

Review

Applications of Ionic Liquids in the Field of Agriculture: A Review

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Abstract: This review delves into the diverse applications of ionic liquids (ILs) in modern agriculture, focusing on their pivotal roles in the extraction of natural products and pesticides, as well as their substantial significance in sustainable pesticide delivery systems. The reported extraction methods include ILs and their modified materials as solvents in dispersive liquid–liquid microextraction, solid-phase dispersion, and solid-phase microextraction. The study categorizes ILs according to their utility as herbicides, microbicides, food repellents, and plant growth regulators. This review investigates the use of ILs as plant immunity inducers to elevate the systemic acquired resistance in crops, thereby augmenting their intrinsic ability to defend against plant pathogens. Furthermore, the review explores the application of ILs in pesticide delivery systems, emphasizing their ability to enhance efficacy while promoting environmental sustainability. The biodegradability and toxicity aspects of ILs are also discussed, shedding light on their potential as eco-friendly alternatives in agricultural practices. In conclusion, this comprehensive overview underscores the multifaceted contributions of ILs in agriculture, from efficient extraction methods to the development of innovative and sustainable pesticide delivery systems. As the agricultural landscape evolves towards environmentally conscious practices, the integration of ILs presents a promising avenue for enhancing productivity while minimizing ecological impact. As the agricultural industry seeks innovative and sustainable solutions, the nuanced exploration of ILs in this review highlights their potential to address multiple challenges in modern farming practices.

Keywords: ionic liquids; modified materials; chromatographic analysis; isolation; pesticide delivery; toxicity

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1. Introduction

In modern agriculture, the crucial role of pesticides in balancing yield protection and economic viability cannot be overstated, particularly for cost-sensitive crops [1]. 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 [2], 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 [3]. 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 [4]. Consequently, it is imperative to explore novel alternative solvents that offer improved environmental sustainability and efficacy.

Ionic liquids (ILs) represent a class of liquid ionic salts characterized by melting points below 100 °C [5,6], and some can even remain in liquid form near room temperature, known as room temperature ILs [7,8]. These substances are hailed as an environmentally friendly alternative to traditional organic solvents, primarily due to their lower toxicity levels [9]. Common anions found in ILs include inorganic anions (halide, tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)imide, etc.) and organic anions (acetate, amino acid, etc.). Meanwhile, prevalent cations comprise imidazolium, ammonium, pyridinium, phosphonium or sulfonium [10]. The distinctive feature of ILs lies in the diverse combinations of anions and cations, coupled with the tunability of functional groups [11]. 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” [12]. 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 [6,13,14].

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 [15]. Currently, the development of IL technology has undergone three major revolutions [16]. 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. 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 in Figure 1.

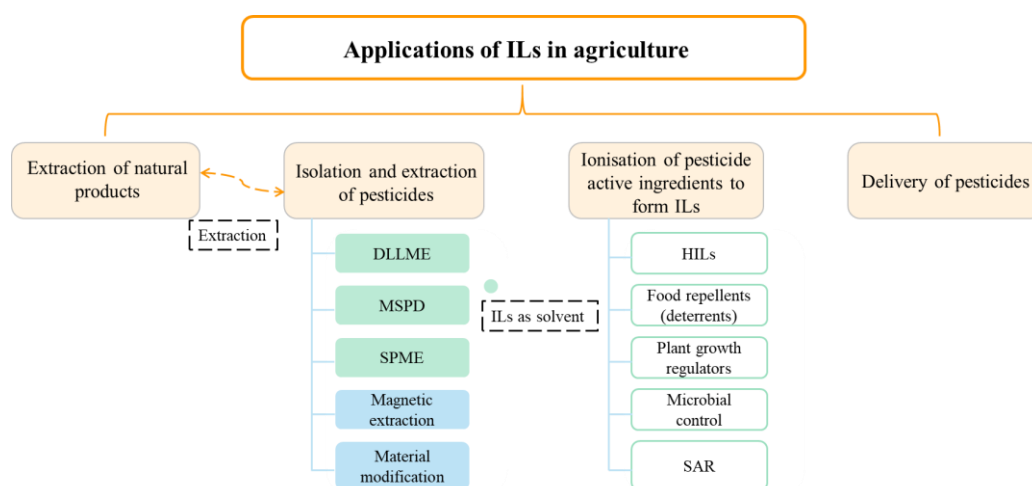


Figure 1. Applications of ILs in agriculture.

2. Extraction of Natural Products

Certain natural plant extracts possess pest- and microbial-inhibition properties, along with herbicidal effects, making them potential substitutes for pesticides to some extent. These extracts, comprising alkaloids, terpenoids, flavonoids, and other compounds, are recognized for their residue-free nature and environmental benefits, aligning with the principles of sustainable agriculture. As a result, the market for these extracts as biogenic insecticides is rapidly expanding. Moreover, natural plant extracts are witnessing a surge in consumer demand across various industries, particularly in the field of food production. The trend underscores the increasing importance of extracting chemicals from natural sources. However, conventional extraction methods for these natural compounds suffer from several drawbacks, including their reliance on significant quantities of non-environmentally friendly organic solvents, as well as their inefficiency, time consumption, and technical complexity [17,18]. Hence, ILs, serving as a green, eco-friendly, straightforward, and cost-effective extraction solvent, have been progressively attracting extensive attention [19,20].

ILs have been extensively investigated for their role in extracting alkaloids such as caffeine [21,22], piperine [23,24], vinblastine [25], neferine [26], and others. The exceptional solubility of most alkaloids in aqueous solutions typically leads to the use of a solvent mixture comprising water and ILs in these extraction studies [27,28]. One of the widely employed techniques for alkaloid extraction using ILs is ultrasound-assisted extraction, which has proven to be particularly effective [25,29,30]. Cao et al. were pioneers in this field, introducing an innovative approach involving IL-based ultrasound-assisted extraction for the isolation of piperine from white pepper [24]. As the field continues to evolve, several new methods have been developed to enhance the extraction of natural products using ILs [31,32]. For instance, Zhu et al. employed cloud point extraction to augment the extraction of alkaloids from lotus leaves with ILs, yielding favorable results for liensinine, isoliensinine, neferine, o-demethyl nuciferine, and nuciferine extraction. The average recovery rates ranged from 80.4% to 93.7%, with relative standard deviation values for extraction and retention time falling within the range of 1.11–4.45% and 0.04–0.28%, respectively [26].

The remarkable effectiveness of ILs in natural product extraction can be attributed to their ability to efficiently dissolve cellulose, a major component of plant cell walls that often presents a significant barrier to the extraction of active ingredients [33,34]. ILs facilitate the extraction of active ingredients from plants by disrupting the molecular or intramolecular hydrogen bonds within or between cellulose fibers in the plant cell wall. This disruption leads to the decomposition of cellulose, making the active components more accessible for extraction [35]. The solubilization mechanism of cellulose by ILs is primarily explained by two main factors. Firstly, the anion within ILs plays a significant role in cellulose solubilization. The anion forms hydrogen bonds with the hydroxyl protons of cellulose, and the strength of these hydrogen bonds in ILs correlates with their capacity to dissolve cellulose [36–38]. Lu et al. have demonstrated that the presence of an acidic proton on the cationic heterocycle directly impacts cellulose solubility in ILs. Secondly, the cation can indirectly influence cellulose solubility by affecting the anion through spatial constraints and strong interactions [39]. Moreover, research by Zhao et al. suggests that the hydroxyl group on the cation of some ILs may compete with the anion for binding to cellulose, forming hydrogen bonds [40,41].

The group of compounds known as flavonoids serves to color various plant parts and significantly contributes to human health [42]. These compounds are known for their diverse pharmacological effects, including antioxidant properties, antibacterial activity, antitumor potential, and cardiovascular protection [43]. Over recent years, there has been a growing focus on the study of flavonoids in natural products, reflecting their increasing importance in various fields [44,45]. Research has revealed that both flavonoids and alkaloids feature hydroxyl and aromatic groups that form hydrogen bonds with the anions present in ILs, thereby enhancing their solubility in these solvents. Du et al. demonstrated that the choice of cation within ILs impacts the extraction efficiency of flavonoid compounds, as evidenced by the differing extraction efficiencies between pyridinium-based

ILs and imidazolium-based ILs [46]. Similarly, the study of Zuo et al. highlighted how the alkyl lengths and positions of the cations in ILs influence the extraction efficiency of flavonoid compounds [47]. It is worth noting that ILs significantly enhance the extraction efficiency of flavonoids. A comparison was made by the extraction efficiency between IL-based microwave-assisted extraction and conventional microwave-assisted extraction for flavonoids in *Bauhinia championii* (Benth.) Benth. The results indicated that IL-based microwave-assisted extraction exhibited superior extraction efficiency with a considerably reduced extraction time (from 1.5 h to 10 min) [48]. Additionally, the IL-based microwave-assisted extraction method outperformed IL-heating extraction, IL-magnetic extraction, and IL-ultrasound-assisted extraction due to its capacity to efficiently absorb microwave energy [49].

Owing to the high toxicity, non-biodegradability, and considerable costs associated with traditional extraction methods, numerous studies have explored the utilization of ILs for the extraction of various other natural products, including terpenoids and lignin lipids [50–53]. For instance, Chen et al. employed 1-butyl-3-methylimidazolium tetrafluoroborate in an IL-ultrasound-assisted extraction method to extract lignans from *Eucommia* bark, showcasing the potential of ILs in the extraction of lignans [54]. Similarly, Li et al. utilized the IL 1-butyl-3-methylimidazolium bromide to extract five ginsenosides from *Panax* ginseng through ultrasound-assisted extraction with a double aqueous phase [55]. Hence, ILs offer an efficient and potentially environmentally friendly approach compared to traditional solvent extraction, ensuring the effective extraction of valuable constituents from plants.

3. Isolation and Extraction of Pesticides

Traditional organic solvents are known for their excellent dissolving and extraction properties; however, their significant drawbacks, including high toxicity, non-biodegradability and considerable cost, are not in line with the principles of green chemistry [56]. Consequently, the exploration and development of alternative eco-friendly solvents have emerged as a key focus for researchers [57]. ILs have gained traction in separation techniques in recent years, primarily due to their customizable physical and chemical properties, making them a promising candidate for sustainable solvent alternatives [58,59]. In the field of pesticide testing, the simplicity, efficiency, and time-saving attributes of IL extraction, compared to conventional organic solvents, have positioned them as viable replacements for organic solvents in the extraction and enrichment of analytes [60]. Furthermore, apart from their role as solvents, ILs can enhance the extraction efficiency of various materials by modifying and functionalizing sorbent materials such as silica and carbon nanotubes. The strong extraction capability of ILs extends to a broad spectrum of aqueous contaminants, including heavy metals, dye molecules, and organic compounds. This ability underscores their potential for efficient wastewater treatment and remediation. Consequently, the versatile nature of ILs holds great promise for advancing sustainable and environmentally friendly practices in various fields, including extraction processes and wastewater treatment [61]. As in the previous section, all details of described examples of IL-based analytical protocols are included in Table 1.

