A Study of Extraction of Metals with Aqueous Two Phase System for Ionic Liquids

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Abstract: This review focuses on the research and development of using ionic liquids (ILs) as extractants and diluents in solvent extraction for metals. The emphasis is placed on the efficiency and selectivity of metal extraction from industrial wastewater using ILs composed of various cations and anions. ILs show great potential for metal extraction due to their favorable properties, such as low vapor pressure and high electrical conductivity, which enhance safety and mitigate risks. However, challenges arise from their high viscosity, slower phase separation, and cost, especially for ILs with long alkyl chains. The review highlights emerging trends in IL research and applications for metal extraction and emphasizes the importance of considering factors like cost, purity, stability, viscosity, solubility, conductivity, and selectivity for engineering requirements. Chemoinformatics methods offer a promising approach to address these challenges. The review also discusses the use of functionalized ILs, which incorporate functional groups into cations or anions, to improve their physicochemical properties and extraction efficiency. Challenges related to toxicity, biodegradability, complex chemical processes, and cost must be overcome for widespread industrial adoption. Further research is needed to optimize IL properties, synthesis techniques, and scalability to achieve efficient and cost-effective metal extraction.

Keywords: Ionic liquids, Extractants, Metal extraction, Solvent extraction, purification

I. Introduction:

Ionic liquids (ILs) are versatile and effective in the extraction and separation of metals, serving as both diluents and extractants [1]. By combining different anions and cations, ILs can be tailored to possess specific properties and characteristics [2].Compared to organic solvents, ILs offer several advantages such as low toxicity, thermal and chemical stability, non-flammability, absence of vapor release, and excellent solvation capacity. Their interactions with analytes involve electrostatic, hydrophobic-hydrophilic, dipole-dipole, π - π interactions, ion exchange, and hydrogen bonding, resulting in high sensitivity and selectivity towards various analytes [3]. Consequently, ILs are increasingly employed in solvent extraction processes for metal recovery [4], particularly for heavy, rare earth, alkali, noble, and radioactive metals.

Studies have demonstrated that ILs can significantly enhance the efficiency and selectivity of metal extraction, making them attractive alternatives to traditional organic solvents [5]. ILs have been explored for the hydrometallurgical extraction of metals, including platinum-group metals, from urban mines [6]. Their ability to separate metal ions from aqueous solutions via electrostatic, van der Waals, and ion-pair interactions has also been demonstrated [7]. Furthermore, ILs can be easily isolated through back-extraction and reused in various extraction techniques, adsorption, and membrane separation.ILs have proven effective in the recovery of rare earth elements from magnets, luminophores, electronic waste, and other scraps [8]. With careful selection of extraction systems and IL properties, it becomes feasible to isolate and separate nearly all metals across the periodic table, from Li(I) to Pu(IV).

2.1. Ionic Liquids as Promising Extractants for Sustainable Metal Extraction

Ionic liquids (ILs) have gained increasing attention as extractants in hydrometallurgical processes for metal recovery [10]. However, their high cost demands that ILs offer superior characteristics compared to existing industrial extractants in terms of distribution ratios, selectivity, reusability, and stability. To mitigate the issue of high viscosity, ILs are often dissolved in molecular solvents, leading to the development of efficient extraction systems. For instance, electronic waste can be a valuable source for recovering indium(III) and gold(III) using IL-based extraction systems [11], while molybdenum(VI) can be extracted with high yields exceeding 99% [12]. Although undiluted ILs have been utilized as extractants in some studies, they tend to become saturated with water during extraction, resulting in a significant reduction in viscosity. This approach has proven effective in extracting tantalum(V) with high efficiency from aqueous solutions, and achieving over 99% recovery efficiency for palladium(II).IL extractants containing bulky cations with positively charged heteroatoms, such as phosphonium, ammonium, and imidazolium cations, are frequently employed due to their

low melting points (below 100°C) and environmentally friendly properties. In the subsequent sections, we will delve into a more detailed examination of these extractants.

a. Phosphonium Ionic Liquids for Metal Extraction

According to published research, phosphonium-based ionic liquids have shown great potential as extractants for a wide range of metals, including noble metals, rare earth elements, transition metals, and radionuclides. They have also demonstrated the ability to separate different transition and rare earth metals effectively.

Among the phosphonium-based ionic liquids, Cyphos 104 and Cyphos 101 have emerged as popular and promising options. Cyphos 104, in particular, has proven to be highly efficient in extracting gallium(III), indium(III), zinc(II), and tin(II) from electronic waste, which is crucial for both environmental and economic considerations. Studies have reported extraction efficiencies of up to 99.8% for gallium from 3 mol L^{-1} HCl [13]. Additionally, the extraction of alkaline waste from LCD screen leach liquor using Cyphos 104 resulted in the recovery of indium(III), zinc(II), and tin(II) with purities of 100%, 98.9%, and 100%, respectively [14].

