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# Application of a cashew-based oxime in extracting Ni, Mn and Co from aqueous solution

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## Abstract

**Background:** Cashew nut shell is a by-product of cashew (*Anacardium occidentale*) production, which is abundant in many developing countries. Cashew nut shell liquor (CNSL) contains a functional chemical, cardanol, which can be converted into a hydroxyoxime. The hydroxyoximes are expensive reagents for metal extraction.

**Methods:** CNSL-based oxime was synthesized and used to extract Ni, Co, and Mn from aqueous solutions. The extraction potential was compared against a commercial extractant (LIX 860N).

**Results:** All metals were successfully extracted with  $\text{pH}_{0.5}$  between 4 and 6. The loaded organic phase was subsequently stripped with an acidic solution. The extraction efficiency and  $\text{pH}_{0.5}$  of the CNSL-based extractant were similar to a commercial phenol-oxime extractant. The metals were stripped from the loaded organic phase with a recovery rate of 95% at a pH of 1.

**Conclusions:** Cashew-based cardanol can be used to economically produce an oxime in a simple process. The naturally-based oxime has the economic potential to sustainably recover valuable metals from spent lithium-ion batteries.

**Keywords:** Cashew nut shell liquor, Nickel extraction, Cobalt extraction, Lithium-ion battery recycling

## Background

Solvent extraction is commonly used in hydrometallurgical processes to separate the desired metal from aqueous solutions. With the use of careful pH control and a series of selective extraction and stripping stages, the separation of multiple desirable streams can be achieved [1]. Solvent extraction is considered a lower cost and more environmentally friendly option than traditional pyrometallurgical processes [2]. In addition to mineral production, solvent extraction is also used in metal recycling. Currently, the recycling process of lithium-ion

batteries (LIBs) and many types of electronic waste relies on solvent extraction [3].

With the increasing demand for LIBs and the high production of electronic waste, there is an urgent need for effective recycling both to recover valuable materials and for more environmentally acceptable disposal. While LIBs recycling facilities are available in developed countries, economic feasibility remains a challenge. These facilities are only available in countries with strict LIB regulations [3]. On the other hand, wastes from developed countries are often shipped to developing countries for processing and disposal. According to a CSIRO report, only 2% of Australian spent LIBs were recycled, whereas the majority of the remainder was shipped overseas [4]. LIBs' disposal in landfills can cause severe ecological and health damages [3]. Recycling of many types of e-waste faces similar challenges [5]. The lack of recycling facilities is a