Table 1. Applications of IL-based hybrid materials in various extraction methodologies.

Types of Separation Technology	Sample Type	Analyte(s)	Evaluated IL(s)	Limits of Detection (µg/kg)	Reference
DLLME	Water; Tea beverage	Benzoylurea insecticides	[N ₈₈₈₁][PF ₆]	0.29–0.59	[62]
DLLME	Coarse cereals	Organophosphorus pesticide	[C ₆ MIM][BF ₄]	2.5–5.5	[63]
DLLME	Wine	Sulfonylurea herbicides	[C ₆ MIM][PF ₆], [C ₄ MIM][PF ₆]	3.2–6.6	[64]
DLLME	Honey	Benzoylurea insecticides	[N ₄₄₄₄][PF ₆]	0.21–0.42	[65]
DLLME	River water	Organophosphorus pesticides	[MCOOC ₂ MIM][NTf ₂]	0.7–2.7	[66]
DLLME	Water	Triazole fungicides	[C ₄ C ₄ MIM][Br], [C ₄ C ₅ MIM][Br], [C ₄ C ₆ MIM][Br], [C ₄ (C ₄ MIM) ₂][Br ₂], [C ₄ (MIM) ₂][Br ₂],	0.74–1.44	[67]
DLLME	Oilseeds	Triazine herbicides	[C ₄ MMIM][FeCl ₄]	1.20–2.72	[68]
ILFF-SPE	Milk	Sulfonylurea herbicides	[C ₄ MIM][BF ₄]	0.6–1.3	[69]
SB-µ-SPE	Agricultural wastewater	Organochlorine pesticides	[1-NA][FeCl ₄] [4-MA][FeCl ₄]	0.25–3.4	[70]
D-µSPE	Water	Organophosphate pesticides	SiO ₂ @MIM–PF ₆	0.3–0.6	[71]
SPME	Grape juice	Volatile endocrine-disruptor pesticides	[C ₈ MIM][Br], [C ₁₂ MIM][Br], [C ₁₈ MIM][Br]	0.002–0.667	[72]
SPME	Wine; Juice	Organophosphorus pesticides	[C ₁₆ MIM][NTf ₂]	0.57–4.13	[73]
HS-SPME	Soil	Epoxiconazole, fluroxypyr, metribuzin, and oxyfluorfen	[VBIMC ₁₆][NTf ₂], [VIMC ₁₀ OH][NTf ₂], [(VBIM) ₂ C ₁₂] ₂ [NTf ₂], [(VB(BIM)) ₂ C ₁₂] ₂ [NTf ₂]	0.2–2	[74]
DI-SPME	Water	20 pesticides	[VIMC ₈][NTf ₂], [VIMC ₁₂][NTf ₂], [(VIM) ₂ C ₁₂] ₂ [NTf ₂], [VBIMC ₈][NTf ₂],	1–200	[75]

			[(VBIM) ₂ C ₁₂] ₂ [NTf ₂]		
SPME	Soils, ground and river waters, and bottom sediments	2,4-D, 2,4-D ester, and metabolites	Fe ₃ O ₄ @SiO ₂ -MIM, Fe ₃ O ₄ @SiO ₂ -MMIM, Fe ₃ O ₄ @SiO ₂ -C ₄ MIM	1×10^{-4} – 3×10^{-2}	[76]
ILMB-ME	Tap, lake and rain water	Carbamate pesticides	[C ₄ MIM][PF ₆], [C ₆ MIM][PF ₆]	1.4–3.4	[77]
MSPD	Naked oat	Acetanilide herbicides	[C ₄ MIM][BF ₄], [C ₆ MIM][BF ₄], [C ₈ MIM][BF ₄], [C ₄ MIM][PF ₆], [C ₆ MIM][PF ₆], [C ₈ MIM][PF ₆]	0.29–0.59	[78]
MSPD	Vegetables	Organophosphate, organochloride and triazine pesticides	[P ₆₆₆₁₄][Gd(III)(hfacac) ₄], [P ₆₆₆₁₄][Dy(III)(hfacac) ₄], [P ₆₆₆₁₄][Co(II)(hfacac) ₃], [P ₆₆₆₁₄][Mn(II)(hfacac) ₃], [P ₆₆₆₁₄][Ni(II)(hfacac) ₃]	0.002–0.009	[79]
MEPS	Brewed coffee	Polycyclic aromatic hydrocarbons	zIL@T@SiO ₂	4.5–6.7	[80]
PT-SPE	Egg	Fipronil	IL@T@GO	4.76	[81]
ILE-MSPE	Water	Organophosphorus pesticides	Fe ₃ O ₄ @Na ₂ CO ₃ @[C ₆ MIM][PF ₆] effervescent tablet	0.14–0.22	[82]

3.1. ILs as Solvent

Pesticide residues pose a significant threat not only to non-target organisms but also to the overall ecology of soil and water [83–85]. Therefore, conducting tests for pesticide residues in soil, water, and food is crucial for mitigating potential health risks [86,87]. However, analyzing trace amounts of polar contaminants accurately in samples, owing to the complexity of the matrix and the low concentration of the target analytes, has long been a challenging and critical area in separation techniques. Accordingly, the development of simple and efficient sample pretreatment techniques has become a top priority. The application of ILs for sample pre-concentration and extraction is widely considered the future direction of pesticide residue analysis, and numerous studies have already been conducted in this area. These studies encompass various techniques, including dispersive liquid–liquid microextraction (DLLME) [62–68], solid-phase extraction (SPE) [69–71], solid-phase microextraction (SPME) [72–76], and so on. ILs demonstrate significant potential for improving the efficiency and accuracy of pesticide residue analysis, presenting a promising avenue for addressing the challenges associated with trace polar contaminant analysis in diverse samples.

3.1.1. DLLME

To achieve ecologically sound, environmentally friendly, and cost-effective sample analysis, the incorporation of sample pre-concentration steps and the miniaturization of analytical instruments is imperative in the pesticide analysis process [57]. DLLME, a novel liquid-phase extraction method, utilizes only a small quantity of extraction solvent. The typical DLLME process comprises three solvent systems: the dispersant, the extraction solvent, and the aqueous sample [88]. This method involves the rapid injection of the dispersant and extractant into the aqueous sample, generating turbulence that disperses the extractant into numerous small droplets, resulting in a large emulsified droplet interface area, which accelerates the mass transfer process of the analyte. ILs are increasingly utilized as extraction solvents in the DLLME technique [89].

In IL solutions, the anions are predominantly tetrafluoroborate $[\text{BF}_4]^-$, hexafluorophosphate $[\text{PF}_6]^-$, and bis[(trifluoromethyl)sulfonyl]imide $[\text{Tf}_2\text{N}]^-$, imparting hydrophobic properties to the ionic solution, facilitating the formation of a biphasic system with aqueous samples. The hydrophobicity of the anions increases in the order of $[\text{Br}]^-$ to $[\text{Cl}]^-$ to $[\text{BF}_4]^-$ to $[\text{PF}_6]^-$ to $[\text{TFSI}]^-$ to bis(perfluoroethanesulfonyl)imide ($[\text{BETI}]^-$) [90]. For instance, Wang et al. utilized the hydrophobic IL ($[\text{N}_{8881}][\text{PF}_6]$) as an extraction solvent [62], developing an innovative in-syringe solidified IL–DLLME method for the rapid screening and quantification of benzoylurea insecticides in water and tea. Its analytical range was 2–500 ($\mu\text{g/L}$) with a minimum density of 0.29–0.59 ($\mu\text{g/L}$) and extraction recoveries between 85.9% and 90.52%. The method demonstrated a simple, effective, and environmentally friendly approach, eliminating the need for tedious vortexing, ultrasound, magnetic stirring, evaporation, or centrifugation, thereby reducing the operating time of the extraction method.

In the case of some pesticides containing aromatic substituents, such as organophosphorus pesticides, the interaction between them and ILs revolves around both hydrophilic and hydrophobic interactions [91]. Zhang et al. combined DLLME with high-performance liquid chromatography (HPLC), utilizing $[\text{C}_6\text{MIM}][\text{PF}_6]$ as the extractant and $[\text{C}_6\text{MIM}][\text{BF}_4]$ as the dispersant for the determination of five organophosphorus pesticide residues (trichlorfon, chlorpyrifos, phoxim, fenthion, and diazinon) in coarse grains. The method exhibited high sensitivity and reproducibility, with limits of detection ranging from 2.3 to 8.6 $\mu\text{g/kg}$ and recoveries between 85.3% and 107.3%. This approach proved suitable for the rapid detection of organophosphorus pesticides in coarse grains [63].

The increase in the chain length of the cationic alkyl substituents enhances the lipophilicity of the ILs, facilitating the solubilization of organic matter. However, an increase in the alkyl chain length leads to IL aggregation in aqueous solutions, resulting in larger microemulsion droplet sizes, which adversely affect viscosity and the mass transfer effect

of the extraction process [92,93]. Li et al. compared three ILs with different cations and ultimately selected $[C_4MIM]^+$, with the shortest alkyl chain, for their IL design. The developed method involved the in situ reaction of $K[PF_6]$ and $[C_4MIM][Br]$ in the sample solution, utilizing the hydrophobic IL $[C_4MIM][PF_6]$ as the extraction solvent. Unlike conventional DLLME methods, this technique does not necessitate a dispersive solvent, showcasing limits of detection and quantification in the range of 0.30–0.62 and 1.20–2.50 $\mu\text{g/L}$, respectively. The method demonstrated high enrichment factors of 74–115 and recoveries ranging from 81.0% to 103.4% [94].

Furthermore, temperature is a crucial factor influencing IL viscosity. Generally, IL viscosity decreases with rising temperature, allowing for the reduction of IL viscosity through temperature elevation [95]. Zhang et al. developed a method for the determination of five pyrethroid residues in herbal tea using IL–DLLME with $[C_6MIM][PF_6]$ as the extraction solvent and acetonitrile as the dispersant. Typically, the high viscosity of ILs poses challenges in dispersing them in sample solutions. Therefore, in this experiment, ultrasonically enhanced temperature control was employed to enhance the dispersion process, improving the ability of ILs to extract analytes. The method exhibited limits of detection and quantification of 1.25–1.35 $\mu\text{g/L}$ and 5 $\mu\text{g/L}$, respectively, with mean recoveries ranging from 74.02% to 109.01% and relative standard deviations below 9.04% [96].

3.1.2. Solid-Phase Dispersion (MSPD)

In solid-phase extraction, the stationary phase, typically a sorbent or resin, forms a strong yet reversible interaction with the target analyte or contaminant, enabling the reliable and rapid extraction of the desired analyte from complex samples [97]. This method is renowned for its selectivity and versatility, offering a diverse array of sorbents and elution conditions suitable for various analytes and matrices. However, traditional solid-phase extraction methods are often criticized for their slow speed, labor-intensive nature, and substantial reliance on organic solvents, rendering them environmentally unfriendly. To address these concerns, the integration of ILs into the solid-phase extraction process has been deemed a significant improvement [98].

