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Extraction of gallium from Bayer liquor using extractant produced from cashew nutshell liquid

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ABSTRACT

Oximes of alkyl salicylaldehydes were synthesized from cardanol extracted from cashew nutshell liquid with $SnCl_4$ as a catalyst. Molecular structures, physical and chemical properties of these oximes were investigated by spectroscopic data. These oximes were used as gallium extractant from a concentrated Bayer liquor of Alumina Tanrai (Vietnam). Results indicated that about 80% of gallium was recovered. This study opens up new opportunities to employ an environmentally friendly extractant for recovery of precious metals from industrial waste.

1. Introduction

Gallium is an irreplaceable metal for electronic industry (Moskalyk, 2003). Gallium demand has grown strongly it the last decade due to its application in LED and smartphones (Nakamura and Krames, 2013). A major source for the recovery of gallium is the spent caustic solution, which is recycled in the Bayer process. In the literature, different processes have been developed to recover gallium from Bayer solutions as reviewed by Zhao (Zhao et al., 2012). These include (1) fractional precipitation, (2) electrochemical deposition, and (3) solvent extraction. The fractional precipitation method is based on Al—Ga precipitation with CO_2 and subsequent separation of Al and Ga with lime milk or sodium aluminate solutions, which is a complicated process. The electrochemical method includes both mercury cathode electrolysis and cementation. The electrolysis with mercury cathode has been prohibited in most countries because of high toxicity. Cementation is an electrochemical process realized by a displacement reaction between gallium and reductants, such as sodium amalgam, aluminum and aluminum–gallium alloy. As a result, solvent extraction of gallium from the concentrated sodium aluminate solutions is the most feasible method.

It should be noted that the available gallium in bauxite is excessively higher than the global demand. Currently, only 10% of available Ga in alumina refineries is extracted (Phipps et al., 2008). Consequently, the economical constrain of Ga extraction is the extractant. The recovery of gallium from Bayer process sodium aluminate solutions by liquid–liquid extraction was reported three decades ago (Leveque and Helgorsky, 1977). The extractant Kelex-100, which is a 7-alkyl-substituted-8-hydroxyquinoline, was found to have effective gallium selectivity from highly alkaline sodium aluminate solutions. The following reactions were proposed during the extraction by Kelex-100 (Leveque and Helgorsky, 1977):

$$Ga(OH)^{4-} + 3HQ(org) = GaQ_3(org) + OH^- + 3H_2O \quad (1)$$

$$Al(OH)^{4-} + 3HQ(org) = A1Q_3(org) + OH^- + 3H_2O \quad (2)$$

$$Na^+ + OH^- + HQ(org) = NaQ(org) + H_2O \quad (3)$$

Typically, the organic phase was 8.5 vol% of Kelex-100, 10.0 vol% of *n*-decanol and 81.5 vol% of kerosene, which were used as extractant, modifier and diluent, respectively. The organic to aqueous ratio was maintained at 1:1, at 28 °C, when over 80% of gallium was reported to be extracted in 3 h (Zhao et al., 2012). Since large quantity of Al (up to 3%) is co-extracted, scrubbing is required before selective stripping. The optimal conditions for scrubbing and the stripping of the organic phase were 6 M HC1

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and 2 M HC1, respectively. The underlining mechanism for the scrubbing selectivity is that Ga can form large chloro-complex species at high HCl concentration, which are trapped by extractant (Kekesi, 2007). On contrast, Al cannot form such complex and consequently is scrubbed at high acidic conditions. The threshold of Ga stripping is reportedly ~2 M HCl, at which no Ga complex is formed.

It has been demonstrated (Sato and Oishi, 1986) that the reaction kinetics for gallium recovery depends on the sodium hydroxide concentration. The rate limiting step in absence of mass transfer limitations has been attributed to the slow interfacial formation of intermediate activated species, such as $Na^+[Ga(OH)_4]^-$ and $Na^+{\cdot}Na^+[Ga(OH)_3]$. Furthermore, the recovery rates (Pesic and Zhou, 1988) also depends strongly on the nature of diluent/modifier in the organic phase. Of the various kerosene based diluents studied from a kinetic perspective (Kermac-470 B, Escaid-200, Aromatic-150 and Cyclohexane), Kermac-470 B was found to be the best. The same study reported that ketones were superior to alcohols as the modifier. However, without decanol, problems with third phase formation persisted during acidic stripping. In addition to synthetic Bayer liquor, industrial Bayer process liquor of a Brazilian bauxite refinery has been used (Borges and Masson, 1994), in which over 90% of gallium was extracted.

