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# Ionic Liquids in Agriculture: From Green Extraction to Sustainable Pesticide Development

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Agriculture, pivotal for sustaining the global population, faces challenges in achieving efficiency, economic viability, and environmental friendliness. Nano-modified stimulants offer promise for sustainable agricultural development, crucial for addressing food security and quality. Ionic Liquids (ILs), known as "designer solvents" with unique physicochemical properties, have gained attention across diverse industries, including agriculture. The evolution of IL technology, from customizable physical properties to bioactive ILs, opens avenues for their application in agriculture, spanning extraction of natural products, pesticide isolation, ionization of active ingredients, and controlled pesticide delivery. ILs contribute to sustainable analyte extraction in modern science, offering eco-friendly alternatives to traditional solvents. In the microextraction of pesticides, ILs feature prominently in techniques like Dispersive Liquid-Liquid Microextraction (DLLME) and Single-Drop Microextraction (SDME), demonstrating advantages such as rapid extraction and high recoveries. In modern sample preparation techniques, ILs integrated into Solid-Phase Extraction (SPE) enhance speed and environmental compatibility. IL-modified materials find application in various microextraction settings, showcasing improved efficiency and environmental compatibility. Pesticides developed using ILs exhibit diverse applications, from herbicidal ILs with dual-ion systems to ILs acting as food repellents, plant growth regulators, and microbial control agents. Furthermore, ILs show promise in pesticide delivery and controlled release, advancing pesticide development for sustainable agriculture. The biodegradability and toxicity of ILs are critical aspects, necessitating a comprehensive understanding. The toxicity of bioactive ILs is influenced by factors such as cation structure and anion nature. Imidazolium cations' biodegradability has been explored, providing insights into potential environmental impacts. Addressing gaps in toxicological research, particularly regarding combined toxicity in agrochemical products, remains a challenge. While certain ILs show limited toxicity in agricultural soils, further studies on IL transport and degradation dynamics are essential. In summary, the multifaceted applications of ILs in agriculture, spanning extraction, microextraction, pesticide development, and environmental considerations, present a dynamic landscape for future research and advancements in sustainable agricultural practices.

**Keywords**: Ionic Liquids, Toxicity of Bioactive, Microextraction of Pesticides, Microbial Control Agents, Imidazolium Cations.

**Abbreviations:**

Ionic Liquids (ILs)
Single-Drop Microextraction (SDME)
Liquid-Liquid Microextraction (DLLME)
Solid-Phase Extraction (SPE)
Liquid-phase microextraction (LPME)

Hollow Fiber-Protected Liquid-Phase Microextraction (HF-LPME)
Herbicidal ILs (HILs)

**Introduction:**

Agriculture has historically stood as the most significant industry, providing essential resources to the feed and food sectors. Given the increasing global population and limited natural resources, the growth of agriculture must be efficient, economically viable, and environmentally friendly. The achievement of numerous objectives in the coming years hinges on this transformation [1]. A major challenge lies in ensuring global food security, with an anticipated rise in global food consumption from 59% to 98% by 2050. The use of nano-modified stimulants in farming has the potential to expedite ongoing efforts for sustainable agricultural development, addressing various components of food security, including soil improvement and food quality [2]. To eradicate hunger and poverty, fostering agricultural growth, the cornerstone of sustainable development is essential. However, agricultural expansion remains inefficient in many rural regions where the majority of the global population resides. In recent times, the application of nanotechnology to agriculture has gained attention, leading to intensive research at different levels. Various well-characterized bulk materials have exhibited intriguing characteristics when investigated at the nanoscale [3].

Nanobiotechnology, an environmentally friendly nanomaterial synthesis technique, holds promise for numerous applications in sustainable agriculture. This innovative technology has found utility in engineering, food technology, medical sciences, and biotechnology over the past few decades, transforming the biosystems of many plants and providing new insights and tools. Green nanomaterial synthesis, an economically viable and sustainable method, has gained prominence for its environmental friendliness and high stability, while chemically synthesized nanomaterials are now considered toxic. Studies indicate that plants and microorganisms can deliver nanoparticles, making Nanotechnological applications a secure method for sustainable agricultural development. The utilization of renewable resources in manufacturing these items is advantageous, as these procedures have no negative environmental effects. Noteworthy achievements in green nanotechnology have rendered nanomaterials ecologically sustainable [4].

Pesticides, which are intentional releases of toxic or harmful substances into the environment to control pests, play a crucial role in enhancing agricultural productivity by eliminating weeds, molds, insects, rodents, and other pests. Herbicides, insecticides, fungicides, acaricides, nematicides, and rodenticides are among the various compounds utilized for this purpose. The escalating global population and the growing food demand have led to increased pesticide usage throughout the agricultural cycle, from planting to shipping and storage of farm produce. While pesticides contribute significantly to pest control and increased agricultural yield, their widespread use has resulted in environmental pollution and the presence of residues in food. Improper management, overuse, and unintentional release into the environment contribute to this issue [5]. Consequently, chemical residues accumulate in food and the environment, leading to severe health issues in humans and animals. Adverse effects include acute neurological toxicity, impairment of neurological development, potential dysfunction of immunological, reproductive, and endocrine systems, malignancies, chronic renal diseases, and other disorders linked to pesticide exposure. Given these risks, the detection of pesticide residues in food and environmental samples is crucial for remedial actions by relevant authorities [6].

