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Exploring Ionic Liquid-based Liquid-Liquid Extraction as Benign Alternative for Sustainable Wastewater Treatment

Sachind P Padinhattath, M Shaibuna, Ramesh L Gardas.

Affiliations below.

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Corresponding Author:
Ph.D. Ramesh L Gardas, Indian Institute of Technology Madras, Deprtment of Chemistry, IIT Madras, 600036 Chennai, India, gardas@iitm.ac.in

Contributors‘ Statement: Conception and design of the work: S.P. Padinhattath, M. Shaibuna, R.L. Gardas;
Data collection: S.P. Padinhattath, M. Shaibuna;
Analysis and interpretation of the data: S.P. Padinhattath, M. Shaibuna, R.L. Gardas;
Statistical analysis: S.P. Padinhattath, M. Shaibuna, R.L. Gardas;
Drafting the manuscript: S.P. Padinhattath, M. Shaibuna;
Critical revision of the manuscript: S.P. Padinhattath, M. Shaibuna, R.L. Gardas.

Affiliations:
Sachind P Padinhattath, Indian Institute of Technology Madras, Deprtment of Chemistry, Chennai, India
M Shaibuna, Indian Institute of Technology Madras, Deprtment of Chemistry, Chennai, India
Ramesh L Gardas, Indian Institute of Technology Madras, Deprtment of Chemistry, Chennai, India

Thieme

Exploring Ionic Liquid-based Liquid-Liquid Extraction as Benign Alternative for Sustainable Wastewater Treatment

Sachind Prabha Padinhattath, M. Shaibuna, Ramesh L. Gardas*
Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India.
*Corresponding author: Phone: +91 44 2257 4248; Fax: +91 44 2257 4202
E-mail: gardas@iitm.ac.in ; Web: https://iitm.irins.org/profile/48355

Significance

This review article emphasizes the significant potential of ionic liquid-based liquid-liquid extraction (IL-LLE) in tackling the issues associated with wastewater treatment. IL-LLE enables the effective and selective removal of various contaminants from aqueous environments by simplifying the experimental setup, minimizing energy requirements, facilitating recyclability, and deepening mechanistic insights. This review article consolidates current advancements, identifies research gaps, and proposes future directions in this burgeoning topic, rendering it a significant resource for researchers and industrialists.

Abstract

The uncontrolled release of industrial effluents containing micropollutants (MPs), dyes, and heavy metal ions contaminates natural water bodies posing threats to health and the environment. Conventional treatment methods often struggle with challenges such as prolonged processing time, low specificity, and risk of producing secondary pollutants. Liquid-liquid extraction (LLE) technique utilizing ionic liquids (ILs) has emerged as a viable alternative for the elimination of contaminants from wastewater. ILs, characterized by minimal volatility and tunable physicochemical properties, facilitate the precise elimination of contaminants from industrial effluent. IL-LLE streamlines the experimental setup, lowers energy consumption, promotes recyclability for reuse, enhances mechanistic understanding, and hence provides a sustainable alternative to industrial effluent treatment. This review provides a comprehensive analysis of IL-LLE approaches for wastewater treatment, commencing with an overview of the historical evolution of ILs, tracing their progression from initial research to contemporary and advanced applications. The article primarily examines the practical applications of IL-LLE, demonstrating how these approaches are employed to efficiently remove diverse contaminants from both simulated and actual industrial wastewater samples. As a whole, the review consolidates the versatility and efficiency of IL-based LLE in addressing various challenges in wastewater treatment.

Keywords: Ionic Liquid; Wastewater; Liquid-liquid extraction; Micropollutants; Dyes; Heavy metals; Reuse

1. Introduction

In the modern era, industrialization has resulted in an abnormal increase in the amounts of hazardous wastes in the environment.[1] Uncontrolled deposition of non-biodegradable and hazardous chemical contaminants into water bodies is harmful to the environment and raises economic concerns.[2] Most of these contaminants are carcinogenic, and they may readily accumulate in living beings via water bodies, either directly or indirectly. Once ingested, it will take a long time for them to be broken down, resulting in phenomena such as biomagnifications.[3] This entire scenario underlines the need for more effective, sustainable, and environmentally friendly water treatment techniques. Wastewater treatment, in general, refers to the processes used to remove biogenic contaminants, undesired chemical pollutants, organic or inorganic particulates, and gases from water.[2,4] The nature and extent of the purification approach are mainly determined by the type of contamination and its utility. Even though several existing chemical methods (e.g., ozone treatment, distillation, ion exchange, neutralizing filtration, sediment filtration, membrane filtration, reverse osmosis) are already available, their efficacy in removing trace metals and micro contaminants is not particularly satisfactory.[5–7] Conventional wastewater treatment methods, though widely used, face several limitations in effectively addressing modern pollution challenges. These techniques in general are energy-intensive, costly, and generate secondary pollutants, which require further treatment or disposal.[8] Moreover, they may not be adaptable to the increasing complexity and variability of industrial waste streams, limiting their overall efficiency and sustainability.

These observations indicate the dire need for the development of novel industrial wastewater treatment methods that can get around the drawbacks of existing techniques while offering enhanced environmental sustainability, efficiency, and selectivity. Extraction techniques serve as an effective means for separation and purification due to their simplicity, low energy requirements, and great efficiency.[9] LLE, commonly referred to as solvent extraction, is a straightforward and environmentally sustainable procedure among extraction methods. LLE is a separation process wherein a solute is moved from one liquid phase to another immiscible liquid phase, typically utilizing a solvent that selectively separates the desired solute from the initial solution.[10] LLE provides simplicity, cost-efficiency, and mitigates the creation of secondary pollutants, rendering it progressively appealing. Nonetheless, the selection of solvents in liquid-liquid extraction presents difficulties, particularly with the attainment of quantitative extraction while maintaining environmental sustainability. Conventional organic solvents used in liquid-liquid extraction can pose significant risks, highlighting the need for more environmentally friendly alternatives. Recently, alternative solvents such as ionic liquids (ILs) and deep eutectic solvents (DESs) have gained significant attention due to their wide range of potential applications.[11-16] They have benefits like low volatility, high stability, and tunability, rendering them optimal selections for sustainable extraction methods in industrial wastewater treatment.[17-20] Their compatibility with various pollutants and capacity for efficient separation further highlight their significance in this field.[21]

Owing to the distinctive properties of ionic liquids, IL-based liquid-liquid extraction has attracted considerable attention as a feasible alternative to traditional solvents. Recent research has examined the application of ionic liquids for the extractive elimination of diverse contaminants, including micropollutants, medicines, personal care product residues, dyes, and heavy metal ions from industrial effluents.[22] These findings highlight the effectiveness of IL-based LLE in facilitating efficient and selective extraction while minimizing environmental impact. A primary obstacle in advancing IL-based LLE was the complexity of comprehending the fundamental mechanisms of extraction. The complex interactions between ILs and contaminants sometimes hinder the accurate prediction of extraction outcomes. Recent advancements in computational methodologies, such as Density Functional Theory (DFT) and the Conductor-like Screening Model for Real Solvents (COSMO-RS), have provided critical insights into these systems.[23,24] These computational approaches have enabled researchers to comprehend and forecast the behaviour of ILs in LLE processes, leading to improved solvent design and process optimization. A fundamental element of IL-based LLE is the recyclability and reusability of the ILs employed in the procedure. Although ILs have various benefits, their high costs and possible environmental repercussions demand the development of techniques for solvent recovery and reuse.[25] Recent studies have begun addressing this difficulty, demonstrating effective solutions for IL recovery and reusability without considerable loss in extraction efficiency (EE). This advancement is crucial for guaranteeing the long-term sustainability and economic feasibility of IL-based LLE in industrial applications.

As a whole, this review aims to offer an extensive overview of IL-based LLE for wastewater treatment by analyzing the evolution of this approach from its initial stages to its present state.

The emphasis will be on the fundamental components of IL design, the intricacies of the process, mechanism analysis, recyclability, and sustainability, offering insights into potential future advancements for this promising technology. This review aims to identify research gaps and highlight opportunities for further innovation in the field of IL-based LLE for industrial wastewater treatment.