The incorporation of ILs in the solid-phase extraction procedure expedites and streamlines the sample preparation process. These ILs are frequently employed as sorbents in solid-phase extraction and can be immobilized on solid-phase carriers through physical adsorption or chemical bonding. In the context of solid-phase extraction, ILs serve as a dissolution system or primary extractant for the sample, enhancing the efficiency and effectiveness of the extraction process [99].

For instance, Zhang et al. utilized $[C_8MIM][BF_4]$ 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 employed an IL-based matrix MSPD-foam flotation solid-phase extraction approach in combination with high-performance liquid chromatography. The method exhibited limits of quantification ranging from 2.62 to 7.28 $\mu\text{g/kg}$. The average recoveries of acetanilide herbicides spiked at 10, 100, and 500 $\mu\text{g/kg}$ ranged from 92.1% to 104.7%. This study serves as an example of how the utilization of ILs in the SPE process can significantly enhance its efficiency and environmental compatibility, paving the way for more sustainable and eco-friendly extraction techniques [78].

3.1.3. Solid-Phase Microextraction (SPME)

Solid-phase microextraction stands out as an advanced, environmentally friendly sample pre-concentration technique that amalgamates sampling, extraction, concentration, and sample introduction into a single step, making it particularly attractive to researchers [98]. One of its most appealing features is its solvent-free pre-concentration process, contributing to the overall eco-friendliness of the solid-phase microextraction procedure [57,100]. This technique operates on the principle of analyte partitioning between the

sample phase and a solid extraction phase (sorbent), typically consisting of a coated polymer fiber that extracts the pesticide from the food matrix [60].

While both solid-phase extraction and solid-phase microextraction procedures frequently incorporate IL-based modifications as a solid phase, some ILs are still used as solvents or directly applied to the solid phase. Zeger et al. developed a novel method for the separation of universally regulated pesticides and cannabinoids from water samples, employing sorbent coatings of imidazolium-based polymeric ILs for direct immersion solid-phase microextraction. In this study, the selectivity of four PIL sorbent coatings for 20 pesticides and six cannabinoids was investigated in comparison with commercial PDMS/DVB fibers. The [VBIMC₈][NTf₂] adsorbent coating exhibited the most favorable selectivity for pesticides, achieving a limit of detection as low as 1 µg/L, with relative recoveries ranging from 95% to 141%, compared to 50% to 114% obtained using conventional PDMS/DVB fibers. This method effectively enhances the extraction of pesticides while minimizing the extraction of cannabinoids [75].

Micro-solid-phase extraction protected by porous membranes represents an extraction technique that utilizes minimal solid phase, enclosed within a membrane bag formed by heat-sealing a flat membrane sheet resembling an envelope [70,71]. Hassan et al. synthesized two novel ILs, namely 4-methylbenzenammonium tetrachloroferrate (III) and 1-naphthylammonium tetrachloroferrate (III). These compounds, characterized by their capacity to exist in the solid phase at temperatures below 65 °C, were utilized as adsorbent phases in stir-bar supported micro-solid-phase extraction (SB-µ-SPE) for extracting organochlorine pesticides from environmental water samples. SB-µ-SPE exhibited outstanding performance in terms of analytical quality factors, with the limits of detection ranging from 0.25 to 3.4 ng/mL [70].

3.2. Magnetic Extraction

Magnetic separation has gained popularity as an extraction method in recent years [101]. It relies on the application of a magnetic field and the rate of magnetization of the extracted phase to separate analytes from complex mixtures. Magnet-assisted microextraction techniques, including those involving ILs, have emerged as a promising approach. For instance, pure liquid magnetic ILs have been rapidly extended to magnet-assisted microextraction operations, providing an alternative to solid magnetic particles that tend to agglomerate. Magnetic ILs are ILs that contain one or more paramagnetic components in their chemical makeup, enabling them to exhibit magnetic properties while maintaining some of the distinctive physicochemical characteristics of ILs [102,103].

Magnetic ILs with iron(III)-based anions, such as tetrachloroferrate(III) ([FeCl₄]⁻) or bromoferric trichloride(III) ([FeCl₃Br]⁻), have been predominantly used in various applications. For example, Wang et al. developed a novel sample pretreatment technique called magnetic MSPD-magnetic IL and used it to extract triazine herbicides from oilseeds. In this method, liquid fat samples were subjected to microextraction via DLLME using [C₄MMIM][FeCl₄] as the magnetic IL. Magnetic separation was employed to streamline the separation process, resulting in intra-day and inter-day relative standard deviations ranging from 2.1% to 6.8%. The recoveries of the analytes ranged from 88.6% to 106.3%. This approach offers an efficient and effective means of extracting triazine herbicides from oilseeds [68].

Furthermore, magnetic ILs can be directly incorporated into matrix solid-phase dispersion practices. For instance, Chatzimitakos et al. designed an experimental approach for the identification of various pesticide residues in raw lettuce and vegetables based on matrix solid-phase dispersion using magnetic ILs. This innovative method eliminated the need for solid dispersion materials or co-sorbents, which facilitated its combination with the matrix, and the hydrophobicity of magnetic ILs can simplify the separation and recovery process. The relative recoveries of pesticide residues in samples of cucumber, potato, and courgette ranged from 92% to 105%. This approach significantly streamlines the MSPD process by eliminating the requirement for co-sorbents or solid dispersion ingredients, making it a more efficient and environmentally friendly extraction technique [79].

3.3. Material Modification

The use of ILs in microextraction settings is subject to two common limitations [104,105]. On one hand, the viscosity of ILs can impede extraction kinetics and complicate their integration into liquid chromatography systems. On the other hand, their low volatility poses a challenge for compatibility with gas chromatography, necessitating the development of specialized interface solutions. Additionally, the inherent characteristics of ILs render them theoretically incompatible with certain specialized techniques, such as evaporative light-scattering detectors.

Material modification is a technique that involves altering the original properties of a material through physical and chemical means, thereby imparting different characteristics to the material [61,92,99]. Due to their superior physical properties and design flexibility for structural purposes, ILs are commonly employed in material modification processes [71–76,80–82,106]. In modes such as solid-phase extraction, solid-phase microextraction, and dispersive micro-solid-phase extraction, IL-modified materials are currently utilized as extraction phases. For example, Galán-Cano et al. developed the dispersive micro-solid-phase extraction mode for the extraction of organophosphorus pesticides from water samples using an ionic solution (methylimidazolium hexafluorophosphate)-modified $[\text{SiO}_2@\text{MIM-PF}_6]$ as a sorbent [71]. The average recovery was 94%, and the lowest detection limit was 0.3 g/L. Fang et al. synthesized an innovative ion-liquid-functionalized silica by chemically bonding methylimidazolium IL to the silica surface. The ion-liquid-functionalized silica was utilized as an adsorbent in solid-phase extraction processes for the separation of 12 sulfonylurea herbicides. The average recoveries of each analyte in water samples and soil samples ranged from 53.8% to 118.2% and from 60.9% to 121.3%, respectively [107].

IL-modified materials can also be employed in magnetic extraction procedures [108]. For instance, Gubin et al. developed a magnetic absorbent based on magnetite nanoparticles modified with an IL [76]. The pollution levels of soil, groundwater, river water, and bottom sediment due to 2,4-DB and its metabolites were assessed using a combination of magnetic solid-phase extraction (MSPE) and gas chromatography–mass spectrometry (GC-MS). In addition to their role in extracting trace pesticide residues from laboratory samples, ion-liquid-modified materials can also be employed for the recovery and reuse of agricultural wastewater. Zulfiqar et al. 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% [106].

4. Types of ILs Based Pesticides

The diverse combinations of anions and cations in pesticides offer a wide range of potential qualities, providing ample opportunities for pesticide development. Traditionally, the isolation of pesticides involved the mono-ionization of the active molecule present in the original active ingredient, with the other ion in the system typically serving to support the characteristics. As research progressed, dual-ion system ILs emerged, which can be categorized as follows: (1) a system with two anions and cations with diverse effects (such as herbicidal, antibacterial, or repellent properties); and (2) a system with one cation and multiple anions with synergistic effects. Pesticides with various biological functions (e.g., insecticides, fungicides, herbicides) can also be ionized to form an IL system that acts in an integrated manner [15,109]. This innovative approach has the potential to revolutionize the pesticide industry and lead to more sustainable and effective agricultural practices. Figure 2 describes the important journey of ILs in the pesticide sector.

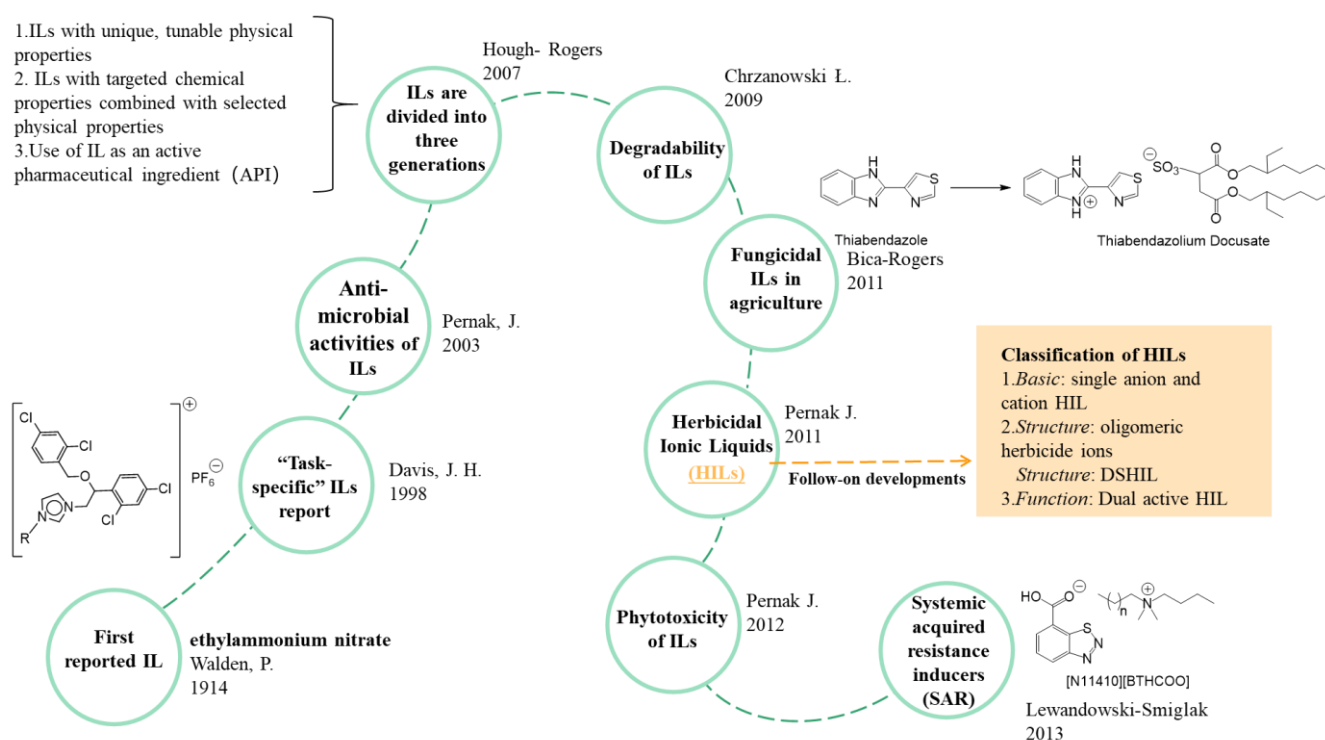


Figure 2. The developmental history of pesticides based on ILs [15,110–117].