The development of analytical procedures to determine pesticide residues is essential, but the significance of sample preparation cannot be overstated, particularly when dealing with complex matrices like food and environmental samples [7]. Despite technological advancements in analytical instruments, sample preparation remains a vital step as most instruments cannot directly analyze compounds in their native matrices. The need for extraction or isolation of analyses from potential interferences in matrices, along with preconcentration for analysis, underscores the importance of sample preparation. In recent times, there has been a notable shift towards ecologically friendly sample preparation methods for pesticides in food and environmental samples. Many of these methods rely on solvent extraction techniques, with microextraction, specifically Liquid-Phase Microextraction (LPME) and solid-phase microextraction (SPME), being associated with environmental friendliness [8].

ILs (ionic liquids) have emerged as promising solvents for extracting pesticides due to their unique features that contribute to significant improvements in extraction performance. In LPME, ILs have been utilized in various modes such as SDME, Hollow Fiber-Protected Liquid-Phase Microextraction (HF-LPME), and DLLME. SPME, which involves using a surface coating as a medium, has also leveraged ILs as coatings for extraction. ILs, considered advanced solvents, offer distinct advantages in terms of selectivity, sensitivity, repeatability, and precision, making them intriguing alternatives to conventional organic solvents for extraction purposes. The tailoring of IL characteristics to extract specific analyses of interest enhances their overall effectiveness in extraction procedures. While there is a wealth of research on the use of ILs in DLLME, there is a growing focus on their application in the extraction of pesticides, with ongoing exploration of their capabilities and potential benefits in this context [9].

In contemporary agriculture, the indispensable role of pesticides in balancing yield protection and economic viability cannot be overstated, particularly for cost-sensitive crops. According to data released by the FAO, global pesticide usage surged to 2.7 million tonnes in 2020, with the United States alone accounting for 15% of this usage, underscoring the pivotal role of pesticides in sustaining the food industry. While pesticides are vital for averting crop production declines, their overuse poses significant threats to environmental ecology, leading to issues related to residue, resistance, and runoff [10]. Conventional methods of pesticide application contribute to uncontrolled releases, low precision in targeting, and substantial losses through volatilization, leaching, and runoff, exacerbating the environmental impact. Furthermore, the use of auxiliaries and traditional organic solvents in the production of pesticide raw materials further compounds the ecological challenges. Consequently, it is imperative to explore novel alternative solvents that offer improved environmental sustainability and efficacy [11].

Ionic liquids represent a class of liquid ionic salts characterized by melting points below 100 °C, and some can even remain in liquid form near room temperature, known as room temperature ILs. These substances are hailed as an environmentally friendly alternative to traditional organic solvents, primarily due to their lower toxicity levels. Common anions found in ILs include inorganic anions (halide, tetrafluoroborate, hexafluorophosphate, bistrifluoromethylsulfonylimides, etc.) and organic anions (acetate, amino acid, etc.). Meanwhile, prevalent cations comprise imidazolium, ammonium, pyridinium, phosphonium, or sulfonium [12]. The distinctive feature of ILs lies in the diverse combinations of anions and cations, coupled with the tenability of functional groups. This unique characteristic allows for a wide array of properties that can be customized and tailored for specific applications, earning them the moniker "designer solvents." Moreover, these solvents boast several advantageous physicochemical properties, including low vapor pressure, exceptional solubility in both organic and inorganic chemicals, high thermal stability, and a benign environmental footprint [13].

With the growing prevalence of green chemistry over the past decades, ILs have garnered attention for their exceptional properties in a multitude of fields, including pharmaceuticals, materials science, electrochemistry, industrial applications, and the food industry. Currently, the development of IL technology has undergone three major revolutions. The first generation encompasses ILs with customizable physical properties. The second generation of ILs primarily focuses on improving the chemical properties and functionalities of the first generation of ILs. The third generation primarily focuses on the development and utilization of bioactive ILs, with a particular emphasis on reducing their toxicity levels [14]. As research into the bioactivity of ILs has intensified, their potential applications in agriculture have also garnered significant interest. Presently, ILs find extensive use in agriculture and can be broadly classified into four categories based on their application scopes: 1) Extraction of natural products, 2) Isolation and extraction of pesticides, 3) Ionization of pesticide active ingredients to form ILs, and 4) Delivery of pesticides. Applications of ILs in agriculture have been schematically presented.

**Sustainable Analyte Extraction in Modern Science:**

Scientists have dedicated considerable effort over decades to explore substances for analyte extraction that can enhance the selectivity, sensitivity, and accuracy of analytical techniques while also being environmentally friendly. In this regard, addressing the consumption of toxic organic solvents in sample preparation or extraction has become a major focus. A notable and eco-friendly solution is the use of ILs, considered "green" substitutes for traditional organic solvents, earning them the designation of solvents of the 21st century [15]. ILs are a category of chemical compounds classified as ionic salts, characterized by a melting point below 100 °C. They consist of a large organic cation paired with a smaller organic or inorganic anion, resulting in an electrically neutral composition with equal numbers of positive and negative ions. ILs exhibit good thermal stability and remain in a liquid state over a wide temperature range. Those with melting points at or below room temperature are referred to as "room temperature ionic liquids," adding to their technological significance [16].

