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Solvent Extraction of Toxic & Heavy Metal Ions by Extractants from Wastewater Solutions

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Abstract

Industrial wastewater often contains toxic heavy metals that pose severe environmental and health hazards. The recovery and removal of these metals are essential for both ecological protection and resource sustainability. Among several treatment techniques, solvent extraction (SX) or liquid–liquid extraction (LLE) has emerged as an efficient and selective method for separating metal ions from aqueous effluents. This chapter explores the principles, mechanisms, and types of extractants involved in solvent extraction, as well as factors affecting extraction efficiency and recent advances such as green extractants and ionic liquids. The integration of solvent extraction into circular economy frameworks for metal recovery and recycling is also highlighted.

Keywords: Solvent extraction, extractants, metal ions, wastewater, green solvents, circular economy, ionic liquids

Introduction

Industrialization and urbanization have significantly increased the generation of wastewater containing heavy metals such as copper (Cu^{2+}), nickel (Ni^{2+}), zinc (Zn^{2+}), chromium (Cr^{3+}/Cr^{6+}), cadmium (Cd^{2+}), and lead (Pb^{2+}). These metal ions are toxic, non-biodegradable, and tend to bioaccumulate in aquatic organisms, posing severe risks to human health and ecosystems (Fu & Wang, 2011). Therefore, the removal and recovery of metal ions from industrial effluents have become an essential component of environmental management and sustainable resource utilization (Zhang et al., 2019).

Conventional wastewater treatment techniques such as chemical precipitation, coagulation–flocculation, ion exchange, membrane filtration, and adsorption are commonly used; however, these methods often suffer from drawbacks like incomplete removal, low selectivity, high operational cost, and sludge generation (Mareš et al., 2020). To overcome these challenges, solvent extraction (SX), also known as liquid–liquid extraction (LLE), has emerged as a highly efficient and selective technique for separating and recovering metal ions from aqueous solutions (Rydberg et al., 2004).

In the solvent extraction process, a metal ion from the aqueous phase is transferred to an organic phase containing a specific extractant, forming a metal–extractant complex. This process is based on the distribution of solutes between two immiscible phases, governed by thermodynamic equilibrium (Sato, 2020). The efficiency of metal extraction depends on factors such as pH, extractant concentration, temperature, and phase ratio. The organic extractant plays a crucial role in determining the selectivity and efficiency of the process (Li et al., 2020).

Different types of extractants—acidic, basic, neutral, and chelating—are used depending on the metal ion and extraction mechanism. For instance, acidic extractants such as di-(2-ethylhexyl) phosphoric acid (D2EHPA) and P507 are widely used for transition metals, while neutral extractants like tributyl phosphate (TBP) work via solvation mechanisms (Zhao et al., 2018). Recently, green extractants such as ionic liquids (ILs) and deep eutectic solvents (DES) have been introduced to reduce the environmental impact of conventional organic solvents (Mao et al., 2022). These eco-friendly alternatives offer low volatility, high thermal stability, and reusability, aligning the process with circular economy principles (Fu & Wang, 2011; Mao et al., 2022).

In summary, solvent extraction provides a versatile, scalable, and effective method for the separation and recovery of metal ions from wastewater. By integrating green chemistry and sustainable extractants, solvent extraction contributes to both environmental protection and resource recovery, supporting the transition toward a circular and sustainable industrial economy.

Principles of Solvent Extraction

Solvent extraction is governed by the equilibrium distribution of solutes between two immiscible phases — an aqueous phase containing metal ions and an organic phase containing the extractant dissolved in an organic diluent such as kerosene. When both phases are mixed, the extractant interacts with metal ions, forming an organometallic complex that migrates to the organic layer (Rydberg et al., 2004). The efficiency is represented by the distribution ratio (D):

$$\mathbf{D} = \frac{[\mathbf{M}]\mathbf{org}}{[\mathbf{M}]\mathbf{aq}}$$

The percentage extraction (E%) can be expressed as:

$$\mathbf{E}\ (\%) = \frac{\mathbf{D}}{\mathbf{D} + (\mathbf{Vaq/Vorg})} \times \mathbf{100}$$