4.1. Herbicidal ILs (HILs)

HILs are developed from various well-known herbicides, including compound such as 2,4-dichlorophenoxyacetic acid (2,4-D) [118], 4-chloro-2-methylphenoxyacetic acid (MCPA) [119,120], 2-(4-chloro-2-methylphenoxy)propanoic acid (MCP) [121], glyphosate [120], clopyralid [122], dicamba [123,124], sulfonyleurea derivatives [125,126], and so on. In the initial stages of HIL development, an “anti-crystalline engineering” approach was employed, where cations were selected to enhance salt mobility and prevent crystallization [127]. In subsequent stages, the focus shifted to improving herbicidal activity and modifying the physical properties of the compounds, such as water solubility and adhesion. The variation of cations significantly affects the overall physical properties of ILs. Numerous studies have reported that the alkyl chain length of cations influences the adhesive properties of ILs [128], while the hydrophilicity/hydrophobicity of cations affects the solubility of ILs [129]. A new direction in HIL design involves introducing new biological functions into HILs by adding cations to create a dual-active HIL system [130]. Additionally, researchers have combined herbicidal anions with different herbicidal activities using the same cation to form a double-salt HIL (DSHIL) system with synergistic effects [125]. Recent studies have also delved into synthesizing HILs with growth regulators [131], glyphosate [132], and cinnamic acid [133] as key components.

4.1.1. Single Anion and Cation HILs

The simplest form of herbicidal ionic solutions consists of a single pair of anions and cations, which are structurally uncomplicated and typically serve a single herbicidal function. In this type of system, the anion usually possesses herbicidal activity, while the cation plays a role in modifying the final physical properties of the ionic solution. A unique subtype of these single anionic HILs is known as a dicationic IL, where the cation has two positively charged centers and can thus bind with two anions [134]. This characteristic allows for a more complex interaction between the cation and anion. For instance, Niu et al. devised a dicationic IL containing 2,4-D with potent herbicidal activity, surpassing that of 2,4-D against two common broadleaf weeds. This innovative IL effectively decreased

the volatility and water solubility of 2,4-D, resulting in a substantial increase in weed fresh weight inhibition, ranging from 74.46% to 84.2%. These findings underscore the promising potential of dicationic ILs in augmenting the herbicidal efficacy of active compounds [135].

4.1.2. Double-Salt HILs

The HIL with double salts is composed of compounds that form a charge-balanced system, encompassing three or more ions [136]. Since the first report of double-salt HILs in 2017, researchers have shown increasing interest in exploring this field [125,132]. Various combinations of double-salt HILs have been developed, including those based on synthetic herbicidal agents such as 4-chloro-2-methylphenoxyacetic acid [131,137,138] and dicamba [132]. In-depth studies on dicamba-based double-salt HILs have revealed synergistic effects between the two herbicidal ions in the double-salt HIL, making them more efficient than single-component systems. Furthermore, it has been observed that herbicides containing both active ingredients can effectively inhibit the development of resistance in target plants compared to conventional herbicides [139,140]. Researchers have designed double-salt HILs with multiple herbicides, each having the same mechanism of action, and found that their herbicidal activity surpasses that of commercially available formulations and most tested ILs containing only one bioactive anion. These novel double-salt HILs have demonstrated enhanced weed control in various species, making them valuable tools in agriculture and weed management. Rzemieniecki et al. reported combining three herbicides with similar mechanisms of action (4-chloro-2-methylphenoxyacetic acid, dicamba, and mecoprop-P) to create a dual-salt HIL. Each individual herbicide in this combination operates with the same mechanism of action. The study found that the weed control activity of this formulation exceeded that of commercially available formulations and most tested ILs containing only a single biologically active anion [138].

4.1.3. Dual-Activity HILs

Dual-activity HILs refer to a category of HILs in which both the anions and cations exhibit distinct biological activities. This classification can be further subdivided into two types. Firstly, the anions and cations have separate biological activities, typically with the anions possessing herbicidal activity and the cations having secondary biological activities [141–144]. Secondly, both the anions and cations individually demonstrate herbicidal activities. For the first type of dual-activity HILs, Ciarka et al. reported four new types of HIL composed of the anion (2-chloro-6-(1-methylphenoxy)acetate) and cation (N-alkyl-N,N-dimethylphenoxyammonium). The coexistence of antimicrobial domifen derivatives and herbicidal 4-chloro-2-methylphenoxyacetate in the IL results in a synergistic effect on weed control and antibacterial activity. This synergy leads to an improved herbicidal efficacy against cornflower (*Centaurea cyanus* L.) compared to individual compounds [145].

In the case of the second type of HILs, Syguda et al. previously developed dicamba as a surface-active cation containing an ester substituent. The cation was subsequently paired with herbicidal anions, including 4-chlorophenoxyacetate, 2, 4-dichlorophenoxyacetate, 4-chloro-2-methylphenoxyacetate, 3-(4-chloro-2-methylphenoxy)propionate and 3,6-dichloropyridine-2-carboxylates. This engineered dual-action HIL facilitates the continuous release of respective herbicides into the soil, thereby prolonging their effectiveness and minimizing the environmental impact of compound exposure. Ultimately, this innovative approach demonstrated superior weed control effects. The design and development of these dual-activity HILs signify significant progress, offering promising prospects for the innovation and efficacy of sustainable herbicides in agricultural practices [146].

4.2. Food Repellents (Deterrents)

Controlling pest impacts on crop yields while minimizing the use of highly toxic chemicals is essential to maintain ecological balance and reduce the unintended consequences of pest control. Using low-level pest repellents or deterrents is an important

approach to achieve this [147]. ILs can play a significant role in this context, not only for extracting plant secondary metabolites with deterrent effects but also by designing cations within ILs that possess deterrent properties. ILs containing antifeedants may incorporate natural anions, such as lactate [148], fatty acids salts [149], or abietic acid sodium salt [150]. Additionally, compounds based on artificial sweeteners have shown effective deterrent activity. Researchers have found that ILs with didecyl dimethyl ammonium cations can exhibit deterrent activity that surpasses that of standard azadirachtin. By using sweet anions (acesulfamate and saccharinate) and naturally occurring anions (lactate and pyroglutamate), and gemini surfactant cations, researchers have synthesized new quaternary bis(ammonium) salt ILs. The ILs showed good deterrent activity against *Trogoderma granarium* [116]. These findings highlight the potential of ILs as an environmentally friendly and efficient approach to pest control through deterrence, thereby contributing to the promotion of more sustainable agricultural practices.

4.3. Plant Growth Regulators

Plant growth regulators (PGRs), which are natural or synthetic plant hormones, have the capacity to influence plant development by initiating or altering various life processes, including flowering and fruit formation. Building on the widespread use of ILs in pharmaceutical applications, researchers have explored the concept of ionizing plant growth regulators and designing them as ILs [151,152]. Indole-3-butyric acid (IBA) is a growth factor used to stimulate rapid rooting and plug growth in numerous trees, shrubs, and plants. Researchers, inspired by the enhanced biological activity observed when converting herbicides into ILs, successfully transformed IBA into an IL form. The IL version not only retained its biological activity but also demonstrated an increase of approximately 10–20% in lettuce biomass upon application. Furthermore, the nutrient content of trace and macronutrients was found to be higher, resulting in a more sustainable lettuce product for consumers [152,153].

In terms of plant growth regulator considerations, ensuring extended shelf-life is paramount, particularly when substances used during cotton growth can be easily washed away by rain, rendering them ineffective. Tang et al. illustrated sustained activity in controlling the lateral branch length and height of cotton plants through the development of an IL based on mepiquat chloride [153]. This resulted in a more compact cotton plant structure compared to cotton treated with a non-IL based on mepiquat chloride. Drawing from the applications and studies of ILs as growth regulators, researchers, such as Weigt et al., have begun exploring the possibility of using ILs for in vitro plant culture. Microspore embryogenesis (ME) is crucial in agricultural breeding for obtaining pure plants, often necessitating external growth factors for induction. In their work with wheat anthers, they found that ILs similar to 2,4-D improved the efficiency of EM induction and plant regeneration. Notably, Weigt et al. observed plant regeneration in genotypic recalcitrance, previously thought to be incapable of undergoing such regeneration [154]. Despite the success, the mechanism behind the role of ILs in inducing ME and promoting plant regeneration remains unclear, calling for further investigation in this area.

4.4. ILs for Microbial Control

The study conducted by Pernak et al. provided valuable insights into the connection between the cations found in certain ILs and the antibacterial activity of the resulting salts. Specifically, the research shed light on how the length of the cationic alkyl chains influences the biological activity of the tested compounds [155]. This study marked the inception of investigations into ILs with antimicrobial properties. Since then, the exploration of ILs with antimicrobial activity has expanded into various domains, encompassing food preservation, wood processing, medicine and pharmaceuticals, as well as agricultural sterilization and disinfection. This research has diversified and extended the potential applications of ILs in combating microbial threats and preserving the integrity of various products and materials.

4.4.1. Antibacterial Activity

One of the confirmed explanations for the heightened antibacterial efficacy of IL lies in its ability to augment the permeability of biofilms [156,157]. Recent investigations into IL bactericides in agriculture have concentrated on two primary avenues: the integration of ions sourced from natural elements to mitigate the inherent toxicity of IL, and ILs with dual biological functionalities.

Regarding the first approach, the inclusion of anions such as mandelate or proline typically does not compromise the bactericidal potency of common cations such as didecyltrimethylammonium, benzalkonium, and domiphen. Furthermore, this incorporation renders them more biocompatible, facilitating their absorption by bacteria [158].

In the second direction, ILs that possess combined antibacterial and antifungal attributes have been subject to extensive scrutiny. For instance, long-chain 3-alkyl carbonate-functionalised 1-methylimidazolium chloride, as well as long-chain 3-alkyl carbamoyl-substituted 1-methylimidazolium and pyridinium bromide, exhibit both antibacterial and antifungal activities, alongside their surfactant properties. Similarly, salicylaldehyde-substituted imidazolium chloride and poly(1-norbornylmethylene-3-methylimidazolium hexafluorophosphate) have demonstrated substantial efficacy as bactericides and fungicides [159,160].