The history of ILs dates back to 1914 when the first stable IL, ethyl ammonium nitrate, was described by Walden, featuring a melting point below room temperature. However, minimal research on ILs occurred until the early 1950s. A breakthrough came in 1982 with the discovery of a new class of ILs with a melting point at or below 100 °C, known as dialkyl imidazolium chloroaluminate. Yet, due to sensitivity to moisture and other compounds, these chloroaluminate ILs did not gain widespread attention. The development of air- and moisture-stable imidazolium salts in 1992 marked the actual emergence of ILs as broadly useful solvents, sparking increased interest in their applicability across sample preparation techniques and various scientific disciplines [17]. Common anions in ILs include hexafluorophosphate, tetrafluoroborate, halides, alkyl sulfate, trifluoromethyl sulfonate, and bis [(trifluoromethyl)sulfonyl] amide, while cations are based on imidazolium, phosphonium, ammonium, pyrrolidinium, and pyridinium. The combinations of these cations and anions allow for the synthesis of numerous ILs, facilitating tailored formulations. Various methods, such as metathesis processes, acid-base neutralization, direct combination, microwave or ultrasonic irradiation, and synthesis using supercritical $CO_2$ or other bio-renewable sources, are employed to synthesize new ILs [18]. Compared to classical organic solvents, ILs offer several advantages, with the ability to customize their physical characteristics based on the intended application and field, earning them the moniker "designer solvents." Over 800 commercially available ILs exist, and the number of known ILs continues to grow, surpassing 1500.

**Eco-Friendly Solvents Revolutionizing Green Extraction of Natural Plant Compounds**:

Certain plant extracts, rich in alkaloids, terpenoids, and flavonoids, exhibit properties that can substitute pesticides to some extent, offering a residue-free and environmentally friendly solution aligning with sustainable agriculture principles. This has led to a growing market for these extracts as biogenic insecticides, driven by increasing consumer demand, particularly in the food production industry. However, conventional extraction methods for these compounds face drawbacks such as reliance on non-environmentally friendly solvents, inefficiency, time consumption, and technical challenges. ILs have emerged as green, eco-friendly, straightforward, and cost-effective solvents for extraction, gaining extensive attention for their role in extracting alkaloids like caffeine, piperine, vinblastine, and others [19].

ILs, especially in ultrasound-assisted extraction, have proven effective for isolating various alkaloids. Continuous advancements, such as cloud point extraction, have further improved IL-based extraction methods, demonstrating favorable results for liensinine, isoliensinine, neferine, o-demethyl nuciferine, and nuciferine extraction. The remarkable effectiveness of ILs in natural product extraction can be attributed to their ability to dissolve cellulose, a major component of plant cell walls. ILs disrupt molecular or intramolecular hydrogen bonds within cellulose fibers, decomposing cellulose and making active components more accessible for extraction [20]. Flavonoids, known for their diverse pharmacological effects, have gained attention in recent years. Research indicates that both flavonoids and alkaloids form hydrogen bonds with IL anions, enhancing their solubility. The choice of IL cation influences the extraction efficiency of flavonoid compounds, and IL-based extraction methods, such as microwave-assisted extraction, have demonstrated superior efficiency compared to traditional methods. ILs have also shown promise in extracting other natural products, including terpenoids and lignin lipids, presenting an efficient and potentially environmentally friendly alternative to traditional solvent extraction for obtaining valuable constituents from plants [21].

**Applications of Ionic Liquids in Microextraction of Pesticides**:

In recent decades, significant modifications to conventional extraction techniques have led to the development of miniaturized methods, such as LPME and Micro-Solid-Phase Extraction (SPE), to address the increasing demands of practical sample preparation applications. Researchers have focused on creating more direct, economical, and rapid techniques in line with the principles of green analytical chemistry. This section discusses the applications of ILs in the microextraction of pesticides, specifically highlighting studies involving DLLME and SDME [22].

**Dispersive Liquid-Liquid Microextraction (DLLME)**:

DLLME, introduced in 2006 by [23]and colleagues, utilizes a ternary solvent system consisting of an aqueous phase (sample), a non-polar water-immiscible solvent (extraction solvent), and a polar water-miscible solvent (disperser solvent). This technique, essentially conventional liquid-liquid extraction at the microscale, offers advantages such as high recoveries, rapid extraction times, and good selectivity. Ionic Liquids, such as 1-hexyl-3-methylimidazolium hexafluorophosphate ([C6MIM][PF6]), have been employed as extract ant solvents in DLLME for the isolation of various pesticides from water samples. Studies have reported successful applications in the extraction of triazine and phenylurea polar herbicides, isoprocarb, diethofencarb, fenothiocarb pesticides, fungicides in fruit juices, and organophosphorus pesticides from water [24].

**Single-Drop Microextraction (SDME)**:

SDME, one of the simplest and most versatile microextraction procedures, involves the use of a conventional GC micro syringe. It allows extraction from both the aqueous sample (direct immersion mode) and the vapor phase above the sample surface (headspace mode). Ionic Liquids, such as 1-hexyl-3-methylimidazolium hexafluorophosphate ([C6MIM] [PF6]), have been applied in SDME for the extraction of aromatic amines, phenolic compounds, limonene, and various pesticides like pyrethroids in vegetables, alkylbenzenes in wastewater, and tributyltin/triphenyl tin in water. Table 1 provides a summary of applications of ILs in the microextraction of pesticides, including sample types, extraction techniques, ILs used, analytical and detection techniques, linear ranges, and limits of detection. These studies showcase the potential of ILs in enhancing the efficiency and selectivity of micro-extraction techniques for pesticide analysis [25].

