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# SELECTIVE EXTRACTION OF MOLYBDENUM, NICKEL, AND COBALT FROM SECONDARY RESOURCES USING BIFUNCTIONAL IONIC LIQUIDS

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**ABSTRACT** –The increasing demand for molybdenum, nickel, and cobalt in high-tech industries has led to a need for efficient and sustainable metal recovery from secondary sources. Conventional solvent extraction methods face environmental concerns, high reagent consumption, and limited selectivity. Ionic liquids (ILs) have emerged as promising alternatives due to their low volatility, high thermal stability, and exceptional metal ion selectivity. In this study, the bifunctional ionic liquids [TOA][CY272] and [A336][P204] were investigated for selective extraction of molybdenum, nickel, and cobalt from synthetic solutions simulating industrial waste leachates. The ILs were dissolved in kerosene, and their extraction efficiencies were compared with raw components to evaluate improvements in selectivity and efficiency. Key operational parameters, such as metal ion concentration, extractant concentration, and pH, were optimized for maximum recovery. Two stripping agents, acidic and alkaline, were tested to enhance selective metal recovery. Results showed [A336][P204] achieved over 95% extraction efficiency for molybdenum with less than 4% co-extraction of nickel and cobalt, while [TOA][CY272] exhibited a maximum efficiency of less than 75% and lower selectivity. The appropriate stripping agent facilitated efficient metal separation. These findings highlight the potential of bifunctional ionic liquids as sustainable and environmentally friendly extractants for recovering strategic metals from secondary sources.

**Keywords:** Metal Recovery, Ionic Liquids, Circular Economy, Sustainable Extraction, Industrial Waste Recycling.

## INTRODUCTION

Molybdenum (Mo), nickel (Ni), and cobalt (Co) are key components of hydrodesulfurization (HDS) catalysts, such as Ni-Mo/γ-$Al_2O_3$ and Co-Mo/γ-$Al_2O_3$ [1], widely used in petroleum refining to remove sulfur and produce cleaner fuels [2]. During HDS process, molybdenum facilitates sulfur removal via hydrogenation. However, prolonged exposure to high temperatures and contaminants leads to catalyst deactivation through poisoning and sintering [3], resulting in spent catalysts that require recovery and management.

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The growth of the petrochemical industry has led to a significant increase in spent HDS catalysts, classified as hazardous due to their toxic and flammable content [4]. However, they also contain valuable metals like Mo, V, Ni, and Co, making their recovery both an environmental necessity and an economic opportunity [5]. Various treatment approaches, such as pyrometallurgical and hydrometallurgical methods, are being explored to efficiently recover metals while minimizing environmental impact [6, 7]. Hydrometallurgical processes are increasingly preferred over pyrometallurgical techniques due to their superior efficiency, ability to selectively separate target elements, lower energy consumption, and reduced greenhouse gas emissions [8]. A review of the literature indicates substantial research efforts aimed at optimizing the recovery and separation of Mo, Ni, and Co from the pregnant leach solution (PLS).

Several techniques, including precipitation, ion exchange, Membrane systems, adsorption, and solvent extraction [9], have been investigated for this purpose. Among these, solvent extraction has emerged as one of the promising methods due to its high selectivity and efficiency in metal separation [10].

Ionic liquids have emerged as promising alternatives to conventional organic solvents in metal extraction due to their unique and environmentally favorable properties. These include excellent chemical and thermal stability, negligible vapor pressure, non-flammability, and high solvation capacity. Such characteristics make them ideal candidates for enhancing extraction efficiency while minimizing environmental impact [11].

Numerous studies have demonstrated the effective use of ionic liquids for the selective extraction of Mo, Ni, and Co. For instance, trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate achieved a remarkable cobalt-to-nickel separation factor of 1097 from an HCl-leached solution. At an ionic liquid concentration of 0.8 mol/L, pH 5.0, and 60°C, over 99% of cobalt was selectively extracted, highlighting the high efficiency and selectivity of ionic liquids in metal separation processes [12].

In this study, two ionic liquids, [TOA][CY272] and [A336][P204], were investigated as alternative extractants for the recovery of Mo, Ni, and Co from synthetic solutions designed to simulate PLS and wastewater derived from spent catalyst processing. The extraction performance was evaluated across varying metal concentrations, and both acidic and alkaline stripping agents were applied to recover the metals from the loaded organic phase.

## EXPERIMENTAL

### Chemicals and reagents

Cobalt, nickel, and molybdenum stock solutions were prepared by dissolving cobalt(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate (98%), and sodium molybdate dihydrate in deionized water. These reagents, obtained from Sigma-Aldrich and Merck. Extractions were performed in a kerosene medium (Carlo Erba), and metal recovery was achieved using $NH_4OH$ (36.6%, VWR) and HCl (25%, Carlo Erba) as stripping agents.

