Hydrometallurgy 150 (2014) 144–152

Contents lists available at ScienceDirect

Hydrometallurgy

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

On the application of bulk-supported liquid membrane techniques in hydrometallurgy

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ARTICLE INFO

Article history:
Received 3 June 2014
Received in revised form 6 October 2014
Accepted 12 October 2014
Available online 22 October 2014

Keywords:
Solvent extraction
Combined liquid membrane technique
Separation
Mixer-settlers
Extraction of lanthanide chlorides

ABSTRACT

A theory of bulk-supported liquid membrane extraction has been developed. The process is performed sequentially in a series of three-phase mass-transfer stages. In each stage the extractant circulates in a closed circuit and alternately contacts a donor (feed) phase and an acceptor (stripping) phase. Special cases have been analyzed in which the phases in the chambers move countercurrently in plug-flow mode; contact chambers represent perfectly-mixed cells; contact chambers consist of a series of theoretical stages; each contact chamber represents a theoretical stage. Experimental and computational studies on extraction and separation of lanthanide chlorides have been carried out using two schemes of a cascade of mixer-settlers: (1) connected in the usual way with external circulation of the extractant (the extractant first passes through all the stages of extraction and then through all the stripping stages) and (2) based on a bulk-supported liquid membrane (the extractant recycles between each pair of extraction and stripping stages). The effectiveness of the bulk-supported liquid membrane extraction scheme was considerably greater than that of the conventional scheme. Experiments on the extraction of lanthanide chlorides from neutral aqueous solutions in the system involving methyltrioctylammonium di (2-ethylhexyl)phosphate were carried out. The experimental results are in satisfactory agreement with the data calculated, which confirms the agreement between theory and experiment. The bulk-supported liquid membrane extraction can be applied to other systems and heavy metals as well.

1. Introduction

Selective separation of metals from industrial and waste solutions is frequently required in hydrometallurgical processing. Solvent extraction is one of the most popular hydrometallurgical separation methods used for recovery and separation of metals from aqueous solutions (Bart, 2005). As an alternative, the liquid membrane separation technique, a non-equilibrium process combining extraction and stripping in a single operation, has been proposed (Li, 1968). A significant increase in the application of liquid membrane techniques is due to their characteristics such as ease of operation, low energy consumption, high selectivity, possible usage of expensive carriers, lower chemical losses and competitive operation costs (Agreda et al., 2011; Arslan et al., 2009; Chakraborty et al., 2010; Cox, 2008; Kocherginsky et al., 2007; Lopez-Lopez et al., 2010).

Liquid membranes can be generally classified into four types: bulk, emulsion, supported liquid membranes and multistage three-phase extraction. In each case, the extractant involved in the organic phase is similar to those used in solvent extraction. The metal extraction stoichiometry is mainly the same as that in solvent extraction but the overall process is governed by kinetic parameters, that is, it is characterized by non-equilibrium mass transfer (Fournier-Salaun and Salaun, 2009; Leon and Guzman, 2004).

Bulk liquid membranes usually consist of an aqueous feed and stripping phase, separated by a water-immiscible liquid membrane phase (Alpaydin et al., 2011; Candela et al., 2013; Jafari et al., 2009; Koter et al., 2013; Reddy et al., 2013; Shaik et al., 2010; Singh et al., 2011). The liquid membrane contacts with two other aqueous liquids and affects the transfer between them.

From a practical point of view, supported (or flat sheet supported) liquid membranes are of particular interest because of their stability and simplicity (Ata, 2005; Belkhouche et al., 2006; Dutta et al., 2012; Gaikwad et al., 2003; Gaikwad, 2004; Joshi et al., 2009; Kumric et al., 2006; Mohammadi et al., 2008; Moreno and Valiente, 1999; Pei et al., 2009a,b, 2012; Rehman et al., 2012; Swain et al., 2006). In supported liquid membranes, an organic liquid is usually absorbed in the small pores of a polymer support and is kept there by capillary forces. Flat sheet supported liquid membranes are being explored for the selective separation, purification, and concentration of toxic wastes and valuable metals in

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http://dx.doi.org/10.1016/j.hydromet.2014.10.011
0304-386X/

aqueous solutions (Alguacil et al., 2000; Altin et al., 2010; Benzal et al., 2004; Bhattacharyya et al., 2006; Candela et al., 2013; Gasser et al., 2008; Kandwal et al., 2011; Panja et al., 2008; Valenzuela et al., 2005).

Emulsion liquid membranes (Hasan et al., 2009; Kumbasar, 2008, 2009a; Kumbasar and Kasap, 2009; Nosrati et al., 2011) comprise water-in-oil or oil-in-water emulsions (formed by the organic solvent and surfactant-stabilized water) stirred into the aqueous feed solution. Mass transfer occurs between the aqueous continuous and inner phases through the immiscible membrane phase. Because of the need to use several unit operations (preparation and breaking the emulsion) this process becomes practically not very attractive. However emulsion liquid membranes have shown great potential, especially in cases where solute concentrations are relatively low and other techniques cannot be efficiently applied (Ambe et al., 1998; Kumbasar, 2009b; Tian et al., 2011).

