Synthesis of oxime from a renewable resource for metal extraction

**Anh Son Hoang*,†, Thi Huong Tran*, Hong Nhung Nguyen*, Hong Son Vu*,
Thanh Phong Vo*, Chi Phan**, and Thanh Vinh Nguyen*****

*Institute of Materials Science, 18 Hoang Quoc Viet, Hanoi, Vietnam
**Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia
***Department of Chemistry, Curtin University, Perth, WA 6845, Australia

Abstract−A new method for semi-synthesis of alkyl salicylaldoximes from cardanol is reported. Cardanol was extracted from decarboxylation process of cashew nutshell liquid, an abundant agricultural by-product. Molecular structures, physical and chemical properties of cardanol and oxime derivatives were confirmed by spectroscopic analyses. The produced oximes were successfully employed to extract copper(II) cation from aqueous copper salt solutions, offering a practical and economical pathway to effectively recover metals using agricultural by-products.

Keywords: Copper Extraction, Oxime, Cashshew Nutshell Liquid, Cardanol

INTRODUCTION

Solvent extraction is an irreplaceable method in the mineral industry [1,2] that has been widely applied to extract valuable metals from ore processing, such as copper, zinc, uranium, molybdenum, vanadium, germanium, nickel and other rare earth metals [3]. The utilization of highly selective and stable extractants for a specific metal is critical to reducing production cost, improving product quality and minimizing environmental impact [4,5]. In the past few decades, commercial extractants such as ACORGA®, LIX®, MOC® and Cyanex® [4,6-8] have been commonly used in the mineral industry, especially for copper extraction. These products

consist of phenolic ketoximes or aldoximes or mixtures of these oxime compounds [9], which can coordinate well to copper(II) cations in solution and, therefore, are responsible for the extraction activity. These phenolic oximes products have also been employed in electrowinning of copper ore [10].

The selective formation and stability of the complexes between these bidentate phenolic oxime ligands and copper(II) cations arise from the favorable hydrogen bonds, as shown in Fig. 1 [11]. For phenolic oxime systems with the same number and type of substituents on the aromatic ring, the acidity decreases in the order: 2-hydroxybenzaldoximes>aliphatic-aromatic hydroxyoximes>2-hydroxybenzophenone oxime derivatives [12]. Parallel to that, cop-
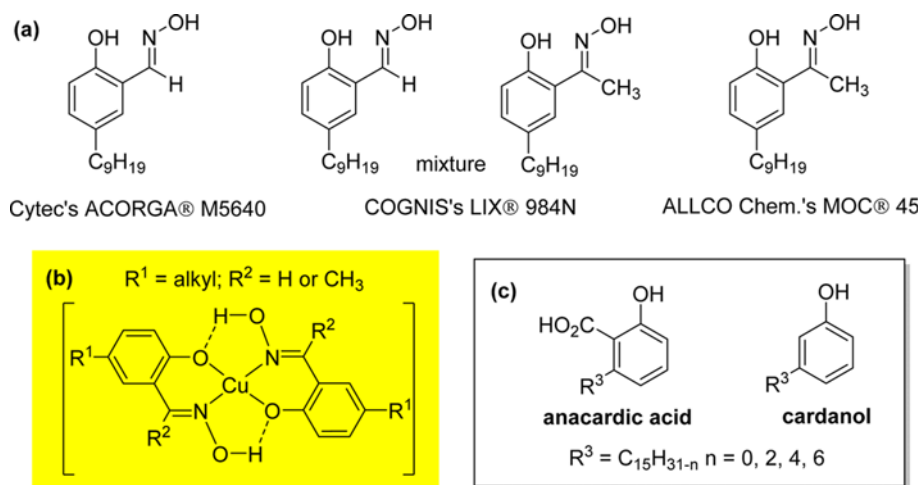

Fig. 1. Examples of (a) commercially available extractants, (b) general structure of their complexes with copper(II) and (c) anacardic acid and cardanol.

---

†To whom correspondence should be addressed.
E-mail: sonha@ims.vast.ac.vn, hoangsonmstv@yahoo.com

per-ligand association constants and the extraction ability of hydroxyoxime products also decrease in the same order [1]. Commercial oxime extractants are generally prepared by the formylation reaction of alkylphenols, which were derived from alkylation reaction of phenolic intermediates of petrochemical processes [10]. There have been several initiatives to find renewable sources for economical and environmentally friendly production of these oxime extractants [11,13].