### Instrumentation and Analytical Techniques

The structural characterization of the synthesized ionic liquids and their precursors was carried out using FT-IR (Thermo Nicolet Nexus 670). Metal concentrations (Mo, Ni, Co) in all solution phases were analyzed by ICP-OES (Agilent 5100).

### Preparation of Bi-Functional Ionic Liquids

Bi-functional ionic liquids [TOA][CY272] and [A336][P204] were synthesized through stoichiometric neutralization reactions. The molecular structures of the final products are presented in Figure 1.

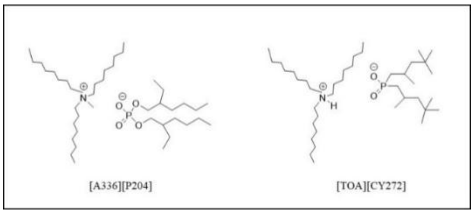


**Figure 1** Chemical structures of [TOA][CY272] and [A336][P204]

## RESULTS AND DISCUSSION

### Metal Extraction Performance

The extraction behavior of the synthesized ILs toward Mo, Ni, and Co was examined under varying conditions. Factors such as IL type and concentration, metals content, and pH were explored to optimize performance.

### Selection of Extractant and Comparison with Precursors

To evaluate the separation efficiency of the synthesized ILs and benchmark them against their precursors, extractions were performed using 35% extractant in kerosene, with a 1:1 A/O ratio and 1000 ppm of each metal at room temperature. As shown in Figure 2, [A336][P204] achieved nearly complete Mo extraction (~100%) but was ineffective for Co and Ni, extracting only 2.3% and 1%, respectively. In contrast, [TOA][CY272] showed moderate Mo extraction (72%) and balanced performance for Co (60–63%) and Ni (50–55%). These results demonstrate [A336][P204]'s strong selectivity for Mo and [TOA][CY272]'s broader applicability for multi-metal separation.

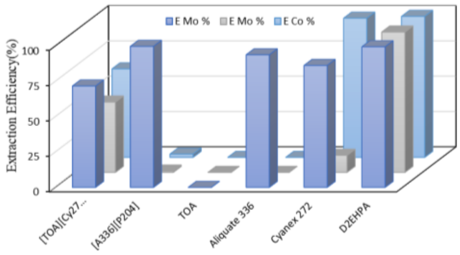


**Figure 2** Extraction efficiency of [A336][P204] and [TOA][CY272] and their precursors

**Effect of Metal Concentration on Extraction Performance**

To simulate various real-world scenarios such as metal-rich catalysts, secondary sources, and dilute wastewaters, extraction tests were conducted at initial metal concentrations of 100, 1000, and 2500 ppm. These levels reflect typical compositions of pregnant leach solutions (PLS) and post-treatment effluents. Figure 3 presents the extraction efficiencies of [TOA][CY272], and [A336][P204] across these concentration ranges. All experiments were performed under consistent conditions.

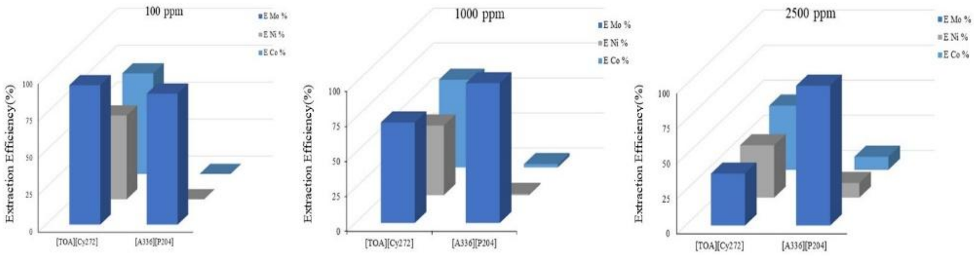


**Figure 3** Extraction efficiency of ionic liquids in different metal concentrations

**Influence of Extractant Concentration on Metal Extraction**

The effect of ionic liquid concentration on metal extraction was assessed using ILs diluted in kerosene at 10%, 20%, 35%, and 50% concentrations, keeping the A/O phase ratio at 1:1. As shown in Figures 4(a and b), extraction efficiency generally increased with extractant concentration, particularly between 10–35%. Beyond 35%, improvements plateaued, likely due to increased viscosity limiting mass transfer. Notably, [A336][P204] showed remarkable selectivity for Mo, achieving 98.5% extraction even at 10%, with minimal gains at higher concentrations. Ni and Co extractions remained below 4%, underscoring the IL's strong affinity for Mo and minimal co-extraction of other metals. In contrast, [TOA][CY272] achieved a maximum extraction efficiency of 74.6%, with lower selectivity.

