JOURNAL OF INTERNATIONAL SCIENTIFIC RESEARCH
Volume 3, Issue 5, October 2025 **Online ISSN: 3030-3508**
https://spaceknowladge.com

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SELECTIVE SEPARATION OF COPPER AND ZINC IONS FROM INDUSTRIAL EFFLUENTS USING ORGANIC COMPLEXING AGENTS: MECHANISMS AND PROCESS DESIGN

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Received:04.11.2025
Revised: 05.11.2025
Accepted:06.11.2025

KALIT SO'ZLAR:

Copper ions; Zinc ions; Organic complexing agents; Selective separation; Solvent extraction; Industrial wastewater; Chelation mechanism; Kelex 100; Bibenzimidazole; Hydrometallurgy.

ANNOTATSIYA:

Industrial effluents often contain elevated concentrations of heavy-metal ions, including copper (Cu^{2+}) and zinc (Zn^{2+}). The selective removal and recovery of these ions are critically important from both environmental and resource-recovery perspectives. This article reviews current knowledge of organic complexing agents (chelators, extractants) applied to the selective separation of copper and zinc ions from industrial wastewater streams and secondary process liquors, analyzes underlying mechanisms (complexation, solvent extraction, ion exchange, selective stripping), and discusses process design considerations and challenges. Particular attention is given to factors influencing selectivity between Cu(II) and Zn(II), including ligand structure, aqueous phase chemistry (pH, chloride, sulfate, competing ions), organic-phase modifiers, phase ratio, stripping strategy, and regeneration. Case studies of solvent extraction systems (e.g., 1,1'-didecyl-2,2'-bibenzimidazole, bifunctional extractants such as Kelex 100) are analysed, and prospects for integration into industrial wastewater treatment and metal recovery schemes are considered.

Introduction

The contamination of industrial wastewater by heavy metals is a serious global environmental issue. According to recent reviews, industrial wastewaters may carry significant loads of heavy metals which pose toxicity risks to human health and ecosystems. Amongst these, copper and zinc ions are common by-products of numerous industrial operations (electroplating, brass manufacture, leaching of printed circuit boards, mining by-products). For example, selective separation of Cu and Zn in hydrometallurgical solutions has been demonstrated. The dual goals of this removal are: (i) reducing environmental discharge and associated regulatory burdens; (ii) recovering valuable metals for reuse, in line with circular economy principles. To achieve these goals efficiently, selective separation techniques using organic complexing agents have gained interest. These agents enable preferential binding or extraction of one metal ion over another, facilitating separation even in mixed-metal environments. This article focuses therefore on the mechanistic basis of selectivity in such systems, process variables, and case studies of industrially relevant systems.

Organic complexing agents (which may act as chelating ligands, extractants in solvent extraction systems, or functionalised adsorption/ion-exchange resins) operate by forming metal–ligand complexes that differ in stability, charge, hydrophobicity or extractability depending on the target metal ion. Several mechanistic features contribute to selectivity for Cu(II) vs Zn(II):

Different metal ions exhibit different coordination preferences (e.g., ligand denticity, donor atoms, ionic radius, charge density). An organic ligand may form a stronger or more stable complex with Cu(II) relative to Zn(II), thereby enabling selective uptake. For instance, in chloride media, the extractant 1,1′-didecyl-2,2′-bibenzimidazole (diC10) was shown to selectively extract Cu^{2+} over Zn^{2+} when the chloride concentration is sufficiently high, due to preferential formation of binuclear Cu–chloro complexes $(CuCl_2)_2L_2$ in the organic phase and suppressed Zn extraction (<4 %) under those conditions. Similarly, extractants based on 8-hydroxyquinoline derivatives (e.g., Kelex 100) were used in selective extraction cycles of Cu, Zn and Fe from acid chloride media. When ligand structure is optimised (alkyl chain length, hydrophobicity, donor group acidity), extraction selectivity can be enhanced.

Selectivity is not only a feature of ligand–metal affinity, but also of the aqueous and organic phase environment. Key variables include pH of the aqueous feed, chloride (or other anion) concentration, presence of competing ions, temperature, aqueous-to-organic (A:O) phase ratio, organic diluent and phase-modifier. For example, the study with diC10 showed that a high chloride concentration (>6 M LiCl) and the presence of benzyl alcohol as organic modifier improved Cu(II) extraction and suppressed Zn(II) extraction. In the Kelex 100 system, the separation of Zn(II) from Cu(II)/Fe was achieved via a multistage extraction–scrubbing–stripping cycle where the scrubbing pH (2.5–3.5) enabled selective release of Zn from the organic phase while Cu and Fe remained bound. Thus, control of the physicochemical medium is essential to achieve high selectivity.

