Application of diffusion dialysis in separation of sulfuric acid and copper from pickling wastewater.

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Summary:

Electroplating industry creates large volumes of wastewater that contain acids and heavy metallic ions which are toxic but valuable. Diffusion dialysis (DD) can be used to separate acids from heavy metals. In this work, two single-cell DD modules equipped with Fumasep FAD membranes were used for the first time for the separation of sulfuric acid from copper. The first module consisted of a laboratory-scale DD unit operated in a batch configuration to study the effect of process parameters on the efficiency of sulfuric acid recovery. The latter one was a large-scale DD unit operated in a continuous configuration to simulate the process operation at the industrial scale. Results showed that Fumasep FAD was suitable to recover sulfuric acid separated from copper salt. In addition, a mathematical model was developed and validated with experimental data obtained in this work. A good agreement between experimental results and model was obtained both in batch and continuous operations.

Keywords: Diffusion dialysis, crystallization, industrial wastewater treatment.

Introduction

Electroplating is a technique widely used in the metal coatings industry. This treatment generates large volumes of wastewater containing acids and heavy metals (Agrawal, Sahu, 2009; Negro et al, 2001). Several techniques are used to recover acids (Xu et al, 2009). Among these, diffusion dialysis (DD), which is a membrane separation process where the driving force is the concentration gradient at both sides of the ion exchange membrane, was selected in this work. In this particular study, an anion exchange membrane (AEM) was adopted. A very few researchers studied the performances of the AEM Fumasep FAD (Palatý and Bendová, 2017). This work focused on the treatment of waste acid solutions generated in copper electroplating to purify sulfuric acid contaminated by copper. To achieve this goal, two DD units equipped with Fumasep FAD membranes were used. Moreover, a mathematical model was developed from the model developed and validated for the hydrochloric acid recovery (Gueccia et al, accepted).

Material and Methods

Experiments were carried out in two different equipment in a batch and continuous operations respectively. For the discontinuous operation, the DD module had a plate and frame configuration with two transparent polymethyl methacrylate shells of 20 cm long and 5 cm thick. In each shell, 6 screw holes of $12^{1/4”}$ were built, 3 inlets and 3 outlets. These allowed the distribution and collection of the fluid present inside the module. Moreover, a spacer was placed in each shell to create a channel through which the solution circulated. These spacers had a thickness of 270 µm and a width and length equal to 100 mm. Between the two spacers, the Fumasep FAD membrane was inserted. For the continuous operation, a plate and frame DD module was used too. However, in this case, the module was composed of 18 Fumasep FAD membranes (80 cm length, 10 cm width and 0.03 cm thickness) and 19 spacers leading to 10 diffusate channels and 9 retentate channels.

Results and Conclusions

Results showed Fumasep FAD was suitable to separate sulfuric acid from copper salt. An acid recovery and copper rejection of 95% were obtained in continuous operation. In batch operation, a higher sulfuric acid recovery was observed as the initial acid concentration decreased. In fact, the maximum value was obtained at 20 g/l (range investigated 20-200 g/l) When copper was added, the sulfuric acid recovery was reduced aproximately 10 % (range investigated 10-70 g/l). Regarding the model, a good agreement between experiments and model results was obtained, both in batch and in continuous operations, for the acid and copper concentration and volume trends.

a) b)

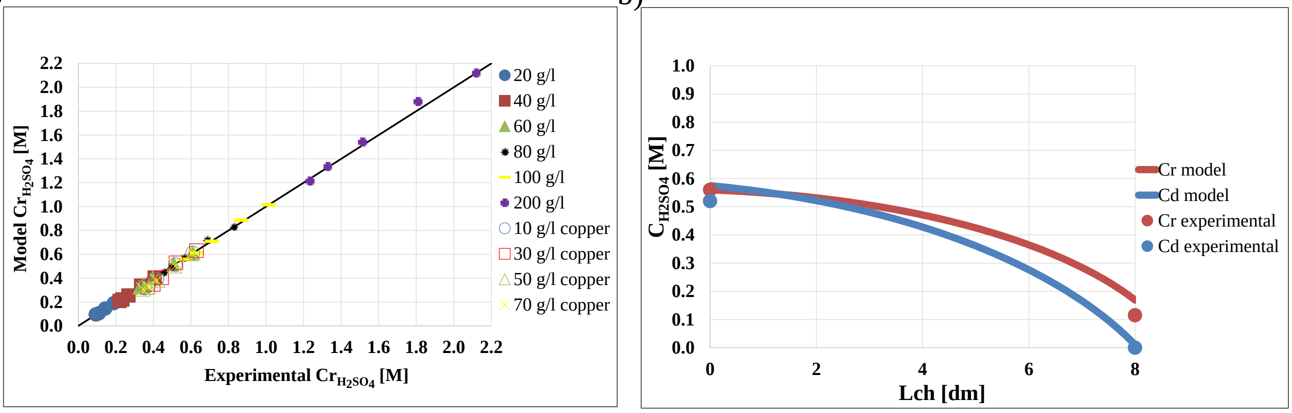

Figure 1.1. a) Batch operation: calculated retentate sulfuric acid concentration versus experimental retentate sulfuric acid concentration for different initial sulfuric acid concentrations (filled marker) and for a constant initial sulfuric acid concentration of 60 g/l for different initial copper concentration. b) Continuous operation: calculated and experimental sulfuric acid concentrations along the retentate (r) and diffusate (d) channels.

References

Agrawal, A, Sahu, K. K. (2009), An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, J. *Hazard. Mater*, 171, 61-75.

Gueccia, R., Randazzo, S., Chillura Martino, D., Cipollina, A., Micale, G., Experimental investigation and modelling of diffusion dialysis for HCl recovery from waste pickling solution. Accepted.

Negro, C, Blanco, M. A., López-Mateos, F., DeJong, A. M. C. P., LaCalle, C., Van Erkel, J., Schmal, D. (2001), Free acids and chemicals recovery from stainless Steel pickling baths, *Separ. Sci. Tech*, 36, 1543-1556.

Palatý, Z., Bendová, H. (2017), Permeability of a Fumasep-FAD membrane for selected inorganic acids, *Chem. Eng. Techol*, 41, 385-391.

Wei, Z., Xiong, Y., Chen, J., Bai, J., Wu, J., Zuo, J., Wang, K. (2018), Recovery of Cu(II) from aqueous solution by induced crystallization in a long-term operation, *JES*, 69, 183-191.

Xu, J., Lu, S., Fu, D. (2009), Recovery of hydrochloric acid from the waste acid solution by diffusion dialysis, *J. Hazard. Mater*, 165, 832-837.