

Zn(II) AND Cu(II) UPTAKE FROM ACID SOLUTIONS WITH MICROCAPSULES CONTAINING A NON-SPECIFIC ALKYL PHOSPHONIC EXTRACTANT

FERNANDO VALENZUELA^{1}, MEHRDAD YAZDANI-PEDRAM², CLAUDIO ARANEDA¹, CARLOS BASUALTO¹, EIJI KAMIO³ AND KAZUO KONDO³*

¹ Laboratorio de Operaciones Unitarias, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, P.O.Box 233, Vicuña Mackenna 20, Santiago, Chile

² Laboratorio de Química de Polímeros, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, P.O.Box 233, Olivos 1007, Santiago, Chile

³ Department of Chemical Engineering and Material Science, Doshisha University, Kyotonabe, Kyoto, 610-0321, Japan

ABSTRACT

It is studied the uptake of Zn(II) and Cu(II) from acid aqueous solutions using microcapsules containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, a non-specific extractant, as an alternative method for metals separation in place of current techniques as ion-exchange solid resins or solvent extraction. The microcapsules employed in this study were prepared by an in situ radical polymerization method. The amount of extractant held within each microcapsule was determined by potentiometric titration. Many experimental tests were carried out to measure the hydrometallurgical capacity of the microcapsules to remove these metallic ions from the aqueous solutions.

Keywords: Copper, Zinc, Extractant, Hydrometallurgy, Microcapsules

INTRODUCTION

Among the most serious difficulties of mining and metallurgy activities, it is possible to indicate a) the generation in its processes of a great variety of aqueous waste solutions and b) the natural formation of acid mine drainages due to geochemical oxidation and microbial causes [1]. These resulting solutions are usually high in acidity and dissolved metals, becoming an environmental problem that is very difficult to clean up. However, these solutions can also constitute a potential source of many valuable and scarce metals. The technical challenge is how to remove them from this type of solutions by means of simple and economical manner. In this respect, we have come studying during many years different alternatives for metal recovery and uptake from dilute mine waters, including current solvent extraction in mixer-settler reactors [2], the use of both supported liquid membranes [3-5] and surfactant liquid membranes [6,7].

This short communication reports in advance on the uptake of zinc and copper ions from acid solutions using a novel method based on the use of microcapsules containing non-specific commercial extractant. This technique would present advantages in many cases with respect to other conventional methods [8,9].

Experimental procedure and results

As extractant was employed the commercial compound PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) supplied by Daihachi Chemical Industry Co. which was used without further purification. Styrene and divinylbenzene were used as monomer to prepare the microcapsules. Grade chemical, toluene and benzoyl peroxide were utilized as a diluent and a polymerization initiator, respectively. All other chemicals, including sodium silicate and minerals acids were of reagent grade and used as received. The metals-containing aqueous solutions were prepared by dissolving appropriate amount of each metal-sulfate salts in distilled water whose pH was adjusted with sulfuric acid and measured in a pH meter (Corning 320).

The synthesis of microcapsules were carried out in a batch-type reactor having a 500 cm³ capacity. A mixture of distilled water and sodium silicate was added as the continuous phase being stirred by magnetic bars driven by synchronous motor. When the temperature of this aqueous solution reached a value of 70°C, it was added the organic solution composed of the monomers, the polymerization initiator and the organophosphorus acid extractant, mixture that behaves as the dispersed phase. Both phases (continuous and dispersed) were intensely agitated for almost 3 h in an inert nitrogen atmosphere, enough to attain the experimental conditions for the polymerization reaction. Once obtained, the polymerized microcapsules were repeatedly washed with distilled water and then dried at room temperature. Moreover, the following potentiometric titration method was accomplished to measure the amount of the organophosphorous extractant retained within each microcapsule: 1.0 g of the microcapsules was mixed with 50 cm³ of methanol during a week, being after separated from the organic liquid by filtration. The alcoholic solution was divided into portions 10 cm³ each, which were titrated with a 0.052 mol/L NaOH solution. From a hydrometallurgical point of view, it is necessary to test the capacity of microcapsules to remove metallic ions from acid aqueous solutions. Then, the next step was to carry out some metal uptake equilibrium experiments. They were made in a batchwise by contacting in a Polyscience orbital-shaker apparatus 0.2 g of microcapsules containing the extractant and 20 cm³ of the aqueous solution containing zinc and copper ions. The sorption runs were carried out during 24 h enough to allow equilibrium to be reached. Once filtrated the metal concentration in the resulting aqueous solution was measured by atomic absorption spectrophotometry in a Perkin Elmer 3110 apparatus.

