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Emulsion ionic liquid membrane for recovery process of lead. Comparative study of experimental and response surface design

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ABSTRACT

The technique of emulsion ionic liquid membrane (EILM) was used as chemical process for Pb(II) recovery, from nitrate medium, using Aliquat336 as ionic liquid carrier. The Tween20 as a dispersive non-ionic surfactant was used for the emulsion formation. The optimization of the extraction and pre-concentration of Pb(II) was determined by optimizing one parameter at the time. So, several experimental parameters as: carrier concentration, surfactant concentration, time and stirring speed of feed phase, initial concentration and pH of feed phase, were studied. The results showed that the lead ions were extracted at 82.61% by Aliquat336 and recovered at 82.16%, in aqueous solution of the nitric acid, from a feed phase of lead(II) nitrate of 207.2 ppm at pH equal to 5.5, in presence of 1% w/w Aliquat336 and 0.5% w/w of Tween20 under 30 min of stirring at 210 rpm. The tests of separation experiments of Pb(II) and Cu(II) were carried on the basis of the optimal conditions of lead (II) recovery. Thus, the separation factor of lead over copper was equal to 1.30, obtained from their equimolar synthetic mixture. Indeed, the recovery of Cu(II) can be advantageous towards of Pb(II) if the molar composition of Cu/Pb in mixture was of 0.65. Response surface methodology (RSM) using Box–Benheken Design (BBD) was used for the statistical study. So, the reduced cubic of the quadratic model showed that the predicted values were in good agreement with those found experimentally and the parameter of ionic liquid concentration has an important individual effect on the response. Therefore, the recovery of Pb(II) can be predicted at 82.14% with the best desirability of the chosen model under our experimental conditions.

1. Introduction

Lead is a heavy metal widely used in the metallurgical activities since ancient times and rediscovered at the time of the industrial revolution. It is mainly found in the ores as galena and lead sulfide (PbS). Currently a good part of lead production is based on the recovery of vehicle batteries (Mohammadi et al., 2016). Lead is generally associated with copper in the most ores (Liu et al., 2013; Tchounwou et al., 2012). In hydrometallurgy field, extraction and pre-concentration of metals constitute a challenge and an important economic issue. Usually, the processes which are extensively used in the recovery techniques of metal ions from their dilute leachate solutions are: solvent extraction, precipitation; ion exchange, adsorption and electrochemical recovery. Sometimes these techniques become ineffective when they presents technical, economical and/or environmental constraints (Chaouchi and Hamdaoui, 2014; Kumbasar, 2010; Tchounwou et al., 2012). The extraction techniques based on the liquid membranes can be an alternative solution to overcome these constraints (Hou et al., 2015; Lu and Dreisinger, 2014). The technique of emulsion liquid membrane (ELM) was invented by Li in 1968. This technique has drawn a great attention

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by many scientific and industrial researchers for the hydrometallurgical processes of heavy metals recovery. ELM has presented a high efficiency, compared to conventional techniques, in the recovery of metal ions and hydrocarbons from wastewater (Chakrabarty et al., 2010; Kitagawa et al., 1977). ELM process consists in a three-phase format (W/O/W). A continuous aqueous phase (W) enters in contact with a hydrophobic organic liquid; called, a membrane phase (O) containing a strip agent solution (W), dispersed in the form of fine droplets to create the emulsion globule which offers an important mass transfer due to the high interfacial area (Gameiro et al., 2007). An adequate surfactant should be added to the organic liquid to ensure the formation and stability of emulsion, and enhance the selectivity and permeability of the membrane (Frankenfeld and Li, 1987). So, the metal ion will be extracted from the feed phase and pre-concentrated in the stripping aqueous solution in the same stage (Frankenfeld and Li, 1987; Srivastava et al., 2017). The pre-concentration operation (emulsion breaking) is realized by electrostatic, heating, dilution and shear techniques (Frankenfeld and Li, 1987; Gameiro et al., 2007). The concentration of metal ion at membrane/aqueous interface must be maintained at zero to keep a continuous driving force of permeation (Park and Chung, 2003). The transport of metal ion is governed by the kinetic rather than the conditions of equilibrium as in solvent extraction processes (Frankenfeld and Li, 1987; Pellegrino and Noble, 1990). Thus, different elements and compounds can be treated at industrial scale with a high efficiency where the possibility to use an expensive carrier in small quantities namely in separation process of metal ions (Gameiro et al., 2007; Kumbasar, 2010; Zhao et al., 2010).