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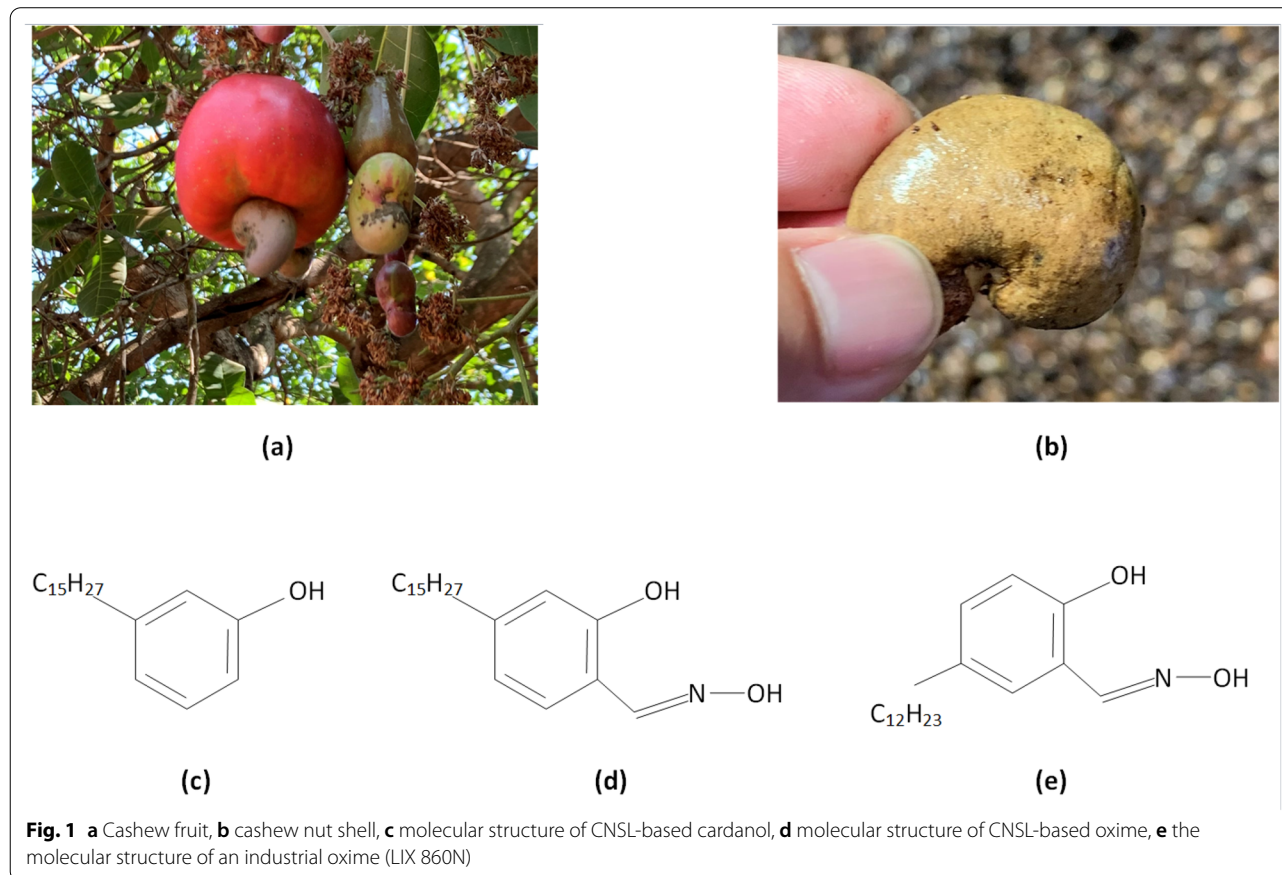
particularly pressing issue for developing countries with weak environmental regulations. Recycling metals, especially nickel and cobalt, avoid associated environmental impacts from the mining activities [6] and provides a method to recover valuable materials.

These problems show an urgent need to develop an economical and practical process with potential application for localized or small-scale collection and recycling facilities. To facilitate this, a move away from industrial chemicals, which are effective but expensive, is needed. In addition to affordable costs, the chemicals should have lower toxicity and lower risks in handling and transportation. For instance, organic and less hazardous acids, citric acid [7], malic acid [8], and oxalic acid [9], have been used in leaching processes.

The extractant is the most specialized and expensive chemical among the required reagents for the processes [10]. Commonly used extractants are based on either a hydroxyoxime group [10] (such as the Acorga and LIX series) or phosphonic groups (Cyanex series) [11, 12], although a wide variety exists for specific metal selectivity. The extractants are often made from petrochemicals. For instance, the hydroxyoximes are synthesized via several reaction steps such as oligomerisation and oximation

[13]. The solvents (diluent) and extractants in current use represent a high operating cost alongside the generation of hazardous (organic) waste [14].

In this study, we utilize a natural-based chemical in extracting metals from LIBs. The chemical is made from natural cardanol, which is an alkyl-phenol found in the cashew nut shell liquor (CNSL) [15]. The cashew tree (*Anacardium occidentale*) is a native of Brazil and the Lower Amazons [16]. The tree is a valuable cash crop in tropical parts of Africa and Asia (Fig. 1a). The cashew nut shell (Fig. 1b) is a by-product of cashew processing and is typically treated as a waste stream. CNSL contains a high fraction of cardanol (Fig. 1c), up to wt. 25% [15]. It should be noted that the CNSL cardanol contains a 15-carbon chain in the alkyl branch, whereas most industrial alkylphenols have 12 or fewer carbons [17]. Furthermore, the CNSL cardanol has the hydrocarbon chain situated in the *meta*-position (Fig. 1c), which is distinct from most synthesized alkyl phenols [15]. The CNSL cardanol thus creates an oxime where the hydrocarbon chain is in the *meta*-position relative to the phenol group, as (Fig. 1d) distinct from the overwhelming majority of reported oxime-type extractants (including the common ACORGA and LIX series) which have an *ortho*-structure