Cashew nutshell liquid (CNSL), an abundant agricultural byproduct, contains roughly 70% anacardic acid and 5% cardanol [14]. The cashew nutshell liquid is commercially available up to 300,000 tons per annum [15]. It is known that the thermal decarboxylation of CNSL and distillation results in an oil rich in cardanol [14], which can be used as precursors to synthesize phenolic aldoxime extractants and other industrial products [15,16]. The alkyl or alkenyl substituents of natural occurring cardanol are at *meta*-position of the phenol group, a feature not easy to obtain for synthesized alkylphenols from petrochemical intermediates [16], which can be advantageous in the metal extraction process. Seidl [13] and Tyman[14] have carried out elegant studies in which they established the principle for the three-step semi-synthesis of oxime derivatives from CNSL-derived cardanol. However, the efficiency and effectiveness of these processes have yet to be quantified. Vietnam produces approximately 290,000 tons cashew nut (with shell) per year [17], making it the fourth biggest producer of this product worldwide. Vietnam is also the third highest territory in yield (tons per hectares) in the top ten producers, after Nigeria and Philippines. Hence, transforming the abundant local CNSL byproduct to useful products is highly desirable. Herein, we would like to report our new method to produce phenolic aldoximes from CNSL. The extraction capacity of the compound was also verified with copper(II) cations, with an intention to apply the method to recover other valuable metals.

EXPERIMENTAL METHODS

1. Materials

Cashew nutshell liquid for our studies was obtained from a local company (Thao Nguyen Co. Ltd., Ho Chi Minh City, Vietnam). Solvents such as toluene, *n*-hexane; reagents such as tin(IV) chloride, triethylamine and paraformaldehyde were purchased and used directly in analytical grade from chemical suppliers. $CuSO_4$ solution was prepared at Cu^{2+} concentration of $5\,g\,L^{-1}$.

2. Experimental Methods

This section describes the production of oximes from cashew nutshell liquid and the application of those oximes in the solvent extraction of copper(II) cation. The semi-synthesis of chemicals and products from CNSL has been reviewed in detail [18]. In this study, oximes were produced by the decarboxylation of cashew nutshell oil, mostly containing anacardic acid, followed by the Lewis acid catalyzed formylation reaction to the *ortho*-position of the phenol group and finally the oximation reaction with hydroxylamine.

^{1}H NMR spectra were recorded at 298 K unless otherwise stated using 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 unless otherwise stated using 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 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 spectrometer with neat thin films on KBr plates.

2-1. Decarboxylation of CNSL and Distillation of Cardanol (Scheme 1)

To a round bottom flask fitted with a distillation head/condenser, a stirrer bar and a thermometer was added cashew nutshell liquid (500 mL). The flask content was heated slowly to 180 °C under reduced pressure (5 mmHg). Mist of carbon dioxide, which resulted from the decarboxylation of anacardic acid (Scheme 1(a)), started to form on the distillation head when it reached 180 °C. The reaction mixture was maintained at this temperature to complete decarboxylation (20 minutes). The reaction mixture was subsequently heated to 200 °C and fractional distillation of the reaction mixture was carried out between 200-230 °C. The first fraction before the temperature reached 220 °C was discarded as spectroscopic analyses revealed that it contained only a small fraction of cardanol. The fraction between 220-230 °C, a light yellow liquid (352 mL, 70% yield based on volume) was collected. Spectroscopic analyses of this fraction confirmed that it was a cardanol mixture. After this fraction, the temperature rose again to 250-270 °C, a red oil as the distillate at this temperature range was also discarded, as it was a mixture of cardanol (minor) and cardol (major).

We have developed a new synthetic method in which cardanol is carbonylated via a Lewis-acid catalyzed formylation reaction with paraformaldehyde before undergoing subsequent oximation reaction. After screening numerous common Lewis acids, we were delighted to find that stannic chloride ($SnCl_4$) can effectively catalyze this formylation reaction. In previous studies [9,12], the unsaturated side-chain of cardanol needed to be hydrogenated to avoid the formation of slurry in the reaction mixture during their Reimer-Tiemann formylation reaction. With our new method, however, we found that slurry formation did not take place in the presence of the unsaturated side-chain. Therefore, we decided to skip the hydrogenation step [13] to saturate cardanol ring-substituents with the anticipation that the unsaturated hydrocarbon side chains will not interfere the carbonylation/oximation or the metal extraction process. Indeed, the unsaturated side-chain tolerated all subsequent chemical transformations.

2-2. Synthesis of Oximes (Scheme 1)

To a multi-neck round bottom flask fitted with a condenser and a stirrer bar was added cardanol (20 mL) and triethylamine (20 mL). A solution of stannic chloride (1.0 mL, 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 minutes before being heated to 100 °C for 5 h. The reaction mixture was then cooled 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
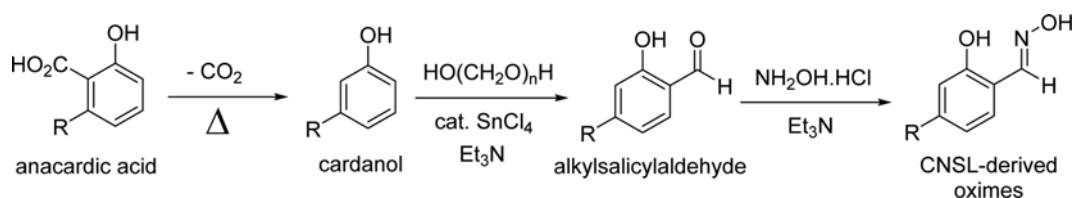
Scheme 1. Two-step synthesis of phenolic oximes from CNSL cardanol.
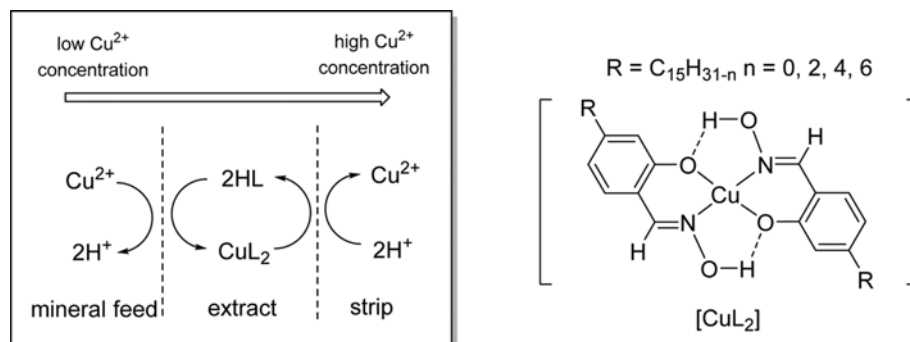
Scheme 2. Extraction of copper(II) by CNSL-derived phenolic oxime products.