The mechanism of indium extraction from a chloride medium has been described by the following equation [14]:

 $In^{3+}_{aq.} + 3Cl^-_{aq.} + 2[R_3P'P^+A^-]_{org.} \leftrightarrow [InCl_3, 2R_3R'P^+A^-]_{org.}$

 $R_3P'P^+$ is trihexyl(tetradecyl)phosphonium, and A is bis(2,4,4-trimethylpentyl) phosphinate.

D2EHPA (organophosphorus), Cyphos 104 (ionic liquid), and a mixture of both. Only the mixture of 0.05 mol L-1 D2EHPA and 0.02 mol L-1 Cyphos 104 achieved complete europium recovery. The authors observed that Cyphos 104 has a higher loading capacity than D2EHPA, but D2EHPA is more suitable for separating yttrium(III) and europium(III). The extraction with D2EHPA yielded the highest separation factor β (Y(III)/Eu(III)) of 10,546, while Cyphos 104 had a separation factor of 629.7 [15].

Cyphos 101 IL and its analogs have applications in the separation of rare earth metals from transition metals, including iron(III), cobalt(II), copper(II), manganese(II), and zinc(II). These liquids are utilized in their concentrated form and serve as both the organic phase and the extractant.Cyphos 101 dissolved in toluene demonstrates high effectiveness as an extractant for gold(III) from thiosulfate solutions, achieving an extraction efficiency of 99%. Additionally, undiluted Cyphos 101 enables complete recovery of platinum(IV) and palladium(II) from acidic leaching solutions of discarded catalytic converters [16].

A modified ionic liquid, $[P_{66614}][MA]$, which is similar to Cyphos 101 but with the N,N,N,N'-tetra(2ethylhexyl)malonate anion, is combined with the $[P_{66614}][NO_3]$ ionic liquid as a diluent. This combination is utilized for the extraction of europium(III) and other trivalent rare earth elements from a nitric acid solution. The study investigated the extraction behavior of europium under various conditions, including solution pH, temperature, extractant and salting-out agent concentrations, and metal content in the aqueous medium. The results indicated that this ionic liquid system is capable of effectively separating rare earth metal ions from transition metal ions, commonly found together in luminophore lamps and magnets [17].

A team of researchers based in the Netherlands has proposed the utilization of a low-melting ionic liquid called tetraoctylphosphonium oleate [P_{8888}][oleate] for the selective extraction of transition metals, specifically cobalt(II), from chloride solutions. The process takes advantage of the ionic liquid's favorable properties, such as low viscosity and environmental stability, enabling continuous operation at room temperature with high efficiency (96% extraction achieved within 15 minutes). However, it should be noted that the continuous-flow setup described in this study is suitable primarily for treating wastewater with low metal ion concentrations. Additionally, this method is more costly compared to the current setup utilizing ion exchange resins, as it requires additional membrane filters to minimize the potential leakage of the ionic liquid into the aqueous phase [18].

The extraction of lithium was carried out using a specific ionic liquid called tetrabutylphosphonium bis(2,4,4-trimethylpentyl) phosphinate [P_{4444][}BTMPP] in toluene. The extraction efficiency of lithium using this synthesized ionic liquid was significantly higher (94.07%) compared to the extraction with the molecular analog, bis(2,4,4-trimethylpentyl)phosphinic acid. An additional advantage of the [P_{4444]}[BTMPP] ionic liquid is its complete regenerability and reusability without any deterioration in its extraction properties. Researchers have found that Trihexyl(tetradecyl)phosphonium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate [P₆₆₆₁₄][hfac] dissolved in toluene is effective for the recovery of U(VI), Pu(IV), Am(III), and Eu(III) radionuclides from acidic waste solutions. In a study conducted by Liu et al. [19], they were able to back extract 98.99% of Am(III), 99.12% of Eu(III), 99.64% of U(VI), and 99.89% of Pu(IV) from a solution containing 0.03 mol L–1 of [P66614][hfac] into a mixture of 1 M guanidine carbonate and 0.05 mol L–1 EDTA within a short timeframe of 15 minutes.

The use of undiluted phosphonium ILs in combination with thiosalicylate derivatives showed significant extraction rates for cadmium(II) and copper(II). In particular, $[P_{66614}][BTB]$ and $[P_{66614}][PTB]$ ILs demonstrated high efficiency in extracting copper, cadmium, and zinc from aqueous solutions, achieving extraction rates of over 90% [20].

2.2. Exploring Ammonium-Based Ionic Liquids for Metal Extraction

Ionic liquids that incorporate ammonium cations have shown great potential as extractants for a wide range of metals, including Group 5 and 6 metals, noble metals, and alkali metals.