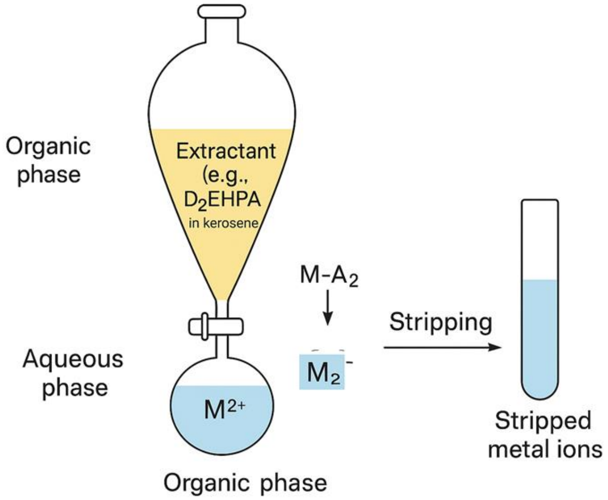

Figure 1: Schematic representation of solvent extraction process

The aqueous phase contains metal ions, and the organic phase contains extractant (e.g., D2EHPA in kerosene). On shaking, metal–extractant complexes form and migrate to the organic layer. The loaded organic phase is stripped with acid to recover metals.

Mechanism of Metal Extraction

The mechanism of metal extraction in solvent extraction (liquid–liquid extraction) involves the transfer of metal ions from an aqueous phase (usually containing dissolved metal salts) into an organic phase that contains an extractant. This process is governed by equilibrium reactions involving ion exchange, solvation, or chelation depending on the type of extractant used (Rydberg et al., 2004; Sato, 2020). The goal is to selectively form a metal–extractant complex that is soluble in the organic phase, enabling separation from other ions present in the wastewater.

1. Basic Principle

The extraction mechanism is based on the partitioning of solutes between two immiscible phases—typically water and an organic solvent. When the extractant is mixed with the aqueous metal ion solution, a chemical equilibrium is established between the two phases (Mareš et al., 2020). The metal ion interacts with the extractant molecules to form a neutral or hydrophobic complex, which preferentially dissolves in the organic phase.

The extraction equilibrium can be represented as follows:

$$\mathbf{M^{n+}(aq) + n(HR)(org) \rightleftharpoons M(R_n)(org) + nH^+(aq)}$$

where:

- M^{n+} = metal ion in aqueous phase
- HR = extractant (acidic type)
- $M(R_n)$ = metal–extractant complex in organic phase
- n = number of extractant molecules participating in the complexation

This equation shows that extraction efficiency depends on the pH, extractant concentration, and the formation constant of the complex (Fu & Wang, 2011).

2. Ion Exchange Mechanism

In many systems involving acidic extractants such as di-(2-ethylhexyl) phosphoric acid (D2EHPA), P204, or P507, the extraction proceeds via an ion-exchange mechanism. The metal cation in the aqueous phase replaces hydrogen ions from the extractant to form a neutral complex in the organic phase (Zhao et al., 2018).

$$\mathbf{M^{2+}(aq) + 2(HR)(org) \rightleftharpoons M(R_2)(org) + 2H^+(aq)}$$

Here, the metal ion (M^{2+}) displaces protons (H^+) from the extractant, releasing them into the aqueous phase. The equilibrium is pH-dependent—higher pH favors extraction as the reaction shifts rightward (Sato, 2020).
Such mechanisms are widely used for the extraction of Zn^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+} from industrial effluents and plating wastewater (Li et al., 2020).

3. Solvation Mechanism

For neutral extractants such as tri-n-butyl phosphate (TBP) or methyl isobutyl ketone (MIBK), the mechanism is typically solvation-based. The metal ion forms an association with anions (like Cl^- or NO_3^-) in the aqueous phase, creating a neutral species that is solvated by the extractant molecule (Rydberg et al., 2004).

$$\mathbf{MCl_n + mS(org) \rightleftharpoons MCl_n \cdot mS(org)}$$

Where S represents a neutral extractant such as TBP. For example, uranyl nitrate [$UO_2(NO_3)_2$] forms solvated complexes with TBP during uranium extraction from nitric acid solutions (Mareš et al., 2020 Kumar et al., 2020).

4. Chelation Mechanism

Chelating extractants, such as β-diketones (e.g., acetylacetone) or oximes (e.g., LIX reagents), form stable ring-like structures with metal ions through donor atoms like oxygen or nitrogen (Li et al., 2020). The resulting chelate complexes are highly stable and hydrophobic, favoring migration to the organic phase.

$$\mathbf{M2+ (aq) + 2HL (org) \rightleftharpoons M(L2) (org) + 2H+(aq)}$$

These reactions exhibit high selectivity and are extensively used for copper and nickel recovery from electroplating and leach solutions (Zhao et al., 2018).

