CHEMICAL ENGINEERING RESEARCH AND DESIGN 89 (2011) 2761–2769

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Uptake of copper (II) ions from acidic aqueous solutions using a continuous column packed with microcapsules containing a β-hydroxyoximic compound

C. Araneda[a], C. Basualto[a], J. Sapag[a], C.Tapia[a], D. Cotorás[b], F. Valenzuela[a,*]

[a] Laboratorio de Operaciones Unitarias e Hidrometalurgia, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Vicuña Mackenna 20, Santiago, Chile
[b] Laboratorio de Microbiología, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Vicuña Mackenna 20, Santiago, Chile

ABSTRACT

In this paper, the uptake of Cu(II) ions from an acidic aqueous solution using a continuous column packed with microcapsules containing the chelating extractant LIX-860 N-IC was examined. A simple, economical method was employed to synthesise the microcapsules' polymeric matrix consisting of an *in situ* radical polymerisation method followed by the subsequent impregnation of the extractant compound 5-nonylsalicylaldoxime. The microcapsules had a spherical shape with a rough surface and a strong hydrophobic character that assured that the organic extractant was immobilised on the microspheres' porous structure. During the metal sorption experiments, three different columns were used, and the aqueous feed solution circulated through them at different flow rates in repetitive sorption–desorption cycles. The results of these experiments revealed that the metal extractability was improved when the flow rate of the feed phase decreased and when the largest column was used, likely because of the higher residence time of the solution in the column improving the solution's contact with the microcapsules and also because of an increase in the vacant sites for the sorption process.

The experimental data of the metal sorption onto the microcapsules in the fixed bed columns were explained by three different models (Wang, Thomas and dose–response). In general, the three predictive equations fit the dynamic behaviour of the breakthrough curves well. However, the modified dose–response model correlated better with the experimental data than the other model equations, as shown by the statistical parameters determined from the experimental conditions used.

Keywords: Sorption; Microcapsules; Packed columns; Copper (II); LIX-860 N-IC

1. Introduction

In most countries, the development of industrial zones causes the generation of enormous amounts of wastes of various natures. Among the most complex wastes are those from the effluents of the chemical and mining industries. The liquid wastes have a troublesome impact on the quality of life of the population and cause great damage to the environment. The adequate management of these wastes is a challenge of increasing complexity. Because the law is becoming very strict with respect to the regulation and treatment of these industrial liquid residues, new technological processes that allow for the efficient removal of the polluting agents, even of very low concentrations, are necessary.

The many waste waters from mining and metallurgical processing (Nedved and Jansz, 2006) and the acidic mine drainage (AMD) formed by sulphide oxidation after exposure to the air and water (Sheoran and Sheoran, 2006), are recognised as the largest environmental problem facing the mining industry. Most of these residuals are acidic waste waters containing various amounts of dissolved metals, mostly iron, copper and zinc, which must be removed due to their toxic charac-

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[*] *Corresponding author*. Tel.: +56 02 9781660; fax: +56 02 2227900.
E-mail address: fvalenzu@uchile.cl (F. Valenzuela).

Received 27 January 2011; Received in revised form 16 May 2011; Accepted 19 May 2011
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doi:10.1016/j.cherd.2011.05.008