2.2.1. Group 5 and 6 Metals of the Periodic Table of Elements

The use of Aliquat 336, an ionic liquid, has shown efficiency in the extraction of vanadium and molybdenum across a wide pH range. Wang et al. [21] employed Aliquat 336 dissolved in sulfonated kerosene and achieved complete recovery of trace amounts of vanadium(V) from an aqueous solution of ammonium tungstate. The researchers observed the formation of a third phase when using 1 vol.% Aliquat 336 and 1 vol.% 2-octanol as a modifying agent. However, increasing the concentration of 2-octanol to 5 vol.% prevented the formation of the third phase and led to faster extraction. Nonetheless, this increase in 2-octanol concentration resulted in decreased efficiency in the extraction of vanadium(V), attributed to the inhibitory effect of 2-octanol on the ionic liquids. Compared to vanadium precipitation using calcium(II) salts, this method offers benefits such as high selectivity and rapid extraction, as noted by the authors [21].

Researchers have developed a flow diagram for the separation of vanadium(V) and aluminum(III) using Aliquat 336 dissolved in sulfonated kerosene [22]. Through their study, they determined that an initial pH of 0.78, an organic-to-aqueous phase ratio of 1:2, an IL concentration of 40 vol.%, and an equilibrium time of 3 minutes resulted in a 99.06% extraction efficiency for vanadium and only 7.95% for aluminum. This led to a separation factor β (V(V)/Al(III)) of 1221. The proposed mechanism for the extraction of vanadium(V) from the oxalic acid leachate of shale using Aliquat 336 involves anion exchange between the VO(C₂O₄)₂²⁻ anion and the chloride anion present in the IL.

$$2[R_4N^+Cl^-]_{org.} + VO(C_2O_4)_2^{2-}aq. = [(R_4N)_2VO(C_2O_4)_2]_{org.} + 2Cl_{aq.}^{-}$$

For the back extraction of vanadium, 8 mol L^{-1} HCl was proposed.

The authors of the study concluded that the developed setup is environmentally friendly, as it eliminates the need for pH control and enables faster vanadium extraction compared to systems involving inorganic acids. They highlighted the potential application of this setup for the processing of vanadium-bearing shale.

Aliquat 336, when diluted with kerosene, has the potential to recover molybdenum(VI) from an alkaline solution that also contains aluminum(III), copper(II), and nickel(II) [23]. It was observed that increasing the extractant concentration to 0.1 mol L-1 resulted in an enhanced molybdenum extraction efficiency of 98.5%. The extraction process was found to be largely unaffected by variations in temperature.

The authors of the study [23] highlighted the use of Aliquat 336 for the hydrometallurgical recovery of molybdenum from spent hydrotreating catalysts. However, they acknowledged that the separation of molybdenum from other elements present in spent catalysts, such as cobalt, rhodium, platinum, palladium, and vanadium, was not considered in their research.

2.2.2. Noble Metals

Aliquat 336, an ionic liquid, has demonstrated its efficiency as an extractant for noble metals including gold(III), platinum(IV), and palladium(II) [24]. In experiments, Aliquat 336 achieved recoveries of 100.0% for gold(III), 99.8% for platinum(IV), and 99.97% for palladium(II) from 0.1 M aqueous solutions of HCl within a short duration of 5 minutes.

Vereycken et al. [25] introduced a one-stage separation method for noble metals (Pd(II), Pt(IV), and Au(III)) from impurities such as Fe(III), Cu(II), Ni(II), and Rh(III) using undiluted Aliquat 336 IL and its bromide and iodide derivatives, [A336][Br] and [A336][I]. The study demonstrated that platinum(IV) and palladium(II) were quantitatively recovered through extraction with Aliquat 336, [A336][Br], and [A336][I], while gold(III) was quantitatively extracted with Aliquat 336 and [A336][Br]. However, the authors did not provide data on the efficiency of gold extraction with [A336][I]. The authors consider this method promising for the processing of electronic waste and analytical purposes. The proposed method offers advantages such as the utilization of a single extraction phase in the flow diagram, the absence of volatile and highly flammable organic diluents, and minimal contamination of the aqueous phase due to the low water solubility of Aliquat 336, [A336][Br], and [A336][I]. However, there are certain drawbacks to the method, including the requirement for relatively small volumes of the aqueous phase, the higher viscosity of the ILs, and the potential limitations in mass transfer rates when scaling up to larger volumes.

Ionic liquids formed by combining tetrahexylammonium $(C_6H_{13})_4N^+$ (THN) and tetraoctylammonium $(C_8H_{17})_4N^+$ (TON) cations with different anions like Br⁻, SCN⁻, and bis(trifluoromethylsulfonyl) imide anion $[NTf_2]^-$ have shown potential as extractants for noble metals, including Au(III), Pt(II), and Pt(IV), from industrial wastewater.

