



Evaluation of magnetic nanoparticles coated by oleic acid applied to solvent extraction processes



Natália Cristina Candian Lobato^a, Ângela de Mello Ferreira^{b,d}, Marcelo Borges Mansur^{a,c,d,*}

^a Universidade Federal de Minas Gerais (UFMG), Postgraduate Program on Metallurgical, Materials and Mining Engineering, Brazil

^b Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG), Department of Chemistry, Brazil

^c Universidade Federal do Rio de Janeiro (UFRJ), Program of Metallurgical and Materials Engineering, Brazil

^d National Institute of Science and Technology on Mineral Resources, Water and Biodiversity (INCT-Acqua), Brazil

ARTICLE INFO

Article history:

Received 18 February 2016

Received in revised form 17 May 2016

Accepted 26 May 2016

Available online 27 May 2016

Keywords:

Solvent extraction

Magnetic nanoparticles

Ferrofluid

Oleic acid

Magnetic separation

ABSTRACT

In this study, a magnetic organic liquid called ferrofluid was used to improve the speed and efficiency of the phase disengagement of solvent extraction processes applied to hydrometallurgical systems. The ferrofluid consisted of magnetic nanoparticles (mean diameter of 10.2 nm), comprised of magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which were coated by oleic acid and dispersed in an organic diluent. The nanoparticles were characterized by applying various methods: transmission electron microscopy, X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy, and thermogravimetric and magnetic analysis. The effect of the nanoparticles on the solvent extraction of cobalt sulfate with Cyanex 272 was investigated using ferrofluids at different concentrations (0, 10, 20, and 30 g/l of magnetic nanoparticles in commercial aliphatic kerosene Exxsol D80). It was observed that, under the conditions studied, the presence of nanoparticles does not interfere in the efficiency of metal extraction and stripping, and that the time necessary for phase disengagement can be up to five times faster. However, the ferrofluid containing nanoparticles coated solely by oleic acid is not stable when in contact with aqueous solutions at $\text{pH} \leq 2.0$. Limited stability restricts the application of the magnetic fluid used in the present study in solvent extraction processes that operate at a pH level beyond 2.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Solvent extraction, also known as liquid-liquid extraction, has become an important step in hydrometallurgy for the separation, purification, and concentration of metal ions from an aqueous solution. The method involves a specific chemical reaction between the metal species and a given extractant dissolved in an organic solvent. Different types of extractants exist for the selective purification of industrial liquors and the concentration of non-ferrous metals, such as zinc, nickel, cobalt, copper, uranium, and rare earth metals [1].

In general, a solvent extraction process consists of three steps: extraction, scrubbing, and stripping. In the extraction step, the aqueous phase, containing the metal of interest (feed phase), is mixed with the organic phase, containing the extractant dissolved in an organic diluent. The contact between both phases is produced

by stirring in order to promote the dispersion of one phase into the other, consequently causing the selective transfer of the metal from the aqueous to the organic phase. The separation of the two liquids normally occurs by gravitational settling. After phase disengagement, the aqueous phase, or raffinate, is treated to recover the remaining metals, either recycled to some point of the process or discarded as waste, while the metal loaded organic phase proceeds to the next step of the solvent extraction circuit. If the selectivity in the extraction step is low, the loaded organic solvent is forwarded to the scrubbing step in order to remove co-extracted impurities. Finally, in the stripping step, the metal is transferred from the loaded organic phase to another aqueous phase, which is free of contaminants and with an aqueous/organic volume ratio so as to obtain a concentrated solution. The organic phase is regenerated and reused in the same solvent extraction circuit, enabling greater economy and less environmental impact, while the aqueous phase proceeds to subsequent operations, such as crystallization or electrowinning, in order to recover the metal of interest with high purity [1,2].

These steps, industrially speaking, normally occur in mixer-settler units. Each mixer-settler consists of two compartments,

* Corresponding author at: Postgraduate Program on Metallurgical, Materials and Mining Engineering, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Campus da Pampulha, 31270-901 Belo Horizonte, MG, Brazil.

E-mail address: marcelo.mansur@metalmat.ufjf.br (M.B. Mansur).

thus corresponding to a single stage: the first compartment, in which mixing of the aqueous and organic phases takes place, and the second compartment, where phase disengagement occurs [2]. During the stirring, the higher the agitation, the smaller the droplets of the dispersion phase; consequently, faster mass transfer rates are obtained. However, since the phase disengagement occurs by gravity sedimentation, such a process can be slow and ineffective. As a result, larger areas for sedimentation are required, increasing investment cost [1,3].

To accelerate and increase efficiency between the separation of liquid phases during the process of sedimentation, the use of a magnetic organic solution was proposed [4,5] so that the disengagement between the organic and aqueous phases could be aided by a magnetic field. The magnetic organic phase was obtained by mixing the extractant with a magnetic liquid (ferrofluid). This kind of fluid is a colloidal system containing superparamagnetic nanoparticles, usually comprised of magnetite (Fe_3O_4) and/or maghemite ($\gamma\text{-Fe}_2\text{O}_3$), with dimensions between 5 and 25 nm, and coated by a hydrophobic component, such as oleic acid, in order to dissolve them in an organic diluent [4,6–9]. With the use of a magnetic solvent extraction process, the phase disengagement rate would be faster when compared to the traditional system. Therefore, when compared to the current dimensions, the required size for the settler compartment would be smaller, and an increase in productivity would occur [10]. Moreover, the efficiency of phase disengagement is also increased. Due to the influence of the applied magnetic field, the droplets of the magnetic organic phase are drawn towards the magnet, increasing the coalescence rate and decreasing the entrainment losses [5,11,12]. Entrainment loss may occur when the droplets of the organic phase remain in the aqueous phase even after long periods of settling [1].