was removed under reduced pressure to give a brown crude oil containing mainly alkylsalicylaldehyde. 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, 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).

2-3. Copper(II) Extraction (Scheme 2)

The newly produced oximes were used to extract copper(II) cations from aqueous copper salt solutions based on a literature procedure [4]. The oxime mixture (1.0 g) was dissolved in amyl alcohol (10 mL) and the solution was mixed well with an aqueous solution of $CuSO_4$ (18 mL, Cu^{2+} concentration of 5 g L^{-1}) in a separatory funnel. The concentration of Cu^{2+} in this primary aqueous phase was quantified to evaluate the efficiency off the extraction process. The organic phase was subsequently mixed with an aqueous solution of H_2SO_4 (14 mL, 1 M, pH~0.3) and the mixture was

heated for 2 h to strip back copper(II) cations to the aqueous phase. This secondary aqueous layer was separated and deionized water (36 mL) was added. An excess amount of concentrated aqueous ammonium hydroxide solution was used neutralize this solution and completely transform copper(II) cations to its complexation with ammonia $[Cu(NH_3)_4]^{2+}$. The final volume of this solution was recorded. Three samples of 10 mL each were put in Erlenmeyer flasks and the Cu^{2+} was titrated with standard 0.001 N EDTA solution, using murexide as indicator. The average value of three titrations was used to calculate the extracted amount of Cu^{2+} in this solution [19].

RESULTS AND DISCUSSION

1. Characterization of Intermediates and Products

1-1. The Distillation Product

The IR spectrum of cardanol (Table 1 and Fig. 2) showed a broad absorption band at 3,100-3,600 cm^{-1}, which can be assigned to stretching vibration of the phenolic O-H bond. Several strong absorption bands at 2,800-3,030 cm^{-1} can be assigned to the aromatic, alkyl

Table 1. Structural information from IR spectra of the CNSL-derived products

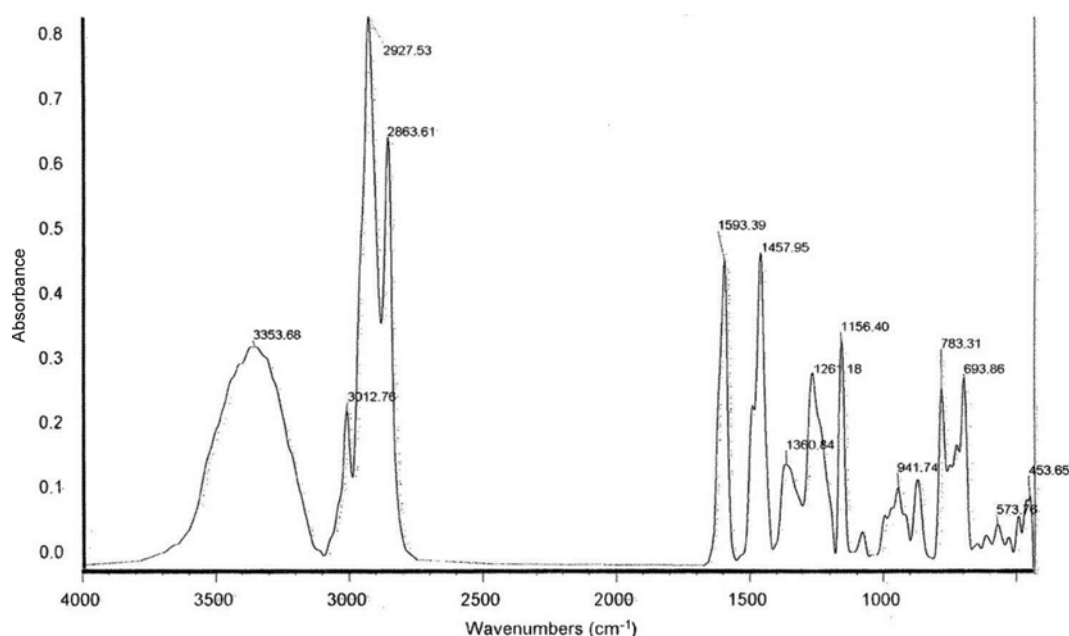| Compound	IR signal	Structural information
The distillation product	- 3100-3600 cm^{-1} (broad)	- O-H stretching
	- 2800-3030 cm^{-1} (strong)	- C-H stretching
	- 1593 and 1457 cm^{-1} (strong)	- C=C bending
	- 693, 783 and 850 cm^{-1}	- 1,3-Disubstituted benzene
The carbonylation product	- 3447 cm^{-1} (broad)	- O-H stretching
	- 1635 cm^{-1} (strong)	- C=O stretching
The oximation product	- 3453 cm^{-1} (broad)	- O-H stretching
	- 1621 cm^{-1} (strong)	- C=N stretching