4.4.2. Antifungal Activity

In the field of agriculture, fungal diseases represent a more significant threat compared to bacterial ailments, prompting a burgeoning interest in the antifungal capabilities of ILs [161]. The groundbreaking work of Davis et al. brought forth the notion of amalgamating ILs with antifungal ions. Miconazole, a widely employed pharmacologically active substance for treating fungal infections on the skin or mucous membranes, was utilized in the synthesis of ILs. This process involved the reaction of miconazole (containing an imidazolium ring in its structure) with an alkylate, followed by an exchange of the iodide anion with $[PF_6]^-$ anion, resulting in the deliberate creation of the first documented IL incorporating antifungal ions [110]. Bica's research delved further into the application of fungicidal ILs in agriculture, employing thiabendazole docusate and imidazolium docusate for in vitro evaluations against 10 plant pathogenic fungi. Not only did the ILs retain their antifungal potency, but they also exhibited enhanced efficacy against various potato tuber pathogens in comparison to commercially available precursors [114]. In terms of their deterrent properties, Kaczmarek et al. developed acetylsulphonate ILs with deterrent properties against *Trogoderma granarium* (larvae) and *Tribolium confusum* (beetles), displaying inhibitory activity against micro-organisms [161]. Lactate serves as an exceptionally effective antibacterial and antifungal agent against *Streptococcus mutans* and *Candida albicans*, while Cybulski et al. identified a novel long alkyl chain quaternary ammonium lactate-based IL with repellent properties [162]. Piotrowska et al. discovered a dicamba-based IL with antibacterial activity against *Pseudomonas putida*, inducing resistance [163]. The group of Stolte proposed a fusion of antimicrobial activity and systemic acquired resistance (SAR) inducers, wherein their antiviral action is not exerted directly on the virus but rather stimulates resistance in the plant, enabling the plant to independently resist infection after activation [164].

4.4.3. IL with Inherently Antifungal and Bacterial Properties

The diverse combination of anions and cations present in ILs contributes to their chemical versatility, leading to the possibility that some non-pesticide ILs may possess antibacterial, antifungal, or herbicidal properties. The incorporation of ions with herbicidal attributes in the synthesis of HILs was previously discussed in our earlier section. In terms of bacterial inhibition, imidazolium, pyridinium, pyrrolidinium, piperidinium, ammonium, and other ILs have exhibited capabilities in inhibiting both bacteria and fungi. In the context of food production, certain ILs have been identified to impede the growth

of yeast. For instance, 1-alkoxymethyl-X-dimethylaminopyridinium-base ionic liquids were found to hinder the growth and ethanol production of the model yeast *Saccharomyces cerevisiae* in the hydrolysis products of pretreated lignocellulosic biomass. Conversely, the addition of small quantities of 1-ethyl-3-methylimidazolium acetate prompted a metabolic shift from respiration to fermentation (ethanol production), while higher concentrations of the ILs inhibited yeast growth. In the field of wood protection, ILs can serve as wood preservatives against fungi and molds, with their antifungal efficacy being influenced by the specific cation and anion composition of the salt molecule. Pyridinium-based ILs examined by Stasiewicz et al. demonstrated activity against *Coniophora puteana* and *Trametes versicolor*, with their effectiveness against the tested fungi being linked to the position of the substituent in the pyridinium ring [165].

The findings from the research conducted by Zabielska-Matejuk et al. highlighted the dependence of ammonium and triazolium-based ILs on their cationic and anionic structure for their antifungal properties, with the ammonium IL featuring a nitrite anion demonstrating a more potent fungal inhibition compared to ammonium nitrate. Additionally, imidazolium chloride derivatives (such as 1-alkyl-3-benzylloxymethylimidazolium, 3-alkoxymethyl-1-benzylimidazolium, and 1-alkyl-3-(3-phenyl-propoxymethyl)imidazolium chlorides) displayed activity against *Coniophora puteana*, *Trametes versicolor*, and *Chaetomium globosum* in agar dilution tests, with their antifungal effects contingent upon the chain length and the hydrophobicity. Conversely, imidazolium compounds containing alkoxymethyl and cycloalkoxymethyl substituents with various anions (formates, acetates, propionates) exhibited activity against *Coniophora puteana*, *Trametes versicolor*, *Chaetomium globosum*, *Aspergillus niger*, and *Penicillium funiculosum*, with their antifungal effect being correlated to the number of alkyl chains and cycloalkyl rings within the IL molecule [166].

4.5. Plant Immunity Inducers (SAR)

Systemic acquired resistance (SAR) serves as the natural defense mechanism employed by plants against a broad spectrum of pathogens [167]. However, the excessive and unscientific use of agrochemicals has hastened the development of pathogen resistance, rendering these chemicals ineffective and exacerbating the misuse of pesticides. The establishment of plant resistance can curtail the need for pesticides and often offers longer-lasting protection, presenting a more eco-friendly and safer approach to plant defense. Among the most effective SAR inducers are derivatives of benzothiadiazole (BTH) [168]. Regrettably, the current commercially available SAR inducer BTH has limited applicability in agriculture, primarily due to its exceedingly low solubility in water.

Notably, Smiglak et al. have enhanced the physical properties of the neutral BTH by converting it into its carboxylate form and pairing it with cations. The outcome of this modification is a substantial increase in the water-solubility of the compounds, rising from 0.007 g/L to over 10 g/L, while maintaining or even surpassing the efficacy of these ILs in inducing plant resistance [169]. Additionally, some researchers have endeavored to enhance the biodegradability and mitigate the toxicity of these compounds by designing IL-based plant systemic acquired resistance (SAR) inducers [163,170].

5. Applications in Pesticide Delivery

By employing various combinations of cations and anions, ILs can undergo structural modifications and be cross-linked with different chemical groups, thus enabling them to function as trigger-release carriers. The development of IL-based drugs, renowned for their exceptional biocompatibility and long-term stability, has shown promise as effective delivery vehicles [171,172]. This has led to frequent reports on their pharmaceutical applications and associated studies, suggesting a broad spectrum of prospects for exploring their potential in pesticide controlled release as well. Yang et al. pioneered the preparation of gelatin cross-linked core-shell microcapsules by dissolving avermectin as a functional additive with phosphorus-containing IL. This innovative approach not only endowed the

microcapsules with slow-release properties but also enhanced the solubility of avermectin, resulting in exceptional insecticidal activity [173]. Furthermore, Zhang et al. developed a novel pre-drug IL-thiabendazole, designed to respond to water and enzymes as triggers for the release of thiabendazole. This pre-drug was synthesized by coupling IL 1-methyl-4-formyl pyridinium iodide via hemiacetal with derivatized thiabendazole, using chloroacetyl chloride and ethanolamine. The results of this study highlighted the pre-drug's significant responsiveness to various pH levels, humidity, and enzymatic conditions, in addition to its lower toxicity to aquatic organisms [174].

6. Biodegradability and Toxicity

6.1. Toxicity

ILs have long been lauded as “green solvents,” implying that they are entirely non-toxic and benign. However, as research has advanced, it has been suggested that certain ILs exhibit residual toxicity and biodegradability that do not align with initial expectations, potentially having adverse implications for the environment [175,176].

Before delving deeper into this issue, it is crucial to clarify that ILs constitute a rather broad classification. While these solutions share certain characteristics, the diverse array of anion and cation types, along with the variety of chemical structures, can result in considerable variation among different ILs. Consequently, discussions regarding the toxicity and degradability of ILs are complex, and understanding the toxicity (including ecotoxicity) of each IL and predicting the broader correlation between the toxic properties and structure of salts present a fundamental challenge within the field of IL science today.

The toxicity of ILs manifests in two primary ways: firstly, through their capacity to destroy living cells, and secondly, through their impact on the proliferative activity of pathogenic micro-organisms [177]. Several studies have identified various factors influencing the toxicity of bioactive ILs, including (i) the “alkyl side-chain effect” in the cation structure, (ii) the number of functional groups on the cation side chain, (iii) the nature of the anion, encompassing factors such as hydrophobicity or stability, and (iv) the nature of the cation, such as lipophilicity [178].

Presently, certain gaps exist in the research concerning the toxicological mechanisms of ILs in agrochemical products. These gaps include the lack of exploration into the toxicological effects of ILs on the final agrochemical product as a whole, with excessive focus directed toward the toxicological effects of ILs on individual pesticide active ingredients. Additives in pesticide products generally outweigh the pesticide active ingredients, and despite the potential reduction in additive use due to IL application, complete avoidance of additives remains unfeasible [179]. Nevertheless, few studies have illuminated the impact of ILs on the toxicity of additives and whether ILs alter the combined toxicity between pesticide prodrugs and additives. Addressing this aspect could emerge as a crucial focus area for the future elucidation of toxicological mechanisms pertaining to ionic solution pesticides.

6.2. Biodegradation

The biodegradability of imidazolium cations was initially examined by Czerwicka et al. in 2007, providing insights into its potential environmental impact [180]. Pernak et al. continued this research in 2014, assessing the biodegradability of raw ionic liquids in relation to the primary biodegradation efficiency of both cations and anions [181]. To assess the biodegradability of ILs, researchers commonly employ the OECD 301 D or F test, which entails measuring dissolved oxygen levels or oxygen consumption in bacterial media over a 28-day period. However, the lack of uniformity in the bacterial flora of activated sludge used in these tests poses a challenge, as it may not fully reflect the actual degradation process. Consequently, the establishment of uniform standards and novel evaluation methods remains a pressing concern in this field.

Recent studies have provided further insights into this matter. Markiewicz et al. investigated the degradability of IL-based plant systemic acquired resistance (SAR)

inducers [171], finding that the synthesized compounds exhibited low degradability. Additionally, Marta Woźniak-Karczewska et al. examined the transport of ILs in agricultural soils. They designed three ILs—[Bet][2,4-D], [C₁₂Bet][2,4-D], and [CAPBet][2,4-D]—to assess the effects of increasing the length of the cationic alkyl chain on the hydrophobicity of the ILs. Their study revealed that these ILs did not display a significant increase in toxicity compared to the original betaine toxicity. Notably, they observed that cations and anions adsorbed independently of each other, suggesting that IL cations and anions undergo distinct chemical–physical processes during soil degradation [182].

7. Summary and Outlook

Certainly, the current research on ILs in the agricultural sector encounters several challenges, which include: (i) Limited understanding of the mechanism of action of IL-based pesticides, including the uncertainties regarding the differential effects between IL and the original compound, and potential alterations in the mechanism of action following ionic liquidization. (ii) Ongoing nascent research on ILs containing natural ingredients, indicating the need for further exploration to comprehend their potential applications in agriculture. (iii) Insufficiently defined criteria and understanding of the toxicology and biodegradability of ILs, emphasizing the necessity for comprehensive research to establish relevant standards and elucidate the underlying mechanisms. (iv) Overlooking the role of additives in toxicological studies on IL-based pesticides, suggesting the importance of considering their impact for a more comprehensive understanding of the overall toxicity.