2.2.3. Lithium

The use of two ionic liquids, tetrabutylammonium bis(2-ethylhexyl) phosphate $[N_{4444}]$ [DEHP] and tetraoctylammonium bis(2-ethylhexyl) phosphate $[N_{8888}]$ [DEHP], dissolved in toluene, demonstrated over 80% efficiency in extracting lithium from hydrogen chloride solutions. Subsequently, lithium was efficiently back-extracted from the organic phase using 0.5 mol L–1 hydrochloric acid in four stages, achieving a 95% efficiency [26].

Due to its high lithium extraction capacity, tetrabutylammonium mono-2-ethylhexyl 2-ethylhexyl phosphate, $[N_{4444}][EHPMEH]$, dissolved in methylbenzene, enables the separation of lithium ions from other alkali metal ions such as sodium, potassium, and rubidium [27]. The distribution ratio of lithium (7) was found to be twice as high as that of Na, K, and Rb (3.5). This discrepancy is attributed to the stronger electrostatic interaction between the IL anion and the cation with a higher charge density. When the ionic liquid concentration exceeded 0.6 mol L–1, the lithium extraction efficiency exceeded 90%. Zhao et al. [27] also investigated the mechanism of lithium extraction and determined that the formed complex had a composition of $3\text{LiCl}\cdot4[N_{4444}][EHPMEH]$. Consequently, $[N_{4444}][EHPMEH]$ IL shows promise as an extractant for lithium in the processing of lithium-ion batteries.

2.3. Imidazolium Ionic Liquids for Metal Extraction

2.3.1. Transition Metals

Ionic liquids based on imidazolium cations have demonstrated potential for the extraction and separation of transition metals.

A study conducted on the extraction of zinc(II), cadmium(II), copper(II), and iron(III) from a hydrochloric acid solution using various imidazolium ionic liquids revealed that selective separation of Zn and Cd from Fe and Cu can be achieved using 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄]. The researchers also observed that 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([omim][NTf₂]) enable selective separation of Zn/Cd and Zn/Fe pairs [28].

Imidazolium-based ionic liquids incorporating butyl ([bmim][NTf₂], [C₄C₁im][OTf], [C₄C₁im][MeSO₄], [C₄C₁im][Me₂PO₄], and [C₄C₁im][OAc]) and octyl ([C₈C₁im][Cl] and [C₈C₁im][OTf]) groups were employed for the extraction of zinc(II) and copper(II) from diesel fuel. The study demonstrated that these compounds can achieve recovery rates of up to 99.3% for zinc and up to 99.7% for copper, even when present in the fuel at concentrations as low as 2 mg kg⁻¹ and 1 mg kg⁻¹, respectively [29]. The researchers found that the solubility of ILs in the fuel phase is minimal, thereby reducing the loss of the extractant.

In comparison to ILs based on ammonium and phosphonium cations, imidazolium-based ILs have higher costs, exhibit toxicity, and exhibit lower efficiency in extracting transition metals from aqueous phases with low acidity. To achieve quantitative extraction of transition metals, solutions with acid concentrations of at least 5 mol L^{-1} are required.

2.3.2. Metals of Period 5 of the Periodic Table of Elements

As an alternative to methyl isobutyl ketone, imidazolium ionic liquids containing a keto group in the cation, namely [EPipMIBK][NTf₂] and [MImMIBK][NTf₂], were utilized for the liquid-liquid extraction of tantalum(V) from a sulfuric acid solution. These ionic liquids offer several advantages over methyl isobutyl ketone, which is highly soluble in water and poses fire and explosion hazards. In contrast, the ionic liquids are non-flammable, non-volatile, possess low viscosity, exhibit poor water solubility, and readily dissolve in organic solvents like kerosene. The extraction efficiency of tantalum using these ILs achieved 96% [30].

A concentrated undiluted ionic liquid consisting of the imidazolium cation and diethyl phosphate anion, specifically 1-ethyl-3-methylimidazolium diethyl phosphate [EMIM]-DEP, was suggested for the extraction of vanadium(V) from diluted oil sands, where vanadium exists as a porphyrin complex [31]. To displace the VO^{2+} ion from the porphyrin anion, the ionic liquid was acidified using 37% hydrochloric acid. However, the recovery of vanadium using this method was only 26%. The authors did not provide an explanation for this observation

III. Ionic Liquids as Diluents in Extraction Systems

The use of different classes of ionic liquids as diluents for extractants is a topic of significant interest. This approach has the potential to enhance various aspects of the extraction process.