Fig. 2. IR spectrum of distilled cardanol.

Table 2. Structural information from NMR spectra of the CNSL-derived products

Compound	NMR signal	Structural information
The distillation product	^{1}H NMR	
	- 7.14 ppm (t, 1H), 6.76 ppm (d, 1H), 6.66 ppm (s, 1H), 6.64 ppm (d, 1H)	- 1,3-Disubstituted benzene
	- 5.50-5.30 ppm (m, 2.2H)	
	- 5.00 ppm (bs, 1H)	- CH=CH moieties in $C_{15}H_{31-n}$
	- 2.60-0.80 ppm (m, ~25H)	- Phenolic OH
		- $C_{15}H_{31-n}$ side chain
The carbonylation product	^{1}H NMR	
	- 11.04 ppm (s, 1H)	- Aldehyde CHO
	- 9.83 ppm (s, 1H)	- Phenolic OH
	- 7.45 ppm (d, 1H), 6.83 ppm (d, 1H), 6.80 ppm (s, 1H)	- 1,2,4-Trisubstituted benzene
The oximation product	^{1}H NMR	
	- 10.30 ppm (s, 1H)	- Aldehyde CHO
	- 8.17 ppm (s, 1H)	- Phenolic OH
	^{13}C NMR	
	- 157 ppm	- C=N-OH group

and alkenyl C-H stretch. Two strong absorption bands at 1,593 and 1,457 cm^{-1} can be assigned to the bending vibration of the aromatic C=C double bonds. The aromatic ring with two substituent groups at 1,3 positions is characterized by three bands at 693, 783 and 850 cm^{-1}. ^{1}H NMR spectrum of the distillate (500 MHz, CDCl$_3$, 25 $^\circ$C, Table 2 and Fig. 3) clearly reveals that it consists of cardanol in high purity. Four aromatic protons of the 1,3-disubstituted system are evidenced by a triplet (7.14 ppm, 1H), a doublet (6.76 ppm, 1H), a singlet (6.66 ppm, 1H) and another doublet (6.64 ppm, 1H) signals in the range from 6.6 to 7.2 ppm. The multiplet (5.50-5.30 ppm, ~2.2H) represents the hydrogens of CH=CH moieties in the $C_{15}H_{31-n}$ side chains of cardanol. The broad singlet (5.00 ppm, 1H) accounts for the phenol group. The rest of the spectrum (2.60-0.80 ppm, ~25H) represents the $C_{15}H_{31-n}$ side chains of cardanol.

1-2. The Carbonylation Product

The IR spectrum of the produced aldoxime (Table 1 and Fig. 4) has two strong characteristic bands: 3,447 cm^{-1} (broad, O-H stretch) and 1,635 cm^{-1} (C=O double bond stretch). ^{1}H NMR spectrum of the carbonylated cardanol (500 MHz, CDCl$_3$, 25 $^\circ$C, Table 2 and Fig. 5) also confirms the identity of the alkylsalicylaldehyde products formed. The aldehyde group is evidenced by a downfield singlet (11.04 ppm, 1H). The other singlet (9.83 ppm, 1H) accounts for the phenol group, probably in hydrogen-bonding interaction with the aldehyde functionality. The resonance signals representing the aromatic protons can be found as a doublet (7.45 ppm, 1H), another doublet (6.83 ppm, 1H) and a singlet (6.80 ppm, 1H).

