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# Synergistic green extraction of nickel ions from electroplating waste via mixtures of chelating and organophosphorus carrier

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## HIGHLIGHTS

- Synergistic extraction of nickel via LIX63-D2EHPA mixture system.
- Maximum synergistic enhancement factor, $R_{Ni,max}$ of 29.56 at $X_{LIX63}$ = 0.8.
- Palm oil as green diluent for synergistic green extraction of nickel.

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## ABSTRACT

The discharge of electroplating waste containing nickel ions has led to environmental issues owing to the toxicity problem mainly to the aquatic organisms and humans. Liquid-liquid extraction offers a great potential treatment for nickel removal with several advantages of simple, high efficiency and high separation factor. In this study, a green synergistic liquid–liquid extraction of nickel ions from electroplating waste solution using chelating oxime (LIX63) and organophosphorus (D2EHPA) carriers individually as well as their synergistic mixture has been studied. The result demonstrated that about 83% of nickel ions have been successfully extracted via the mixture system of 0.08M LIX63 +0.02M D2EHPA with the maximum synergistic enhancement factor, $R_{max}$ of 29.56. Meanwhile, the back extraction study also revealed that $HNO_3$ was the most suitable stripping agent while the diluent screening also showed that palm oil has high potential to be incorporated as a diluent in the green synergistic liquid–liquid extraction of nickel.



## 1. Introduction

The electroplating industry is one of the heavy metal sources which discharges into the environment since it is using high volume of water in various steps of the process. Nickel is a hazardous and toxic heavy metal which comes from the electroplating industry. Basically in the electroless nickel plating (ENP), nickel metal is deposited via chemical reduction of nickel ions by certain reducing agents. During the plating process, about 5000 ppm of nickel sulfate is added with certain proportions of reducing agents, hypophosphite compounds in the plating bath. For quality purposes, after several runs of plating, the plating solution will be discharged to the wastewater treatment plant in higher concentrations [1]. Meanwhile, the concentrations of the metal ions also increase over time due to the repeated recirculation of the rinsing liquid. For instance, the rinsewater from the nickel plating industries has nickel concentrations from 900 to 1583 ppm of nickel in the concentrated stream [2,3]. The high concentrations of nickel in natural water may cause severe damage to the lungs and kidneys causing gastrointestinal distress, nausea, pulmonary fibrosis, and skin dermatitis [4,5]. The discharge of nickel into wastewater has led to environmental issues as they have caused a great damage to aquatic and human life systems. Therefore, it is important to extract nickel ions from the wastewater before releasing into the environment.

The selection of the separation method strongly focuses on the efficiency and cost of the operation treatment. Various methods have been introduced for nickel extraction includes precipitation, ion exchange and electrochemical. For instance, Pinto et al. [6] who reported the nickel separation using EDTA leachate revealed that the process is simpler and easy to handle with lower operation cost. Nevertheless, this process seems inefficient for a bigger industry

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due to the large quantity of precipitated sludge production, hence leading to the secondary pollution. Through the electrochemical method, there are some advantages such as high selectivity with no sludge production. However, this process involves high energy consumption although for a treatment of low concentration wastewater, sometimes the treated effluents do not meet the standard discharge limit [7]. Solvent extraction or liquid–liquid extraction method is widely known method for various metals extraction owing to the simpler method with a higher extraction efficiency. In this process, there are many types of carrier are used which are highly dependent on the desired solute extracted. Mostly the metal cations and anions are extracted by acidic and basic carriers, respectively [8–10]. Principally, this process solely depends on the carrier concentration used since the extraction reaction will stop when the equilibrium is reached.

Nevertheless, the use of single carriers in the extraction system have suffered from the drawback of small loading capacity of metal ion into the organic phase. Hence, to improve the extraction efficiency, the mixtures of carrier are employed in the extraction due to their synergistic relationship. Basically, synergism is a cooperation of two carrier molecules in helping the transportation of metal ions from the aqueous to the organic media in order to satisfy the metal-carrier complexation [11]. One carrier will form a complex with the metal ion while the other carrier may replace the water molecule or occupy the coordinate of the free site. The synergistic extraction can be performed with any combinations such as acidic and neutral carriers, two acidic carriers, two neutral carriers, anionic and neutral carriers, cationic and anionic carriers and two anionic carriers. A synergistic liquid–liquid extraction for vanadium (IV) extraction was performed using the mixed carrier consisting of D2EHPA and EHEHPA [12]. It was found that the maximum synergistic factors was obtained at mole fraction of D2EHPA, $X_{D2EHPA}$ of 0.2 and the reaction of the synergistic extraction is exothermic. Besides, Li et al. [13] also reported the mixture system of D2EHPA-TBP for vanadium extraction where D2EHPA and TBP act as a carrier and modifier, respectively. Meanwhile, the solvent extraction of manganese(II) has been studied from chloride solutions using a mixture of Cyanex 272 and Cyanex 301 which provided a significant synergistic effect at mole fraction of Cyanex 272, $X_{Cyanex272}$ of 0.6 with synergistic enhancement factor of 14 [14]. In addition, the separation of zinc and manganese were reported using the synergistic effect of Cyanex 302 and D2EHPA [15]. Henceforth, Singh et al. [16] also reported the extraction of uranium from aqueous phosphoric acid medium using PC88A and TBP individually as well as their synergistic mixture in different diluents. The results indicate that a synergistic mixture of 0.90 M PC88A + 0.15 M TBP in xylene can be used for the extraction of uranium from low phosphoric acid medium.