3.1. Ionic Liquid Diluents: Exploring Phosphonium Cations for Enhanced Extraction Processes

The combination of Cyanex 272 extractant dissolved in the Cyphos 101 ionic liquid offers a selective extraction method for cobalt(II) and nickel(II) from acidic chloride solutions. The use of Cyphos 101 as a diluent provides several advantages, including excellent selectivity, high extraction efficiency, and the beneficial properties of ionic liquids such as low saturated vapor pressure and high thermal stability. These characteristics contribute to an overall enhancement of the extraction efficiency.

A notable illustration involves the utilization of a 0.5 mol L–1 solution of Cyanex 272 in Cyphos 101 at a temperature of 323 K. This setup facilitated the rapid and selective extraction of cobalt(II) from an aqueous chloride solution with a pH of 6, which also contained Ni(II). The cobalt extraction efficiency achieved an impressive 90%. Subsequently, 100% of the cobalt was successfully back-extracted using 0.1 mol L⁻¹ sulfuric acid at a temperature of 298 K [32].

In a study conducted by Song et al. [33], triethyl (pentyl) phosphonium bis (trifluoromethylsulfonyl) imide $[P_{2225}][NTf_2]$ was employed as a diluent for trioctylamine $(C_8H_{17})_3N$, which is an extractant for tungsten(VI) and cobalt(II). The authors observed that the trioctylamine- $[P_{2225}][NTf_2]$ system exhibited higher separation efficiency, selectivity, and distribution ratio compared to the trioctylamine-kerosene system. Additionally, M. Matsumiya, a Japanese scientist, employed a similar system using triethyl (hexyl) phosphonium bis (trifluoromethylsulfonyl) imide $[P_{2226}][NTf_2]$ for the extraction of platinum(IV) from a chloride medium.

IV. Ionic Liquids as Effective Agents for Solid-Phase Metal Extraction

The use of ionic liquids for metal extraction extends to solid-phase sorbents, including water-insoluble polymers. These polymers offer advantages such as environmental friendliness, non-volatility, non-toxicity, and ease of separation and regeneration from the liquid phase. Solid-phase extraction resins can be modified by grafting or impregnating them with liquid extractants, with the latter method being preferred due to its simplicity.

Zhang et al. proposed a novel approach for enhancing the extraction efficiency of mercury ions from aqueous solutions containing Hg(II), Pb(II), and Cu(II) by modifying solid-phase sorbents [34]. They developed a resin based on polyvinyl alcohol and sodium alginate, incorporating an ionic liquid, tricapryl(methyl)ammonium 2-methylthiobenzoate [A336][MTBA], as the extractant. By optimizing the ratio of ionic liquid volume to polyvinyl alcohol weight, they achieved 100% recovery of Hg(II) from a solution with a mercury concentration of 50 mg/L. The extraction efficiency of mercury was found to be unaffected by increased impurity ion concentrations, and the optimal pH was determined to be 5.8. The designed sorbent aimed to remove mercury ions from wastewater, and the researchers also investigated the regenerability and reusability of the extractant.

Two different resins were synthesized using tetrabutylammonium dihydrogen phosphate (TBAH2P) ionic liquid in combination with natural cellulose and commercial Amberlite XAD-7 polymer as sorbents [35]. The performance of these resins as extractants for europium was evaluated, considering factors such as pH, contact time, initial concentration of Eu(III) in the solution, and temperature, in order to assess their adsorption capacity. It was observed that the maximum adsorption efficiency of europium extractants was achieved at pH values below 6, with an optimal contact time of 30 minutes. Further increasing the contact time did not significantly affect the adsorption capacity. While both materials exhibited favorable adsorption properties, experimental findings indicated that functionalized Amberlite XAD-7 demonstrated higher selectivity (71.99 mg of Eu(III) per gram of the polymer) compared to modified cellulose. This difference was attributed to the chemical composition and porous structure of Amberlite XAD-7 particles, which offered greater porosity than cellulose.

Novel polyionic liquids were synthesized by cross-linking poly-N-vinylimidazole and poly-4vinylpyridine with 1,4-dichlorobutane ($[PVIm-(CH)_2)_4PVIm][Cl^-]_2$ and $[PVP-(CH_2)_4-PVP][Cl^-]_2$ ILs) as well as with 1,6-dichlorobutane ($[PVIm-(CH)_2)_6-PVIm][Cl^-]_2$ and $[PVP-(CH_2)_6-PVP][Cl^-]_2$ ILs) for the purpose of arsenic removal from aqueous solutions [36]. These polyionic liquid gels exhibited excellent capability to quantitatively remove As(V) ions, even at both low and high concentrations in water, indicating a high affinity for the target ions. It is worth mentioning that the gels $[PVIm-(CH)_2)_6-PVIm][Cl^-]_2$ and $[PVP-(CH_2)_6-PVP][Cl^-]_2$ showed enhanced extraction rates due to improved accessibility of active sites for As(V) ions.