In Table 1 are listed the different experimental conditions employed to prepare the microcapsules, the mass of microcapsule obtained and the results of the metallurgical tests for zinc and copper removal from an acid aqueous solution. In Table 1 **St**, **DVB** and **MC** denote styrene, divinylbenzene and microcapsule respectively. It is observed that the production of microcapsules was enhanced as the proportion of divinylbenzene monomer was increased. However, as the amount of extractant used in the synthesis was the same in all cases, the content of the phosphonic compound held in the microcapsules resulted to be lower as the microcapsules yield increased since the weak acid-type extractant was dispersed in a higher mass of capsules. Furthermore, it was observed a quite good uptake of Zn(II) and a regular extraction of Cu(II), what can be explained considering that the zinc extraction runs were carried out at a pH value for

feed solution where this extractant present a maximum activity [7]. However, the copper uptake runs were accomplished using an initial pH for feed solution around 3.8 looking for improve this metal extraction with PC-88A under a acidity condition where is not efficiently extracted [2].

Table 1: Uptake of Zn(II) and Cu(II) from acid solutions with microcapsules containing PC-88A

zinc sorption initial conditions: 87.3 mg/L Zn(II), pH = 4,09 copper sorption initial conditions: 107.0 mg/L Cu(II), pH = 3.85. mass of microcapsule: 0.2 g								
	St (%)	DVB (%)	MC production (%)	Zn (II) Extraction (%)	pH equilibrium	[mol Zn extracted/ mol PC-88A]	[mol Zn extracted / g MC]· 10 ⁴	[mol PC-88A / g MC]· 10 ³
Zn	70.05	29.94	39.64	99.10	3.03	0.073	1.32	1.813
	49.49	50.90	66.78	98.78	2.99	0.086	1.32	1.528
	29.38	70.61	69.32	98.72	2.97	0.098	1.32	1.347
	14.93	85.07	89.55	97.09	2.90	0.119	1.30	1.088
	0.00	100	87.82	97.21	2.87	0.119	1.30	1.088
	St (%)	DVB (%)	MC production (%)	Cu (II) Extraction (%)	pH equilibrium	[mol Cu extracted/ mol PC-88A]	[mol Cu extracted / g MC]· 10 ³	[mol PC-88A / g MC]· 10 ³
Cu	70.05	29.94	39.64	49.00	3.34	0.046	8.24	1.813
	49.49	50.90	66.78	44.65	3.36	0.049	7.51	1.528
	29.38	70.61	69.32	40.86	3.36	0.051	6.88	1.347
	14.93	85.07	89.55	37.37	3.42	0.058	6.29	1.088
	0.00	100	87.82	33.89	3.40	0.052	5.70	1.088

In Figure 1 are shown the potentiometric titration curves for many microcapsules synthesized varying the proportion between both monomers, styrene and divinylbenzene. It can be appreciated that the higher the proportion of divinylbenzene employed to prepare the microcapsules the lower the acid extractant held in them, confirming the dispersion effect of the extractant when a bigger amount of product was obtained. Therefore, in order to determine the actual capacity of microcapsules to extract metals, it is necessary to determine the dependence between the amount of metal adsorbed in each gram of microcapsule and the content of extractant held in them. This can be analyzed by observing the both most right-handed columns in [Table 1](#) which show the results observed for Zn(II) and Cu(II) ions sorptions expressed in that manner. It is appreciated that the zinc uptake from the acid solution was very high no matter the content of extractant in the microcapsules, meanwhile the copper sorption was increased as the content of the phosphonic compound in the capsule was increased.