5. Stripping and Regeneration

After extraction, the loaded organic phase containing the metal–extractant complex undergoes a stripping process to recover the metal. This is typically achieved using an acidic aqueous solution (e.g., H_2SO_4, HCl, or HNO_3), which reverses the extraction equilibrium and releases the metal ion back into the aqueous phase (Mao et al., 2022). The regenerated organic phase can then be recycled for further use, enhancing the sustainability of the process.

$$M(Rn)(org) + nH+(aq) \rightleftharpoons Mn+(aq) + n(HR)(org)$$

This cyclic operation underlies the closed-loop metal recovery systems widely employed in hydrometallurgical and wastewater treatment industries.

6. Schematic Representation of the Extraction Mechanism

Metal ions in the aqueous phase interact with extractant molecules in the organic phase at the interface, forming metal–extractant complexes that transfer to the organic layer. The loaded organic phase is then subjected to stripping to recover pure metals.

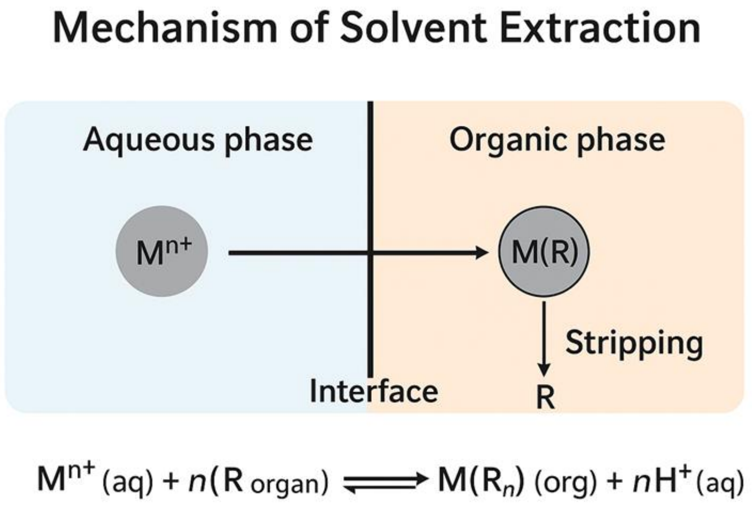

Figure 2: A simplified schematic of the solvent extraction mechanism.

Thermodynamics and Kinetics

The extraction mechanism is controlled by both thermodynamic equilibrium and kinetic factors. The equilibrium constant (Kex) of the extraction reaction determines the distribution of metal ions between the phases (Sato, 2020). Meanwhile, the rate of mass transfer across the phase boundary dictates how fast equilibrium is achieved (Fu & Wang, 2011). Factors such as interfacial area, agitation, and temperature directly influence the kinetics of extraction.

$$\mathbf{K_{ex}} = \frac{\left[\mathbf{M(R_n)}_{\boldsymbol{org}}\right][\mathbf{H^+}]^{\mathbf{n}}}{[\mathbf{M}_{\boldsymbol{aq}}^{\boldsymbol{n+}}]\,[\mathbf{HR}]^{\boldsymbol{n}}}$$

Understanding these relationships allows researchers to predict and optimize extraction performance under varying conditions.

Types of Extractants

The efficiency and selectivity of solvent extraction processes largely depend on the nature of the extractant, which is the key chemical responsible for transferring metal ions from the aqueous phase to the organic phase. Extractants are broadly classified into acidic, basic, neutral, and chelating types based on their functional groups and extraction mechanisms (Rydberg et al., 2004). Each class operates through a distinct interaction with metal ions, influencing both selectivity and extraction efficiency.

1. Acidic Extractants

Acidic extractants are among the most widely used in metal ion extraction processes. These reagents typically contain carboxylic, phosphoric, or phosphonic acid functional groups that undergo ion exchange reactions with metal cations in the aqueous phase. During extraction, the metal ion replaces a proton from the extractant to form a neutral metal–extractant complex that migrates into the organic phase (Sato, 2020).

Common acidic extractants include di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507), and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272). These extractants have been extensively applied for the recovery of metals such as Fe^{3+}, Zn^{2+}, Cu^{2+}, Co^{2+}, and Mn^{2+} from industrial effluents (Zhao et al., 2018). The high extraction efficiency and selectivity of these compounds make them particularly suitable for hydrometallurgical recycling and wastewater treatment applications (Fu & Wang, 2011).