Another approach for solid-phase extraction of metals involves the utilization of Fe_3O_4 magnetic particles coated with a polymer shell containing ionic liquids [36]. This composite material facilitates the separation process as the magnetic particles can be easily separated from the aqueous phase or soil using a

magnet. The polymer shell ensures the stability of the magnetic particles in acid media, making them suitable for metal extraction applications.

Phosphonium-based ionic liquids have shown great potential for the functionalization of polymer sorbents. In a study by Mokhodoeva et al. [37], magnetite nanoparticles derived from PEG 4000 and Cyphos 101 IL were proposed for the extraction of Pd(II) and Pt(IV) from wastewater. The extraction process involved multicomponent chloride solutions containing Cu(II), Ni(II), Au(III), Rh(III), along with the platinum-group metals. Remarkably, the system exhibited selective recovery, extracting 98% of Pt(IV) and 99% of Pd(II) within a short time frame of 30 minutes. The authors suggested that the presence of a PEG shell enhanced the hydrophilicity of the nanoparticles, thereby expediting the ion exchange process. Furthermore, this approach demonstrated the capability to extract trace concentrations of platinum-group metals (around 10⁻⁵ mmol L⁻¹). Additionally, the magnetite nanoparticles functionalized with ILs exhibited stability in concentrated hydrochloric and nitric acid solutions. However, further investigations are necessary to elucidate the structure and binding mechanism of the obtained sorbents, particularly regarding the involvement of polymers and the underlying sorption mechanism.

Solid-phase extraction on an impregnated polymer support offers the combined advantages of liquidliquid extraction and ion-exchange chromatography. However, it should be noted that impregnated resins are more susceptible to the washing out of the organic extractant from the polymer pores. On the other hand, grafted extraction polymer resins exhibit high stability, resulting in longer service life for these materials.

Solid-phase extraction holds great promise for metal extraction from wastewater due to the reusability of the sorbent after desorption of the adsorbed metal and its ease of operation. It eliminates the need for toxic and combustible organic solvents and complex equipment like mixer-settlers.Nevertheless, solid-phase extraction may encounter certain challenges, such as difficulties in dispersing the sorbent in the analyte solution. Moreover, for quantitative extraction of an analyte, the sorbent must possess specific properties, including a large specific surface area, appropriate porosity, and ease of modification.

V. Conclusions

Ionic liquids show great promise for metal extraction and can serve as extractants or diluents, depending on process conditions and metal ions involved. They offer advantages such as low vapor pressure, improved safety compared to traditional diluents, and prevention of static charge accumulation. However, challenges include high viscosity, slower phase separation, and high cost, especially for ionic liquids with long alkyl chains. Future research and development of ionic liquids for metal extraction should consider various characteristics like cost, purity, stability, viscosity, solubility, density, conductivity, extraction efficiency, selectivity, and the underlying extraction mechanism. Given the wide range of available ionic liquids, chemoinformatics methods can be employed to address these complex issues effectively.

Methods such as quantitative structure-property relationships, molecular dynamics modeling, databases, combinatorial chemistry, and computer-aided molecular design are valuable for investigating ILbased separation. Functionalized ILs have gained attention for their enhanced extractability, selectivity, and physicochemical properties. While functionalized ILs with modified cations have been extensively studied, research on modified anions is less explored. The selection of cations and anions allows tailoring IL properties to specific tasks, considering density, viscosity, polarity, and water solubility. However, challenges remain, including toxicity, biodegradability, complexity of chemical processes, and high cost, limiting industrial use. Standard synthetic methods and large-scale production are essential for reproducibility and industrial applications. The hydrophobicity of imidazolium ILs can be improved, but care must be taken to avoid environmental hazards. Ongoing efforts focus on developing more cost-effective and readily available ILs with improved extraction properties. Further studies are needed to fully evaluate the potential of ILs.

References:

- [1]. Rajyaguru, YashesH, Vijay et al. Ionic Liquids, an Asset in Extraction Techniques–a Comprehensive Review. Reviews and Advances in Chemistry 12, 107 (2022).
- [2]. Frederik Philippi, Tom Welton, Targeted modifications in ionic liquids from understanding to design, Phys. Chem. Chem. Phys., 23, 6993 (2021).
- [3]. Ruiz-Ángel MJ, Carda-Broch S. Recent Advances on Ionic Liquid Uses in Separation Techniques, Separations, 9(4):96, (2022).
- [4]. Masmoudi, A., Zante, G.Trébouet, Barillon, R.,Boltoeva, M. Solvent extraction of lithium ions using benzoyltrifluoroacetone in new solvents, Sep. Purif. Technol. 255, 117653 (2021).
- [5]. Jae-chun Lee, Kurniawan Kurniawan, Sookyung Kim, Viet Tu Nguyen & Banshi D. Pandey Ionic Liquids-Assisted Solvent Extraction of Precious Metals from Chloride Solutions, Separation & Purification Reviews, **52**(3), 242(2023).
- [6]. Grace Inman, Ikenna C. Nlebedim, Denis Prodius, Application of Ionic Liquids for the Recycling and Recovery of Technologically Critical and Valuable Metals, Energies, 15, 628 (2022).
- [7]. Sameer Imdad, Rajeev Kumar Dohare, A Critical Review On Heavy Metals Removal Using Ionic Liquid Membranes From The Industrial Wastewater, Chemical Engineering and Processing-Process Intensification, **173**, 108812 (2022).
- [8]. Chao Huang, Yabing Wang, Bin Huang, Yamin Dong, Xiaoqi Sun, The recovery of rare earth elements from coal combustion products by ionic liquids, Minerals Engineering, **130**,142 (2019).