teristics or recovered due to their intrinsic value. However, the metal ion concentration in them is often low because of the dilution by the natural surface water and groundwater, making their removal difficult. Furthermore, these waste waters often contain a variable but high concentration of sulphate and others anions that surpass the legal regulations (NormN°90/2000, Chile 2000). The chemical industries also generate various residual waters that may contain many types of metallic ions and anionic pollutants from the chemical steps employed in the process. Thus, the challenge is how to extract these pollutants from these types of aqueous solutions using simple, economical methods. Among the technological alternatives that can be used to uptake metals from aqueous solutions, are chemical precipitation (Matlock et al., 2002), solid ion-exchange resins (Hu et al., 2009), natural adsorbents (Choksi and Joshi, 2007) and solvent extraction (SX) processes including conventional liquid–liquid extraction (Li et al., 2008) and their variants of surfactant liquid membranes (Valenzuela et al., 2009) or solid-supported liquid membranes (Yang and Kocherginsky, 2007). However, all of these methods have advantages as well as multiple operational and economical limitations. In recent years, different methods have been studied to overcome these disadvantages. One of the most promising technological alternatives is the use of hydrophobic porous microcapsules composed of polymeric matrices that act as a suitable support for immobilising the same liquid organic extractants used in SX technology. Therefore, the microencapsulation of non-specific extractants corresponds to a methodology based on the current solvent extraction process, but the microencapsulation has some features that make it appropriate to treat dilute solutions (Kamio et al., 2008; Yang et al., 2005). In previous work, we successfully used efficient methods to synthesise these microcapsules. The best synthesis route was the chemical method based on an *in situ* polymerisation in which the monomers utilised to produce the polymeric matrix and the initiator of the reaction were mixed with the extractant and a dispersant compound in a suitable solvent, as was reported by Fonseca et al. (2010). With this method, a polymeric matrix was obtained in which the liquid extractant has the chemical activity to selectively or collectively react with the metals that exist in the aqueous solution feed for the treatment. Also, the microcapsules act as granular adsorbents with the advantages and features of IX resins and those of the liquid extractants widely used currently in SX processing. These microspheres that are used as supports for the extractants are a relatively new technology that has been developed rapidly in recent years. Several research groups have made important progress in this field, and the initial studies have been concerned with the synthesis of the microcapsules using physical and chemical methods followed by their chemical and morphological characterisation (Ochoa et al., 2006; Kamio et al., 2002; Ozcan et al., 2010; Wu et al., 2008; Singh and Srivastava, 2005). In a previous paper, we reported on a comparative extraction of Cd(II) and Cu(II) from acidic aqueous solutions by sorption onto microcapsules containing the extractant compound, 2-ethylhexy phosphonic acid mono-2-ethylhexyl ester and whose matrix was synthesised using the monomers ethylene glycol dimethacrylate (EGDMA) and styrene (St) (Araneda et al., 2008). A kinetics analysis showed that the sorption of the metallic ions followed a pseudo-second-order model, which fit well with the observed experimental results. In another recent study, we removed Cr(VI) ions from an acidic aqueous solution using microcapsules containing a long-chain quaternary ammonium salt-type extractant immobilised in their hydrophobic pore structure (Barassi et al., 2009). An equilibrium study showed that the Langmuir's isotherms correlated well with the experimental sorption data. The kinetics analysis showed that the sorption process was controlled by a chemisorption mechanism, and the measurements of the thermodynamic parameters indicated that the chemisorption process was spontaneous and exothermic. The microcapsules presented a large specific interfacial area per volume unit and required a minimal inventory of organic solvents for the extraction of the metals from dilute solutions, especially in those where their concentrations exceeded the maximum concentration permitted by the environmental regulations. Additionally, the microcapsules were easily separated from the solution by conventional filtration or sedimentation and have become a convenient alternative for use in separation processes with respect to the current technologies.

All our previous studies were performed using discontinuous batchwise reactors but from an industrial standpoint, it is absolutely necessary to consider the use of continuous columns packed with adequate microcapsules. Normally, the main challenge in designing and operating a column-system, beyond the use of efficient chemical adsorbents, is to determine the correct packing density of the solids in it and to achieve a suitable and uniform distribution of the fluids in the column. The simplicity of the reactor previously used and the ease of operation of the columns lead to the conclusion that a column packed with the microcapsules could be easily adapted to industrial applications. In this paper, the experimental results are presented for the uptake of copper (II) ions from acidic aqueous solutions using small, continuous columns packed with microcapsules containing a β-hydroxioximic compound. The results were analysed using several adsorption isothermal models that presented various ways to explain the experimentally observed data.

2. Experimental

2.1. Reagents and solutions

5-Nonylsalicylaldoxime ($C_{16}H_{25}O_2N$; commercially known as LIX-860 N-IC) was supplied by Cognis-Chile and was used without further purification as the copper extractant. It was a brownish, transparent liquid with a molecular weight of 263.38, a specific gravity of 0.965 (25 °C) and an absolute viscosity of 130 cp at 30 °C. This compound, which is widely used in SX industrial plants, is an acid chelating extractant. To synthesise the polymeric matrix, styrene (C_8H_8, molecular weight 104.15) and ethylene glycol dimethacrylate ($C_{10}H_{14}O_4$, molecular weight 198.2), which were supplied by Aldrich, were used as the monomers. They had a purity higher than 98% and were used as received. Their structures were shown previously (Araneda et al., 2008).

USP-grade benzoyl peroxide, which was supplied by Aldrich, was used as the polymerisation initiator and had a molecular weight of 242.2 and a specific gravity of 0.67 (20 °C). Toluene was used as the solvent for the organic compounds and gum arabic was used as a dispersant during the preparation of the microcapsules. Both the toluene and gum arabic were reagent grade. Due to the risk of thermal degradation of the β-hydroxyoxime during the synthesis, the active sorbent extractant was impregnated into the polymeric matrix after the polymer synthesis using dichloromethane (CH_2Cl_2, 99.5%