1-3. The Oximation Product

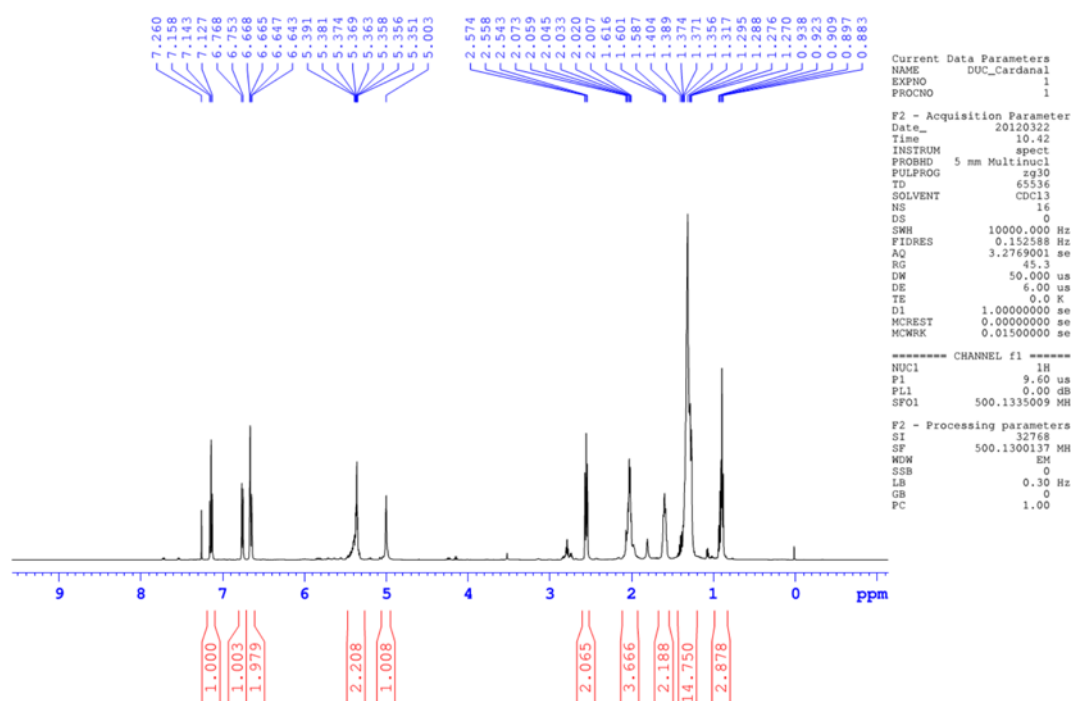The IR spectrum of the produced aldoxime (Table 1 and Fig. 6)

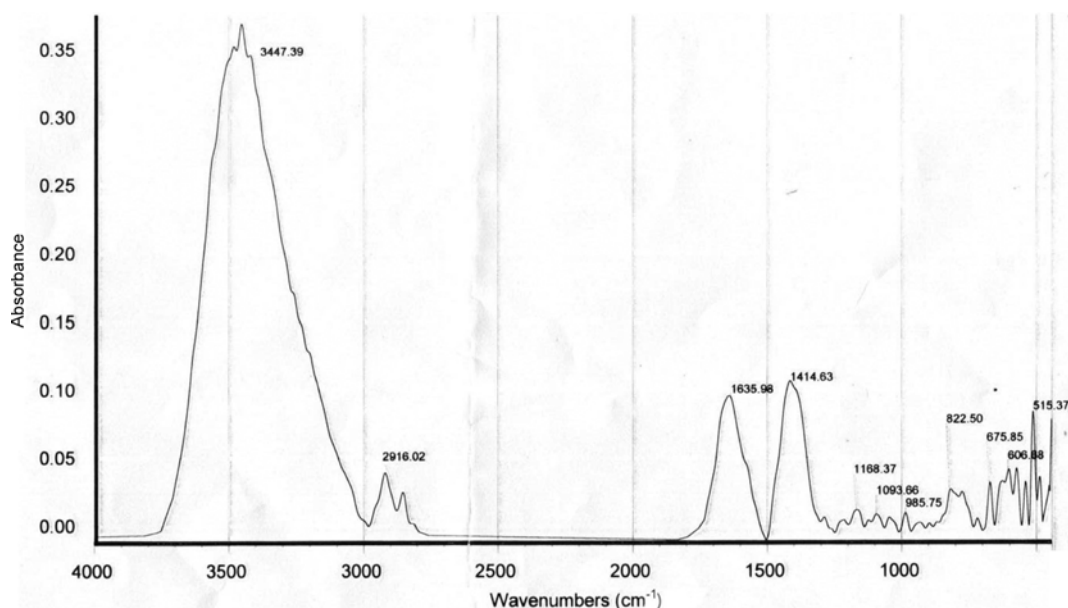**Fig. 3.** ^{1}H NMR spectrum of distilled cardanol.

Fig. 4. IR spectrum of carbonylated cardanol.

has two strong characteristic bands: 3,453 cm^{-1} (broad, O-H stretch) and 1,621 cm^{-1} (C=N double bond stretch). The ^{1}H-NMR spectrum (500 MHz, CDCl$_3$, 25 °C, Table 2 and Fig. 7) shows two singlets at 10.30 and 8.17 ppm corresponding to the oxime and phenolic OH groups, respectively. The ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C, Table 2 and Fig. 8), DEPT-90 and DEPT-135 spectra suggest the absence of the aldehyde C=O group in the 180-220 ppm region and give the evidence of the presence of the C=N-OH group at 157 ppm.