Despite these challenges, it is important to recognize the vast scope of applications and the research value of ILs in the agricultural domain. A promising direction for future IL research in agriculture is to explore the impact of ILs on pesticide delivery. This area is particularly intriguing due to the existing research on the involvement of ILs in pharmaceutical delivery and the close relationship between various nanomaterials involved in pesticide release and ILs. Moreover, the regulation of light and pH in the controlled release of pesticides holds relevance to the application of ionic solutions in the agricultural context.

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Abbreviations

ILFF-SPE	Ionic-liquid-based foamflotation solid-phase extraction
SB- μ -SPE	Stir-bar supported membrane protected micro-solid-phase extraction
D- μ SPE	Dispersive micro-solid-phase extraction
HS-SPME	Headspace solid-phase microextraction
DI-SPME	Direct immersion solid-phase microextraction
ILMB-ME	Ionic liquid magnetic bar microextraction
MEPS	Microextraction by packed sorbent
PT-SPE	Pipette-tip solid-phase extraction
ILE-MSPE	Ionic-liquid-based effervescence-enhanced magnetic solid-phase extraction
2,4-DB	Butyl 2,4-dichlorophenoxyacetate

Bet	Betaine
[N ⁸⁸⁸¹][PF ₆]	Methyltriethylammonium bis(trifluoromethylsulfonyl)imide
[C ₆ MIM][BF ₄]	1-Hexyl-3-methylimidazolium tetrafluoroborate
[C ₆ MIM][PF ₆]	1-Hexyl-3-methylimidazolium hexafluorophosphate
[C ₄ MIM][PF ₆]	1-Butyl-3-methylimidazolium hexafluorophosphate
[N ⁴⁴⁴⁴][PF ₆]	Tetrabutylammonium hexafluorophosphate
[MCOOC ₂ MIM][NTf ₂]	3-Methyl-1-(ethoxycarbonylmethyl) imidazolium bis(trifluoromethylsulfonyl)-imide
[C ₄ C ₄ MIM][Br]	1,3-Dibutylimidazolium bromide
[C ₄ C ₅ MIM][Br]	1-Pentyl-3-butylimidazolium bromide
[C ₄ C ₆ MIM][Br]	1-Hexyl-3-butylimidazolium bromide
[C ₄ (C ₄ MIM) ₂][Br ₂]	1,1'-(Butane-1,4-diyl)bis(3-butylimidazolium) bromide
[C ₄ (MIM) ₂][Br ₂]	1,1'-(Butane-1,4-diyl)bis(3-methylimidazolium) bromide
[C ₄ MMIM][FeCl ₄]	1-Butyl-3-methylimidazolium tetrachloroferrate
[C ₄ MIM][BF ₄]	1-Butyl-3-methylimidazolium tetrafluoroborate
[1-NA][FeCl ₄]	4-Methylbenzenaminium tetrachloroferrate (III)
[4-MA][FeCl ₄]	1-Naphthylammonium tetrachloroferrate (III)
SiO ₂ @MIM-PF ₆	Methylimidazolium-hexafluorophosphate functionalized silica
[C ₈ MIM][Br]	1-Methyl-3-octyl-imidazolium bromide
[C ₁₂ MIM][Br]	1-Methyl-3-undecyl-imidazolium bromide
[C ₁₈ MIM][Br]	1-Methyl-3-octadecyl-imidazolium bromide
[C ₁₆ MIM][NTf ₂]	1-Hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[VBIMC ₁₆][NTf ₂]	1-Vinylbenzyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide
[VBIMC ₁₀ OH][NTf ₂]	1-Vinyl-3-(10-hydroxydecyl)imidazolium bis[(trifluoromethyl)sulfonyl]imide
[(VBIM) ₂ C ₁₂][2][NTf ₂]	1,12-Di(3-vinylbenzylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide
[(VB(BIM)) ₂ C ₁₂][2][NTf ₂]	1,12-Di(3-vinylbenzyl(benzimidazolium))dodecane bis[(trifluoromethyl)sulfonyl]imide
[VIMC ₁₂][NTf ₂]	1-Vinyl-4-dodecylimidazolium bis(trifluoromethanesulfonyl)imide
[(VIM) ₂ C ₁₂][2][NTf ₂]	1,12-Di(3-vinylbenzylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide
[VBIMC ₈][NTf ₂]	1-Vinylbenzyl-3-octylimidazolium bis[(trifluoromethyl)sulfonyl]imide
Fe ₃ O ₄ @SiO ₂ -MIM	Magnetite nanoparticles modified with 1-carboxymethyl-3-methylimidazolium chloride
Fe ₃ O ₄ @SiO ₂ -MMIM	Magnetite nanoparticles modified with 1,3-dimethylimidazolium-2-carboxylate
Fe ₃ O ₄ @SiO ₂ -C ₄ MIM	Magnetite nanoparticles modified with 1-butyl-3-methylimidazolium-2-carboxylate
[C ₈ MIM][BF ₄]	1-Octyl-3-methylimidazolium tetrafluoroborate
[C ₈ MIM][PF ₆]	1-Octyl-3-methylimidazolium hexafluorophosphate
[P ⁶⁶⁶¹⁴][Gd(III)(hfacac) ₄]	Trihexyl(tetradecyl)phosphonium tetrakis(hexafluoroacetylaceto)gadoliniate(iii)
[P ⁶⁶⁶¹⁴][Dy(III)(hfacac) ₄]	Trihexyl(tetradecyl)phosphonium tetrakis(hexafluoroacetylaceto)dysprosate(iii)
[P ⁶⁶⁶¹⁴][Co(II)(hfacac) ₃]	Trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)cobaltate(ii)
[P ⁶⁶⁶¹⁴][Mn(II)(hfacac) ₃]	Trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)manganate(ii)
[P ⁶⁶⁶¹⁴][Ni(II)(hfacac) ₃]	Trihexyl(tetradecyl)phosphonium tris(hexafluoroacetylaceto)nickelate(ii)
zIL@T@SiO ₂	1-Vinyl-3-(butyl-4-sulfonate) imidazolium-thiol-SiO ₂
IL@T@GO	1-Allyl-3-(perfluorobenzyl)-imidazolium bromide-thiol-graphene oxide
Fe ₃ O ₄ @Na ₂ CO ₃ @[C ₆ MIM]	Ionic-liquid-based magnetic effervescent tablet composed of magnetic nanoparticles (Fe ₃ O ₄), sodium carbonate (Na ₂ CO ₃) as an alkaline source, and an ionic liquid ([C ₆ MIM][PF ₆])

References

- Gavrilescu, M. Fate of pesticides in the environment and its bioremediation. *Eng. Life Sci.* **2005**, *5*, 497–526. <https://doi.org/10.1002/elsc.200520098>.
- Rajan, S.; Parween, M.; Raju, N.J. Pesticides in the hydrogeo-environment: A review of contaminant prevalence, source and mobilisation in India. *Environ. Geochem. Health* **2023**, *45*, 5481–5513. <https://doi.org/10.1007/s10653-023-01608-6>.
- Costanzini, S.; Teggi, S.; Bigi, A.; Ghermandi, G.; Filippini, T.; Malagoli, C.; Nannini, R.; Vinceti, M. Atmospheric dispersion modelling and spatial analysis to evaluate population exposure to pesticides from farming processes. *Atmosphere* **2018**, *9*, 38.
- Ma, J.; Hong, X. Application of ionic liquids in organic pollutants control. *J. Environ. Manag.* **2012**, *99*, 104–109. <https://doi.org/10.1016/j.jenvman.2012.01.013>.
- Hayes, R.; Warr, G.G.; Atkin, R. Structure and nanostructure in ionic liquids *Chem. Rev.* **2015**, *115*, 6357–6426.
- Kaur, G.; Kumar, H.; Singla, M. Diverse applications of ionic liquids: A comprehensive review. *J. Mol. Liq.* **2022**, *351*, 118556. <https://doi.org/10.1016/j.molliq.2022.118556>.
- Hallett, J.P.; Welton, T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508–3576. <https://doi.org/10.1021/cr1003248>.
- Nasirpour, N.; Mohammadpourfard, M.; Zeinali Heris, S. Ionic liquids: Promising compounds for sustainable chemical processes and applications. *Chem. Eng. Res. Des.* **2020**, *160*, 264–300. <https://doi.org/10.1016/j.cherd.2020.06.006>.
- Procopio, D.; Siciliano, C.; Trombino, S.; Dumitrescu, D.E.; Suciu, F.; Di Gioia, M.L. Green solvents for the formation of amide linkages. *Org. Biomol. Chem.* **2022**, *20*, 1137–1149. <https://doi.org/10.1039/D1OB01814K>.
- Zhang, C.; Qu, P.; Zhou, M.; Qian, L.; Bai, T.; Jin, J.; Xin, B. Ionic liquids as promisingly multi-functional participants for electrocatalyst of water splitting: A review. *Molecules* **2023**, *28*, 3051. <https://doi.org/10.3390/molecules28073051>.
- Lei, Z.; Chen, B.; Koo, Y.-M.; MacFarlane, D.R. Introduction: Ionic liquids. *Chem. Rev.* **2017**, *117*, 6633–6635. <https://doi.org/10.1021/acs.chemrev.7b00246>.
- Ahmed, M.; Rao, S.S.; Filippov, A.; Johansson, P.; Shah, F.U. Aromatic heterocyclic anion based ionic liquids and electrolytes. *Phys. Chem. Chem. Phys.* **2023**, *25*, 3502–3512. <https://doi.org/10.1039/D2CP05272E>.
- Shukla, M.K.; Tiwari, H.; Verma, R.; Dong, W.-L.; Azizov, S.; Kumar, B.; Pandey, S.; Kumar, D. Role and recent advancements of ionic liquids in drug delivery systems. *Pharmaceutics* **2023**, *15*, 702. <https://doi.org/10.3390/pharmaceutics15020702>.
- Veríssimo, N.V.; Vicente, F.A.; de Oliveira, R.C.; Likoza, B.; Oliveira, R.P.d.S.; Pereira, J.F.B. Ionic liquids as protein stabilizers for biological and biomedical applications: A review. *Biotechnol. Adv.* **2022**, *61*, 108055. <https://doi.org/10.1016/j.biotechadv.2022.108055>.
- Hough, W.L.; Smiglak, M.; Rodríguez, H.; Swatloski, R.P.; Spear, S.K.; Daly, D.T.; Pernak, J.; Grisel, J.E.; Carliss, R.D.; Soutullo, M.D.; et al. The third evolution of ionic liquids: Active pharmaceutical ingredients. *New J. Chem.* **2007**, *31*, 1429–1436. <https://doi.org/10.1039/B706677P>.
- Cho, C.-W.; Pham, T.P.T.; Zhao, Y.; Stolte, S.; Yun, Y.-S. Review of the toxic effects of ionic liquids. *Sci. Total Environ.* **2021**, *786*, 147309. <https://doi.org/10.1016/j.scitotenv.2021.147309>.
- Ten, A.; Zazybin, A.; Zolotareva, D.; Dauletbaev, A.; Rafikova, K.; Yu, V.; Giner, B. Ionic liquids in agrochemistry. *Curr. Org. Chem.* **2020**, *24*, 1181–1195. <https://doi.org/10.2174/1385272824999200608135522>.
- Murador, D.C.; de Souza Mesquita, L.M.; Vannuchi, N.; Braga, A.R.C.; de Rosso, V.V. 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.* **2019**, *26*, 25–34. <https://doi.org/10.1016/j.cofs.2019.03.002>.
- Passos, H.; Freire, M.G.; Coutinho, J.A.P. Ionic liquid solutions as extractive solvents for value-added compounds from biomass. *Green Chem.* **2014**, *16*, 4786–4815. <https://doi.org/10.1039/C4GC00236A>.
- Tang, B.; Bi, W.; Tian, M.; Row, K.H. Application of ionic liquid for extraction and separation of bioactive compounds from plants. *J. Chromatogr. B* **2012**, *904*, 1–21. <https://doi.org/10.1016/j.jchromb.2012.07.020>.
- Cláudio, A.F.M.; Ferreira, A.M.; Freire, M.G.; Coutinho, J.A.P. Enhanced extraction of caffeine from guaraná seeds using aqueous solutions of ionic liquids. *Green Chem.* **2013**, *15*, 2002–2010. <https://doi.org/10.1039/C3GC40437D>.
- Carciochi, R.A.; Dieu, V.; Vauchel, P.; Pradal, D.; Dimitrov, K. Reduction of environmental impacts of caffeine extraction from guarana by using ultrasound assistance. *Food Bioprod. Process.* **2021**, *127*, 266–275. <https://doi.org/10.1016/j.fbp.2021.02.014>.
- Hassan, S.A.; Gad, S.F.; Abdu-Allah, H.H.M.; Qayed, W.S.; AbouElmagd, S.A.; Ibrahim, E.A. Ionic liquid of ketoprofen-piperine modulates the pharmaceutical and therapeutic characters of ketoprofen. *Int. J. Pharm.* **2022**, *620*, 121724. <https://doi.org/10.1016/j.ijpharm.2022.121724>.
- Cao, X.; Ye, X.; Lu, Y.; Yu, Y.; Mo, W. Ionic liquid-based ultrasonic-assisted extraction of piperine from white pepper. *Anal. Chim. Acta* **2009**, *640*, 47–51. <https://doi.org/10.1016/j.aca.2009.03.029>.
- Yang, L.; Wang, H.; Zu, Y.-g.; Zhao, C.; Zhang, L.; Chen, X.; Zhang, Z. Ultrasound-assisted extraction of the three terpenoid indole alkaloids vindoline, catharanthine and vinblastine from *Catharanthus roseus* using ionic liquid aqueous solutions. *Chem. Eng. J.* **2011**, *172*, 705–712. <https://doi.org/10.1016/j.cej.2011.06.039>.
- Zhu, S.-C.; Shi, M.-Z.; Yu, Y.-L.; Cao, J. Simultaneous extraction and enrichment of alkaloids from lotus leaf by in-situ cloud point-reinforced ionic liquid assisted mechanochemical extraction technology. *Ind. Crops Prod.* **2022**, *183*, 114968. <https://doi.org/10.1016/j.indcrop.2022.114968>.
- Jiang, Y.; Wang, Z.; Lei, Z.; Yu, G. Structural effects on thermodynamic behavior and hydrogen bond interactions of water-ionic liquid systems. *Chem. Eng. Sci.* **2021**, *230*, 116186. <https://doi.org/10.1016/j.ces.2020.116186>.