(Fig. 1e) [18]. The underlying reason is that industrial oligomerisation tends to form *ortho*- and *para*-alkyl-phenol only [13].

Previously, we synthesized an oxime from CNSL and successfully used it to extract gallium from bauxite processing liquor [19]. This study explores the feasibility of the chemical to extract valuable metal from recycling LIBs and e-waste. Among the current LIBs, Lithium Nickel Manganese Cobalt Oxide (NMC) is the most common cathode due to its high capacity [20]. Consequently, the extraction of the natural-based extractants with three divalent metals,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$ , is investigated. Among a myriad of structures, complexes between phenolic oxime extractants and a large number of transition metals, including vanadium, nickel, cobalt, copper, platinum, and palladium, have been reported [18], which is promising for their use in recovering valuable metals as part of the recycling process. Ultimately, this study aims to provide an economical and environmental friendly extractant for LIBs' recycling.

## Methods

### Synthesis and characterization of CNSL-oxime

Cardanol was received from a cashew nut shell processing facility in Binh Phuoc Province, Vietnam. Cardanol was dissolved in triethylamine (volume ratio 3:2). The cardanol solution was stirred for 30 min and added to a mixture of  $\text{SnCl}_4$  and toluene ( $\text{SnCl}_4$ :toluene volume ratio of 1:4) at the volume ratio of 1:1. The solution was stirred for 30 min before adding a mixture of formaldehyde and methanol (formaldehyde to methanol volume ratio of 3:2). This solution was stirred constantly for 24 h at 25 °C. The resulting alkyl salicylaldehyde product was rinsed and filtered using toluene and deionized water.

The recovered alkyl salicylaldehyde was employed for the oximisation reaction (step 2 in Fig. 2). Alkyl salicylaldehyde was dissolved into deionized water (1:1 weight ratio), mixed with the same amount of hydroxylamine hydrochloride, and stirred for 30 min. A mixture constituting triethylamine and methanol (trimethylamine to methanol volume ratio of 1:2) was added into the solution to start the oximisation reaction [21]. The reaction was maintained for 6 h at 25 °C under constant stirring

(at 200 rpm). The final oxime product was filtered and heated at 80 °C for 30 h to remove the organic solvent.

The intermediate (alkyl salicylaldehyde) and final (oxime) products were diluted in toluene at 5% for IR characterization (Spectrum Two PerkinElmer). The IR spectra are shown in Figs. 3 and 4. The characteristic bands of the aldehyde group are clearly identified in Fig. 3:  $1607\text{ cm}^{-1}$  (C=O bond) and three peaks in the range  $3033\text{--}2882\text{ cm}^{-1}$  (C–H bonds). The characteristic bands of the oxime group were confirmed in Fig. 4:  $1643\text{ cm}^{-1}$  (C=N–OH bond) and  $3418\text{ cm}^{-1}$  (O–H bond).