**ContLs as Solvent**:

Pesticide residues pose a considerable threat not only to non-target organisms but also to the overall ecology of soil and water. Therefore, it is crucial to conduct tests for pesticide residues in soil, water, and food to mitigate potential health risks. However, accurately analyzing trace amounts of polar contaminants in samples has been a longstanding challenge due to the complexity of the matrix and the low concentration of the target analytes. Consequently, the development of simple and efficient sample pretreatment techniques has become a top priority. The utilization of ILs for sample pre-concentration and extraction is widely seen as the future direction for pesticide residue analysis. Numerous studies have already been conducted in this area, employing various techniques such as DLLME, SPE, SPME, and others. ILs show significant potential for enhancing the efficiency and accuracy of pesticide residue analysis, offering a promising avenue to address the challenges associated with trace polar contaminant analysis in diverse samples [26].

**Table 1:** Summary of Applications of IL(s) in Microextraction of Pesticides [27].

| Sample type/Analyte(s) | Extraction Technique | Ionic Liquid(s) Used | Analytical and Detection Techniques | Linear Range (R2) | LOD |
|---|---|---|---|---|---|
| Triazine and phenyl urea polar herbicides from a water sample | DLLME | [C6MIM][PF6]a | HPLC-DAD | 5–200 µgL−1 (0.9947–0.9973) | 0.46–0.89 µgL−1 |
| Isoprocarb, diethofencarb, and methiocarb pesticides from water | DLLME | [C6MIM][PF6]a | HPLC | 3.1–1000 µgL−1 (0.9989–0.9993) | 0.45–1.40 µgL−1 |
| Fungicides in fruit juices (apple and grape) | DLLME | [C6MIM][PF6]a | HPLC | 0.02–2 mgL−1 (0.9902–0.9979) | 3.1–10.2 µgL−1 |
| Carbendazim/benomyl, thiabendazol, fuberidazole, carbaryl and triazophos | DLLME | [C6MIM][PF6]a | HPLC-FD | 0.07–5500 ng/g (0.994–0.999) | 0.02–27.07 ng/g |
| Organophosphorus pesticides (OPPs) (parathion, phoxim, phorate, and chlorpyrifos) from water | DLLME | [C8MIM][PF6]b | HPLC | 10.2–1089 µgL−1 (0.9961–0.9990) | 0.1–5.0 µgL−1 |
| Glyphosate and aminomethylphosphonic acid in water samples | DLLME | [DMIM[BF4]c | HPLC-FD | 0.8–13.44 µgL−1 (>0.99) | 0.22–0.27 µgL−1 |
| Aromatic amines (3-chloroaniline, 2-nitroaniline, and 4-bromoaniline) in water | SDME | [C6MIM][PF6]a | LC-UV | 5–1000 µgL−1 (0.9983–0.9989) | 1.00–2.50 µgL−1 |
| Phenolic compounds (4-chlorophenol, 3-nitrophenol and 2-nitrophenol) | SDME | [BMIM][PF6]d | CE | 0.05–50 µg/mL (0.9994–0.9998) | 0.005–0.050 µg/mL |
| Limonene (and non-pesticides hexyl acetate, and geranyl acetate) from fruit juices | HS-SDME | [HMIM][BF4]e | GC–MS | 0.02–7.16 µg/mL (0.9986–0.9998) | 0.00437 µg/mL (limonene) |
| Fungicides (kresoxim-methyl, chlorothalonil, | SDME | [HMIM][PF6]f | HPLC | 0.5–100 ng/mL | 0.13–0.19 ng/mL |

| | | | | | |
|---|---|---|---|---|---|
| and famoxadone) in water | | | | (0.996–0.998) | |
| 2,4,6-Trichloroanisol in water and wine | SDME | [HMIM][NTF2]g | IMS | 0.1–100 ngL−1 | 0.2 ngL−1 |
| Tributyltin and triphenyltin in water | HS-SDME | [C4MIM][PF6]h | HPLC-FD | 1–200 µgL−1 (0.990–0.992) | 0.62–0.95 µgL−1 |
| Alkylbenzenes in wastewater and tap water | HS-SPME | [C4MIM][BF4]i | GC | 0.04–400 µgL−1 (0.9921–0.9995) | 9.3–48.1 ngL−1 |
| Diazinon, fenitrothion, malathion, fenvalerate, phosalone, and tridemorph from water and pretreated human hair | HF-SPME | [C4MIM][OH]j | HPLC-DAD | 0.01–25,000 ng/mL (0.9950–0.9994) | 0.004 and 0.095 ng/mL |
| OPPs (diazinon, fenitrothion, and malathion) in hair samples | HF-SPME | [(Py BS)3PW12O40]k | HPLC-PDA | 0.02–50,000 µg/g (0.9975–0.9983) | 0.00034 ng/mL-1.3000 µg/g |
| Pyrethroids in vegetables | SPME | [ViHDIm+PF6−]l | GC-ECD | 0.1–100 µgL−1 (>0.9904) | 0.07–0.29 µgL−1 |