Diluent is one of the important components in the organic phase of liquid–liquid extraction process. Diluent provides several criteria such high solute capacity, inert toward extraction system, miscible with carrier, immiscible with aqueous phase, has a low surface tension for good dispersion performance, low viscosity, nontoxic and non-corrosive [17]. Several researchers have carried out the formulation study for metal extraction using petroleum based diluents such as Exxol D-100, kerosene, hexane, toluene and dodecane [18–22]. The petroleum based diluents are usually toxic, non-renewable, flammable and volatile in nature. Although high extraction percentages are achieved, they are not environmentally friendly and non-biodegradable. Thus, the use of green materials such as vegetable oils, sunflower oil, and corn oil instead of chemical diluent in liquid- liquid extraction are another alternative which lead to the green and environmentally friendly process. Very few literatures are available on the use of biodegradable oil such as palm oil as a diluent in liquid–liquid extraction processes. Previously, some studies have proven that the vegetable oils could be an ideal replacement for the conventional volatile organic diluents. For instance, Jusoh et al. [23] have used the combination of 30/70 kerosene to palm oil for succinic acid extraction which has led to a high separation factor (57.82). Othman et al. [24] reported about 83% of phenol was removed in the emulsion liquid membrane extraction process using a green palm oil based organic solvent. Meanwhile, Ahmad et al. [25] also revealed that about 98.6% of Cd (II) ions were successfully removed by employing corn oil instead of kerosene in emulsion liquid membrane process. Vegetable oils loaded with both D2EHPA and TBP were found to be the most effective for Cu (II) extraction and are potential greener substitutes for the conventional petroleum-based organic solvents [26].

**Table 1**
The typical properties of vegetable palm oil [17].

| Properties | Palm Oil |
|---|---|
| Viscosity, $\mu$ (mPa s) | 77 |
| Dielectric Constant | ~3 |
| Specific Gravity | 0.918 |
| Flash Point, $T_f$ (°C) | 174 |
| Melting Point, $T_m$ (°C) | 35 |

In this present research, the synergistic extraction of nickel ions from electroplating waste using the mixture system consisting of D2EHPA with other several types of carriers was discussed. Besides, the screening for stripping agent type and effect of the composition mixture kerosene-palm oil also were carried out. On the other hand, the effect of the nickel extraction using the regeneration of the organic phase were investigated as well.

## 2. Materials and methods

### 2.1. Reagents

Nickel electroplating waste was obtained from one of the companies in Johor Malaysia. 5, 8-diethyl-7-hydroxydodecan-6-one oxime (LIX63, purity 99%) was procured from Cognis INC, Australia. Di-2-ethylhexyl phosphoric acid (D2EHPA, purity 95%), Diisooctylthiophosphinic acid (Cyanex 302, purity 85%), Tridodecylamine (TDA, purity 98%), Tributylphosphate (TBP, purity 99%), Octanol (purity 99%), kerosene, and nitric acid ($HNO_3$, purity 65%) were purchased from Sigma-Aldrich. Sulfuric acid ($H_2SO_4$, purity 97%) and hydrochloric acid (HCl, purity 37%) were supplied from Merck. The commercial vegetable palm oil was obtained from one of the companies in Malaysia. The typical properties of the vegetable palm oil used in this research are tabulated in Table 1. All these materials were used directly as received from the manufacturer without further purification.

### 2.2. Analytical method

The apparatus used in this study include a Mettler Toledo pH Meter for pH measurement of the aqueous waste solutions. The equilibrium experiments were carried out using a mechanical shaker. Then, the concentration of nickel ions in the aqueous solution was analysed by the Atomic Absorption Spectrophotometer (AAS).

### 2.3. Liquid-liquid extraction procedures

Liquid–liquid extraction (LLE) process was performed by mixing an equal volume (10 mL) of organic phase (carrier in organic diluent) and feed phase (electroplating waste solution) which thereafter was stirred using a mechanical shaker at 320 rpm for 18 h to attain the equilibrium. The solution was then carefully poured into a separation funnel for phase separation for about 30 min. After