2. Ionic Liquids

Ionic liquids (ILs) are chemical entities consisting of organic cations combined with organic or inorganic anions, exhibiting distinctive chemical and structural characteristics. These characteristics encompass an extensive liquid range, thermal stability, low vapour pressure, a broad electrochemical window, and the capacity to solubilize various compounds.[26] An ionic IL is defined as a chemical composed exclusively of ions, generally existing in a liquid state at temperatures below 100 °C. Categorizing an ionic liquid exclusively as a category of salts with a melting point below 100 °C is not universally endorsed. ILs can be regarded as a separate class of solvents, alongside water and organic solvents.[27]

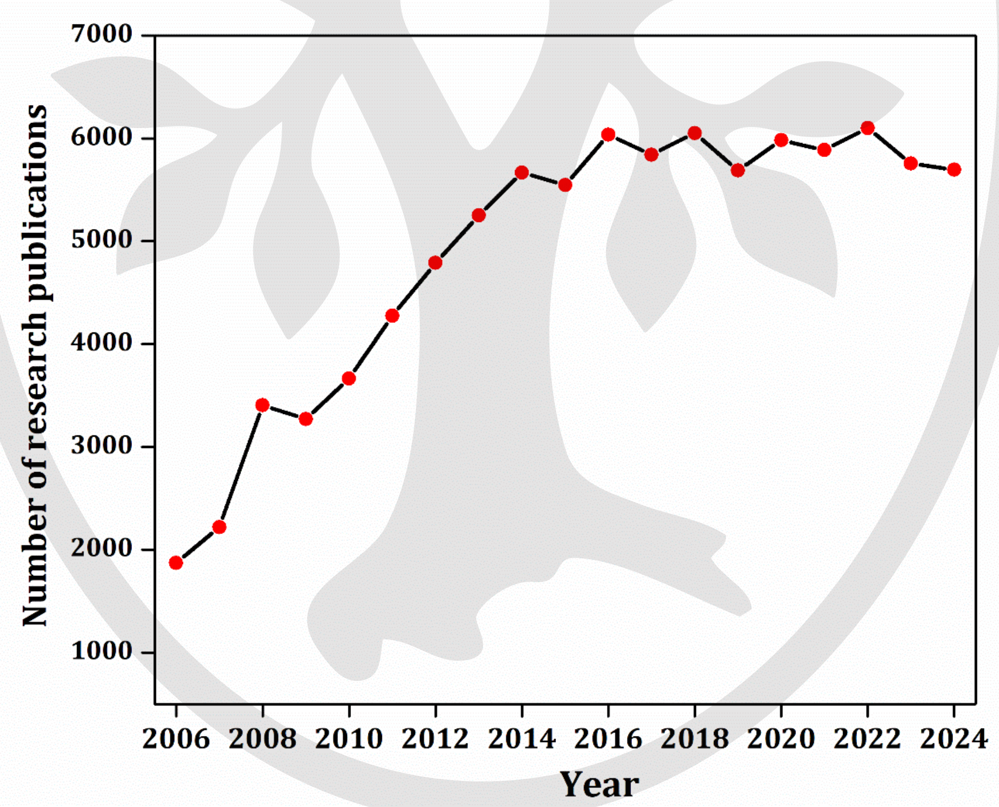

Figure 1 Year-wise publications on ionic liquids from 2006 to 2024*

(*Source: SCOPUS, as of 13th December 2024)

In recent times, ILs have deeply influenced different scientific fields and technologies, displaying notable growth in both research output and practical applications. Their versatility in properties has engrossed substantial attention from various sectors, fostering several scientific developments and inventions. The steady increment in the number of publications based on IL- chemistry over the years underlines the increasing significance and widespread application of ILs across key areas (Figure 1). The highly tunable structure of ILs provides remarkable versatility, allowing them to be custom-made for a wide array of applications. Additionally, their potential for reuse makes them a sustainable option in numerous fields.[28]

2.1 History and Classifications

The voyage of IL research finds its roots in the ground-breaking investigations of Paul Walden in the early 20th century.[29] Ethylammonium nitrate ($[EtNH_3][NO_3]$), the first discovered IL, was prepared by the neutralization of ethylamine by nitric acid. This IL had a surprisingly low melting point of 12 °C. Nevertheless, the actual potential of ILs remained mostly unmapped for the next four decades. Hurley and Wier, In 1951, found that a 2:1 mixture of 1-ethylpyridinium bromide and aluminum chloride, $[C_2py]Br\text{-}AlCl_3$, persisted as a liquid at room temperature.[30] This finding led to further analysis, including the development of phase diagrams and the invention of novel liquid state compositions. Building upon this, the limitations of the current mixture were later refined. This particular research study was focused on formulating a broader range of liquid compositions at room temperature, which ended up in the discovery of 1-butylpyridinium chloride-aluminum chloride, $[C_4py]Cl\text{-}AlCl_3$. This compound possessed improved properties as an IL in comparison to the former one.[31] During this period, the research on IL revolved around halo aluminate-based ILs, which can be regarded as the first generation of ILs.

A significant milestone in the history of ILs occurred with the introduction of moisture-stable ILs by Wilkes and Zaworotko in 1992. These ILs replaced aluminium chloride with other stable anions, rapidly expanding the room-temperature IL family.[32] Following this advent of air and water-stable ILs- characterized by anions such as tetrafluoroborate, nitrate, methyl sulfonates, trifluoromethane sulfonate, hexafluorophosphate, and halides-there arose a surge in the concept of designer solvents. This surge was fuelled by the tunable physical and chemical properties inherent in ILs. Beyond the widely favoured imidazolium category, the cationic selection of ILs extended to include ammonium, phosphonium, triazolium, pyridinium, morpholinium, cholinium, and beyond. Figure 2 depicts different categories of cations and anions generally used in ILs. Task-specific ionic liquids (TSILs) mark a significant evolution in the field of

ILs.[33] TSILs are specifically designed to perform specific tasks or functions with high efficiency and selectivity. TSILs have found various applications across different fields. Apart from their role in conventional chemical processes, TSILs have also been widely explored in biological and environmental contexts.[34] Another noteworthy evolution in the field of ILs was the advent of a new generation of ILs as mixtures of ILs and molecular solvents.[35] This development from traditional IL formulations signified a paradigm shift in the understanding of solvent systems.

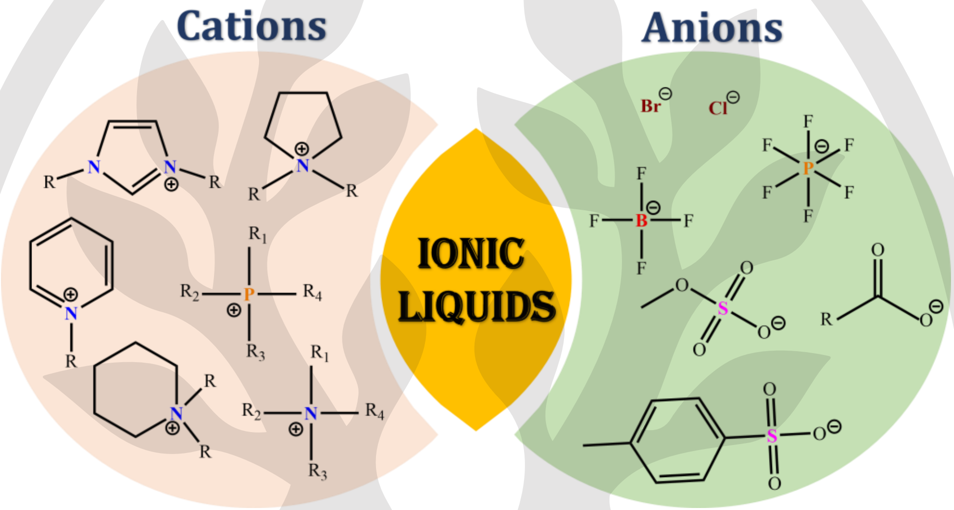

Figure 2 Pictorial representation of commonly used cations and anions in ILs

Classifying ILs presents a challenging task. Still, in accordance with the method of preparation and chemical nature, ILs can be categorized into different groups. Aprotic ionic liquids (AILs) are typically synthesized through quaternization reactions followed by anion metathesis (when required). These ILs are usually produced by the alkylation of phosphine, amine, etc., which produces intermediate salts. Subsequently, the desired anions are often introduced, resulting in the displacement of those produced during the intermediate stage.[36] AILs represent a significant portion of publications in the field of IL chemistry and exhibit superior thermal stability relative to other IL categories.[37] Another major category, protic ionic liquids (PILs) are generally formed through the proton transfer from a Brønsted acid to a Brønsted base.[38] The process leads to the formation of sites that can donate and accept protons, thereby promoting hydrogen bonding within the PIL structure. A significant difference in the pK_a values of the involved acids and bases is really essential, and that governs the extent of proton transfer during PIL formation. Commonly employed cations in PILs include phosphonium, ammonium, caprolactam, and imidazolium, combined with anions such as trifluoroacetate, triflate, and nitrate. In PILs, the cations possess a proton bonded to either nitrogen or phosphorus. PILs exhibit superior conductivity relative to other classes of ILs, attributed to the presence of free protons that facilitate hydrogen bonding interactions.[39] The enhancement in conductivity is accompanied by a trade-off in stability, as the potential for backward reactions resulting in back proton transfer, which diminishes the stability of PILs at higher temperatures.