**MSPD**:

In SPE, the stationary phase, usually a sorbent or resin, establishes a robust yet reversible interaction with the target analyte or contaminant. This allows for the dependable and swift extraction of the desired analyte from complex samples. This method is well-regarded for its selectivity and versatility, offering a diverse range of sorbents and elution conditions suitable for various analytes and matrices. Nevertheless, traditional SPE methods have faced criticism for their slow speed, labor-intensive processes, and heavy reliance on organic solvents, making them environmentally unfriendly. To address these concerns, the integration of ILs into the SPE process has been considered a significant improvement. The inclusion of ILs expedites and streamlines the sample preparation process. These ILs are often used as sorbents in SPE and can be immobilized on solid-phase carriers through physical adsorption or chemical bonding. In the context of SPE, ILs act as a dissolution system or primary extractant for the sample, thereby enhancing the efficiency and effectiveness of the extraction process. For example, [28] employed [C8MIM][BF4] as the extraction solvent and foaming agent in the analysis of seven acetanilide herbicides (alachlor, metazachlor, propanil, acetochlor, pretilachlor, metolachlor, and butachlor) in naked oats. They utilized an IL-based matrix MSPD-foam flotation solid-phase extraction approach in conjunction with high-performance liquid chromatography. The method demonstrated limits of quantification ranging from 2.62 to 7.28 µg/kg. The average recoveries of acetanilide herbicides spiked at 10, 100, and 500 µg/kg and ranged from 92.1% to 104.7%. This study serves as an illustrative example of how the incorporation of ILs into the SPE process can significantly enhance its efficiency and environmental compatibility, paving the way for more sustainable and eco-friendly extraction techniques [29].

Magnetic extraction methods have gained prominence in recent years, relying on the application of a magnetic field and the magnetization rate of the extracted phase to separate analytes from complex mixtures. Magnet-assisted microextraction techniques, including those involving ILs, have emerged as a promising approach [30]. Liquid magnetic ILs, as an alternative to solid magnetic particles prone to agglomeration, have been rapidly extended to magnet-assisted microextraction operations. Magnetic ILs, containing paramagnetic components, exhibit magnetic properties while retaining the distinctive physicochemical characteristics of ILs. IronIII-based anions, such as tetrachloroferrate (III$FeCl_4$]−or bromoferric trichloride$FeCl_3Br$]−, have been prominently used. For example, [4] introduced a novel sample pretreatment technique called magnetic MSPD-magnetic IL, using [$C_4$MMIM][$FeCl_4$] for the microextraction of triazine herbicides from oilseeds. Magnetic separation streamlined the process, resulting in relative standard deviations ranging from 2.1% to 6.8% and analyte recoveries from 88.6% to 106.3%. Moreover, magnetic ILs can be directly integrated into matrix solid-phase dispersion practices. [4] developed an approach for identifying pesticide residues in lettuce and vegetables using magnetic ILs in matrix solid-phase dispersion. This method eliminated the need for co-sorbents, simplifying the separation and recovery process. Recoveries of pesticide residues in cucumber, potato, and courgette samples ranged from 92% to 105%, making it a more efficient and environmentally friendly extraction method. Material modification addresses common limitations of ILs in microextraction settings, such as viscosity hindering extraction kinetics and challenges in integration with chromatography systems. IL-modified materials are utilized in solid-phase extraction, solid-phase microextraction, and dispersive micro-solid-phase extraction. For instance, [12] employed methylimidazolium hexafluorophosphate-modified [$SiO_2$@MIM-$PF_6$] in dispersive micro-solid-phase extraction for extracting organophosphorus pesticides from water samples. Fang et al. used ion-liquid-functionalized silica in solid-phase extraction for the separation of sulfonylurea herbicides. IL-modified materials find application in magnetic extraction procedures as well. [8] developed a magnetic absorbent based on magnetite nanoparticles modified with an ionic liquid for assessing pollution levels of soil, groundwater, river water, and bottom sediment due to 2,4-DB and its metabolites. Additionally, ion-liquid-modified materials can be employed for recovering and reusing agricultural wastewater, as demonstrated by [13] who synthesized an imidazolium-based IL and cellulose acetate–supported membrane for the removal of "pyrimethoprim" from agricultural wastewater, achieving an improved removal rate of 74%.

