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Abstract: *Phosphonium-based room temperature ionic liquids (ILs) have demonstrated remarkable properties for metal extraction applications. In this study, we investigated the potential of these ILs as environmentally friendly materials for extracting metals from mine tailings. Specifically, we synthesized Trihexyltetradecylphosphonium salicylate* $[PR_4][TS]$ *through a straightforward metathesis process employing thiosalicylic acid as the source of the anion. The synthesized IL was characterized using various techniques including FTIR, TGA, and UV-VIS. To evaluate its effectiveness in metal extraction, we varied the incubation time, temperature, and concentration, and observed simultaneous extraction of Cd, Cr, Cu, Pb, and Mn. Remarkably, the highest extraction efficiency reached 95.9% within 120 minutes at a 30% IL concentration under room temperature conditions. These results provide valuable insights into the potential use of phosphonium-based ILs as green materials for highly efficient metal extraction.*

Keywords: heavy metal, ionic liquids, phosphonium, removal, thiosalicylate

1. INTRODUCTION

The mining industry plays a crucial role in the global economy by providing essential raw materials for various industrial sectors. However, the extraction and processing of minerals pose significant environmental challenges. One of the major concerns is the accumulation of large amounts of metallurgical wastes, including tailings, which are the residues from mineral processing and metal extraction. If not properly handled and stabilized, mine tailings could pose a serious risk to ecosystems and human health by releasing toxic metals, acid drainage, and contamination of soil and water sources. For the past decades, there has been an increased interest in the recovery of metals from ores and mine tailings using less expensive and environmentally friendly technologies [1-3].

Conventional metal extraction methods from mine tailings involve the use of hazardous chemicals and energy-intensive processes, exacerbating the ecological footprint of mining operations. For instance, pyrometallurgy which is the oldest extractive metallurgical process employs thermal energy to induce physical and chemical changes on materials making it possible to recover valuable metals from their solid sources [4-6]. This method usually entails a very high cost of energy required in all the pyrometallurgical processes in extracting metals [5]. Furthermore, the emission of toxic gases [7] and carbon dioxide [8] is the major disadvantage of pyrometallurgy, which made it unpopular with much environmental organization due to its contribution to the greenhouse effect and climate change. Another conventional method of extracting and recovering metals from their ores or from other source is hydrometallurgy which deals with using aqueous chemistry as well as some elements of organic chemistry. Using hydrometallurgical processes, a complete recovery of metals with high purity is possible with low energy requirements [9]. For instance, the leaching of solders has been investigated using sodium hydroxide and sodium persulfate, organic solvents, and nitric acid (HNO3) as leaching agents [10-11]. Notably, organic solvents are harmful to the environment [11]. The strong acid leachates release toxic gases like Cl_2, SO_3, and NO_x [12,13]. The waste acid solution generated during the process is also harmful to the environment. For the sustainable management of natural resources and to reduce environmental pollution, it is important to develop a simple recycling process to recover as much of the valuable metals as possible [12-14].

In recent years, the concept of green chemistry has gained momentum to address these challenges and promote sustainable mining practices. Green chemistry aims to minimize or eliminate the use of hazardous substances, reduce energy consumption, and generate less waste during chemical processes. In this context, the use of ionic liquids (ILs) as extracting solvents has emerged as a promising avenue for environmentally friendly metal extraction. Ionic liquids are a class of molten salts that exist in a liquid state at or near room temperature. They possess unique properties such as low volatility, high thermal stability, and tunable solubility, making them attractive alternatives to conventional organic solvents. Ionic liquids have been introduced to leaching and solvent extraction processes in the extraction of various metals. For instance, ionic liquids can be an alternative leaching agent for copper ore to the existing leaching techniques based on hydrochloric acid leaching agent, high temperature/pressure operation, or bleaching. 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) ionic liquid as a solvent and $Fe(BF_4)_3$ as an oxidizer was used for chalcopyrite leaching, and 90% of copper was gained at 100 °C after 8 h leaching [6]. Also, [Bmim]HSO_4 ionic liquid was used with $Fe(SO_4)_3$ in the leaching of gold and silver, which demonstrates the potential of ionic liquids as a selective leaching agent for precious metals with an advantage of replacing toxic acid agents [15].