28. Freire, M.G.; Neves, C.M.S.S.; Marrucho, I.M.; Canongia Lopes, J.N.; Rebelo, L.P.N.; Coutinho, J.A.P. High-performance extraction of alkaloids using aqueous two-phase systems with ionic liquids. *Green Chem.* **2010**, *12*, 1715–1718. <https://doi.org/10.1039/C0GC00179A>.
29. Wang, W.; Li, Q.; Liu, Y.; Chen, B. Ionic liquid-aqueous solution ultrasonic-assisted extraction of three kinds of alkaloids from *Phellodendron amurense* Rupr and optimize conditions use response surface. *Ultrason. Sonochem.* **2015**, *24*, 13–18. <https://doi.org/10.1016/j.ultsonch.2014.10.009>.
30. Peng, X.; Sui, X.; Li, J.; Liu, T.; Yang, L. 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.* **2021**, *168*, 113596. <https://doi.org/10.1016/j.indcrop.2021.113596>.
31. Ma, W.; Lu, Y.; Hu, R.; Chen, J.; Zhang, Z.; Pan, Y. Application of ionic liquids based microwave-assisted extraction of three alkaloids *N*-normuciferine, *O*-normuciferine, and nuciferine from lotus leaf. *Talanta* **2010**, *80*, 1292–1297. <https://doi.org/10.1016/j.talanta.2009.09.027>.
32. Li, Q.; Wu, S.; Wang, C.; Yi, Y.; Zhou, W.; Wang, H.; Li, F.; Tan, Z. Ultrasonic-assisted extraction of sinomenine from *Sinomenium acutum* using magnetic ionic liquids coupled with further purification by reversed micellar extraction. *Process Biochem.* **2017**, *58*, 282–288. <https://doi.org/10.1016/j.procbio.2017.04.030>.
33. Liu, X.; Yu, D.; Luo, H.; Li, C.; Li, H. Efficient reaction systems for lignocellulosic biomass conversion to furan derivatives: A minireview. *Polymer* **2022**, *14*, 3671.
34. Zhang, P.; Dong, S.-J.; Ma, H.-H.; Zhang, B.-X.; Wang, Y.-F.; Hu, X.-M. Fractionation of corn stover into cellulose, hemicellulose and lignin using a series of ionic liquids. *Ind. Crops Prod.* **2015**, *76*, 688–696. <https://doi.org/10.1016/j.indcrop.2015.07.037>.
35. Miyafuji, H. Application of ionic liquids for effective use of woody biomass. *J. Wood Sci.* **2015**, *61*, 343–350. <https://doi.org/10.1007/s10086-015-1489-4>.
36. Youngs, T.G.A.; Holbrey, J.D.; Mullan, C.L.; Norman, S.E.; Lagunas, M.C.; D'Agostino, C.; Mantle, M.D.; Gladden, L.F.; Bowron, D.T.; Hardacre, C. Neutron diffraction, NMR and molecular dynamics study of glucose dissolved in the ionic liquid 1-ethyl-3-methylimidazolium acetate. *Chem. Sci.* **2011**, *2*, 1594–1605. <https://doi.org/10.1039/C1SC00241D>.
37. Youngs, T.G.A.; Hardacre, C.; Holbrey, J.D. Glucose solvation by the ionic liquid 1, 3-dimethylimidazolium chloride: A simulation study. *J. Phys. Chem. B* **2007**, *111*, 13765–13774. <https://doi.org/10.1021/jp076728k>.
38. Zhang, J.; Xu, L.; Yu, J.; Wu, J.; Zhang, X.; He, J.; Zhang, J. Understanding cellulose dissolution: Effect of the cation and anion structure of ionic liquids on the solubility of cellulose. *Sci. China Chem.* **2016**, *59*, 1421–1429. <https://doi.org/10.1007/s11426-016-0269-5>.
39. Lu, B.; Xu, A.; Wang, J. Cation does matter: How cationic structure affects the dissolution of cellulose in ionic liquids. *Green Chem.* **2014**, *16*, 1326–1335. <https://doi.org/10.1039/C3GC41733F>.
40. Zhao, H.; Baker, G.A.; Song, Z.; Olubajo, O.; Crittle, T.; Peters, D. Designing enzyme-compatible ionic liquids that can dissolve carbohydrates. *Green Chem.* **2008**, *10*, 696–705. <https://doi.org/10.1039/B801489B>.
41. Zhang, Z.; Song, J.; Han, B. Catalytic transformation of lignocellulose into chemicals and fuel products in ionic liquids. *Chem. Rev.* **2017**, *117*, 6834–6880. <https://doi.org/10.1021/acs.chemrev.6b00457>.
42. Tao, H.; Zhao, Y.; Li, L.; He, Y.; Zhang, X.; Zhu, Y.; Hong, G. Comparative metabolomics of flavonoids in twenty vegetables reveal their nutritional diversity and potential health benefits. *Food Res. Int.* **2023**, *164*, 112384. <https://doi.org/10.1016/j.foodres.2022.112384>.
43. Chand, P.; Kumar, H.; Jain, R.; Jain, A.; Jain, V. Flavonoids as omnipotent candidates for cancer management. *S. Afr. J. Bot.* **2023**, *158*, 334–346. <https://doi.org/10.1016/j.sajb.2023.05.025>.
44. Ji, S.; Wang, Y.; Gao, S.; Shao, X.; Cui, W.; Du, Y.; Guo, M.; Tang, D. Highly efficient and selective extraction of minor bioactive natural products using pure ionic liquids: Application to prenylated flavonoids in licorice. *J. Ind. Eng. Chem.* **2019**, *80*, 352–360. <https://doi.org/10.1016/j.jiec.2019.08.014>.
45. Wang, R.; Chang, Y.; Tan, Z.; Li, F. A novel combined process for extracting, separating and recovering flavonoids from flos sophorae immaturus. *Sep. Purif. Technol.* **2017**, *172*, 422–432. <https://doi.org/10.1016/j.seppur.2016.08.038>.
46. Du, F.-Y.; Xiao, X.-H.; Luo, X.-J.; Li, G.-K. Application of ionic liquids in the microwave-assisted extraction of polyphenolic compounds from medicinal plants. *Talanta* **2009**, *78*, 1177–1184. <https://doi.org/10.1016/j.talanta.2009.01.040>.
47. Zuo, L.; Ao, X.; Guo, Y. Study on the synthesis of dual-chain ionic liquids and their application in the extraction of flavonoids. *J. Chromatogr. A* **2020**, *1628*, 461446. <https://doi.org/10.1016/j.chroma.2020.461446>.
48. Xu, W.; Chu, K.; Li, H.; Zhang, Y.; Zheng, H.; Chen, R.; Chen, L. Ionic liquid-based microwave-assisted extraction of flavonoids from *Bauhinia championii* (Benth.) Benth. *Molecules* **2012**, *17*, 14323–14335. <https://doi.org/10.3390/molecules171214323>.
49. Zeng, H.; Wang, Y.; Kong, J.; Nie, C.; Yuan, Y. Ionic liquid-based microwave-assisted extraction of rutin from Chinese medicinal plants. *Talanta* **2010**, *83*, 582–590. <https://doi.org/10.1016/j.talanta.2010.10.006>.
50. Tashakkori, P.; Tağaç, A.A.; Merdivan, M. Fabrication of montmorillonite/ionic liquid composite coated solid-phase microextraction fibers for determination of phenolic compounds in fruit juices by gas chromatography and liquid chromatography. *J. Chromatogr. A* **2021**, *1635*, 461741. <https://doi.org/10.1016/j.chroma.2020.461741>.
51. Lago, S.; Rodríguez, H.; Arce, A.; Soto, A. Improved concentration of citrus essential oil by solvent extraction with acetate ionic liquids. *Fluid Phase Equilib.* **2014**, *361*, 37–44. <https://doi.org/10.1016/j.fluid.2013.10.036>.