### Chemicals for extractant study

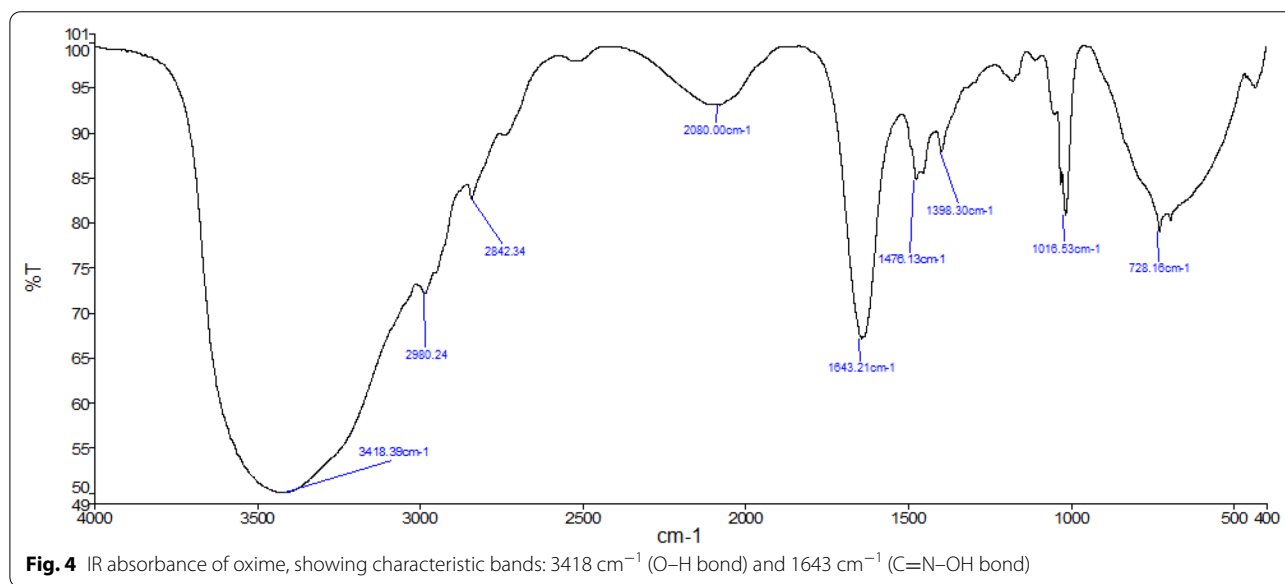
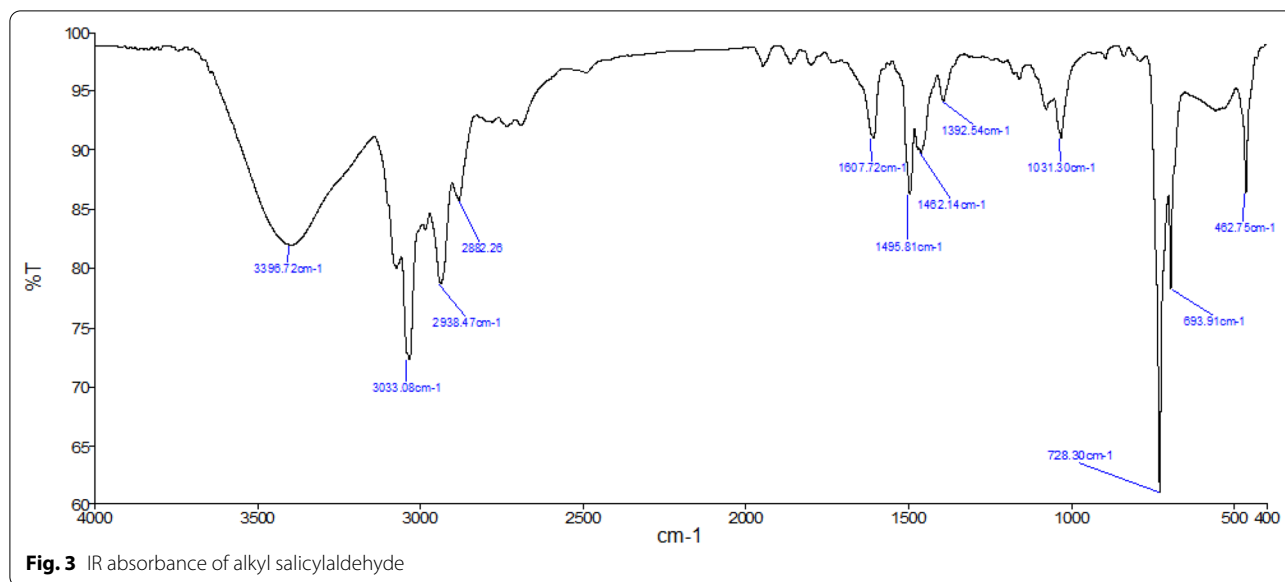
In addition to the CNSL-based oxime, 5-nonylsalicylaldehyde (LIX 860N-IC) was received from BASF Ltd. (Australia). Table 1 presents a list of metal compounds employed in the extraction study. All chemicals were obtained from Chem-Supply (Australia) and used as received, without any further purification.