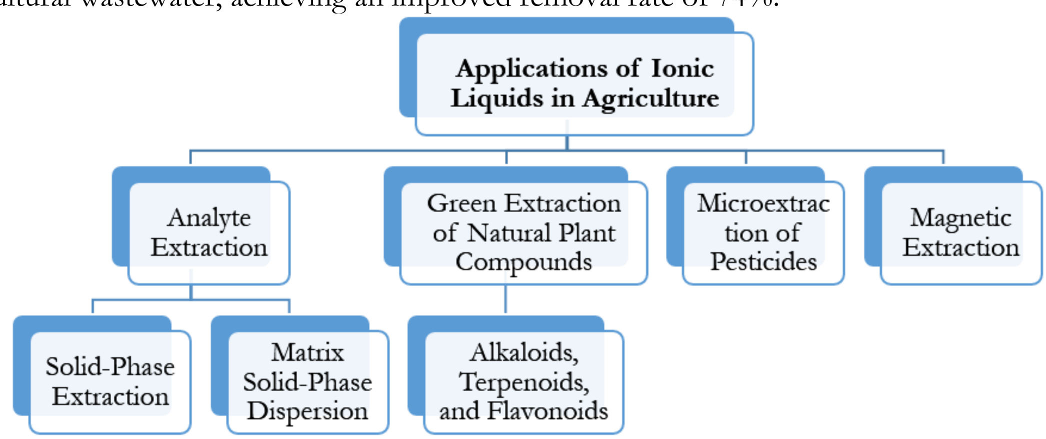


**Figure 1:** Applications of Ionic Liquids in Agriculture.

**Types of ILs Based Pesticides:**

The diverse combinations of anions and cations in pesticides offer a broad spectrum of potential qualities, creating ample opportunities for pesticide development. Traditionally, pesticides were isolated through the mono-ionization of the active molecule in the original ingredient, with the other ion supporting its characteristics. Dual-ion system ionic liquids have emerged, characterized by two anions and cations with diverse effects or one cation with multiple anions, leading to synergistic effects. This innovative approach has the potential to revolutionize the pesticide industry and contribute to more sustainable agricultural practices [31].

**Herbicidal ILs (HILs):**

HILs are developed from various well-known herbicides, including compounds like 2,4-dichlorophenoxyacetic acid (2,4-D), MCPA, MCPP, glyphosate, clopyralid, dicamba, sulfonylurea derivatives, etc. Initially, an "anti-crystalline engineering" approach focused on preventing crystallization, and later stages aimed at enhancing herbicidal activity and modifying physical properties. Cation selection influences adhesive properties, while cation hydrophilicity/hydrophobicity affects solubility. New directions involve dual-active HIL systems with added cations for new biological functions and double-salt HIL systems with synergistic effects [32].

**Single Anion and Cation HILs:**

The simplest herbicidal ionic solutions consist of a single pair of anions and cations, with the anion usually possessing herbicidal activity. Dicationic ILs, where the cation has two positively charged centers, allow for complex interactions. For instance, a dicationic IL containing 2,4-D demonstrated potent herbicidal activity, surpassing that of 2,4-D alone against common broadleaf weeds [33].

**Double-Salt HILs:**

Double-salt HILs, composed of compounds forming a charge-balanced system, have shown increased efficiency compared to single-component systems. Combining herbicides with similar mechanisms of action in double-salt HILs can effectively inhibit resistance development in target plants [9].

**Dual-Activity HILs:**

Dual-activity HILs involve both anions and cations exhibiting distinct biological activities. Anions typically possess herbicidal activity, while cations may have secondary biological activities. This category includes HILs with separate anionic and cationic activities and those where both components individually demonstrate herbicidal activities.

**Food Repellents and Deterrents:**

ILs play a role in controlling pests by acting as deterrents. ILs with antifeedant properties may incorporate natural anions or artificial sweeteners. Didecyl dimethyl ammonium cations in ILs have shown deterrent activity surpassing standard azadirachtin. New quaternary bisammonium salt ILs synthesized with sweet anions and gemini surfactant cations displayed good deterrent activity against pests [11].

**Plant Growth Regulators:**

ILs are explored as plant growth regulators, influencing various plant life processes. Indole-3-butyric acid (IBA) has been transformed into an IL form, retaining biological activity and enhancing lettuce biomass. ILs based on mepiquat chloride demonstrated sustained activity in controlling lateral branch length and height in cotton plants [15].

**ILs for Microbial Control:**

ILs with antibacterial and antifungal properties find applications in various domains, including food preservation, wood processing, medicine, pharmaceuticals, and agricultural sterilization. Different ILs have demonstrated antibacterial and antifungal activities, contributing to the preservation of products and materials.

**Pesticide Delivery and Controlled Release:**

ILs undergo structural modifications to function as trigger-release carriers, offering the potential for pesticide-controlled release. Gelatin cross-linked core-shell microcapsules containing ILs and avermectin demonstrated slow-release properties and enhanced insecticidal activity. Pre-drug ILs designed to respond to water and enzymes as triggers for pesticide release show promise in controlled and targeted pesticide delivery [15].

The study of ILs in the pesticide sector presents a promising avenue for advancing pesticide development, enhancing efficacy, and promoting more sustainable agricultural practices.

**Toxicity of Ionic Liquids:**

ILs, initially celebrated as "green solvents," have been scrutinized for residual toxicity and biodegradability, deviating from early expectations. Their toxicity manifests through cell destruction and influence on pathogenic micro-organisms' proliferative activity. Factors affecting bioactive IL toxicity include cation structure's "alkyl side-chain effect," the number of functional groups on the cation side chain, anion nature (hydrophobicity or stability), and cation lipophilicity. Understanding IL toxicology, especially ecotoxicity, proves complex, with gaps in research on toxicological mechanisms, particularly the combined toxicity of pesticide prodrugs and additives in the final agrochemical product [34].

**Biodegradation of ILs:**

Imidazolium cations' biodegradability has been examined, shedding light on potential environmental impacts. Commonly, OECD 301 D or F tests measure dissolved oxygen or oxygen consumption over 28 days, though challenges persist due to bacterial flora variations. Recent studies delving into IL biodegradability reveal insights, such as assessments of IL-based plant systemic acquired resistance inducers showing some synthesized compounds with low degradability. Studies on IL transport in agricultural soils demonstrate certain ILs maintain limited toxicity compared to original compounds, with independent adsorption of cations and anions during soil degradation.

**References**

[1] S. Lago, H. Rodríguez, A. Arce, and A. Soto, "Improved concentration of citrus essential oil by solvent extraction with acetate ionic liquids," Fluid Phase Equilib., vol. 361, pp. 37–44, Jan. 2014, doi: 10.1016/J.FLUID.2013.10.036.