Pseudoprotic Ionic Liquids (PPILs) are a distinct subclass of PILs. In contrast to conventional PILs, there is an incomplete proton transfer among the components, leading to a distinct ionic composition that may affect their properties and potential applications. This is due to the relatively low pK_a differences.[40] Despite this, PPILs exhibit many properties typical of ILs.[41] The method of synthesis is easier in comparison with multi-stage synthesis and purification needed for commercially available extractants and other RTILs. Commonly employed cations in PPILs include phosphonium, ammonium, caprolactam, and imidazolium, with a variety of anions such as salicylate, benzoate etc.[42] PPILs present a distinctive combination of characteristics, integrating features of both protic and aprotic ionic liquids, and are relevant for multiple applications in extraction, catalysis, electrochemistry, and materials science.[43]

Magnetic ionic liquids (MILs) represent a category of RTILs distinguished by their intrinsic magnetic characteristics, independent of any magnetic particle incorporation.[44] These magnetic properties are induced by either the cation, anion, or their combination. MILs frequently incorporate transition metal or lanthanide complexes in their anion frameworks, which imparts paramagnetic properties. MILs containing the $[FeCl_4]^-$ anion were among the first to be synthesized and have been the subject of extensive investigation.[45] Recently, MILs incorporating transition metals like Co and Mn, as well as lanthanide complexes such as Gd or Dy have gathered attention.[46] Commonly employed cations include phosphonium, ammonium, and imidazolium, paired with a variety of anions such as tetrachloroferrate, tetrachloromanganate etc. MILs generally show potential for different kinds of extraction, optical, and catalytic applications.[47]

2.2 Unique Properties and Applications of ILs

Ionic liquids are distinguished from conventional solvents by their numerous distinctive characteristics. Their intrinsic tunability enables tailored traits which makes them compatible with many domains and applications.[48] Due to their wide solubility range and highly tunable structures, ILs are widely utilized in solubilization applications across several fields. To enhance the bioavailability of poorly dissolvable drugs in pharmaceuticals they are employed.[49] Additionally, ionic liquids are used in the dissolution of biomass, including lignin.[50] Their distinctive features make them efficient solvents for decomposing lignocellulosic biomass into its constituent components, such as cellulose, hemicellulose, and lignin.[51] The dissolution process is vital in numerous biomass conversion technologies, such as the generation of biofuels, biochemicals, and biomaterials.[52]

The remarkable solubility range, tunability, and efficient phase separation properties of ILs are crucial in many extraction and separation processes. ILs are extensively utilized in the extraction and separation of bioactive compounds,[53] valuable metals from electronic waste,[54] pollutants from wastewater,[55] as well as lanthanides and actinides from spent nuclear waste.[56] Their adaptability in various applications arises from their capacity to effectively dissolve substances of interest while facilitating straightforward separation.

The wide electrochemical potential windows and high conductivity of ionic liquids are utilized in electrochemical applications.[57] They are extensively utilized in energy storage devices, such as fuel cells, supercapacitors, and batteries.[58] The versatility of ILs comprises semiconductor applications, metal electrodeposition, and the revolutionizing of electroplating processes.[59] In addition, ILs are included in various electrolyte systems, including polymer or gel polymer electrolytes, and utilized as additives, thereby enhancing their utility.[60] The unique characteristic that makes ILs suitable for sensing applications is their ability to alter physicochemical and biological properties in response to specific conditions. This attribute enables ILs to interact with target analytes in a controlled manner, allowing for their detection with heightened precision and selectivity.[61] Consequently, they have substantial applicability in numerous sensing devices.[62] In addition to sensing, ILs are utilized for the absorption of greenhouse gases. The low volatility and gas absorption capacity of ILs make them appealing candidates for greenhouse gas capture.[63] Specifically formulated ILs have successfully captured various greenhouse gases, including CO_2, CH_4, and N_2O.[64]

Industrial chemical processes like catalysis, which require high temperatures, greatly benefit from the exceptional thermal stability of ILs. In catalysis, ILs can serve as solvent media, catalysts, or co-catalysts. Many studies reported that when ILs are employed in reaction mediums, catalyst exhibits considerable selectivity and activity. Catalytic reactions facilitated by ILs encompass various processes including Diels-Alder cycloadditions, polymerizations, acylation of isobutylbenzene, biomass dissolving, and olefin dimerization.[65] Furthermore, ILs have been employed as additives to enhance the efficiency of various industrial materials, including paints.[66] A widely used feature of ILs is their ability to adjust the viscosity and rheological properties of the product. The flow properties of substances such as paints and shampoo can be modified by tuning the flow properties of ILs. The overall durability and shelf life of the product are improved due to its thermal and chemical stability. Additionally, ILs can protect against degradation from heat, oxidation, and other chemical processes, thereby extending the lifespan of the manufactured product.

Recent research has explored the potential of ILs as alternatives to traditional refrigerants used in refrigeration systems.[67] As hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs) gain popularity as refrigerants for refrigeration and cryogenic applications, concerns regarding their significant environmental impacts are growing. Due to their high gas absorption capacity, negligible vapor pressure, and outstanding thermal stability, ILs present a promising alternative for reducing the environmental impact of refrigeration systems. Another commercialized application of ILs is their use in dispersing crude oil spills.[68] The emergence of magnetic ILs possessing inherent magnetic properties has opened up a new range of potential applications.[69] ILs can be applied to the surface of an oil spill, where they interact with the oil molecules because of their amphiphilic nature. The ILs create a stable emulsion with the crude oil, breaking it into smaller droplets and inhibiting its coalescence into large slicks.[70]

3. Liquid-Liquid Extraction (LLE)

As mentioned earlier, extraction is the process of separating a substance from its matrix by transferring it to a different phase, which can be solid or liquid. The main types of extraction include solid phase extraction, liquid-liquid extraction, acid-base extraction, and supercritical fluid extraction. Liquid-liquid extraction involves the exchange of certain compounds, on the basis of their relative solubility, between two immiscible or partially miscible solvents. The driving force of these extractions is chemical potential which results in the net transfer of compounds from one liquid to another, generally from polar to non-polar medium.[71] A schematic representation of LLE using ionic liquids is given in Figure 3.

Initially, the water layer contains the pollutants and value-added goods. When appropriate IL is added and thoroughly mixed, the system approaches equilibrium and the two solvents split into distinct phases. The solutes will distribute between the phases based on their miscibility and affinity. The solutes' affinity and miscibility will determine how they are distributed among the phases. Several metrics, such as extraction efficiency percentage (EE%), separation factors, distribution ratio (D), and decontamination factor, are used to evaluate how effective the extraction process is.

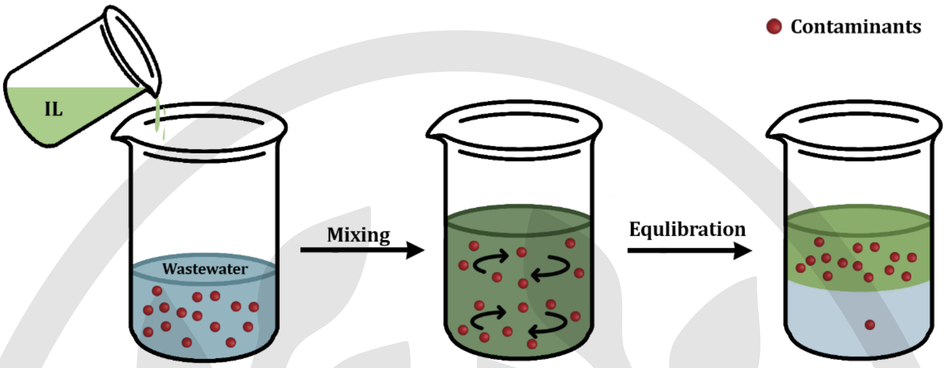

Figure 3 Schematic representation of LLE using ionic liquids

LLE techniques are categorized according to how they are executed and how they work. Classical LLE depends on partitioning solutes between aqueous and organic phases, widely used for purifying compounds and extracting pollutants. Dispersive liquid-liquid extraction (DLLE) involves mixing small amounts of two solvents into a sample, causing tiny droplets to spread throughout the liquid. This increases contact between the solvents and the sample, making extraction faster and more efficient.[72] Temperature-controlled LLE modifies solute distribution by varying the temperature, thereby enhancing selective extraction.[73] Vortex-assisted LLE accelerates phase mixing using mechanical agitation, resulting in rapid and efficient extraction[74]. Aqueous Biphasic Systems (ABS) are eco-friendly versions of LLE that utilize two water-rich phases (e.g., polymers or ionic liquids) for biocompatible, sustainable extractions of biomolecules or pollutants[75]. Microwave-assisted LLE makes use of microwave radiation to heat and intensify phase interactions, achieving fast extraction rates[76]. Ultrasound-assisted LLE improves the process through ultrasonic waves, promoting higher extraction efficiency[77]. Each method offers distinct advantages depending on the target analyte, with every modification focusing on minimizing solvent consumption, improving extraction rates, and enabling greener processes.