### Solvent extraction procedures

The aqueous solution was prepared by dissolving the exact amount of  $\text{MnSO}_4\cdot\text{H}_2\text{O}$ ,  $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ , and  $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$  with the Mn:Co:Ni molar ratio of 1:1:1 in doubly distilled water. The organic phase was prepared by mixing extractant and kerosene (a mixture of  $\text{C}_n\text{H}_{2n+2}$  with  $n$  between 10 and 16). The volumetric ratio between extractant solution (both LIX 860N-IC and natural oxime) and kerosene was 1:9. The extraction and stripping processes were performed by mechanically contacting equal volumes (100 mL) of aqueous and organic solutions in a separating funnel. To generate the pH extraction equilibrium, a 3 M NaOH solution was employed to adjust the pH of the aqueous–organic mixture. Such pH values of the aqueous–organic mixture or emulsion were continuously measured with an intermediate junction pH electrode (Ionode, IJ-44A) connected to a pH meter. After each addition of NaOH into the mixture, the separating funnel was shaken for 10 min using Separatory Funnel Shaker (SR-2DW, Borg Scientific) and followed by its equilibrium at each sample point until the pH was stable to two decimal points.



**Fig. 2** Chemical reactions to produce oxime from cardanol



**Table 1** List of chemicals for extraction study

Name	Formula	Grade (%)
Cobalt (II) sulfate heptahydrate	CoSO <sub>4</sub> ·7H <sub>2</sub> O	≥ 99
Nickel (II) sulfate hexahydrate	NiSO <sub>4</sub> ·6H <sub>2</sub> O	≥ 99
Manganese (II) sulfate monohydrate	MnSO <sub>4</sub> ·H <sub>2</sub> O	≥ 99

The loaded organic phase obtained from the extraction experiments was used for the stripping experiment. The loaded organic was contacted with deionized water at a volume ratio of 1:1. Acidic solution (5 wt. % of sulphuric acid) was added to adjust the pH of the mixture. The

stripping equilibrium was established with a similar procedure of the extraction experiment, that is shaken for 10 min and allowed to separate.

The collected aqueous sample was digested with a 5% HNO<sub>3</sub> solution and analyzed by employing ICP-OES equipment (NexION™ 350D-Optima 8300, PerkinElmer). All measurement was performed at room temperature and in triplicate.

