[443] Experimental investigation and modelling of diffusion dialysis for the recovery of waste acid solutions

R. Gueccia*, S. Randazzo*, D. Chillura Martino**, A. Cipollina*, G. Micale*

*Dipartimento dell'Innovazione Industriale e Digitale (DIID), Università degli Studi di Palermo – Viale delle Scienze Ed.6, 90128 Palermo, Italy.

**Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Università degli Studi di Palermo – Viale delle Scienze Ed.17, 90128 Palermo, Italy.

Introduction

Pickling is widely used as a chemical pre-treatment method for cleaning metal surfaces before other surface treatments and it consumes large amount of acids and water. During the pickling process, the efficiency of the pickling liquor decreases due to the accumulation of metal salts and the consumption of active acid. The exhausted acid solution is discarded completely or partly as a waste, while the pickling bath is maintained active with fresh pickling acid to extend the bath life. The environmental impact and costs of the disposal can be minimized by the recovery and recycling of valuable substances and water from waste pickling solutions.

Among several separation methods, diffusion dialysis (DD) is becoming more and more attractive thanks to the recent important advances in ion exchange membranes (IEMs) and because of its clean nature and operational simplicity, low installation and operating costs, and low energy consumption [1,2].

In this work, we performed experiments and simulations to characterise the behaviour of a DD unit for the separation of HCl, $FeCl_2$ and $ZnCl_2$ from waste pickling solutions.

Experimental methods and results

Two single-cell diffusion dialysis modules with different dimensions equipped with commercial anion exchange membranes were employed. The first one consisted in a laboratory-scale DD unit ($10 \times 10 cm^2$) operated in a batch configuration in order to study the effect of process parameters on the efficiency of HCl recovery and metals rejection. The second one, a large-scale DD unit (80 cm long), was operated in a continuous configuration in order to simulate the process operation at the industrial scale.

We firstly characterized system performances in terms of acid and water fluxes with artificial HCl solutions at different concentration (from 0.1 to 3 M HCl) showing an increasing trend for the acid permeability, as well as the water permeability, as the concentration in the retentate solution increases.

In addition, we investigated the effect of the presence of $FeCl_2$ and $ZnCl_2$ in order to simulate the operation of the system when treating real pickling solutions (see Table 1).

In particular, the acid permeability is affected differently from the two salts. $FeCl_2$ leads to an increase of the acid flux due to the "salt effect". On the other hand, a flux reduction is caused by the competitive passage through the membrane of Zn-Cl complexes.

293

**Table 1**. Operating conditions range for the four different investigated systems.

Sol. types	HCl sol.	HCl and $FeCl_2$ sol.	HCl and $ZnCl_2$ sol.	HCl, $FeCl_2$, $ZnCl_2$ sol.
Conc. range	3.6-110 g/l	0-150 g/l (Fe^{2+})	0-20 g/l (Zn^{2+})	0-150 g/l (Fe^{2+}); 0-20 g/l (Zn^{2+})

Modelling approach and validation

A mathematical model for the DD process was developed and validated with experimental data. The model, also built to simulate time-dependent variations for the batch operation mode, consists of two different parts: a distributed parameter model with spatial differential equations describing the DD unit and a dynamic part including time-differential equations for the concentration variation in the batch tanks.

For the first time, the coupled influence of HCl, $FeCl_2$ and $ZnCl_2$ on the overall process performance was simulated both in terms of concentration profiles of the three components and in terms of volume variation of the retentate and diffusate solutions (thanks to the prediction of water osmotic and entrained flux).

This provides useful and novel insight on the operation of DD with such solutions, offering at the same time an important tool for process optimization and for the design of industrial systems.
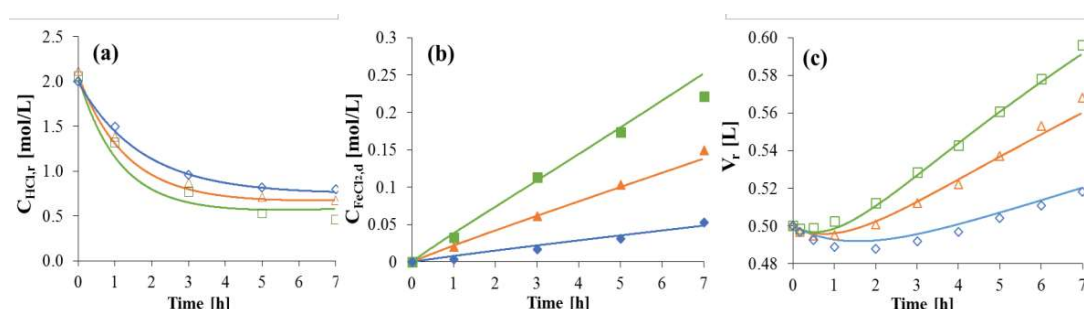
Figure 1. Experimental values and model predictions for the time variation of the: (a) retentate acid concentration; (b) diffusate salt concentration; (c) retentate volume.

Acknowledgments

References

[1] Luo et al., *Diffusion dialysis processes of inorganic acids and their salts: the permeability of different acidic anions*, Separation and Purification Technology 78 (2011), 97-102

[2] Xu et al., *Recovery of hydrochloric acid from the waste acid solution by diffusion dialysis*, Journal of Hazardous Materials 165 (2009), 832-83