2. Basic Extractants

Basic extractants contain amine functional groups that can form ion pairs with negatively charged metal complexes (anions) present in solution. They are typically used for extracting metal oxyanions such as CrO_4^{2-}, MoO_4^{2-}, and WO_4^{2-} (Li et al., 2020). The extraction mechanism involves protonation of the amine to form an ammonium cation, which associates with the metal anion, forming an ion-pair complex that dissolves in the organic phase.

Typical basic extractants include trioctylamine (TOA), Aliquat 336, and Amberlite LA-2, which are effective for the extraction of Cr (VI), Mo (VI), and V(V) from wastewater streams. The selectivity of amine-based extractants can be tuned by controlling pH and the presence of competing anions (Rydberg et al., 2004).

3. Neutral Extractants

Neutral extractants operate through a solvation mechanism rather than ion exchange or ion pair formation. They dissolve metal species by coordinating through oxygen or phosphorus atoms, often in the form of solvated complexes (Mareš et al., 2020). These extractants are particularly effective for metals forming neutral chloride or nitrate complexes, such as UO_2Cl_2 or $FeCl_3$.

Common examples include tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), and di-n-hexyl sulfoxide (DHSO). These reagents are widely used in the extraction of uranium, thorium, and rare earth elements. TBP, for instance, has been employed in the PUREX process for the separation of uranium and plutonium from nuclear waste streams (Rydberg et al., 2004).

4. Chelating Extractants

Chelating extractants form stable ring-like complexes with metal ions through multiple donor atoms such as oxygen, nitrogen, or sulfur. This chelation mechanism provides high selectivity and strong binding affinity, even at low metal concentrations (Mareš et al., 2020).

Notable examples include β-diketones (e.g., acetylacetone), Schiff bases, oxime-based extractants (e.g., LIX 84-I, LIX 984N), and 8-hydroxyquinoline derivatives. Oxime-based reagents are particularly effective for the selective extraction of Cu^{2+} and Co^{2+} from mixed metal solutions (Li et al., 2020). The strong coordination ability of these extractants allows for efficient recovery of valuable metals from dilute wastewater streams.

5. Green and Ionic Liquid Extractants

In recent years, the development of green extractants such as ionic liquids (ILs) and deep eutectic solvents (DES) has gained attention for their environmental compatibility. These solvents possess negligible vapor pressure, high thermal stability, and tunable solvation properties, making them promising alternatives to conventional organic diluents (Mao et al., 2022). For example, choline chloride-based DESs have been successfully used for the extraction of Cu^{2+}, Ni^{2+}, and Zn^{2+} ions from wastewater, demonstrating comparable performance to traditional extractants but with reduced ecological impact (Fu & Wang, 2011; Mao et al., 2022).

The adoption of such sustainable solvents represents a shift toward greener hydrometallurgical processes, aligning solvent extraction technology with circular economy and sustainable development goals.

Factors Affecting Extraction Efficiency

The efficiency of solvent extraction in removing and recovering metal ions from wastewater depends on several physicochemical parameters. These factors influence the distribution equilibrium, complex formation, and phase separation during extraction. Understanding and optimizing these variables are essential for achieving high selectivity and recovery yields (Rydberg et al., 2004; Fu & Wang, 2011). The major factors include pH of the aqueous phase, extractant concentration, phase ratio (O/A), temperature, contact time, and diluent type.

1. pH of the Aqueous Phase

The pH of the aqueous solution is one of the most critical factors influencing metal ion extraction. It determines the degree of ionization of both the extractant and the metal ions, thereby affecting complex formation (Sato, 2020). For acidic extractants such as D2EHPA or P507, higher pH values favor deprotonation of the extractant, enhancing metal–ligand complexation (Zhao et al., 2018). However, excessively high pH values can cause metal hydroxide precipitation, which negatively impacts extraction efficiency (Fu & Wang, 2011).

For instance, the extraction of Cu^{2+} and Zn^{2+} using D2EHPA shows maximum efficiency near pH 4–5, beyond which unwanted species may form (Li et al., 2020). Therefore, maintaining an optimum pH range is crucial for selective extraction and phase stability.

2. Extractant Concentration

The extractant concentration directly affects the distribution ratio (D) and determines the total capacity of the organic phase for metal ion loading (Rydberg et al., 2004). Increasing extractant concentration enhances metal extraction up to a saturation point, beyond which no significant improvement is observed (Mareš et al., 2020). However, excessive extractant use can increase viscosity, reduce mass transfer, and complicate phase separation.