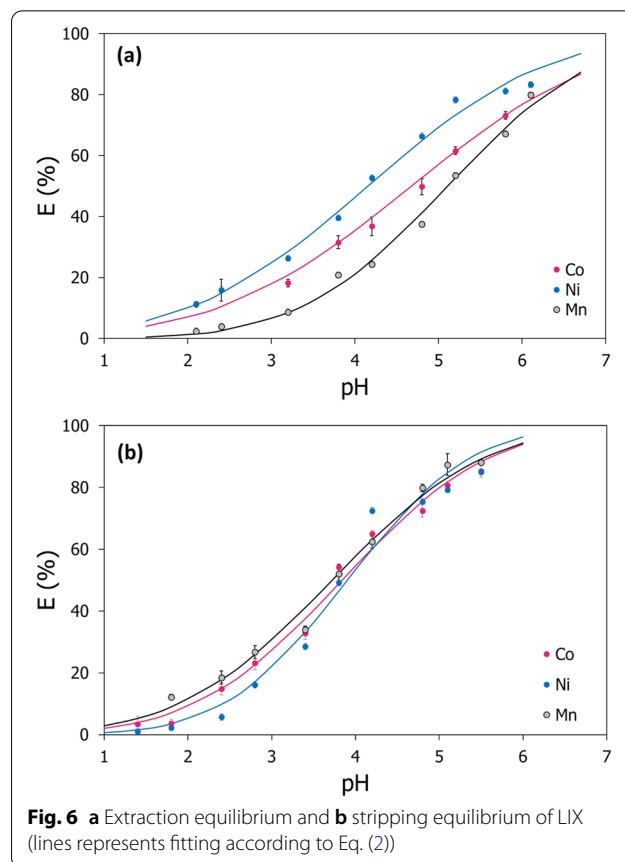
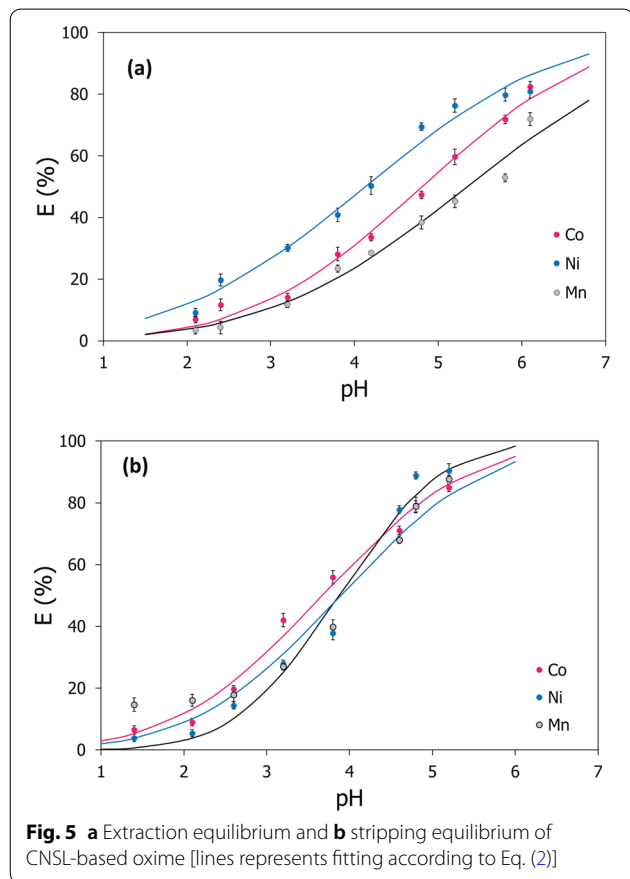
## Results and discussion

The metal loading (oil phase percentage, *E*) of each metal was evaluated by the following equation:

$$E = \frac{[M]_0 V_0 - [M]_e V_e}{[M]_0 V_0} \cdot 100\%, \quad (1)$$

where  $[M]_0$  and  $[M]_e$  ( $\text{mg L}^{-1}$ ) are the initial and equilibrium metal concentration in the aqueous phase, respectively;  $V_0$  and  $V_e$  (mL) are the initial and equilibrium volumes of the aqueous phase, respectively.

The extraction and stripping isotherms of the CNSL-based extractant and commercial (LIX series) extractant are shown in Figs. 5 and 6. As expected, the metals are transferred to the oil phase at higher pH and transferred to the aqueous phase at low pH. The pH-dependent behavior is consistent with the proton ionization of oxime at a high pH [10]. The commercial and naturally based oximes were shown to have similar extracting and stripping capacities. While the CNSL-based molecule has 15 carbons in the hydrocarbon chain, against the nine-carbon chain in LIX 860N-IC, it also has three double bonds. In addition, the 15-carbon “tail” is in the meta- (rather than *ortho*-) orientation to the phenol group. The length of the carbon chain can impact the hydrophobicity of the extractant and complexes [13]. A short carbon chain can increase water solubility, and reduce loading efficiency and phase separation.