4. IL Based LLE for Wastewater Treatment

Conventional methods for treating industrial wastewater have several drawbacks. They often lack specificity, meaning they may not effectively target specific contaminants. These methods can also be time-consuming, require large amounts of chemicals, and sometimes create secondary pollutants as a byproduct. The extraction of various micropollutants, dyes, and heavy metal ions using IL-based LLE has emerged as a highly efficient and environmentally benign technique. This method offers enhanced extraction performance, reduced solvent loss, and potential recyclability, making it an attractive alternative to conventional methods in wastewater treatment applications. In some cases, phase-separation promoters are utilized to segregate the water-IL combination into two immiscible aqueous phases employing hydrophilic ILs. Figure 4 shows a schematic diagram depicting the optimal techniques for IL-based LLE in wastewater treatment.

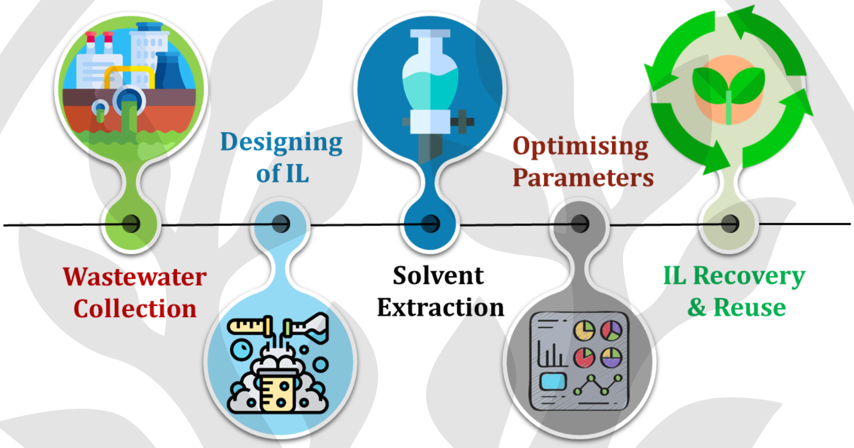

Figure 4 Schematic diagram explaining the IL-based LLE for wastewater treatment

The treatment of wastewater via ionic liquids commences with the acquisition of real wastewater samples or the creation of simulated samples in a laboratory setting. Researchers then develop ILs particularly formulated for the contaminants of concern, using their tunable characteristics to efficiently target pollutants. These pollutants include micropollutants, pharmaceutical residues, personal care product waste, dyes, and heavy metals, which are frequently present in industrial effluent. Subsequently, the most suitable type of LLE is determined, and extensive optimization is conducted to ascertain the optimal extraction conditions. Parameters like temperature, pH, extractant concentration, and extraction duration are optimized to enhance pollutant removal efficiency. A crucial phase entails devising methods to recycle the ILs post-extraction. Solvent recycling is often accomplished by suitable stripping techniques, facilitating numerous extraction cycles. A comprehensive review of the current literature on IL-based LLE techniques in wastewater treatment is carried out, emphasizing recent developments in extraction efficiency, solvent reusability, and overall environmental impacts

4.1 Extractive Removal of Organic Contaminants

Initially, scientists employed IL-based conventional and dispersive liquid-liquid microextraction (DLLME) techniques for the extractive removal of organic pollutants from wastewater, subsequently advancing to more sophisticated liquid-liquid microextraction (LLME) methods utilizing temperature and ultrasound. The predominant research in IL-based water treatment of organic impurities concentrated on the extraction of phenol and phenolic pollutants. Numerous industries have made extensive use of phenols and their derivatives. The main ingredients in personal care products are also phenol derivatives, such as bisphenol-A, naphthol, resorcinol, and catechol.

Khachatryan et al. used an RTIL, 1-Butyl-3-methyl imidazolium hexafluorophosphate, [BMIm][PF_6], to recover phenolic chemicals from industrial wastewater. Specifically, phenols, nitrophenols, and naphthols were the main compounds targeted. LLE was employed in all operations at room temperature, maintaining a 1:3 volume ratio at pH values between 1 and 14. Nitrophenols and naphthols recovered more than 90 %, whereas phenols and polyphenols way lesser amount. The variation in extraction capacity with different ILs was explained by the process's pH dependence.[78] Using a similar collection of ILs, Vidal et al. have also tried to extract phenolic chemicals from aqueous solutions. They achieved this by employing hexafluorophosphates with extended alkyl chains and 1-(n-alkyl)-3-methylimidazolium tetrafluoroborates. Tyrosol, phenol, and p-hydroxy benzoic acid were among the phenolic compounds that were more successfully extracted using tetrafluoroborate-based ILs. An extraction efficiency of about 90 % was observed, and the pH shift found to have no effect on it. Conversely, the effectiveness of ILs based on hexafluorophosphate was comparatively low and was sensitive to pH changes.[79] Egorov et al. investigated the extraction of phenols and aromatic amines using novel quaternary ammonium ILs, comparing their efficiency to that of previously reported imidazolium-based ILs. Ammonium-based RTILs, such as tetrahexylammonium dihexylsulfosuccinate and trioctamethylammonium salicylate, were found to have considerably higher solute distribution ratios than imidazolium-based RTILs.[80] Similarly, Cesari et al. have developed choline bis(trifluoromethylsulfonyl)imide [Ch][NTf_2] as an extractant medium for the extraction of phenolic compounds from aqueous solution.[81]

Emilio et al. investigated the extraction of phenolic compounds from wastewater using aromatic and non-aromatic ILs. They used ILs based on pyrrolidinium and imidazolium with bis(trifluoromethanesulfonyl) imide as the anion to extract phenol, o-cresol, and resorcinol. In addition, they have analyzed the extraction process computationally using COSMO-RS. It was observed that pyrrolidinium-based ILs show improved extraction performance and the efficiency increases in the order for o-cresol>phenol>resorcinol.[82] Sas et al. have established an LLE method utilizing for extracting phenolic compounds using 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl) imide. The phenolic derivatives extracted include o-cresol, resorcinol, 2-chlorophenol, and phenol, from aqueous solutions, with initial concentrations varying from 3 mg L^{-1} to 1000 mg L^{-1}. Furthermore, the extraction of four phenolic compounds from aqueous solutions was evaluated within the identical concentration range. All chemicals, except for resorcinol, were extracted at rates exceeding 90 %, whereas resorcinol was removed at approximately 78 %. Most notably, they successfully regenerated the IL by using NaOH solution.[83] Subsequently, the same group refined their research by developing pyridinium-based ionic liquids including bis(trifluoromethanesulfonyl) imide and bis(trifluorosulfonyl) imide as anions. Upon analyzing the ionic structure of the extracting agent, it was determined that the anion is of paramount importance. The impact of the structure of extracted phenolic contaminants was also examined. Substituted phenols were extracted more efficiently by ionic liquids than by phenol itself. Hydrophobic interactions were identified as essential in the transfer of phenols from the aqueous phase to the ionic liquid-rich phase.[84]