[2] J. Zhang et al., "Understanding cellulose dissolution: effect of the cation and anion structure of ionic liquids on the solubility of cellulose," Sci. China Chem., vol. 59, no. 11, pp. 1421–1429, Nov. 2016, doi: 10.1007/S11426-016-0269-5.

[3] A. Abdi Hassan, M. Sajid, H. Al Ghafly, and K. Alhooshani, "Ionic liquid-based membrane-protected micro-solid-phase extraction of organochlorine pesticides in environmental water samples," Microchem. J., vol. 158, Nov. 2020, doi: 10.1016/J.MICROC.2020.105295.

[4] Y. Wang et al., "Matrix solid-phase dispersion coupled with magnetic ionic liquid dispersive liquid-liquid microextraction for the determination of triazine herbicides in oilseeds," Anal. Chim. Acta, vol. 888, pp. 67–74, 2015, doi: 10.1016/J.ACA.2015.07.028.

[5] D. Lu, C. Liu, J. Deng, X. Zhou, G. Shi, and T. Zhou, "Rational design of an ionic liquid dispersive liquid-liquid micro-extraction method for the detection of organophosphorus pesticides," Analyst, vol. 144, no. 6, pp. 2166–2172, Mar. 2019, doi: 10.1039/C9AN00123A.

[6] S. Peng, J. Xiao, J. Cheng, M. Zhang, X. Li, and M. Cheng, "Ionic liquid magnetic bar microextraction and HPLC determination of carbamate pesticides in real water samples," Microchim. Acta, vol. 179, no. 3–4, pp. 193–199, Nov. 2012, doi: 10.1007/S00604-012-0884-4.

[7] "View of Evaluating Spatio-Temporal Decline to Agriculture through Satellite Imagery from 2010-2022." Accessed: Feb. 22, 2024. [Online]. Available: https://journal.50sea.com/index.php/IJASD/article/view/471/971

[8] A. Gubin, P. Sukhanov, A. Kushnir, K. Shikhaliev, M. Potapov, and E. Kovaleva, "Ionic-liquid-modified magnetite nanoparticles for MSPE-GC-MS determination of 2,4-D butyl ester and its metabolites in water, soil, and bottom sediments," Environ. Nanotechnology, Monit. Manag., vol. 17, May 2022, doi: 10.1016/J.ENMM.2022.100652.

[9] H. Wang et al., "A rapid and simple pretreatment method for benzoylurea insecticides in honey samples using in-syringe dispersive liquid–liquid microextraction based on the direct solidification of ionic liquids," J. Chromatogr. A, vol. 1471, pp. 60–67, Nov. 2016, doi: 10.1016/J.CHROMA.2016.10.027.

[10] Y. Jiang, Z. Wang, Z. Lei, and G. Yu, "Structural effects on thermodynamic behavior and hydrogen bond interactions of water–ionic liquid systems," Chem. Eng. Sci., vol. 230, Feb. 2021, doi: 10.1016/J.CES.2020.116186.

[11] L. Zhang et al., "Separation and concentration of sulfonylurea herbicides in milk by ionic-liquid-based foam flotation solid-phase extraction," J. Sep. Sci., vol. 38, no. 10, pp. 1733–1740, May 2015, doi: 10.1002/JSSC.201401344.

[12] F. Galán-Cano, R. Lucena, S. Cárdenas, and M. Valcárcel, "Dispersive micro-solid phase extraction with ionic liquid-modified silica for the determination of organophosphate pesticides in water by ultra performance liquid chromatography," Microchem. J., vol. 106, pp. 311–317, Jan. 2013, doi: 10.1016/J.MICROC.2012.08.016.

[13] S. C. Zhu, M. Z. Shi, Y. L. Yu, and J. Cao, "Simultaneous extraction and enrichment of alkaloids from lotus leaf by in-situ cloud point-reinforced ionic liquid assisted mechanochemical extraction technology," Ind. Crops Prod., vol. 183, Sep. 2022, doi: 10.1016/J.INDCROP.2022.114968.

[14] N. Nasirpour, M. Mohammadpourfard, and S. Zeinali Heris, "Ionic liquids: Promising compounds for sustainable chemical processes and applications," Chem. Eng. Res. Des., vol. 160, pp. 264–300, Aug. 2020, doi: 10.1016/J.CHERD.2020.06.006.

[15] J. Yang et al., "Synthesis and application of imidazolium-based ionic liquids as extraction solvent for pretreatment of triazole fungicides in water samples," Anal. Bioanal. Chem., vol. 410, no. 6, pp. 1647–1656, Feb. 2018, doi: 10.1007/S00216-017-0820-X.

[16] X. Peng, X. Sui, J. Li, T. Liu, and L. Yang, "Development of a novel functionality for a highly efficient imidazole-based ionic liquid non-aqueous solvent system for the complete extraction of target alkaloids from Phellodendron amurense Rupr. under ultrasound-assisted conditions," Ind. Crops Prod., vol. 168, Sep. 2021, doi: 10.1016/J.INDCROP.2021.113596.

[17] M. G. Freire, C. M. S. S. Neves, I. M. Marrucho, J. N. Canongia Lopes, L. P. N. Rebelo, and J. A. P. Coutinho, "High-performance extraction of alkaloids using aqueous two-phase systems with ionic liquids," Green Chem., vol. 12, no. 10, pp. 1715–1718, Oct. 2010, doi: 10.1039/C0GC00179A.