Phosphonium-based ILs have garnered significant attention for their application in metal extraction processes due to their exceptional stability and solvating abilities. Their ability to selectively extract heavy metals from complex matrices, such as mine tailings, while leaving behind non-toxic residues, makes them ideal candidates for green and efficient metal recovery. These groups of ionic liquids have been "neglected" in the literature comparing to their imidazolium or pyridinium based counterparts. However, during the last decade significant work has been done, pointing out the advantages and broad application spectrum of these types of ionic liquids. Their improved thermal and chemical stability in comparison to *e.g.* pyridinium and imidazolium based ILs, their unique miscibility behavior and solvating properties advances their use in specific applications such as phase-transfer catalysts, solvents, lubricants, gas capture agents, coating materials, or chemical sensors [16]. Thus, we report here the synthesis of phosphonium-based ionic liquids designed for the extraction of heavy metals from mine tailings. These ILs are extensively characterized and evaluated for their heavy metal extraction efficacy.

2. METHODOLOGY

2.1 Chemical and Reagents

Trihexyl(tetradecyl)phosphonium chloride (CYPHOS IL 101) and salicylic acid were purchased from Sigma Aldrich and used as received without further purification. All other reagents used in this study were analytical grade and distilled or deionized distilled water was used in the preparation of all solutions.

2.2 Synthesis of Trihexyl(tetradecyl)phosphonium salicylate [PR4][TS]

The phosphonium-based IL was synthesized in accordance with the synthetic route presented in Figure 1. Herein, appropriate amount of Cyphos IL 101 was placed in a flask, dissolved in acetone, reacted with an equimolar amount of thiosalicylic acid which was dispersed in water, and deprotonated with two-fold excess of sodium hydroxide. The trihexyltetradecylphosphonium chloride [PR_4][Cl] solution was added dropwise with thiosalicylate solution then vigorously stirred at room temperature in a certain amount of time. The formed IL phase was separated, washed several times with small amounts of ice-cold water, and N_2-dried for characterization. The synthesized [PR_4][TS] ionic liquids was clear in color, odorless and viscous liquid at room temperature.

2.3 Extraction Process

The extraction experiments was conducted by mixing the prepared ionic liquid and specific amount of mine tailings sample. The variables being varied were incubation time (120 min and 240 min), temperature (room temperature and 80°C), and IL concentration (10 – 30%). The samples was pre-monitored via XRF and % efficiency was calculated by the following equation:

$$\% \text{ Efficiency} = (C_i - C_f)/C_i \times 100$$

where C_i and C_f represent initial and final metal concentrations, respectively.

2.4 Characterization Techniques

The synthesized ionic liquid was analyzed via Fourier transform infrared radiation (FTIR) spectroscopy, Thermo Gravimetric Analysis (TGA), and Ultraviolet Visible Spectroscopy (UV-VIS) technique and the extraction efficiency was monitored via X-ray Fluorescence (XRF) analysis.

3. RESULTS AND DISCUSSIONS

3.1 Synthesis of Phosphonium-based ionic liquids

The synthesis of trihexyltetradecylphosphonium thiosalicylate ([PR4][TS]) involved a straightforward two-step process as shown in Figure 1. Initially, the phosphonium chloride ([PR4][Cl]) was prepared by mixing trihexyltetradecylphosphonium bromide with a chloride source. This precursor then underwent an anion-exchange reaction with deprotonated thiosalicylic acid, resulting in the formation of [PR4][TS]. The product was obtained as a viscous, clear, odorless liquid at room temperature. The high yield and purity of the synthesized IL indicate the efficiency of the metathesis route employed. The ionic liquid was subsequently purified through repeated washing with ice-cold water and dried under nitrogen to remove residual solvents and unreacted precursors. The success of the synthetic route is attributed to the careful control of stoichiometry, pH, and reaction time. The presence of excess sodium hydroxide ensured complete deprotonation of thiosalicylic acid, facilitating the nucleophilic substitution reaction necessary for anion exchange. Additionally, the use of a biphasic solvent system (acetone for the cationic precursor and water for the anionic component) promoted phase transfer and enhanced reaction kinetics. This biphasic approach minimizes side reactions and enhances product purity. The choice of trihexyltetradecylphosphonium as the cationic moiety is strategic due to its superior hydrophobicity, thermal stability, and previously documented efficacy in metal extraction applications. These attributes not only support the integrity of the IL under operational conditions but also reduce its aqueous solubility, which is advantageous in extraction processes.

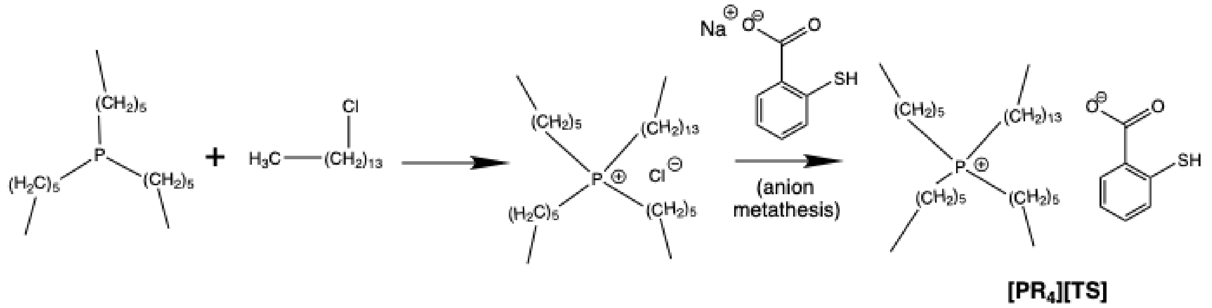

Figure 1. Synthesis of trihexyltetradecylphosphonium thiosalicylate [PR$_4$][TS].

3.2 FTIR Analysis

The Fourier Transform Infrared (FTIR) spectroscopy confirmed the successful synthesis of [PR4][TS] as shown in the obtained FT-IR spectrum depicted in Figure 2. The FTIR spectrum exhibited characteristic absorption bands corresponding to functional groups present in the thiosalicylate anion and the phosphonium cation. The broad band at 3625–3200 cm^{-1} corresponds to O–H stretching, while the peaks between 3100–2800 cm^{-1} are attributed to C–H stretching vibrations from the alkyl chains. The strong band near 1700 cm^{-1} indicates C=O stretching of the carboxyl group. Vibrations in the 1550–1600 cm^{-1} range suggest aromatic ring vibrations, whereas bands in the 1450–1000 cm^{-1} range indicate aromatic C–H bending and stretching. The presence of bands around 700–750 cm^{-1} is indicative of C–O stretching [17]. These spectral features confirm the presence of both the phosphonium cation and the thiosalicylate anion in the synthesized IL. Furthermore, the absence of peaks associated with starting materials such as unreacted thiosalicylic acid or Cyphos IL 101 confirms the high purity of the product. For instance, the disappearance of broad hydroxyl bands typical of unbound thiosalicylic acid suggests successful coordination of the anion within the IL structure. Moreover, the consistent presence of long alkyl chain C–H stretches reinforces the identity of the bulky phosphonium cation. These findings collectively substantiate the structural integrity of [PR4][TS], validating the efficiency of the synthetic protocol. FTIR thus served not only as a qualitative confirmation tool but also as an essential method for detecting potential contaminants or incomplete reactions in the synthesized product.

3.3 Ultra-violet Visible Spectroscopic Analysis

The synthesized ionic liquid [PR4][TS] was also characterized using UV-Vis spectroscopy and the obtained absorption specturm is shown in Figure 3. The UV-visible spectrum of [PR4][TS] displayed absorption peaks at 350 nm and 404 nm with an extended tail up to 430 nm. The band at 404 nm corresponds to the monobasic form of thiosalicylate (HTSal), while the band at 350 nm is attributed to the diacid form (H2TSal). These observations are consistent with literature reports on the tautomerism of thiosalicylate anions [18-19]. The absorption features suggest successful incorporation of the thiosalicylate moiety and provide insights into the electronic transitions within the IL. The electronic absorption spectrum thus serves as a supplementary confirmation of the molecular structure and composition of the synthesized compound.

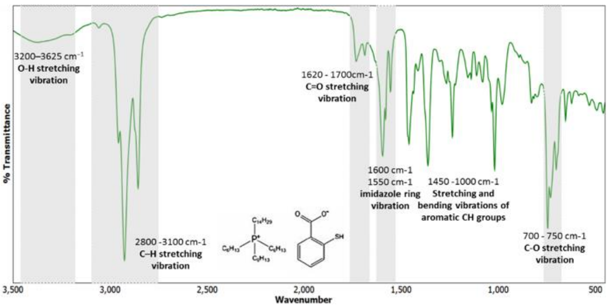

Fig. 2. FTIR spectrum of [PR$_4$][TS].

The distinction between the absorption bands is critical for understanding the acid-base behavior and protonation state of the thiosalicylate moiety within the ionic liquid. Such behavior has implications for metal binding affinity, as the protonation state of the ligand can influence complexation kinetics and selectivity. Additionally, the tailing of the absorption band suggests extended conjugation and potential intramolecular charge transfer, which may affect the redox properties of the IL. These electronic attributes further support the role of [PR4][TS] as an efficient and selective extractant, capable of engaging in complexation mechanisms with transition metal ions through π-donor interactions.

3.4 Thermal Analysis

Thermal stability of [PR4][TS] was evaluated using TGA, where the sample was heated from 30 to 500 °C at a rate of 10 °C/min. The TGA curve, as shown in Figure 4, revealed a two-step weight loss profile. The initial weight loss of 10.19% began around 145.5 °C, likely due to the evaporation of moisture or volatile impurities. The major decomposition occurred between 295.0 °C and 445.0 °C,

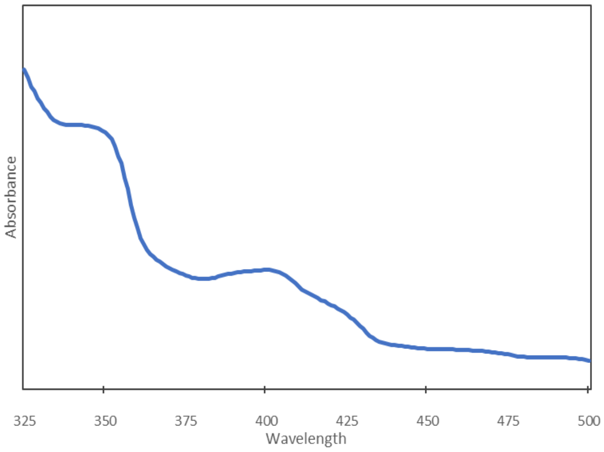

Fig. 3. UV-visible spectrum of [PR₄][TS].

accounting for a weight loss of approximately 80.89%. The high decomposition temperature indicates that [PR4][TS] possesses excellent thermal stability, a desirable trait for industrial applications involving high-temperature operations. This stability enhances its usability as a robust medium for metal extraction under various conditions.

Such thermal resilience makes the ionic liquid suitable for multiple recycling processes, an important criterion for economic and environmental sustainability in industrial metal recovery. The broad decomposition window also reduces the risk of thermal degradation during extraction operations, especially when high temperatures are used to accelerate leaching kinetics. Additionally, the absence of significant degradation below 145 °C confirms that [PR4][TS] can maintain structural integrity under ambient and moderately elevated temperatures, which are typically used in practical extraction settings. TGA results align with earlier reports on the stability of phosphonium-based ILs and further confirm their robustness over more commonly used imidazolium analogs.

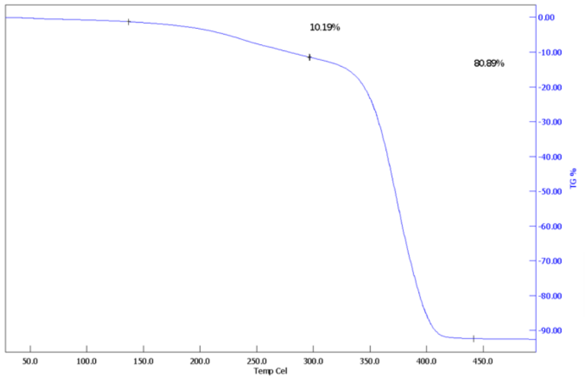

Fig. 4. Thermo-gravimetric analysis (TGA) of [PR₄][TS].

3.5 Extraction of Heavy Metals using Phosphonium-based Ionic Liquids

The synthesized [PR4][TS] was tested for its metal extraction efficiency from mine tailings under varying operational conditions. As shown in Table 1, several extraction experiments were performed with different IL concentrations (10%, 20%, 30%), incubation times (120 and 240 minutes), and temperatures (room temperature and 80 °C). The results showed that [PR4][TS] could extract significant amounts of Cd, Cu, Cr, Pb, and Mn. Notably, the best overall extraction efficiency was achieved at 30% IL concentration, 120 minutes of incubation, and room temperature, with values reaching as high as 95.9% as shown in Figure 5.

Table 2. Calculated extractive efficiency of [PR4][TS] against various selected metals.