Identifying the presence of active pharmaceutical ingredients (APIs) and their removal from water bodies is imperative. In recent years, ionic liquid-based liquid-liquid extraction (IL-based LLE) has been widely investigated for the same. Seven unique functionalized ILs were designed by Yao et al. to extract fourteen organic contaminants including APIs such as acetaminophen and sulfisomidine from aqueous solutions. In their study, the ionic liquid 1-(6-amino-hexyl)-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, demonstrated significant selectivity and sensitivity in the extraction of molecules with tertiary amine functionality.[85] Hou et al. employed a temperature-regulated liquid-liquid extraction approach to isolate eight distinct tetracycline antibiotics from environmental water samples. The antibiotics were initially transformed into hydrophobic complexes utilizing La(III) as a chelating agent, and these complexes were subsequently extracted employing 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids. Trace concentrations of antibiotics were quantified via ultra-high pressure liquid chromatography.[86] Parrilla et al. investigated imidazolium-based ILs with hexafluorophosphate anion for the extraction of nine distinct medicines, including paracetamol, naproxen, and bisoprolol. Subsequent to extraction, the samples were analyzed utilizing a high-performance liquid chromatograph-quadrupole-linear ion trap mass spectrometer.[87] A recent study by Padinhattath et al. has explored the removal of APIs from wastewater using novel n-benzyl ethanolamine based ILs. Four novel N-benzylethanolamine-based hydrophobic ILs were designed for the extractive removal of top-priority pharmaceutical micropollutants from wastewater samples, with a special focus on diclofenac sodium. The structural optimization of the ILs was performed using DFT studies with the B3LYP method and a 6-311++G(d,p) basis set, using Gaussian 16 suite of programs. The interactions between the ILs and diclofenac medium were explored using the integral equation formalism polarizable continuum model (IEFPCM) of solvation. Experimental studies employed the LLE method, with extraction parameters being optimized to ensure efficient extraction. The reusability of the most efficient IL was also assessed. Computational interaction studies and FT-IR analysis were conducted to determine the primary factors driving the extraction process. The primary driving forces of extraction were determined to be hydrophobicity, hydrogen bonding, van der Waals interactions, and π-π interactions between the IL and the pollutant. Moreover, the study's aim was extended to encompass the extractive removal of additional micropollutant pharmaceuticals, including ciprofloxacin and metronidazole.[88]

The extraction of aromatic and non-aromatic hydrocarbons from aqueous samples is a compelling topic. The hazardous traits of specific hydrocarbons were identified as a concern, and the IL-LLE methods surfaced as the most effective solution to address it. The initial attempts of Liu et al. were of great importance. They successfully illustrated the distribution ratios of specific polycyclic aromatic hydrocarbons (PAHs) in water and ILs. Fifteen specific PAHs have been identified as target compounds, with imidazolium-based ILs containing hexafluorophosphate anion utilized as extractants. log D values were recorded between 3.34 and 4.36, exhibiting a gradual increase with the molar mass of PAH.[89] Fan et al. conducted a noteworthy study on the extraction of aromatic amines from river water, wastewater, and tap water utilizing dispersive LLE. The targeted aromatic amines were 1-naphthylamine, 2-methylaniline, 4-aminobiphenyl and 4-chloroaniline, whereas the IL employed was 1-butyl-3-methylimidazolium hexafluorophosphate. They have optimized extraction parameters including extraction duration, pH of the aqueous solution, and amount of IL. Good sensitivity and repeatability were achieved under optimal conditions.[90] Pena et al. introduced an IL (1-octyl-3-methylimidazolium hexafluorophosphate) based technique for the extraction of 18 unique PAHs from various water samples. The extraction method employed was IL-DLLME. This technique leverages the chemical affinity between the IL and the target analytes, facilitating the extraction and preconcentration of PAHs from the sample. Various parameters influencing EE (%), including ionic liquid type and volume, dispersion solvent type and volume, extraction duration, centrifugation duration, as well as ionic strength were optimized. The EE (%) of the optimized method exceeds that of conventional LLE techniques. The present method proved effective in analyzing PAHs in water samples.[91] Saleem et al. conducted a significant study on the IL-based extraction of various halogenated hydrocarbons (HHCs), including CCl_4, $CHCl_3$, and $CHBr_3$, from wastewater. ILs comprising piperidinium, pyrrolidinium, and ammonium cations, with bis(trifluoromethanesulfonyl) imide as the anion, were utilized for this purpose. The applied extraction method was conventional liquid-liquid microextraction. The ILs were chosen for their capacity to solubilize significant pollutants. Moreover, their hydrophobicity, viscosity, and stability in the presence of superoxide ions would be employed to decompose HHCs. The chosen ILs successfully removed harmful HHCs from the aqueous phase, with extraction efficiencies ranging between 83 % and 100 %. The study demonstrated that ILs with octyltriethyl-ammonium and pyrrolidinium cations, along with bis(trifluoromethylsulfonyl) imide anion, efficiently extract particular HHCs. The influence of various parameters, such as the properties of the components (HBA and HBD), temperature, pH, polarizability, and octanol/water partition coefficient on the EE, was thoroughly investigated.[92]

Research into the extraction of pesticides and insecticides from water bodies is equally crucial. Pesticides and insecticides are frequently employed in agriculture, and most of them have significant toxicity and cause substantial damage to aquatic systems. Many of these are not directly extractable using conventional methods due to their low concentrations. As a result, the usage of IL-based LLME gave the study in this field a new perspective. Lijun et al. investigated the extraction of organophosphorus pesticides from tap, well, rain, and yellow river water samples. The pesticides extracted were parathion, phoxim, phorate, and chlorpyrifos, while the extracting agent was 1-alkyl-3-methylimidazolium hexafluorophosphate ILs. The procedure was persuaded by the development of a cloudy solution, which consisted of tiny droplets of IL dispersed completely into the sample solution using the disperser solvent methanol. The extraction solvent volume, the dispersion solvent volume, extraction time, centrifugation time, the influence of salt addition, extraction temperature, and sample pH were all studied and optimized. Because of its higher extraction efficiency, 1-octyl-3-methylimidazolium hexafluorophosphate was found to be the best among ILs.[93] Liu et al. used a similar approach and the same category of ILs to extract and identify four heterocyclic insecticides, namely fipronil, chlorfenapyr, buprofezin, and hexythiazox, from water samples.[94] Zhang et al investigated the feasibility of extracting benzoylurea insecticides (BUIs) from water samples using 1-alkyl-3-methylimidazolium hexafluorophosphate ILs. The team experimented with a rapid dispersive LLE strategy, followed by magnetic retrieval of the ILs utilizing unmodified magnetic nanoparticles (MNPs). Fine IL droplets produced in aqueous samples functioned as an extractant for the extraction of BUIs. The suggested method's repeatability and reproducibility were found to be satisfactory, and it was successfully employed for the rapid determination of BUIs in real water samples.[95]

Several additional organic pollutants were extracted and identified using various classes of ILs. Zhao et al. attempted to extract bactericides from natural water samples using DLLME. Triclosan and triclocarban were the pollutants chosen. They combined hexafluorophosphate and tetrafluoroborate anions with imidazolium-based cations to form ILs. The extraction experiment was highly efficient, with a profound recovery rate.[96] Later, the same group investigated the extraction of hexabromocyclododecane (HBCD) diastereomers in environmental water samples using the same set of ILs. They performed experiments on lake water, river water, rainfall, and snow water to determine the presence of α, β, γ - HBCD. The extraction efficiency using 1-octyl-3-methylimidazolium hexafluorophosphate was found to be higher than that of the other ILs [97]. Bhosale et al. were able to extract energetic materials from industrial effluents using IL-based LLE. TNT (2, 4, 6-trinitrotoluene), RDX (hexahydro-1,3,5trinitro-1,3,5-triazine), and tetryl(2, 4, 6-trinitro-phenyl methylnitramine) were the materials targeted. For this purpose, five different imidazolium-based ILs containing $[NTf_2]^-$ and $[PF_6]^-$ anions were used. They observed that extraction efficiency improves with a change in anionic moiety from $[NTf_2]^-$ to $[PF_6]^-$, pH drop, and an increase in phase volume ratio. After numerous washes with diethyl ether, ILs were regenerated and reused for further cycles.[98]

As previously mentioned, various advanced modifications of LLE have been developed, including in situ dispersive liquid-liquid microextraction, temperature-controlled LLE, ultrasound-assisted LLE, and so on. These innovative techniques have recently gained attention among researchers for their effectiveness in removing organic pollutants from wastewater samples. Yao et al. conducted a noteworthy demonstration of in situ liquid-liquid microextraction, where they designed an experiment to extract aromatic compounds, including biphenyl, 3-tert-butyl phenol, and polyaromatic hydrocarbons, from natural water samples. In situ metathesis was employed to develop a water-immiscible imidazolium-based IL that preconcentrated aromatic compounds in water samples. They observed that, in comparison to conventional IL-based DLLME, the combined extraction and metathesis process in the IL-based extraction phase significantly reduced extraction time while providing higher enrichment factors.[99] In the following years, Darias et al.[100] and Zhong et al.[101] used similar methods to recover a range of organic pollutants from natural water samples. The method of temperature-controlled LLE was effectively utilized by Zhou et al., where they focused on the detection of organophosphorus pesticides in environmental samples using IL-based temperature-controlled LLE. The extraction solvent was 1-hexyl-3-methylimidazolium hexafluorophosphate, and the factors influencing the EE (%), like IL volume, pH of solutions, extraction and centrifugation duration, temperature, and salt effect, were optimized.[102] Later, the team used the same ionic liquid to extract phenols from water samples using temperature-controlled IL-based DLLME.[103]