2. Carbonylation and Oximation Processes

The convenient semi-synthesis of aldoximes from CNSL cardanol and the successful extraction of copper(II) from aqueous solution using these aldoximes confirms the practicality of this newly developed method. As mentioned in section 2.2, we skipped the hydrogenation of the unsaturated side chains step. Seidl and coworker originally hydrogenated the side chains due to the problematic Reimer-Tiemann carbonylation reaction in their synthetic sequence in the presence of the side chain C=C double bonds [13].
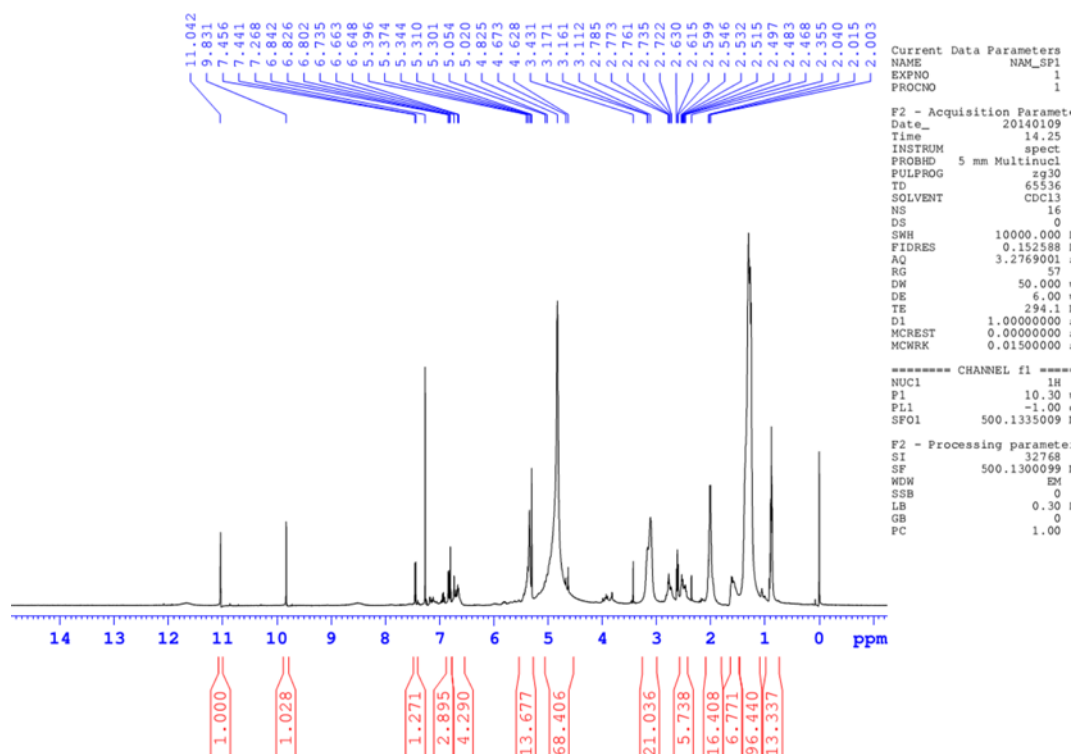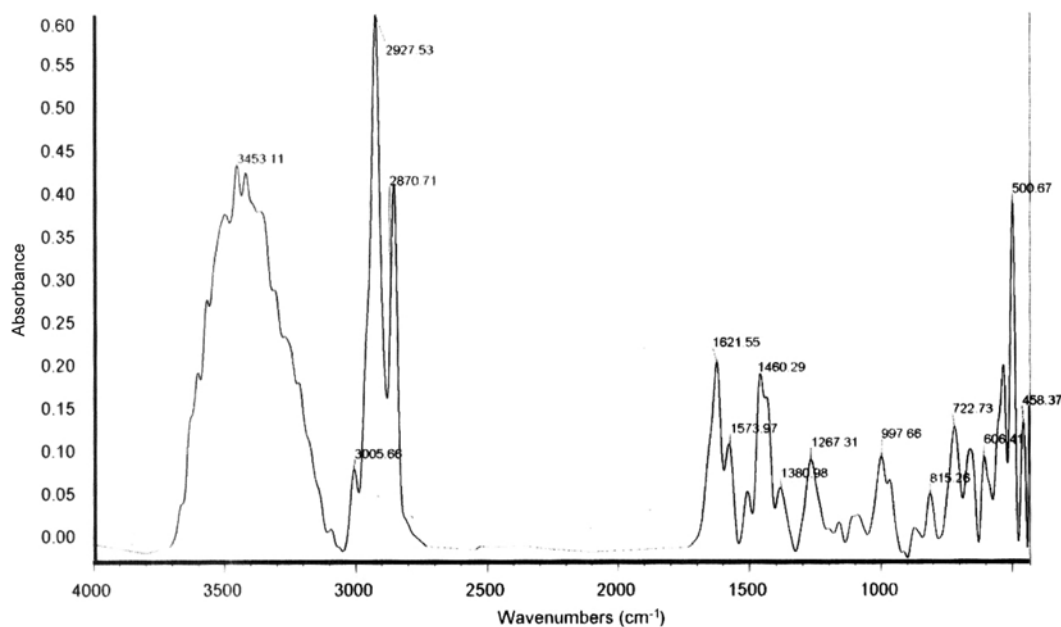
Fig. 5. ^{1}H NMR spectrum of carbonylated cardanol.

Fig. 6. IR spectrum of oximes from CNSL.