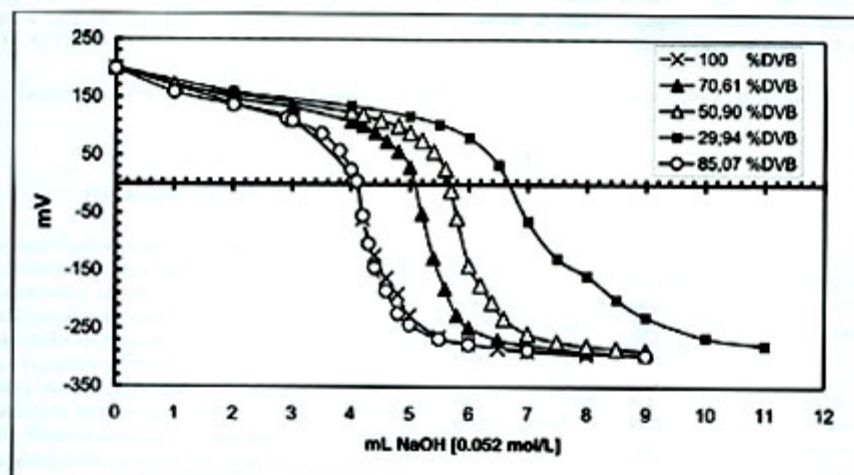


Fig 1.- Microcapsules preparation: potentiometric titration curves

It is clear that the extractant maintains its high metal-loading capacity in the microcapsules in an improved operation system with respect to the conventional liquid-liquid-extraction method today widely industrially used.

It was not measured any extractant leak from microcapsules under the pH condition employed to run the experiments, probably due to the hydrophobicity of the phosphonic extractant what would disable its loss from the microcapsules. This point is being studied in detail in these days for a broad acidity range. The scope of this study also considers to measure the maximum metal adsorption capacities in the microcapsules using a Langmuir or Freundlich-type isotherm model and relate these results with the characteristics of the surface and porosity of microcapsules. However, the most important point is to study the analysis of the possible metal sorption mechanism in the microcapsule based on a mass transfer with chemical reaction-process, what it will be reported shortly in a full communication.

Until this point of the study we can indicate that the extractant microcapsulization procedure is easy in a high efficiency process carried out using a simple reactor. From the viewpoint of an industrial application of this technique to remove metallic ions, the target must be pointed out to the uptake of heavy metal from mine and industrial waste dilute solutions. Probably by using a reactor based on a continuous column packed with microcapsules containing the appropriate selective or collective extractant.

ACKNOWLEDGMENTS

The authors express their thanks to Daihachi Chem. Co. for providing PC-88A extractant. The authors also thank the Japan-Chile Visit Program (JSPS-CONICYT N° RC 20437001) by the financial assistance.

REFERENCES

1. P.A. Weber, W.A. Stewart, W.M. Skinner, C.G. Weisener, J.E. Thomas, R.S. Smart, *Applied Geochemistry* 19, 1953 (2004).
2. F. Valenzuela, J. Andrade, J. Sapag, C. Tapia, C. Basualto, *Minerals Engineering*, 8, 893 (1995).
3. J. Marchese, F. Valenzuela, C. Basualto, A. Acosta, *Hydrometallurgy*, 72, 309 (2004).
4. F. Valenzuela, M.A. Vega, M.F. Yañez, C. Basualto, *J Membrane Sci.* 204, 385 (2002).
5. F. Valenzuela, C. Salinas, C. Basualto, J. Sapag-Hagar, C. Tapia, *J.Chilean Chemical Society*, 48, 79 (2003).
6. F.Valenzuela, C. Fonseca, C. Basualto, O. Correa, C. Tapia, J. Sapag, *Minerals Engineering* 18, 33 (2005).
7. F. Valenzuela, J. Auspont, C. Basualto, C. Tapia, J. Sapag, *Chem. Eng. Research and Design*, 83, 247 (2005).
8. E. Kamio, M. Matsumoto, K. Kondo, *J. Chem. Eng. Japan*, 35, 178 (2002).
9. E. Kamio, M. Matsumoto, F. Valenzuela, K. Kondo, *Ind. Eng. Chem. Res.*, 44, 2266 (2005).

*) To whom correspondence should be addressed

E-mail: fvalenzu@uchile.cl