Recently, IL-based ultrasonic-assisted dispersive liquid-liquid microextraction techniques have emerged as a promising alternative for the separation of organic contaminants from water samples. In this technique, sonication will thoroughly distribute IL into the aqueous sample solution. The analytes would be transferred into tiny IL droplets, resulting in a high enrichment in performance. Zhang et al. employed a similar approach to extract benzophenone-type UV filters from water samples, utilizing 1-alkyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ILs. They have successfully isolated four types of UV filters, identifying 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate as the optimal IL due to its lower viscosity.[104] Wang et al. performed a study in this field, combining ultrasound-assisted technique with in situ solvent formation microextraction and solidification of sedimentary ILs. This technique was used in conjunction with HPLC to identify various triazole pesticides in water and juice samples. In this technique, the tributyloctylphosphonium hexaflurophosphate $[P_{4448}][PF_6]$ is the microextraction solvent, which was synthesized from tributyloctylphosphonium bromide $[P_{4448}]Br$ and potassium hexaflurophosphate. Various parameters influencing the EE (%) like the amount of $[P_{4448}]Br$, the molar ratio of [P4448]Br to KPF_6, salt addition, centrifugation rate and time, and sample pH were all investigated. The recovery rates for these four triazole insecticides range from 85 to 91 %.[105] Zeeb et al. applied a similar method to detect trace amounts of five PAHs in environmental water samples. They added 1-butyl-3-methylimidazolium tetrafluoroborate (hydrophilic), to the sample solution along with an ion-pairing agent ($NaPF_6$), which generated a hydrophobic IL, 1-butyl-3-methylimidazolium hexafluorophosphate. The PAHs were extracted into the IL phase, with ultrasonic radiation dispersing the microextraction solvent throughout the sample. By combining the advantages of both techniques, this innovative method demonstrated high efficiency and potential for broader applications.[106]

4.2 Extractive Removal of Dyes

The extraction and separation of dyes from aqueous solutions utilizing ILs have become widely popular since the early 21st century. Vijayaraghavan et al. put forward a study on the extraction and recovery of acid blue and acid red dyes - azo dyes utilized in the leather industry using N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)amide. A similar experiment was repeated using an actual tanning effluent dye sample. The ILs were back-extracted from the ionic liquid-dye combination utilizing a 1:1 isopropyl alcohol-water solution and subsequently reused.[107] Li et al. have put forward a method for isolating acidic dyes (acid yellow RN and Brilliant Blue RAW) and reactive dyes (Reactive Black KN-G2RC, Reactive Yellow M-5R) using 1-butyl-3-methylimidazolium hexafluorophosphate. The IL effectively extracted acidic dyes.[108] However, the extraction of reactive dyes was improved by the incorporation of dicyclohexyl-18-crown-6. The pH significantly affected the partition coefficient values in the case of acidic and reactive dyes, but it did not impact the extraction of the weak acid dye.[108] Moreover, Othman et al. illustrated the IL-based extraction of remazol brilliant orange 3R from textile effluent utilizing tetrabutyl ammonium bromide. Multiple parameters influencing extraction efficiency were analyzed. The research indicated that extraction utilizing dichloromethane and chloroform as diluents was more efficacious than using toluene, kerosene, n-dodecane, and xylene. The influence of pH on the extraction ratio was determined to be minimal. Following the extraction, a 1:1 ratio of salicylic acid to NaOH was employed for the stripping process.[109]

Zhang et al. conducted significant work utilizing temperature-controlled dispersive liquid-liquid microextraction to examine the extraction of malachite green and crystal violet with 1-octyl-3-methylimidazolium hexafluorophosphate. The examination into the effects of NaCl salinity demonstrated a direct proportionality between the extraction coefficient and NaCl concentration up to 20 %, followed by a subsequent decline afterwards.[110] In the subsequent year, Chen et al. conducted a study on the extraction of methyl orange and methylene blue dyes with quaternary ammonium-based ILs. The influence of the phase ratio on EE (%) was determined to be minimal. The endothermic nature of the procedure resulted in an increased distribution coefficient for the extraction of methyl orange with rising temperature. Conversely, the extraction of methylene blue was an exothermic process, and the distribution coefficient diminished with increasing temperature. The research on the influence of pH on the extraction coefficient determined that pH does not significantly affect the extraction of methylene blue, but it does have a pronounced effect on the extraction of methyl orange. Methylene blue was subsequently extracted using 0.1 molar HCl and recovered from IL with chloroform.[111]

Talbi et al. conducted another intriguing investigation on the removal of cationic dyes from aqueous solutions utilizing ILs and non-ionic surfactant-IL systems, with the results subjected to empirical fitting analysis. The study utilized 1-butyl-3-methylimidazolium hexafluorophosphate for the extraction of methylene blue dye. The results indicate that extraction efficiency decreased with increasing temperature and enhanced with the addition of the non-ionic surfactant, Triton X-114. The dye's ability to easily dissolve into micelles at high pH levels is associated with its improved extraction efficiency in alkaline settings. The addition of K_2CO_3 salt negatively affected extraction efficiency.[112] Fan et al. initiated a study on the influence of imidazolium-derived ILs on the extraction of azo dyes. The distribution ratios (D) were found to be constant with increasing phase ratio after 40 minutes of extraction at pH 1.25 and 10.21, whereas a little decrease was detected at pH 4.32. Thus, the pH of the aqueous phase was recognized as a crucial factor influencing the distribution ratio. An examination of the influence of chemical structure on the D value was conducted. The variation in the hydration capacity of the additional salts resulted in considerable changes to the D values.[113] Ana et al. investigated IL-based ABS for the extraction of chloranilic acid, Sudan III, and indigo blue dyes from water. Phosphonium-based ABS exhibited superior EE compared to imidazolium-based counterparts. Utilizing the appropriate ionic liquid and salt, they accomplished superior dye elimination in a single step and effectively recycled the ionic liquid via filtration.[114] Beatriz et al. employed a liquid-liquid extraction procedure utilizing trihexyltetradecylphosphonium decanoate to remove three textile dyes from water samples. This IL showed exceptional extraction capability while necessitating reduced quantities relative to comparable experiments. The IL showed significant efficacy in removing dyes from contaminated water; nonetheless, the work raises questions about the toxicity of phosphonium ILs and their appropriateness for wastewater treatment.[115]

A recent study by Padinhattath et al. investigated the use of pseudoprotic ionic liquids (PPILs) for the efficient removal of various dye classes from both simulated and real industrial wastewater samples. The study focused on the effective extraction of cationic dyes, including crystal violet, malachite green, methylene blue, and rhodamine, from neutral aqueous solutions using non-stoichiometric PPILs, comprising tri-octyl amine and octanoic acid as the extraction medium. LLE was employed at pH 7 ± 0.1 and 303 ± 1 K, with parameters such as diluent choice, extractant concentration, equilibration time, interference effects, stripping agents, and stripping phase ratios systematically optimized. The dyes were effectively back-extracted from the PPIL-rich phase using dilute citric acid as the stripping agent, allowing for solvent regeneration and reuse in successive extraction cycles. Through pH, conductivity, and titrimetric analyses, proton exchange was identified as the extraction mechanism. The method achieved quantitative extraction and stripping (>99 %) of all cationic dyes, and its circular process design demonstrates significant potential for real-world wastewater treatment applications.[116]

4.3 Extractive Removal of Heavy Metal Ions

The initial experiment utilizing ILs for the LLE of metal ions from wastewater took place in the late 1990s. Since then, the methodology for metal ion extraction from wastewater utilizing ILs has evolved in three specific pathways: (i) ILs functioning as both extracting agents and organic phases, (ii) ILs working as diluents to dissolve extractants, and (iii) functionalized or task-specific ILs used for targeted extraction processes.