In recent years, the ionic liquids (ILs); called "green solvents", presented an alternatives to hydrometallurgical processes of metal ions separation where they begin to replace many organic solvents that are expensive, toxic or non-ecological. This was due to theirs characteristics as: zero volatility, good miscibility and solubility of organic and inorganic compounds and low toxicity. It exists as liquid over a wide range of temperatures (Abbott and McKenzie, 2006; Coll et al., 2012; Tian, 2012). Aliquat336 is a commercial ionic liquid, called as Starks's catalyst. It is a quaternary ammonium salt, insoluble in water used as a catalyst of phase transfer and as carrier of metal ions (Chaouchi and Hamdaoui, 2014; Srivastava et al., 2017). With respect to hydrometallurgical applications, it appears to have only a modest amount of work presented in the literature, reported on the modelling of extraction and pre-concentration of lead by aliquat336 using the emulsion liquid membrane technique.

The present work was devoted to the optimization of Pb(II) recovery process by the experimental and statistical study. The experiments of extraction and pre-concentration of lead(II) and copper(II) were realized by Aliquat336 using the technique of emulsion ionic liquid membrane (EILM). The optimization method of one experimental parameter at the time was adopted for determination of the best conditions of lead(II) recovery, from their nitrate aqueous medium. The results were extrapolated on its recovery tests from their synthetic mixture with copper(II). In the second time, the modelling of process was achieved by response surface methodology (RSM) using Box–Behnken Design (BBD). For this, three parameters such as: initial concentration of Pb(II), concentration of ionic liquid and concentration of stripping solution, were considered as factors of quadratic model to predict the optimal recovery of Pb(II).

2. Experimental

2.1. Reagents

Tricaprylylmethylammonium chloride (Aliquat336) was used without further purification. The non-ionic surfactants used were: TritonX-100 (iso-octyl-phenoxypolyethoxyethanol) with the following properties: the critical micellar concentration is equal to 0.2–0.9 mM (20–25 °C), the HLB balance is of 13.5 and the cloud point temperature is of 65 °C, and Tween20 (Polyethylene glycol sorbitan monolaurate) with the following properties: the critical micellar concentration is equal to 0.06 mM (20–25 °C), the HLB balance is of 16.7 and the cloud point temperature is of 76 °C. These products were purchased from Sigma–Aldrich (Steinheim, Germany). Heptane was purchased from Merck (Darmstadt, Germany). Nitric acid was provided from Prolabo (VWR International France). The stock of lead and copper nitrates were supplied by Fluka (Germany).

2.2. Apparatus

The experiments of metal ion recovery were conducted by a mechanical stirring during the equilibrium time of the extraction reaction using a platform agitator; type A Haier (Beijing, China). The study of the pH effect on extraction and pre-concentration of metal ions, was carried out with a pH-meter; type Consort C831 (Turnhout, Belgium). An analytical balance; type Kern ABS (Balingen, Germany), was used in the weighing operation. The experiments of the emulsion formation were carried out by using a homogenizer; type Vortex (Germany) at 2500 rpm. An Ultra-8TL centrifuge model (LW Scientific, Lawrenceville, USA) was used for the phase separation. Atomic absorption spectromerter; type PerkinElmer PinAAcle 900H, was used for the metal ions analysis.

2.3. Preparation of emulsion

An organic solution of 7.5 mL was prepared in *n*-heptane by mixing the appropriate amounts of surfactant and Aliquat336. The stripping solution of 4.5 mL was added dropwise to the liquid membrane solution under the stirring speed of 1800 rpm during 20 min, to produce the emulsion globules. The aqueous solution of nitric acid at 0.5 M was chosen as stripping solution starting from the preliminary tests with the aqueous solutions of potassium hydroxide and ammonium chloride.

2.4. Batch ELM experiment

The emulsion phase (W/O emulsion) was added to a volume of 62.5 mL of feed solution of metal ions then, obtained solution is mixed during a time of extraction. This block of emulsion liquid membrane was used in the study of the permeation of the metal ion. For the metal pre-concentration operation, emulsion globule phase was separated from the feed phase in the first place, after, it was diluted and centrifuged. The aqueous solutions were prepared with deionized water. Each experiment was repeated three times and the average value was considered in the calculation. The experiments of extraction and pre-concentration of metal ion were carried out in batch system at the room temperature of 20 ± 0.1 °C. Samples of aqueous solutions of metal ion were taken for spectrometer analysis.

2.5. Analytical response

The study of recovery process of metal ion was evaluated by the yield of extraction (Eq. (1)) and the pre-concentration (Eq. (2)).

$$\textit{Yield of extraction},\ Y\,(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

$$\textit{Pre-concentration},\ P\,(\%) = \frac{C_{strip}}{C_0} \times 100 \tag{2}$$