Presumably, sodium hydroxide employed in the Reimer-Tiemann reaction would hydroxylate the alkenyl C=C double bonds, resulting in the formation of inseparable emulsion and significantly reduce the productivity of the process. In our method, the carbonylation of cardanol was via a Lewis-acid catalyzed process, so hydrogenation reaction of the side chains is indeed not necessary. This shorter synthesis of aldoximes from cardanol offers a new pathway to a

more economical and environmentally friendly process to produce metal extractants from renewable sources.

3. Copper(II) Extraction

The copper(II) extraction efficiency for our synthesized oximes was calculated to be ~96% (Table 3), which is comparable to the reported values for MOC® 45 [4] or Cyanex® 301 and 302 [8]. Note that the high extraction was obtained without additional NaOH as
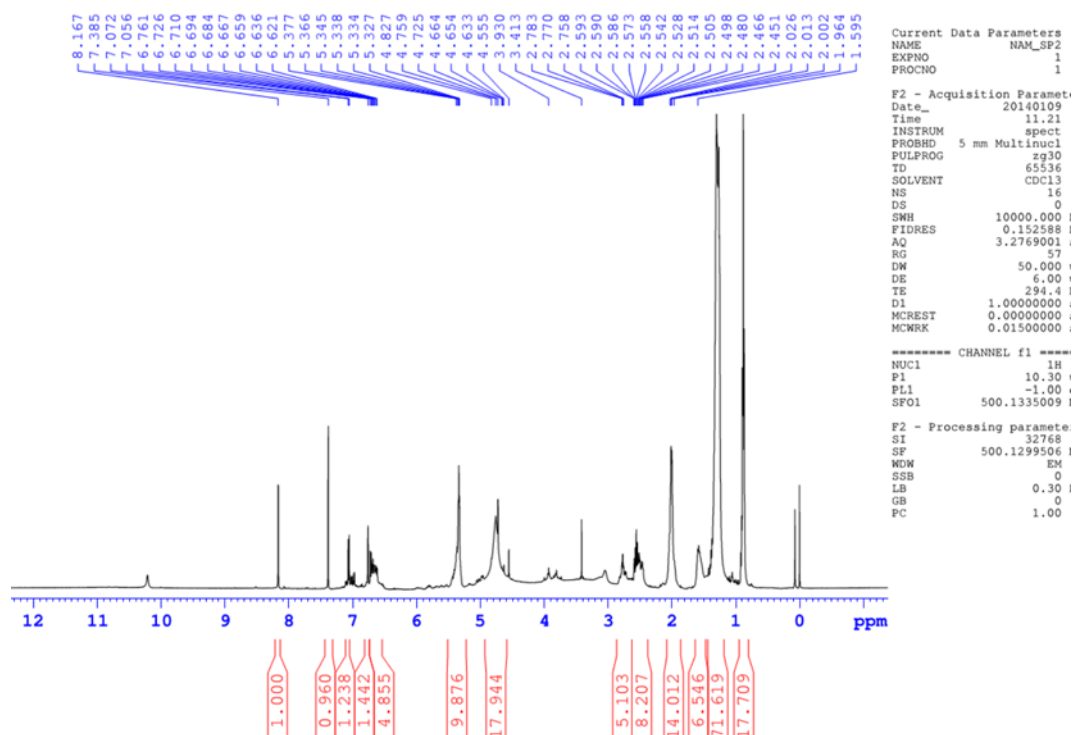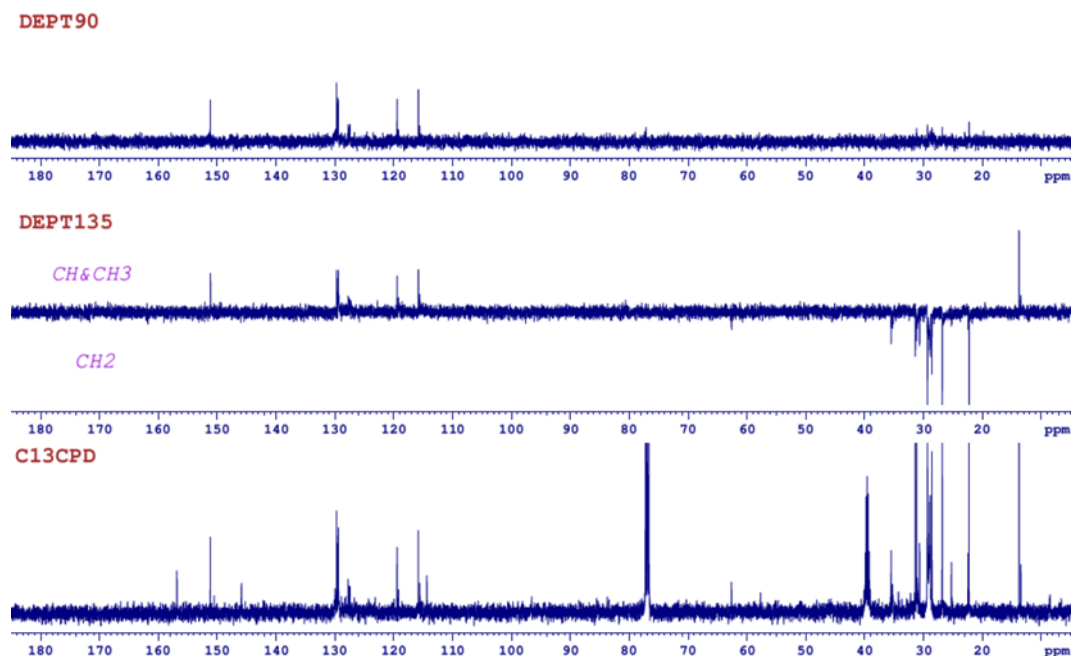
Fig. 7. ¹H NMR spectrum of oximes from CNSL.