The pioneer works on alkali and alkaline earth metal extraction appeared in 1999, which laid the foundation of volatile organic solvents (VOSs) replacement with ILs, which were carried out by Dai and co-workers. They have reported extraction of Sr^{2+} with a combination of dicyclohexane-18-crown-ether-6 (DCH18C6) and a series of imidazolium-based ILs. [117] Sr is a fission product, and until now, there has been no efficient extraction method available for its removal from radioactive waste sites, particularly for samples with a distribution ratio greater than 1. They analyzed the distribution ratio of metal ions with and without the presence of crown ether and found that even without the presence of crown ether, some of the ILs were able to provide a distribution ratio of around 0.9. IL combined with crown ether provided a large hike in the distribution ratio, which was way beyond the conventional results. The selection of IL anions was also very much relevant with $[NTf_2]^-$ and $[PF_6]^-$ based ionic liquids showed dashing efficiency in the extraction process. The efficiency of the ILs was also compared with conventional VOSs such as chloroform and toluene as well.[117] Later, it was found that the EE of the same process was significantly improved by the presence of a second ligand, tri-*n*-butyl phosphate (TBP), because of the formation of a synergistic adduct. These works have become the stepping stone for a slower transition towards the IL era in metal extraction chemistry.[118]

Following this, Luo and co-workers have synthesized sixteen protic amide-based ILs derived from N,N-dimethylformamide and other amide derivatives with bis(trifluoromethanesulfonyl)imide as conjugated anions.[119] These ILs were tested as extraction solvents using DCH18C6 an extractant for the separation of Sr^{2+} and Cs^{+} ions from aqueous solutions. Excellent extraction efficiencies were found for a number of these ILs in comparison with other imidazolium and ammonium-based ILs. In general, it was observed that without the addition of ILs to these compounds, they did not extract M^{2+} cations. The effects of solution acidities, anions, and alkyl chain lengths of cations of ILs in the extraction efficiency were also thoroughly investigated. Similar works were carried out by Turanov et.al, Toncheva et.al and Dukov et.al which affirm the role of ILs as active reagents in synergic extraction systems.[120–122] One of the major factors that influence the alkali and alkaline earth cations from an acidic aqueous phase into the IL phase by a crown ether was the hydrophobicity of both the IL anion and cation. The universality of this discovery was verified by carrying out extraction tests with different families of ILs.[123] The extraction behaviour of Sr^{2+} ion from high-level liquid waste was examined by Takahashi et.al using $[C_1C_nim][Tf_2N]$ (n = 2,4,6) and dichloromethane as diluents.[124]

In 2017, another group developed task-specific ILs for Li-ion capture. They synthesized tetrabutylphosphonium bis(2,4,4-trimethylpentyl)phosphinate ($[P_{4444}]$[BTMPP]) along with two non-fluorinated compounds-tetrabutylammonium/tetraoctylammonium bis(2-ethylhexyl)phosphate ($[N_{4444}]$[DEHP] and $[N_{8888}]$[DEHP]) and evaluated their performance in extracting Li^{+} ions in comparison to molecular ligand analogues. The synthesized ionic compounds demonstrated superior extraction efficiency compared to their molecular counterparts due to an intrinsic synergistic effect. Notably, the $[N_{4444}]$[DEHP] compound exhibited the highest extraction efficiency.[125,126]

Although limited, the extraction of p-block metals from water using ILs is noteworthy. Post-transition p-block metals including Al, Ga, In, Sn and Pb exhibit a wide range of physical and chemical properties. Clio et al. developed a new methodology for the purification of Indium using cyphos IL 101 and aliquat 336. In^{3+} ions showed a strong affinity for the IL phase, resulting in extraction percentages exceeding 95 % across the HCl concentration range of 0.5 to 12 M. An extraction mechanism was proposed based on the relationship between the viscosity of the IL phase and the loading with In^{3+} ions. Indium can be easily recovered as $In(OH)_3$ through precipitation stripping using NaOH solution. This new IL-based extraction avoids the use of volatile organic solvents.[127] Eguchi et.al utilised 1-alkyl-3-

methylimidazolium bis(trifluromethylsulfonyl) Imide to study ionic liquid-chelate based extraction of group 13 metals. 8-quinolinol was the chelate used and they have varied the alkyl chain length to study the effect. Though extraction pattern was similar, the efficiency of extraction was maximum with the most hydrophobic IL amongst.[128] Subsequently, Luo et al. investigated the simultaneous leaching and extraction of Indium from waste LCDs using the functionalized IL, betainium bis(trifluoromethylsulfonyl)imide. In the present work, the IL phase was transferred into an In-rich solution with the aid of oxalic acid, allowing the IL to be recovered. The regenerated IL maintained stable properties, making it suitable for reuse.[129] Recently many other research groups are focusing on IL-based methodologies to extract p-block elements from acidic solutions as well as from aqueous media.[130,131]

IL-based extraction studies of metals predominantly focus on d-block elements and heavy metal ions due to their environmental and industrial significance. The mechanisms underlying these extraction processes are typically driven by either preferential coordination between the functional groups in the ionic liquid and the metal ions, which is often governed by the HSAB principle. Ion exchange is also cited as one of the key driving forces in various studies related to the particular process. In the former, softer acids like transition metals tend to coordinate with softer bases present in the IL, while harder acids prefer coordination with harder bases. In ion exchange mechanisms, the metal ions are replaced by ions from the ionic liquid, facilitating the extraction process.

Papaiconomou et al. carried out a study to extract metal ions using task-specific ILs. The targeted molecules were metal ions like Cu, Hg, Ag and Pd. They have found that Hg and Cu extraction is more efficient with the use of ILs having disulfide functional groups whereas, Ag and Pd can be efficiently extracted using ILs with nitrile functional groups. They have also figured out that the distribution coefficients of metal ions were higher in IL with pyridinium cations and trifluoromethyl sulfonate than imidazolium cation and bis[trifluoromethyl]sulfonyl imide.[132] Kogelnig et al. have performed a thorough investigation on the extraction of Cd^{2+}. Three hydrophobic ionic liquids have been produced from tricaprylmethylammonium chloride through reaction with suitable Brønsted acids. Among these, tricaprylmethyl ammonium thiosalicylate exhibited the highest extraction efficiency for Cd^{2+} from both ultrapure and natural river water.[133] Egorov et al. investigated trioctylmethylammonium salicylate as an extractant for the extraction of transition metal ions Fe^{3+}, Cu^{2+}, Ni^{2+}, and Mn^{2+}. The extraction efficiencies of $Fe^{3+}$and Cu^{2+} were 99 % and 89 % respectively. In contrast, $Ni^{2+}$and Mn^{2+} exhibited lower extraction yields.[134] Subsequently, Rajendran et al. recovered metals, including

Ni, Zn, Pb, Fe, and Cu, from tannery effluents via task-specific ammonium-based ionic liquids.[135] The scientific investigation of extraction of Ag^+ and Pb^{2+} using imidazolium-based ILs by Domanska et al. is worth mentioning, where dithizone [DTZ] was used as the metal chelator as well as organic extractant. The method adopted was classical liquid-liquid extraction of metal-DTZ complex and that was a pH-dependent process. 1 butyl-3-ethylimidazoliumbis [trifluoromethyl sulphonyl] imide $[BEIM][NTf_2]^-$ showed an efficiency of 99.3 %, which was way greater than conventional organic solvents like chloroform. Nonetheless, re-extraction was also carried out which indicated that ILs can be recycled and reused which ensures sustainability.[136]

Fetouhi et al. carried out a study on the extraction of heavy metals 1-butyl-3-methylimidazolium hexafluorophosphate with extracting ligand N-salicylideneaniline. Metals like Cu^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} were extracted. The stoichiometry of these metal complexes with ligand was found to be 1:2. Cu^{2+} extraction was found to be independent of pH, while others depend on changes in pH.[137] Thasneema et al. recently conducted the extraction of hazardous heavy metal ions from their respective standard solutions. The study utilized metal ions As^{3+}, Cr^{3+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and Hg^{2+} together with ionic liquids containing phosphonium cations and hydrophobic anions. UV-visible spectroscopy and ICP-MS analysis were employed to assess the extraction efficiency. The extraction performance was observed to be elevated, and this group of ionic liquids was also determined to be successful in HMI extraction.[138]

Pseudoprotic ionic liquids have lately been investigated for their efficacy in removing heavy metal ions. Matsumoto et al. broadened the utilization of PPILs comprising trioctylamine and decanoic acid for the extraction of rare earth elements.[139] Janssen et al. devised a technique for the extraction of heavy metal ions, including Ni^{2+}, Cu^{2+}, and Co^{2+}, from saline aqueous solution. The PPILs employed in this investigation were trihexylammonium octanoate, trioctylammonium benzoate, and trioctylammonium salicylate at equimolar doses. Their investigation revealed that these ILs facilitate the extraction of heavy metal ions from concentrated sodium chloride brines while minimizing the co-extraction of sodium ions.[140] ILs with carboxylate anions have recently been explored for the removal of HMIs.[141] The study was initially restricted to ILs with aliphatic protic carboxylate anions, which was later extended to both protic and pseudoprotic ILs with cyclic carboxylate anions.[142] These ionic liquids provide the benefit of adjustable coordination centres, allowing for customization that is tailored to the specific properties of the targeted heavy metal ions. Padinhattath et al. recently reported a series of hydrophobic ILs with varying coordinating atoms in their anions for the extractive removal of toxic heavy metal ions from wastewater. The reported ILs were able to extract the metal ions even from their mixtures, mimicking real industrial conditions.[143] These findings further validate the potential of tailored hydrophobic ILs as efficient and selective extractants for heavy metal ion removal in complex wastewater matrices.