- [9]. uijada-Maldonado, E., Olea, F., Sepúlveda, R.; Castillo, J., Cabezas, R., Merlet, G., Romero, J. Possibilities and Challenges for ionic liquids in hydrometallurgy. Sep. Purif. Technol. 251, 117289 (2020).
- [10]. Alguacil, F.J. Liquid-Liquid Extraction of Indium (III) from the HCl Medium by Ionic Liquid A327H+ Cl- and Its Use in a Supported Liquid Membrane System. Molecules 25,5238 (2020).
- [11]. Yudaev PA, Chistyakov EM. Ionic Liquids as Components of Systems for Metal Extraction. ChemEngineering. 6(1),6 (2022).
- [12]. Mochamad L. Firmansyah, Fukiko Kubota, Wataru Yoshida, and Masahiro GotoApplication of a Novel Phosphonium-Based Ionic Liquid to the Separation of Platinum Group Metals from Automobile Catalyst Leach LiquorIndustrial & Engineering Chemistry Research 58 (9), 3845 (2019).
- [13]. Vicente-Martínez Y, Muñoz-Sandoval MJ, Hernández-Córdoba M, López-García I. Using a Simple Magnetic Adsorbent for the Preconcentration and Determination of Ga(III) and In(III) by Electrothermal Atomic Absorption Spectrometry. Molecules,28(6):2549, (2023).
- [14]. Aliakbari, R., Marfavi, Y., Kowsari, E., & Ramakrishna, S., Recent Studies on Ionic Liquids in Metal Recovery from E-Waste and Secondary Sources by Liquid-Liquid Extraction and Electrodeposition: a Review. Materials Circular Economy, **2**, 1(2020).
- [15]. Asadollahzadeh M, Torkaman R, Torab-Mostaedi M. Continuous Extraction of Europium(III) by Ionic Liquid in the Rotating Disk Column with an Asymmetrical Structure Aimed at the Evaluation of Reactive Mass Transfer. ACS Omega, 5(30):18700 (2020).
- [16]. Jae-chun Lee, Kurniawan Kurniawan, Sookyung Kim, Viet Tu Nguyen & Banshi D. Pandey, Ionic Liquids-Assisted Solvent Extraction of Precious Metals from Chloride Solutions, Separation & Purification Reviews, 52(3), 242 (2023).
- [17]. Rout, A.; Binnemans, K. Liquid–liquid extraction of europium (III) and other trivalent rare-earth ions using a non-fluorinated functionalized ionic liquid. Dalton Trans, **43**, 1862(2014).
- [18]. GuilhemArrachart1,* , Julien Couturier 1,2, Sandrine Dourdain 1, Clément Levard 2 and Stéphane Pellet-Rostaing, Recovery of Rare Earth Elements (REEs) Using Ionic Solvents, **Processes 9**, 1202 (2021).
- [19]. Cui X, Wang Y, Wang Y, Zhang P, Lu W. Extraction of Gold Based on Ionic Liquid Immobilized in UiO-66: An Efficient and Reusable Way to Avoid IL Loss Caused by Ion Exchange in Solvent Extraction. Molecules, 28(5), 2165 (2023).
- [20]. Kamaruddin NAL, Taha MF, Wilfred CD. Synthesis and Characterization of Novel Thiosalicylate-based Solid-Supported Ionic Liquid for Removal of Pb(II) Ions from Aqueous Solution. Molecules, 28(2), 830 (2023).
- [21]. Wang, L., Zhang, G., Guan, W., Zeng, L., Zhou, Q., Xia, Y., Wang, Q., Li, Q., Cao, Z. Complete removal of trace vanadium from ammonium tungstate solutions by solvent extraction. Hydrometallurgy **179**, 268(2018).
- [22]. Xiaobo Zhu, Yue Liu, Wang Li, Efficient Separation and Recovery of Vanadium(V) from Hydrochloric Acid Solution Using N1923 as an Extractant, ACS Omega, 7 (6), 5485(2022).
- [23]. Pradhan D, Kim DJ, Sukla LB, Pattanaik A, Lee SW. Evaluation of molybdenum recovery from sulfur removed spent catalyst using leaching and solvent extraction. Sci Rep, 10(1), 1960 (2020).
- [24]. Ning Wang, Qi Wang, YuqiGeng, Xu Sun, Duokun Wu, and Yanzhao Yang, Recovery of Au(III) from Acidic Chloride Media by Homogenous Liquid–Liquid Extraction with UCST-Type Ionic Liquids, ACS Sustainable Chemistry & Engineering, 7 (24), 19975(2019).
- [25]. Vereycken, W.,Riaño, S., Gerven, T.V.;,Binnemans, K. Extraction Behavior and Separation of Precious and Base Metals from Chloride, Bromide, and Iodide Media Using Undiluted Halide Ionic Liquids. ACS Sustain. Chem. Eng., 8, 8223 (2020).
- [26]. Olea F, Durán G, Díaz G, Villarroel E, Araya-López C, Cabezas R, Merlet G, Romero J, Quijada-Maldonado E. Ionic Liquids for the Selective Solvent Extraction of Lithium from Aqueous Solutions: A Theoretical Selection Using COSMO-RS. Minerals, 12(2), 190 (2022).
- [27]. Zhao, X., Wu, H., Duan, M., Hao, X., Yang, Q., Zhang, Q., Huang, X. Liquid-liquid extraction of lithium from aqueous solution using novel ionic liquid extractants via COSMO-RS and experiments. Fluid Phase Equilib.**459**, 129 (2018).
- [28]. De los Ríos, A.P.D.L., Hernández-Fernández, F., Alguacil, F., Lozano, L., Ginesta, A., García-Díaz, I., Sanchez-Segado, S., López, F., Godínez, C. On the use of imidazolium and ammonium-based ionic liquids as green solvents for the selective recovery of Zn (II), Cd (II), Cu (II) and Fe (III) from hydrochloride aqueous solutions. Sep. Purif. Technol., 97, 150 (2012).
- [29]. Pirjo Isosaari, Varsha Srivastav, Mika Sillanpaa, Ionic liquid-based water treatment technologies for organic pollutants: Current status and future prospects of ionic liquid mediated technologies, Science of the total Environment, 690(10), 604 (2019).
- [30]. Turgis, R.,Arrachart, G., Michel, S., Legeai, S., Lejeune, M., Draye, M., Pellet-Rostaing, S. Ketone functionalized task specific ionic liquids for selective tantalum extraction. Sep. Purif. Technol., 196, 174 (2018).
- [31]. Chauhan, G., de Klerk, A. Acidified Ionic Liquid Assisted Recovery of Vanadium and Nickel from Oilsands Bitumen. Energy Fuels, **35**, 5963 (2021).
- [32]. Rafael Manuel Rios-Vera, et. al., Trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl)phosphinate micellar behavior in the extraction of Ag(I) from acidic nitrate media, Journal of Molecular Liquids, **358**, 119132 (2022).
- [33]. Song, Y.; Tsuchida, Y.; Matsumiya, M.; Uchino, Y.; Yanagi, I. Separation of tungsten and cobalt from WC-Co hard metal wastes using ion-exchange and solvent extraction with ionic liquid. Miner. Eng., **128**, 224(2018).
- [34]. Dong, C., Gao, J., Zhao, Y. et al. Preparation of Pickering emulsion hydrogels containing indium(III) extractants and their indium(III) recycling properties. Clean Techn Environ Policy (2023).
- [35]. Andreea E. Gabor, Corneliu M. Davidescu, Adina Negrea, Mihaela Ciopec, Monica Butnariu, CatalinIanasi, Cornelia Muntean, PetruNegrea,Lanthanum Separation from Aqueous Solutions Using Magnesium Silicate Functionalized with Tetrabutylammonium Dihydrogen Phosphate, Journal of Chemical & Engineering Data,61 (1), 535 (2016).
- [36]. Atta AM, Ezzat AO, Moustafa YM, Sabeela NI, Tawfeek AM, Al-Lohedan HA, Hashem AI. Synthesis of New Magnetic Crosslinked Poly (Ionic Liquid) Nanocomposites for Fast Congo Red Removal from Industrial Wastewater. Nanomaterials (Basel), 9(9), 1286 (2019).
- [37]. Olga Lanaridi, Apurba Ranjan Sahoo, Andreas Limbeck, Shaghayegh Naghdi, Dominik Eder, Elisabeth Eitenberger, Zita Csendes, Michael Schnürch, Katharina Bica-Schröder, Toward the Recovery of Platinum Group Metals from a Spent Automotive Catalyst with Supported Ionic Liquid Phases, ACS Sustainable Chemistry & Engineering, 9 (1), 375 (2021).