Since the Ga content in Bayer liquor is typically less than 200 ppm, the selectivity of extractant remains a critical factor. As mentioned above, the use of Kellex-100 remains irreplaceable for gallium recovery. However, this extractant is produced from a complicated and expensive industrial process (Gareil et al., 1989). Recently, we have synthesized new oxime compounds (Hoang et al., 2015) from cardanol (Fig. 1c). The mono-phenols, with molecular formula $C_{21}H_{36-2n}O$ (n = 0, 1, 2, 3), occur naturally in cashew nutshell (Vasapollo et al., 2011; Voirin et al., 2014), an agricultural by-product. Cashew nutshell liquid (CNSL) is commercially available at more than 300,000 tons per annum worldwide (Attanasi et al., 2006). Cardanol can be distilled from CNSL using a routine process. The natural cardanol, with 15 carbon atoms in the hydrocarbon tails, can have different numbers of double bonds, which make them hydrophobic. Structural variations of cardanol can also occur in the position of the hydroxyl group and the aromatic ring. The key structural advantage of cardanol is the *meta*-position of the hydrocarbon chain (Vasapollo et al., 2011), which is difficult to obtain from synthetic alkylphenols. This structural feature can increase metal selectivity, which is a critical factor in Ga extraction from Bayer liquor.

This study employed the produced oximes of alkyl-salicylaldehydes from cashew nutshell liquid to extract gallium from Bayer liquor of Alumina Tanrai plant (Vietnam). We aim to provide an environmentally friendly and economical extractant to reduce the environmental footprint of gallium production.

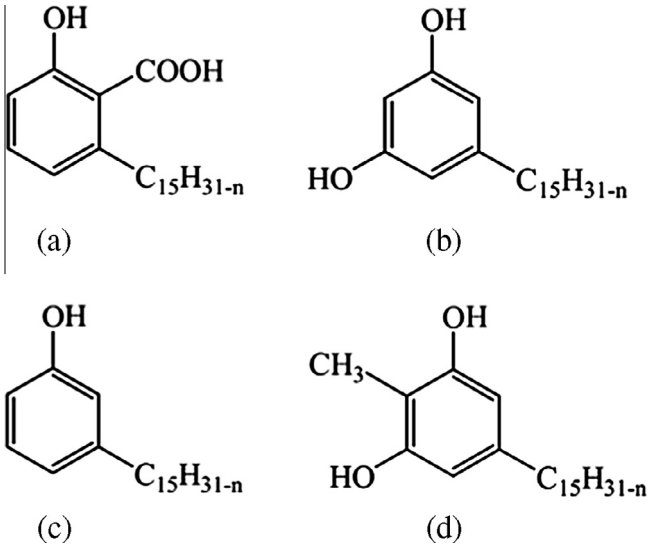

Fig. 1. The components of CNSL: (a) anacardic acid, (b) cardol, (c) cardanol and (d) methylcardol (Yuliana et al., 2012).

2. Experiments

2.1. Materials

Cashew nutshell liquid was obtained from a local company (Thao Nguyen, Hochiminh City, Vietnam). The liquid was distilled at 220–230 °C and used within five days after distillation. The Bayer liquor was obtained from the alumina refinery at TanRai (Vietnam). The Bayer liquor was taken between the filtration and cooling processes in alumina refining loop (Fig. 2a).

The commercial grade kerosene from Exxon Mobil Chemical was used. Analytical grade of isodecanol, ethanol, $SnCl_4$, acetic acid, toluene, chloroform, sodium hydroxide and methanol were used in this study.

2.2. Characterization

^{1}H NMR spectra were recorded at 298 K using a Bruker Avance III 500 MHz spectrometer. Data is expressed in parts per million (ppm) downfield shift from tetramethylsilane with residual solvent as an internal reference (δ 7.26 ppm for chloroform) and is reported as position (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (J in Hz) and integration (number of protons). ^{13}C NMR spectra were recorded at 298 K using a Bruker Avance III 125 MHz spectrometer with complete proton decoupling. Data is expressed in parts per million (ppm) downfield shift relative to the internal reference (δ at 77.2 ppm for the central peak of deuterated chloroform) and is reported as position (δ in ppm). IR spectra were collected by a Nicolet Impact 410 FTIR Spectometer as neat thin films on KBr plates. Concentrations of Ga and other metals were determined by plasma spectrophotometer 7300 DV.

2.3. Synthesis of oximes

A multi-neck round bottom flask, fitted with a condenser and a stirrer bar, was used to contains cardanol (20 mL) and triethylamine (20 mL). A solution of stannic chloride (1.0 mL, as a solution in 50 mL toluene, ~0.12 equiv) was added slowly followed by the addition of paraformaldehyde (4.0 g). The reaction mixture was stirred at room temperature for 15 min before heated to 100 °C for 5 h. The reaction mixture was then cooled down to room temperature. Water (200 mL) was added, and the organic products were extracted with diethyl ether (3 × 50 mL). The solvent of the combined organic phases was removed under reduced pressure to give a brown crude oil. This crude oil (5.0 g) and hydroxylamine hydrochloride (2.0 g) was dissolved in a mixture of water (10 mL) and triethylamine (10 mL) in a round bottom flask fitted with a stirrer bar. The reaction mixture was heated to 50 °C for 3 h with stirring. After cooling down, more water (30 mL) was added and the organic products were extracted with diethylether (3 × 20 mL). The combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure to give a dark yellow solid (82% overall yield from cardanol, see Fig. 3).