5. Future prospects of ILs for wastewater treatment

The futuristic aspects of IL-based techniques for industrial wastewater treatment show significant potential, providing inventive and benign approaches. Even though most of the research studies based on IL-LLE currently remain confined to the laboratory scale, the scope for its application in practical scenarios is extensive. Nonetheless, the efforts to scale up these techniques present a significant challenge. It is crucial to collaborate with industries and sewage treatment to facilitate practical applicability. Grasping the fundamental mechanisms of IL-LLE is also essential for this scale-up. Although computational tools such as DFT and COSMO-RS have advanced in predicting these mechanisms, additional investigation is necessary. Developing more effective recyclization or stripping processes is also critical for the scalability of IL-LLE. Apart from LLE, IL-based materials are also demonstrating notable importance in the realm of wastewater treatment. Integration of these methodologies together can yield even more effective solutions. Exploring the potential of computational tools further in designing methodologies can enhance our comprehension and refine extraction methodologies, thereby facilitating the broader implementation of IL-based technologies in sustainable wastewater management.

6. Conclusions and Outlooks

This review examines the growing interest in ionic liquid research since its beginning, encircling its historical background, classification, recent breakthroughs, and applications in wastewater treatment. The analysis emphasizes the extraction of major contaminants, including organic pollutants, dye residues and metal ions, from both simulated and actual wastewater samples. The analysis indicates that IL-based liquid-liquid extraction has emerged as the primary methodology for contaminant extraction and removal, owing to its higher efficiency and effectiveness compared to alternative methods. The simplicity, cost-effectiveness, and ease of implementation render LLE an appealing alternative to conventional systems in both academic and industrial domains.

Research studies on the extraction of organic contaminants and micropollutants via IL-LLE have largely concentrated on phenolic pollutants, featuring residues from personal care products and other common laboratory chemicals. The removal of active pharmaceutical ingredients through IL-LLE has also been thoroughly explored. In the initial stages of research, ILs with fluorinated anions were utilized to impart hydrophobicity; however, this strategy gradually transitioned to the incorporation of ILs with long-chain cations. The analysis of dye extraction using ILs has featured both cationic and anionic dyes extensively. Previously, protic and aprotic ILs were widely explored for this aim, but more recent investigations have featured the potential of target-specific pseudoprotic ILs. The extractive removal of heavy metal ions from wastewater utilizing ILs has advanced through three primary methods: ILs functioning as both extracting agents and organic phases, ILs working as diluents, and functionalized or task-specific ILs enabling targeted extractions. The mechanism aspects of HMI extraction were found to be either by neutral coordination or by ion exchange processes. The extraction limit is contingent upon the specific type of pollutant. With regards to APIs and personal care product residues, natural contamination levels and corresponding extractable limits generally range from micrograms (µg) to nanograms (ng). Whereas, for pollutants like dyes and HMIs, extractable concentrations often lie within the parts per million (ppm) range. A significant obstacle in contemporary IL-based wastewater treatment is the stripping stage, which has often been overlooked in prior research. However, recent studies have increasingly focused on the final stripping and recycling of ILs, addressing reusability issues and improving overall process quality.

Likewise, the selection of ILs was arbitrary, and the mechanisms underlying extraction and stripping in IL-based systems were not comprehensively investigated in prior research. Recent research has elucidated these processes, frequently corroborated by theoretical studies like COSMO-RS and DFT analysis. The research demonstrates that the primary factors influencing the extraction of organic pollutants include hydrophobicity, hydrogen bonding, van der Waals interactions, and π-π interactions between ILs and the pollutants. In the context of dyes, these parameters similarly influence extraction, with ion exchange or proton exchange also identified as key driving forces. The preferential coordination of metal ions with appropriate functional groups in the ionic liquid cation or anion is fundamentally governed by the HSAB principle. The ion exchange mechanism is primarily observed in the extraction of metal ions. These sophisticated methodologies have facilitated a more profound comprehension and precise interpretation of the extraction and stripping mechanisms, enhancing the general effectiveness of IL-based extraction strategies.

The prospective utilization of IL-based LLE for wastewater treatment might be considerably expanded, creating new opportunities across diverse industrial sectors. Industries can efficiently address complicated contamination issues and reduce environmental impact by adopting advanced IL formulations. This may result in enhanced adherence to environmental standards and foster a cleaner, more sustainable future.

Declaration of generative AI in scientific writing

During the preparation of this research work, ChatGPT was used to improve the readability and language of the manuscript. After using this tool/service, the authors reviewed and edited the content as required and took full responsibility for the publication.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Sachind Prabha Padinhattath: Conceptualization, Data curation, Investigation, Methodology, Formal analysis, Validation, Writing – original draft.

M. Shaibuna: Conceptualization, Data curation, Formal analysis, Methodology, Validation, Writing – original draft.

Ramesh L. Gardas: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Author information

Corresponding Author

*Phone: +91 44 2257 4248. Fax: +91 44 2257 4202. E-mail: gardas@iitm.ac.in ; Web: https://iitm.irins.org/profile/48355

ORCID

Sachind Prabha Padinhattath: 0000-0003-1364-0237

M. Shaibuna : 0009-0002-1622-6031

Ramesh L. Gardas: 0000-0002-6185-5825

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Biosketches:

	**Prof. Ramesh Laxminarayan Gardas**' research group focusses on 'Chemical Thermodynamics' and 'Phase Equilibria' of industrially important solvents and their mixtures. His research group, which is unique in the country, focuses on both 'Science' and 'Technology' part of the contemporary field – "Ionic Liquids/ Deep Eutectic Solvents as an alternative to Volatile Organic Solvents" and significantly contributing in connecting them. His research group strives to design the task-specific ionic liquids and to provide an important insight into physical chemistry to regulate their properties for varied technological applications such as phase change materials, CO_2 capturing, electrolytes in solar cell and supercapacitors, desulfurization of fuels, and also the extraction of metal ions, biomolecules and value-added products. Dr. Gardas has more than 24 years of research and 14 years of teaching experience. So far, he has co-authored more than 240 research publications which received more than 9775 citations with h-index = 51 and i10-index = 166.
	**Dr. Sachind Prabha Padinhattath**, who hails from Kannur district, Kerala, India, completed his B.Sc. in Chemistry from the University of Kannur in 2015 and his M.Sc. in Chemistry from the National Institute of Technology, Tiruchirappalli in 2017. He then pursued his PhD in Chemistry from the Indian Institute of Technology Madras under the supervision of Prof. Ramesh L. Gardas, graduating in July 2024. His main research interests are centered on developing hydrophobic ionic liquid and deep eutectic solvent-based extraction systems for the efficient removal of contaminants from both simulated and industrial wastewater samples. Currently, Dr. Sachind is working as a post-doctoral research associate in the Department of Chemistry, at IIT Madras.
	**Dr. Shaibuna M**, from Malappuram district, Kerala, India, completed her B.Sc. in Chemistry from the University of Calicut in 2012 and her M.Sc. from Mahatma Gandhi University, Kottayam, in 2014. She earned her Ph.D. at Cochin University of Science and Technology, where she investigated the catalytic applications of deep eutectic solvents (DES) to enhance organic reactions. Dr. Shaibuna is currently a postdoctoral researcher in the Department of Chemistry at the Indian Institute of Technology Madras. Her research focuses on developing hydrophobic ionic liquid and deep eutectic solvent-based extraction systems to efficiently remove contaminants from simulated and industrial wastewater. By leveraging these innovative materials, her work aims to provide sustainable and efficient alternatives to conventional solvents, promoting greener and more effective wastewater treatment solutions.

Graphical Abstract: