mixture and real acid waste solution containing hydrochloric acid, Fe^{2+} and Zn^{2+} ions. In the case of real solution, it was proved that the acid recovery yield was higher than 88%, while that of Fe^{2+} ions was in the limits from 11% to 23%. On the other hand, a high leakage of Zn^{2+} ions through the membrane was observed, i.e., over 56%. Wei et al. [15] studied the recovery of sulphuric acid from model solutions (H_2SO_4 + $FeSO_4$, H_2SO_4 + $VOSO_4$) and a real acid solution, which is generated from a black shale pressure acid leaching process in the extraction of vanadium from black shale. It was found that more than 80% of sulphuric acid can be recovered, while V and Fe are effectively rejected. An economic evaluation proved that an investment can be recovered within 27 months. The results on the recovery of nitric acid from acidic effluents discharged by an electrodialysis plant were published by Lan et al. [16]. In the diffusion dialysis experiments, an anion-exchange membrane DF-120 was used, and the effects of the concentrations of nitric acid and metal ions (Li, Na, K, Mg, Ca), and the water to acid flow rate ratio on the performance of the dialysis process were investigated. In a two-compartment counter-current dialyzer with single passes, the transport of sulphuric acid in the presence of magnesium sulphate was studied by Palatý and Bendová [17]. The dialysis process was characterised by the recovery yield of acid and rejection of salt. Moreover, the transport of each component was quantified by phenomenological coefficients. The same characteristics of the dialysis process were used to quantify the simultaneous transport of sulphuric acid and zinc sulphate [18]. Diffusion dialysis with anion-exchange membranes was used to recover sulphuric acid from an acid leaching solution generated in the vanadium producing process [19]. The effects of the liquid flow rates of the feed and stripping agent, the flow rate ratio, and ion concentration on the acid recovery and metal rejection were investigated. Wang et al. [20] presented results on dynamic behaviour of a continuous dialyzer. From the breakthrough curves obtained for various acid concentrations (HNO_3, H_2SO_4, H_3PO_4), the sorbed amount of the individual acids in the membrane was then calculated.

Although diffusion dialysis is mainly used for the separation of liquid mixtures containing inorganic acids and their salts, the aim of this communication is to investigate simultaneous transport of inorganic acids exhibiting different sorption and diffusivities in a polymeric membrane. For this purpose, a model solution of sulphuric and phosphoric acids was used.

2. Theory

Suppose that a ternary mixture (component A, component B and solvent w) is to be dialyzed. The feed enters the bottom of compartment I, while a stripping agent (mostly water) enters the