[18] D. C. Murador, L. M. de Souza Mesquita, N. Vannuchi, A. R. C. Braga, and V. V. de Rosso, "Bioavailability and biological effects of bioactive compounds extracted with natural deep eutectic solvents and ionic liquids: advantages over conventional organic solvents," Curr. Opin. Food Sci., vol. 26, pp. 25–34, Apr. 2019, doi: 10.1016/J.COFS.2019.03.002.

[19] C. W. Cho, T. P. T. Pham, Y. Zhao, S. Stolte, and Y. S. Yun, "Review of the toxic effects of ionic liquids," Sci. Total Environ., vol. 786, Sep. 2021, doi: 10.1016/J.SCITOTENV.2021.147309.

[20] M. Gao et al., "Ionic-liquid-based effervescence-enhanced magnetic solid-phase extraction for organophosphorus pesticide detection in water samples," Anal. Methods, vol. 14, no. 6, pp. 661–671, Feb. 2022, doi: 10.1039/D1AY01698A.

[21] M. Z. Shi, Y. L. Yu, S. C. Zhu, J. Yang, and J. Cao, "Latest Development of Matrix Solid Phase Dispersion Extraction and Microextraction for Natural Products from 2015-2021," Sep. Purif. Rev., vol. 52, no. 3, pp. 262–282, 2023, doi: 10.1080/15422119.2022.2094274.

[22] J. P. Hallett and T. Welton, "Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2," Chem. Rev., vol. 111, no. 5, pp. 3508–3576, May 2011, doi:

10.1021/CR1003248.
[23] M. Li, C. Yang, H. Yan, Y. Han, and D. Han, "An integrated solid phase extraction with ionic liquid-thiol-graphene oxide as adsorbent for rapid isolation of fipronil residual in chicken eggs," J. Chromatogr. A, vol. 1631, Nov. 2020, doi: 10.1016/J.CHROMA.2020.461568.
[24] X. Song et al., "Research progress in the sample pretreatment techniques and advanced quick detection methods of pesticide residues," Process Saf. Environ. Prot., vol. 165, pp. 610–622, Sep. 2022, doi: 10.1016/J.PSEP.2022.07.047.
[25] L. Vidal, M. L. Riekkola, and A. Canals, "Ionic liquid-modified materials for solid-phase extraction and separation: A review," Anal. Chim. Acta, vol. 715, pp. 19–41, Feb. 2012, doi: 10.1016/J.ACA.2011.11.050.
[26] D. Han and K. H. Row, "Recent applications of ionic liquids in separation technology," Molecules, vol. 15, no. 4, pp. 2405–2426, Apr. 2010, doi: 10.3390/MOLECULES15042405.
[27] P. O. Boamah, L. Wang, W. Shen, S. Tang, and H. K. Lee, "Applications of ionic liquids in the microextraction of pesticides: A mini-review," J. Chromatogr. Open, vol. 4, p. 100090, Nov. 2023, doi: 10.1016/J.JCOA.2023.100090.
[28] L. Yang et al., "Ultrasound-assisted extraction of the three terpenoid indole alkaloids vindoline, catharanthine and vinblastine from Catharanthus roseus using ionic liquid aqueous solutions," Chem. Eng. J., vol. 172, no. 2–3, pp. 705–712, Aug. 2011, doi: 10.1016/J.CEJ.2011.06.039.
[29] X. Y. Lin, R. X. Mou, Z. Y. Cao, Z. Z. Cao, and M. X. Chen, "Analysis of pyrethroid pesticides in Chinese vegetables and fruits by GC–MS/MS," Chem. Pap., vol. 72, no. 8, pp. 1953–1962, Aug. 2018, doi: 10.1007/S11696-018-0447-1.
[30] M. Andraščíková, E. Matisová, and S. Hrouzková, "Liquid phase microextraction techniques as a sample preparation step for analysis of pesticide residues in food," Sep. Purif. Rev., vol. 44, no. 1, pp. 1–18, 2015, doi: 10.1080/15422119.2013.872125.
[31] K. D. Clark, M. J. Trujillo-Rodríguez, and J. L. Anderson, "Advances in the analysis of biological samples using ionic liquids," Anal. Bioanal. Chem., vol. 410, no. 19, pp. 4567–4573, Jul. 2018, doi: 10.1007/S00216-018-0898-9.
[32] B. Herce-Sesa, J. A. López-López, and C. Moreno, "Advances in ionic liquids and deep eutectic solvents-based liquid phase microextraction of metals for sample preparation in Environmental Analytical Chemistry," TrAC - Trends Anal. Chem., vol. 143, Oct. 2021, doi: 10.1016/j.trac.2021.116398.
[33] D. J. Eyckens and L. C. Henderson, "A review of solvate ionic liquids: Physical parameters and synthetic applications," Front. Chem., vol. 7, no. APR, 2019, doi: 10.3389/FCHEM.2019.00263.
[34] Q. Li et al., "Ultrasonic-assisted extraction of sinomenine from Sinomenium acutum using magnetic ionic liquids coupled with further purification by reversed micellar extraction," Process Biochem., vol. 58, pp. 282–288, Jul. 2017, doi: 10.1016/J.PROCBIO.2017.04.030.