A few studies have been published regarding the use of nanoparticles in the solvent extraction process on hydrometallurgical systems. Palyska and Chmielewski [10] and Vatta et al. [12,13] conducted solvent extraction tests to evaluate the influence of nanoparticles on the efficiency of metal ion extraction using distinct hydrometallurgical systems. The results, often contradictory, hamper a conclusion on the subject. In some systems, metal extraction was greater when using the magnetic fluid, as in the case of zinc extraction using D2EHPA (di-2-ethylhexyl phosphoric acid) as an extractant dissolved in kerosene. In others the presence of nanoparticles reduced the metal extraction rate, as in the case of cobalt extraction using Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) dissolved in kerosene [12]. In relation to the time of phase disengagement with and without nanoparticles, the magnetic system proved to be faster. According to Vatta et al. [12,13], the time of phase disengagement using magnetic fluid (magnetic nanoparticles coated by oleic acid with unknown concentration) was between 48% and 86% of the separation time of the equivalent traditional solvent extraction system. According to the authors, the variation on efficiency is due to the extractant used. Palyska and Chmielewski [10] also verified that the disengagement rate using magnetic fluid (magnetic nanoparticles coated by oleic acid with concentration ranging between 80 and 120 g/l) was 20–160 times faster than the use of a gravitational field alone.

Although the few studies published on the subject have asserted that the use of magnetic nanoparticles in solvent extraction processes applied to hydrometallurgical systems promotes higher disengagement speed, the data on the efficiency of extraction processes are still insufficient. In addition, no study has shown the relationship between nanoparticle concentrations in the fluid with process efficiency. Furthermore, the chemical stability of such a fluid, when in contact with aqueous solutions of different acidities, has still not been evaluated in the literature. In this context, the present work aimed to present a detailed characterization of nanoparticles coated by oleic acid and evaluate whether or not different

concentrations of such nanoparticles dispersed in the organic liquid influence the extraction and stripping of the metal, and whether or not these have any impact on the separation speed of the two phases. Moreover, this study sought to assess the chemical stability of the magnetic fluid when in contact with varying acidic aqueous solutions by monitoring the contamination of the aqueous phase by iron.

2. Experimental

2.1. Materials

Except for the diluent and the extractant, which were of commercial grade, all remaining reagents used in this work were of analytical grade: ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Vetec, purity 97%), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Neon, purity 99%), ammonium hydroxide (NH_4OH , Neon, 28–30 wt%), oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$, Synth, purity 100%), cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, Synth, purity 99%), sulfuric acid (H_2SO_4 , Synth, purity 98%), ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$, Neon, purity 99.5%), Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid, $\text{C}_{16}\text{H}_{35}\text{PO}_2$, Cytec Canada, purity 85%), and Exxsol D80 (liquid diluent which is essentially an aliphatic hydrocarbon, ExxonMobil Chemical). The water used is distilled or purified by membrane permeation (Milli-Q, Millipore, France), depending on the experiment.

2.2. Synthesis of the organic magnetic fluid containing Cyanex 272

The magnetic nanoparticles were synthesized using the alkaline co-precipitation method [6,14–16]. A solution containing 0.07 mol/l of Fe^{2+} and 0.14 mol/l of Fe^{3+} was mechanically stirred (1000 rpm) and heated to 80 °C. Next, 50 ml of NH_4OH was added, and the solution was stirred for 40 min. Afterwards, the solution was left for cooling at ambient temperature. The magnetic particles were then separated by filtration; washed with distilled water, and later with ethyl alcohol; filtrated; and dried.

The hydrophobic character of the nanoparticles was obtained by coating the magnetic nanoparticles with oleic acid [4]. A given weight of the nanoparticles was mixed with 40 ml of distilled water at 60 °C under stirring (500 rpm). For each gram of nanoparticles, 1 ml of oleic acid was added. The mixture was stirred for 15 min and left to stand until reaching room temperature. In the sequence, the coated particles were washed with distilled water, and later with ethyl alcohol, and then filtered.

The particles coated by oleic acid were mixed with Exxsol D80 in order to obtain ferrofluids with different concentrations (10, 20, and 30 g/l), using an ultrasonic bath (Brasonic, 1210 model, frequency 47 Hz) for 30 min [7]. Finally, Cyanex 272 was added to the ferrofluid in a proportion of 10% v/v.

2.3. Characterization of the magnetic nanoparticles

The magnetic nanoparticles (bare and coated) were characterized using the following methods:

- (i) Transmission electron microscopy, to analyze the morphology and particle size. The analyses were performed using a Tecnai G2-20 equipment - SuperTwin FEI - 200 kV. Sample preparation consisted of the dispersion of the particles in ethyl alcohol for 10 min in an ultrasonic bath, followed by a sample dripping on a carbon grid.
- (ii) X-ray diffraction, to determine the crystalline phases of the materials. The diffractograms were obtained on a Shimadzu 7000 X-ray diffractometer, using a copper anode ($\text{CuK}\alpha$ radiation) and graphite crystal monochromator. Analyses were run with scan range 2 theta from 10 to 80, with increments of 0.02 theta and a scanning speed of 2°min^{-1} .

Download English Version:

<https://daneshyari.com/en/article/640046>

Download Persian Version:

<https://daneshyari.com/article/640046>

[Daneshyari.com](https://daneshyari.com)