According to the version of the liquid membrane separation technique called multistage three-phase extraction (Kostanian, 2000a,b; Kostanyan, 1999, 2013b; Kostanyan et al., 2005), the extraction process is carried out in a cascade of three-phase mass-transfer stages, each comprising two interconnected contact chambers — one extraction chamber and one stripping chamber. The liquid membrane acts as the mass-transfer medium, contacting with a feed stream (or donor phase) in the extraction chambers and with an acceptor stream (or stripping phase) in the stripping chambers building a number of closed circuits. Thus, the liquid membrane is held stationary in the operating system (in a cross-flow mode with the acceptor and donor phases within the same stage), while the donor and acceptor phases are eluted through all of the stages as the mobile phases. The multistage three-phase extraction can be achieved either in a series of mixer-settlers or conventional extraction columns with forced circulation of the membrane phase between the chambers or in special multistage two-chamber extraction columns (Kostanian, 2000a,b, 2013) with natural (convective) membrane phase circulation. In the latter case, circulation of the liquid membrane, which is the continuous phase, between the contact chambers takes place due to the difference in emulsion density in the chambers.

It should be noted that multistage three-phase extraction is actually a combination of bulk and supported liquid membrane techniques, therefore it can be called a bulk-supported liquid membrane. The disadvantages of supported liquid membranes are low productivity and problems associated with implementation on an industrial scale. The advantages of bulk-supported liquid membrane technique are simplicity and high productivity. Moreover, it can be easily implemented in practice using conventional extraction equipment (mixer-settlers and extraction columns).

The aim of the present work was to perform a full theoretical treatment of the bulk-supported liquid membrane extraction and evaluate the prospects of its application in hydrometallurgy.

2. Theory of the bulk-supported liquid membrane extraction processes

2.1. General case

Consider the general case when the process is performed sequentially in a series of N mass-transfer stages, each comprising two interconnected contact chambers — one extraction chamber and one stripping chamber. In each stage the liquid membrane circulates in a closed circuit and alternately contacts in countercurrent mode a donor (feed) phase and an acceptor (stripping) phase. The donor and acceptor phases are flowing through all of the stages in the countercurrent mode (Fig. 1). This process can be implemented in a cascade of pair-wise interconnected conventional extraction columns.

To analyze the extraction process in the described system, we make the following assumptions:

1. The contacting phases in the chambers move counter-currently in the plug-flow mode;
2. Mass transfer between the phases is described by the mass-transfer equations as in the case of conventional extraction;
3. Equilibrium-distribution coefficients of the transferred component in the extraction $D_{ex} = y^*/x_1^*$ and in the stripping $D_{str} = y^*/x_2^*$ chambers are constant.

According to Fig. 1 the model equations for the current mass-transfer stage i can be presented in the following forms:

$$v_1 \frac{dx_1}{dz} = a_1 k_1 \left(x_1 - y_1^*/D_{ex1}\right) = -w \frac{dy_1}{dz} \tag{1}$$

$$v_2 \frac{dx_2}{dz} = a_2 k_2 \left(y_2 - D_{str} x_2^*\right) = -w \frac{dy_2}{dz} \tag{2}$$

$$v_1 x_1 + w y_h = v_1 x_i + w y_1 \tag{3}$$

$$v_2 x_{2,i+1} + w y_2 = v_2 x_2 + w y_h, \tag{4}$$

where a_1 and a_2 are specific surface area of phase contact in the extraction and stripping chambers, respectively; k_1 and k_2 — mass-transfer coefficients in the chambers; v_1 and v_2 — specific flow rates of the donor and acceptor phases, respectively; w is the specific flow rate (circulation rate) of the liquid membrane; x_1 and x_2 are the concentrations of a component in the donor and acceptor phases, respectively; y_1 and y_2 are the concentrations of a component in the membrane phase in the extraction and stripping chambers, respectively (the symbol * stands for equilibrium

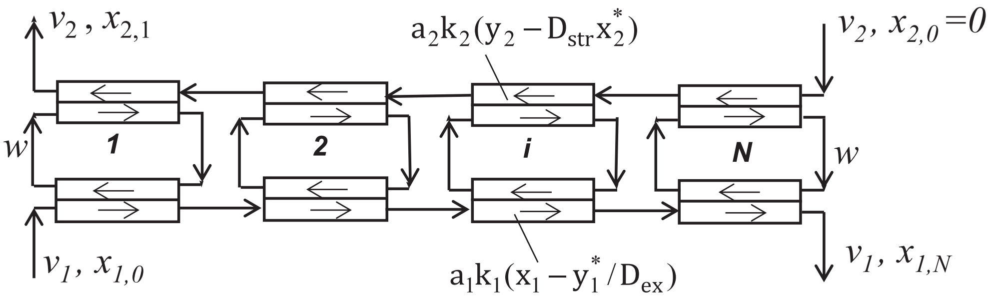

Fig. 1. The scheme of the theoretical model for the general case of the bulk-supported liquid membrane extraction process.