In practice, selective extraction of Cu and Zn often necessitates multi-stage solvent extraction or ion-exchange processes: extraction of metal-ligand complex into the organic phase, scrubbing of unwanted metals, stripping of the target metal into a suitable aqueous phase, then regeneration of the extractant for reuse. For example, in the extraction of Cu, Zn and Fe using a bifunctional extractant, the process consisted of extraction → scrubbing (to release Zn) → stripping (to recover Zn in sulphate medium) → conditioning/regeneration of the extractant. The success of selective separation thus depends on the interplay between ligand design, process architecture, and regeneration strategy.

Industrial effluents present multiple challenges for selective separation systems: Mixed metal composition, high ionic strength and complex anion composition, variable pH and temperature, and the need for cost-effectiveness and sustainability. For industrial deployment, the process must have high selectivity, good capacity, minimal reagent consumption, regenerability of extractant, and minimal generation of secondary waste streams. Given these constraints, the design of selective separation systems must incorporate both mechanistic understanding and process engineering.

1,1′-Didecyl-2,2′-bibenzimidazole (diC10) for Cu(II) from chloride media: Mądrzak-Litwa & Borowiak-Resterna (2019) studied extraction of Cu^{2+} from concentrated chloride solutions by diC10 in toluene (or toluene + benzyl alcohol modifier). They demonstrated that when $[HCl]_{(feed)} \geq 1$ M and $[LiCl]_{(feed)}$ was increased to 6-7 M, Cu extraction approached nearly 100 % while Zn extraction remained <4 %. They found that at pH_feed > 1, the binuclear complex $(CuCl_2)_2L_2$ likely forms in the organic phase. The regenerated extractant retained its extraction ability, suggesting good reusability.

Kelex 100 bifunctional extractant for Cu–Zn–Fe separation: Zhivkova et al. (2017) described a process for simultaneous extraction of Cu(II), Zn(II) and Fe (II/III) from hydrochloric acid solutions via Kelex 100. The extraction mechanism involved first extracting all three metals as anion chloride complexes, then scrubbing at pH ~2.5–3.5 to release Zn into the aqueous scrubbing phase while Cu and Fe remained in the organic phase. After stripping, Zn was recovered in a sulfate medium suitable for electrolysis. This multistage process illustrates how selectivity can be engineered via sequential steps. 4.3 Use of complexing agents in sorption/adsorption systems: Kołodyńska (2013) reviewed the application of "new generation" complexing agents for sorption of Cu(II), Zn(II), Cd(II) and Pb(II). Such adsorbents may offer lower cost and smaller footprint compared to solvent extraction, but achieving high selectivity for Cu vs Zn remains challenging.

When planning a selective separation system for Cu and Zn using organic complexing agents in industrial wastewater, several key design principles apply: feed characterisation, choice of ligand/extractant, phase chemistry optimisation, multi-stage flowsheet, stripping and recovery, regeneration and recycle of extractant, integration with downstream recovery, and economic and environmental assessment. These considerations ensure that laboratory findings can be adapted for industrial-scale performance.

Despite progress, several challenges remain. Many studies focus on binary systems (Cu + Zn) under idealised laboratory conditions. Real industrial effluents contain complex matrices (multiple metals, organics, surfactants) which affect performance. Long-term stability of extractants, solvent losses, phase separation issues under highly loaded conditions require further investigation. Lower-cost, greener ligands and solvents (biobased chelators, ionic liquids) are under-explored. Scale-up of selective extraction/adsorption systems from lab to pilot/industrial scales is limited, especially in wastewater treatment. Coupling of selective separation with circular-economy frameworks needs further development. Nevertheless, selective separation via organic complexing agents offers attractive potential.Selective separation of Cu(II) and Zn(II) ions from industrial wastewater using organic complexing agents is feasible and has been demonstrated in several laboratory studies. Mechanistic control via ligand design, phase chemistry (particularly chloride concentration and pH), and multistage flowsheets enables high selectivity. Process design must consider feed composition, extractant choice, phase chemistries, stripping/regeneration, and integration with downstream recovery. Further work is required to translate laboratory systems into robust, cost-effective industrial applications.

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