For example, extraction of nickel using P507 increases sharply with extractant concentration from 0.1 M to 0.4 M but stabilizes at higher concentrations (Zhao et al., 2018). Thus, an optimal extractant concentration must be maintained for both efficiency and economic feasibility.

3. Organic-to-Aqueous Phase Ratio (O/A Ratio)

The phase ratio, defined as the volume of organic phase to aqueous phase, significantly influences the overall extraction efficiency and recovery rate. A higher O/A ratio allows for better extraction of metal ions by providing a greater amount of extractant, thereby increasing the distribution ratio (Mareš et al., 2020). However, using too much organic phase can be economically unviable and lead to excessive solvent consumption.

Studies have shown that the extraction of Cu^{2+} using LIX 984N and D2EHPA reaches near-complete recovery at an O/A ratio of 1:1 or 2:1 (Li et al., 2020). Optimization of this ratio is essential for industrial-scale applications to balance efficiency and cost-effectiveness.

4. Temperature

Temperature has a dual effect on solvent extraction processes. It can influence both the equilibrium constant of metal–extractant complex formation and the mass transfer rate between phases (Rydberg et al., 2004). For most extraction systems, an increase in temperature enhances the diffusion rate and reduces viscosity, improving phase contact (Sato, 2020). However, extraction reactions are often exothermic, meaning that high temperatures may shift the equilibrium toward the aqueous phase, reducing extraction efficiency (Mao et al., 2022).

For instance, the extraction of Zn^{2+} using P507 decreases slightly as temperature increases from 25 °C to 50 °C due to the exothermic nature of complex formation (Zhao et al., 2018). Therefore, maintaining moderate temperatures is beneficial for both kinetics and equilibrium stability.

5. Contact Time and Mixing Intensity

The duration and intensity of contact between the aqueous and organic phases determine how quickly equilibrium is reached. Adequate contact time ensures complete interaction and complex formation, while mixing intensity improves interfacial area for mass transfer (Fu & Wang, 2011). Typically, equilibrium is achieved within a few minutes for most systems, but insufficient mixing may cause poor phase separation and lower recovery.

According to Sato (2020), efficient agitation during extraction reduces diffusion resistance, while controlled settling time ensures clear phase disengagement. Thus, optimizing both agitation and contact duration is vital for reproducible extraction performance.

6. Type of Diluent

The diluent used to dissolve the extractant plays an important role in determining phase behavior, viscosity, and solubility characteristics. Common diluents include kerosene, xylene, and toluene. The polarity and dielectric constant of the diluent can significantly affect the solvation of the extractant–metal complex (Rydberg et al., 2004).

For example, kerosene-based systems are often preferred due to their low cost, low solubility in water, and favorable phase separation properties (Li et al., 2020). Recently, green diluents such as ionic liquids and deep eutectic solvents have been proposed to minimize environmental risks (Mao et al., 2022).

7. Presence of Competing Ions

The presence of co-existing metal ions in wastewater can strongly influence the extraction selectivity. Competing ions may form similar complexes with the extractant, leading to reduced purity or loading of the target metal (Fu & Wang, 2011). For example, the co-presence of Fe^{3+} can hinder Zn^{2+} extraction using D2EHPA due to similar coordination behavior (Zhao et al., 2018). Therefore, selective extractants and optimized pH conditions are required to minimize such interference.

Applications in Wastewater Treatment

Solvent extraction has been successfully applied for the recovery of various metals from industrial effluents. Copper recovery from electroplating wastewater using LIX 984N-C or D2EHPA achieves >95% efficiency (Li et al., 2020). Chromium can be selectively extracted using trioctylamine (TOA) or Aliquat 336 (Fu & Wang, 2011). P507 extractant separates Zn^{2+} over Ni^{2+} efficiently (Zhao et al., 2018).

Green Solvent Extraction and Sustainable Approaches

Traditional solvents like kerosene pose environmental risks. Green alternatives such as ionic liquids (ILs) and deep eutectic solvents (DES) are gaining popularity for their low volatility, recyclability, and tunable selectivity (Mao et al., 2022). DES systems based on choline chloride efficiently extract Cu^{2+} and Ni^{2+}.