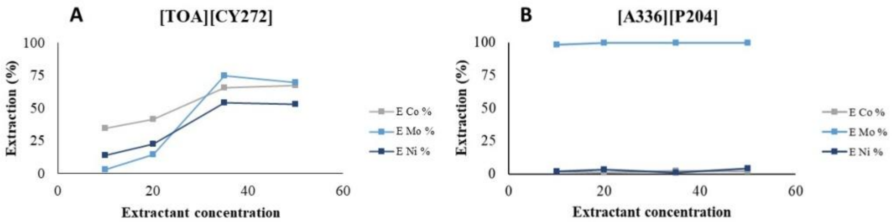


**Figure 4** Effect of varying concentration (10%, 20%, 35%, 50%) of ionic liquid extractants

**Effect of Aqueous Phase pH on Extraction**

The pH of the aqueous phase is a key factor that influences metal speciation and, consequently, extraction behavior. To examine its impact, experiments were performed at pH values of 1.5, 4.5, and 7.5. Higher pH values were excluded to avoid the precipitation of Ni and Co. As shown in Figure 5, extraction efficiency varied notably with pH, reflecting the selective affinity of each ionic liquid for Mo, Co, and Ni under different acidity conditions.

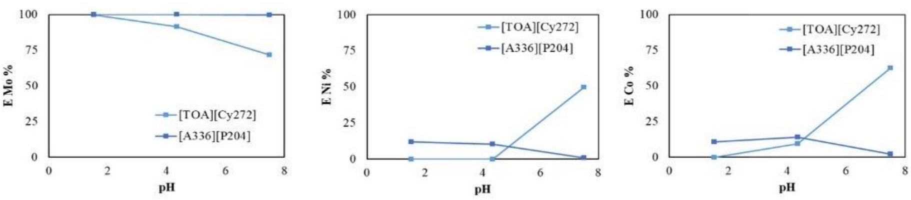


**Figure 5** Effect of aqueous phase pH on extraction efficiency

The effect of pH on extraction efficiency revealed distinct behaviors for [TOA][CY272] and [A336][P204]. For [TOA][CY272], Ni and Co extraction improved significantly with increasing pH, especially from 4.5 to 7.5. In contrast, [A336][P204] showed a steady decline in Ni and Co extraction as pH increased, reaching negligible levels at pH 7.5. Both ILs achieved near-complete Mo extraction at pH 1.5; however, [TOA][CY272] exhibited a gradual decrease in Mo recovery at higher pH, while [A336][P204] maintained consistently high Mo extraction (>99%) across all pH levels, confirming its strong selectivity and stability for Mo.

**Stripping Process and Metal Separation**

Selective recovery of Mo, Ni, and Co from the loaded organic phases was assessed using 2 M HCl and 1 M $NH_4OH$ as stripping agents. The process was performed at room temperature with a 1:1 O/A ratio. Figure 6 shows the stripping efficiencies for each metal using [TOA][CY272] and [A336][P204], highlighting their potential for effective and selective metal separation.

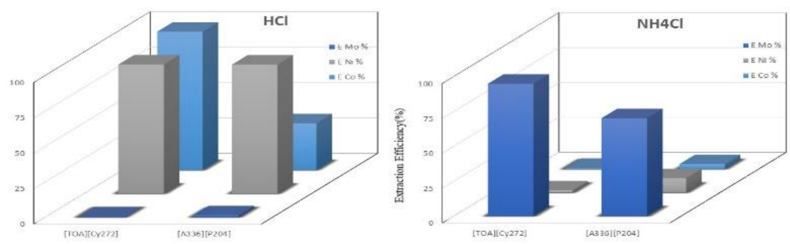


**Figure 6** Acidic and alkaline agents stripping performance

**CONCLUSION**

This study evaluated the extraction performance of two ionic liquids, [TOA][CY272] and [A336][P204], for recovering Mo, Ni, and Co from synthetic solutions mimicking PLS or wastewater derived from spent catalyst processing. [A336][P204] demonstrated exceptional selectivity for Mo, achieving nearly 100% extraction efficiency, with minimal influence from metal or extractant concentration. In contrast, [TOA][CY272] showed improved efficiency with increasing extractant concentration but was less effective at higher metal loadings. pH had a notable impact on extraction behavior, and subsequent stripping with acidic and alkaline agents enabled effective separation of Mo from Ni and Co. These findings support the potential of ionic liquids for efficient and selective metal recovery in hydrometallurgical applications.

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