Fig. 8. ¹³C NMR and DEPT spectra of oximes from CNSL.

Table 3. Efficiency of copper(II) extraction

Initial amount of Cu²⁺ (per 1 g oximes)	Extracted Cu²⁺ (mg/1 g oximes)[a]	Extraction efficiency	Desorbed Cu²⁺ (mg/1 g oximes)[b]	Desorpption efficency
90.0	86.6	96.2%	57.6	66.5%

[a]From the feed solution to the organic phase containing oximes

[b]From the organic phase back to aqueous solution

often employed with normal extractants [4]. The desorption process has an efficiency of 66% (Table 3). Collectively, the overall solvent extraction of copper(II) cations by oximes gave 57.6 mg Cu^{2+}/ g oximes. This result is slightly more favorable than what was obtained by Seidl and co-workers using their three-step synthesis (49.3-49.6 mg Cu^{2+}/1 g oximes) [13].

CONCLUSIONS

We have successfully developed a new catalytic method to produce oxime compounds of alkylsalicyladehyde from cashew nutshell liquid in high yield by (i) decarboxylative pre-treatment of CNSL and distillation of cardanol, and (ii) $SnCl_4$ catalyzed formylation of cardanol and (iii) oximation of the aldehydes. The produced oximes were successfully used to extract copper(II) cation from aqueous copper salt solutions, offering a practical and economical pathway to effectively recover metals using inexpensive agricultural by-products. The produced oximes from the new method have similar extraction capacity to petrochemical extractants. The results demonstrated the potential application of natural-based products in sustainable hydrometallurgical processes. Industrial development and implementation of this new method for the extraction of other metals, especially rare-earths, are currently underway.

ACKNOWLEDGEMENTS

REFERENCES

1. A. M. Sastre and J. Szymanowski, *Solvent Extr. Ion Exch.*, **22**(5), 737 (2004).
2. M. J. Hudson, *Hydrometallurgy*, **9**(2), 149 (1982).
3. D. S. Flett, *J. Chem. Technol. Biotechnol.*, **74**(2), 99 (1999).
4. K. S. Rao, N. B. Devi and B. R. Reddy, *Hydrometallurgy*, **57**(3), 269 (2000).
5. D. Dreisinger, *Hydrometallurgy*, **83**(1), 10 (2006).
6. Z. Lazarova and M. Lazarova, *Solvent Extr. Ion Exch.*, **29**(1), 128 (2011).
7. M. Amores, A. G. Coedo and F. J. Alguacil, *Hydrometallurgy*, **47**(1), 99 (1997).
8. K. C. Sole and J. B. Hiskey, *Hydrometallurgy*, **37**(2), 129 (1995).
9. J. Szymanowski, *Hydroxyoximes and copper hydrometallurgy*, CRC Press (1993).
10. J. H. P. Tyman and S. J. A. Iddenten, *J. Chem. Technol. Biotechnol.*, **80**(11), 1319 (2005).
11. A. G. Smith, P. A. Tasker and D. J. White, *Coord. Chem. Rev.*, **241**(1-2), 61 (2003).
12. J. Szymanowski and A. Borowiak-resterna, *Crit. Rev. Anal. Chem.*, **22**(1-2), 519 (1991).
13. P. R. Seidl, A. R. Menzel and R. O. P. Couto, *Process for preparation of oximes and resulting products*, U.S. Patent, 6,673,969 (2004).
14. J. H. P. Tyman, D. Wilczynski and M. A. Kashani, *J. Am. Oil. Chem. Soc.*, **55**(9), 663 (1978).
15. O. A. Attanasi, S. Berretta, C. Fiani, P. Filippone, G. Mele and R. Saladino, *Tetrahedron*, **62**(25), 6113 (2006).
16. G. Vasapollo, G. Mele and R. Del Sole, *Molecules*, **16**(8), 6871 (2011).
17. *Food and Agriculture Organization of the United Nations. Available online: http://www.fao.org* (Accessed 18-08-2012).
18. C. Voirin, S. Caillol, N. V. Sadavarte, B. V. Tawade, B. Boutevin and P. P. Wadgaonkar, *Polym. Chem.*, **5**(9), 3142 (2014).
19. M. A. Abd El-Ghaffar, Z. H. Abdel-Wahab and K. Z. Elwakeel, *Hydrometallurgy*, **96**(1-2), 27 (2009).