A longer carbon chain, in contrast, decreases solubility and hinders the stripping process. However, there is no noticeable impact of the molecular structure on the extraction capacity in this instance. The natural-based extractant can extract all three metals within the intermediate pH range, indicating that the change in hydrophobicity is too weak to have a significant impact on the loading and stripping processes. Both the commercial (LIX) and CNSL-based extractant show similar equilibrium curves for the three metals (Ni, Co and Mn) due to the complex formation of the oxime group [10]. Conversely, both extractants can collect the three metals at an intermediate pH, making them practical choices for generating a combined product that can be sent off-site to another refinery for further processing.

The data were fitted with Gaussian distribution by an error function (error  $f$ ):

$$E = \frac{1}{2} \left( 1 + \text{error } f \left[ \frac{\text{pH} - \text{pH}_{0.5}}{\delta \sqrt{2}} \right] \right), \quad (2)$$

where  $\text{pH}_{0.5}$  is the equilibrium pH (at which the metal ion is present equally in the two phases), and  $\delta$  is the width of the distribution.

**Table 2** Best-fitted parameters for the extraction systems

Metal	CNSL-based oxime				LIX 860N			
	Extraction		Stripping		Extraction		Stripping	
	pH <sub>0.5</sub>	δ	pH <sub>0.5</sub>	δ	pH <sub>0.5</sub>	δ	pH <sub>0.5</sub>	δ
Co <sup>2+</sup>	4.8	6.6	3.7	9.0	4.6	9.5	3.8	12.0
Ni <sup>2+</sup>	4.2	11.2	3.8	21.0	4.1	8.2	3.9	26.4
Mn <sup>2+</sup>	5.3	12.6	3.9	34.5	5.1	6.0	3.7	11.8

The error function is a well-accepted model for probability theory and given by [22]

$$\text{error } f(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt. \quad (3)$$

The fitting data are tabulated in Table 2.

The results demonstrate the potential of CNSL to recover Ni, Mn, and Co as part of the recycling process. Most of the existing LIBs recycling aims to recover cobalt [3], the most valuable metal in the cathode. However, battery manufacturers tend to increase nickel content to improve capacity [23, 24]. For instance, the LIBs for electric vehicles are now relying on NMC 622 (60% Ni, 20% Mn, and 20% Co) [25] and NMC 811 [20]. Consequently, a recycling facility should recover both Ni and Co. In comparison with these two metals, Mn has a lower economic value and is often a nuisance in Ni–Co production [26]. The natural-based extractant allows the recovery of the metals that could then be sent as a crystalline or matte product for further processing and recovery.

It is important to highlight that CNSL is an abundant by-product in many developing countries in Asia, Africa, and South America [27]. These developing countries can effectively utilize natural resources for metal recovery. The current price of CNSL is around US \$300–400 per tonne, and it is often used as fuel. The synthesizing agents required for the production of the oxime are common chemicals. The overall cost of synthesized oxime is estimated ~US \$2000–3000 per tonne, which is about 20% of the current price of the industrial oxime. In addition to being low cost, the natural oxime has a low carbon footprint and significantly reduces the environmental impact of LIBs' recycling [28].

## Conclusions

A natural-based extractant was synthesized from cashew nut shell liquor and used to extract a mixture of metals from an aqueous solution. It was found that the product has a similar extraction potential as a commercial oxime. The natural chemical is abundant in many developing countries and could be used for economically reclaiming valuable metals from spent batteries.

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Not applicable.

## Authors' contributions

CMP, SAH, and SY designed the study. SAH and SHV synthesized the oxime. HMN, CVN and AEH measured the extraction. The manuscript was written through the contributions of all the authors. All the authors read and approved the final manuscript.

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## Availability of data and materials

Not applicable.

## Declarations

## Ethics approval and consent to participate

Not applicable.

## Consent for publication

Not applicable.

## Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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