	%Efficiency at 120 min incubation time					
[IL, %]	10%		20%		30%	
Temp.	RT	80°C	RT	80°C	RT	80°C
Mn	4.2	4.8	6.0	10.4	14.0	15.0
Pb	2.3	1.7	9.4	8.2	15.7	19.5
Cu	15.5	0.5	0.0	0.0	11.3	0.0
Cr	0.0	0.0	42.3	38.8	95.9	24.7
Cd	14.8	13.3	25.3	11.2	12.2	18.6
	%Efficiency at 240 min incubation time					
[IL, %]	10%		20%		30%	
Temp.	RT	80°C	RT	80°C	RT	80°C
Mn	0.0	7.3	7.3	15.6	9.7	16.9
Pb	1.7	9.7	9.7	15.5	14.1	19.1
Cu	0.0	7.0	7.0	0.0	0.0	0.3
Cr	0.0	80.5	80.5	39.5	0.0	0.0
Cd	19.9	6.3	6.3	16.9	24.9	20.0

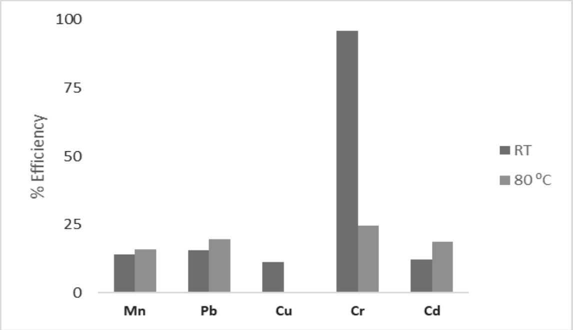

Fig. 5. Graphical illustration of the extractive % efficiency of [PR₄][TS] in 120 min under room temperature condition.

Increasing temperature to 80 °C generally improved extraction for most metals, attributed to increased kinetic energy and diffusion rates. However, chromium exhibited higher extraction efficiency at room temperature, suggesting a distinct interaction mechanism with the IL or potential thermal degradation of Cr-containing species at elevated temperatures. This behavior underscores the importance of tailoring extraction parameters based on the specific target metal. The extraction mechanism is believed to involve both ion exchange and complexation. The thiosalicylate anion provides chelating sites via thiol and carboxylate groups, facilitating selective metal ion coordination. This dual functionality enhances the affinity of the IL for heavy metals, making it a potent extractant for complex matrices such as mine tailings. The phosphonium cation, known for its hydrophobic character, supports efficient phase separation post-leaching, thereby reducing emulsification and simplifying downstream processing.

Furthermore, the extraction capability of $[PR_4][TS]$ is also influenced by the stability of the metal-ligand complex and the partitioning behavior of the metal species between the aqueous and IL phases. The bulky alkyl chains of the phosphonium moiety promote favorable hydrophobic interactions that stabilize the extracted metal complex within the IL phase. This mechanism enhances the selectivity and loading capacity of the IL for heavy metals. The recyclability of $[PR_4][TS]$ is an essential aspect for practical implementation. Preliminary tests suggest that the IL can be regenerated through simple back-extraction techniques using aqueous acid or chelating agents, allowing for multiple cycles without significant loss in efficiency. Such features contribute to its economic and environmental feasibility.

Moreover, the application of $[PR_4][TS]$ aligns with green chemistry principles, minimizing the generation of hazardous waste and avoiding the use of toxic organic solvents. Compared to traditional hydrometallurgical reagents, the use of ILs like $[PR_4][TS]$ presents a safer, more sustainable option for metal recovery from waste streams. The promising results obtained in this study advocate for further exploration into other metal systems and real-world industrial effluents. The integration of IL-based extraction systems into existing mining or recycling operations could revolutionize metal recovery, reducing environmental footprints while improving recovery yields. Additional research into kinetics, thermodynamics, and IL-metal interaction modeling would enhance understanding and optimization of the process. Collectively, these findings solidify the position of phosphonium-based ILs as next-generation extractants in the field of sustainable metallurgy.

4. CONCLUSION

Trihexyltetradecylphosphonium thiosalicylate [PR4][TS] ionic liquids was successfully synthesized using nucleophilic substitution of the alkyl chloride with trihexylphosphene and the subsequent metathesis reaction with thio thiosalicylate anion. The synthesized IL was confirmed via FT-IR and UV–VIS analysis and TGA showed its high thermal stability. The leaching test showed that the heavy metals in the mine tailings can be extracted with ionic liquids as extracting agent. Leaching efficiency depended on the factors such as high concentration of ionic liquid, incubation period and temperature as measured in this study. Nevertheless, the application of an inexpensive ionic liquid based on phosphonium derivatives shows capability of extracting metals ions (Mn, Cu, Cd, Zn, Pb and Cr) simultaneously from mine tailings. Overall, this work demonstrates the green process of recovering precious metals from waste mine tailings using environment-friendly phosphonium-based ionic liquids solvent system.

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