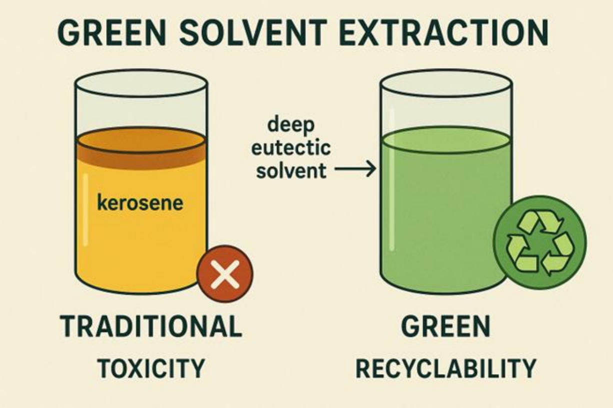

Figure 3: Green solvent extraction concept showing replacement of kerosene with deep eutectic solvent, enhancing recyclability and reducing toxicity.

Advantages and Limitations

1. Advantages of Solvent Extraction

a. High Selectivity and Efficiency

  - Solvent extraction allows selective separation of specific metal ions even from complex mixtures.
  - Extractants can be tailored to target particular oxidation states or ionic forms (Manna et al., 2020).

b. High Purity of Recovered Metals

- The extracted metals are often obtained in very pure form after stripping and regeneration processes (Ritcey & Ashbrook, 2018).

c. Rapid Kinetics and Simplicity

- The process is relatively fast and can be performed at room temperature with simple equipment compared to ion exchange or precipitation methods.

d. Scalability and Industrial Applicability

- Solvent extraction is widely used in hydrometallurgical industries for large-scale metal recovery such as copper, uranium, and rare earths.

e. Reusability of Solvents (Green Approach)

- Use of green solvents such as ionic liquids or deep eutectic solvents (DES) reduces volatility and enhances recyclability, minimizing environmental hazards.

f. Effective for Low Metal Concentrations

- Even trace amounts of metal ions can be extracted efficiently due to high distribution coefficients of certain extractants.

g. Flexibility in Process Design

- Can be easily integrated into multi-stage counter-current systems for better separation and yield optimization.

2. Limitations of Solvent Extraction

a. Toxicity and Volatility of Organic Solvents

- Traditional diluents such as kerosene, toluene, or xylene are toxic and flammable, posing environmental and health risks (Gupta & Krishnamurthy, 2005).

b. Formation of Emulsions

- During phase separation, stable emulsions can form, complicating extraction and reducing efficiency.

c. Solvent Loss and Degradation

- Loss of extractant through volatilization or degradation over multiple cycles can affect both cost and performance.

d. Limited Selectivity for Similar Metals

- Metals with close ionic radii or similar chemical properties (e.g., Ni^{2+} and Co^{2+}) are often difficult to separate effectively.

e. High Cost of Some Green Solvents

- Although sustainable, green solvents (ionic liquids, DES) can be expensive and not yet widely available for industrial scale-up.

f. Waste Generation and Treatment

- The process can still produce secondary wastes such as acid or base effluents during stripping or regeneration steps.

g. Temperature and pH Sensitivity

- The extraction efficiency is highly dependent on parameters like pH, temperature, and ionic strength, requiring precise control.

Future Perspectives

The future of solvent extraction lies in the development of eco-efficient, sustainable, and intelligent extraction systems that reduce environmental impact while maximizing metal recovery and process efficiency. Emerging trends focus on integrating green chemistry principles, including the use of biodegradable solvents, ionic liquids, and deep eutectic solvents, to replace hazardous conventional organic solvents. Advanced extractants with higher selectivity and improved reusability are being designed to enhance separation performance and reduce waste generation. Process intensification techniques, such as membrane-assisted extraction and miniaturized systems, further improve efficiency and reduce energy consumption. These innovations support circular economy goals by promoting resource recovery, waste minimization, and sustainable industrial practices.

Conclusion

Solvent extraction remains a promising and efficient technology for the recovery and removal of heavy metals from wastewater, providing an effective solution for reducing environmental pollution while enabling resource recovery. Its high selectivity allows for the targeted separation of specific metal ions even in complex industrial effluents, ensuring precise and reliable treatment performance. Additionally, its scalability makes it suitable for a wide range of applications, from small-scale laboratory systems to large industrial wastewater treatment plants, enhancing its practical relevance across multiple sectors such as mining, electroplating, and metal processing industries. The compatibility of solvent extraction with green solvents further strengthens its role in circular economy strategies, where waste streams are converted into valuable resources through the recovery and reuse of metals, thereby reducing reliance on virgin raw materials. The shift toward environmentally friendly alternatives such as ionic liquids and deep eutectic solvents (DES) ensures safer, low-toxicity, and energy-efficient processes, promoting sustainable, eco-friendly, and highly effective wastewater treatment practices.

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