52. Ullah, H.; Wilfred, C.D.; Shaharun, M.S. Comparative assessment of various extraction approaches for the isolation of essential oil from *Polygonum minus* using ionic liquids. *J. King Saud Univ. Sci.* **2019**, *31*, 230–239. <https://doi.org/10.1016/j.jksus.2017.05.014>.
53. Li, W.; Fan, Y.; Zhang, S.; Li, J.; Zhang, L.; Wu, H. Extraction of rosmarinic acid from *Perilla* seeds using green protic ionic liquids. *Microchem. J.* **2021**, *170*, 106667. <https://doi.org/10.1016/j.microc.2021.106667>.
54. Chen, G.; Sui, X.; Liu, T.; Wang, H.; Zhang, J.; Sun, J.; Xu, T. Application of cellulase treatment in ionic liquid based enzyme-assisted extraction in combine with in-situ hydrolysis process for obtaining genipin from *Eucommia ulmoides* Olive barks. *J. Chromatogr. A* **2018**, *1569*, 26–35. <https://doi.org/10.1016/j.chroma.2018.07.063>.
55. Wu, K.; Zhang, Q.; Liu, Q.; Tang, F.; Long, Y.; Yao, S. Ionic liquid surfactant-mediated ultrasonic-assisted extraction coupled to HPLC: Application to analysis of tanshinones in *Salvia miltiorrhiza bunge*. *J. Sep. Sci.* **2009**, *32*, 4220–4226. <https://doi.org/10.1002/jssc.200900398>.
56. Clarke, C.J.; Tu, W.-C.; Levers, O.; Bröhl, A.; Hallett, J.P. Green and sustainable solvents in chemical processes. *Chem. Rev.* **2018**, *118*, 747–800. <https://doi.org/10.1021/acs.chemrev.7b00571>.
57. Musarurwa, H.; Tavengwa, N.T. Emerging green solvents and their applications during pesticide analysis in food and environmental samples. *Talanta* **2021**, *223*, 121507. <https://doi.org/10.1016/j.talanta.2020.121507>.
58. Hansen, B.B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J.M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B.W.; et al. Deep eutectic solvents: A review of fundamentals and applications. *Chem. Rev.* **2021**, *121*, 1232–1285. <https://doi.org/10.1021/acs.chemrev.0c00385>.
59. Han, D.; Row, K.H. Recent applications of ionic liquids in separation technology. *Molecules* **2010**, *15*, 2405–2426. <https://doi.org/10.3390/molecules15042405>.
60. Musarurwa, H.; Chimuka, L.; Tavengwa, N.T. Green pre-concentration techniques during pesticide analysis in food samples. *J. Environ. Sci. Health Part B* **2019**, *54*, 770–780. <https://doi.org/10.1080/03601234.2019.1633213>.
61. Nguyen, T.T.; Huynh, T.T.T.; Nguyen, N.H.; Nguyen, T.H.; Tran, P.H. Recent advances in the application of ionic liquid-modified silica gel in solid-phase extraction. *J. Mol. Liq.* **2022**, *368*, 120623. <https://doi.org/10.1016/j.molliq.2022.120623>.
62. Wang, H.; Hu, L.; Li, W.; Yang, X.; Lu, R.; Zhang, S.; Zhou, W.; Gao, H.; Li, J. In-syringe dispersive liquid-liquid microextraction based on the solidification of ionic liquids for the determination of benzoylurea insecticides in water and tea beverage samples. *Talanta* **2017**, *162*, 625–633. <https://doi.org/10.1016/j.talanta.2016.10.035>.
63. Zhang, L.; Yu, R.; Zhang, X.; Zhang, D. Ionic liquid-based dispersive liquid-liquid micro-extraction of five organophosphorus pesticides in coarse cereals. *Food Anal. Methods* **2021**, *14*, 10–17. <https://doi.org/10.1007/s12161-020-01851-y>.
64. Gure, A.; Lara, F.J.; García-Campaña, A.M.; Megersa, N.; del Olmo-Iruela, M. Vortex-assisted ionic liquid dispersive liquid-liquid microextraction for the determination of sulfonylurea herbicides in wine samples by capillary high-performance liquid chromatography. *Food Chem.* **2015**, *170*, 348–353. <https://doi.org/10.1016/j.foodchem.2014.08.065>.
65. Wang, H.; Hu, L.; Li, W.; Lu, R.; Zhang, S.; Zhou, W.; Gao, H. 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* **2016**, *1471*, 60–67. <https://doi.org/10.1016/j.chroma.2016.10.027>.
66. Lu, D.; Liu, C.; Deng, J.; Zhou, X.; Shi, G.; Zhou, T. Rational design of an ionic liquid dispersive liquid-liquid micro-extraction method for the detection of organophosphorus pesticides. *Analyst* **2019**, *144*, 2166–2172. <https://doi.org/10.1039/C9AN00123A>.
67. Yang, J.; Fan, C.; Kong, D.; Tang, G.; Zhang, W.; Dong, H.; Liang, Y.; Wang, D.; Cao, Y. Synthesis and application of imidazolium-based ionic liquids as extraction solvent for pretreatment of triazole fungicides in water samples. *Anal. Bioanal. Chem.* **2018**, *410*, 1647–1656. <https://doi.org/10.1007/s00216-017-0820-x>.
68. Wang, Y.; Sun, Y.; Xu, B.; Li, X.; Wang, X.; Zhang, H.; Song, D. Matrix solid-phase dispersion coupled with magnetic ionic liquid dispersive liquid-liquid microextraction for the determination of triazine herbicides in oilseeds. *Anal. Chim. Acta* **2015**, *888*, 67–74. <https://doi.org/10.1016/j.aca.2015.07.028>.
69. Zhang, L.; Cao, B.; Yao, D.; Yu, R.; Yu, C.; Zhang, H.; Yu, A. Separation and concentration of sulfonylurea herbicides in milk by ionic-liquid-based foam flotation solid-phase extraction. *J. Sep. Sci.* **2015**, *38*, 1733–1740. <https://doi.org/10.1002/jssc.201401344>.
70. Abdi Hassan, A.; Sajid, M.; Al Ghafly, H.; Alhooshani, K. Ionic liquid-based membrane-protected micro-solid-phase extraction of organochlorine pesticides in environmental water samples. *Microchem. J.* **2020**, *158*, 105295. <https://doi.org/10.1016/j.microc.2020.105295>.
71. Galán-Cano, F.; Lucena, R.; Cárdenas, S.; Valcárcel, M. 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.* **2013**, *106*, 311–317. <https://doi.org/10.1016/j.microc.2012.08.016>.
72. Pelit, F.O.; Pelit, L.; Dizdaş, T.N.; Aftafa, C.; Ertaş, H.; Yalçinkaya, E.E.; Türkmen, H.; Ertaş, F.N. A novel polythiophene—Ionic liquid modified clay composite solid phase microextraction fiber: Preparation, characterization and application to pesticide analysis. *Anal. Chim. Acta* **2015**, *859*, 37–45. <https://doi.org/10.1016/j.aca.2014.12.043>.
73. Pang, L.; Yang, P.; Pang, R.; Lu, X.; Xiao, J.; Li, S.; Zhang, H.; Zhao, J. Ionogel-based ionic liquid coating for solid-phase microextraction of organophosphorus pesticides from wine and juice samples. *Food Anal. Methods* **2018**, *11*, 270–281. <https://doi.org/10.1007/s12161-017-0997-9>.
74. Orazbayeva, D.; Koziel, J.A.; Trujillo-Rodríguez, M.J.; Anderson, J.L.; Kenessov, B. Polymeric ionic liquid sorbent coatings in headspace solid-phase microextraction: A green sample preparation technique for the determination of pesticides in soil. *Microchem. J.* **2020**, *157*, 104996. <https://doi.org/10.1016/j.microc.2020.104996>.

75. Zeger, V.R.; Bell, D.S.; Herrington, J.S.; Anderson, J.L. Selective isolation of pesticides and cannabinoids using polymeric ionic liquid-based sorbent coatings in solid-phase microextraction coupled to high-performance liquid chromatography. *J. Chromatogr. A* **2022**, *1680*, 463416. <https://doi.org/10.1016/j.chroma.2022.463416>.
76. Gubin, A.; Sukhanov, P.; Kushnir, A.; Shikhaliev, K.; Potapov, M.; Kovaleva, E. 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. Nanotechnol., Monit. Manag.* **2022**, *17*, 100652. <https://doi.org/10.1016/j.enmm.2022.100652>.
77. Peng, S.; Xiao, J.; Cheng, J.; Zhang, M.; Li, X.; Cheng, M. Ionic liquid magnetic bar microextraction and HPLC determination of carbamate pesticides in real water samples. *Microchim. Acta* **2012**, *179*, 193–199. <https://doi.org/10.1007/s00604-012-0884-4>.
78. Zhang, L.; Ma, Z.; Wang, C.; Yu, R.; Zhang, D. Extraction of acetanilide herbicides in naked oat (*Avena nuda* L.) by using ionic-liquid-based matrix solid-phase dispersion-foam flotation solid-phase extraction. *J. Sep. Sci.* **2019**, *42*, 3459–3469. <https://doi.org/10.1002/jssc.201900541>.
79. Chatzimitakos, T.G.; Anderson, J.L.; Stalikas, C.D. Matrix solid-phase dispersion based on magnetic ionic liquids: An alternative sample preparation approach for the extraction of pesticides from vegetables. *J. Chromatogr. A* **2018**, *1581–1582*, 168–172. <https://doi.org/10.1016/j.chroma.2018.11.008>.
80. Jordan-Sinisterra, M.; Vargas Medina, D.A.; Lanças, F.M. Microextraction by packed sorbent of polycyclic aromatic hydrocarbons in brewed coffee samples with a new zwitterionic ionic liquid-modified silica sorbent. *J. Food Compos. Anal.* **2022**, *114*, 104832. <https://doi.org/10.1016/j.jfca.2022.104832>.
81. Li, M.; Yang, C.; Yan, H.; Han, Y.; Han, D. 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* **2020**, *1631*, 461568. <https://doi.org/10.1016/j.chroma.2020.461568>.
82. Gao, M.; Zhang, X.; Ma, S.; Wang, J.; Mammah, M.; Du, L.; Wang, X. Ionic-liquid-based effervescence-enhanced magnetic solid-phase extraction for organophosphorus pesticide detection in water samples. *Anal. Methods* **2022**, *14*, 661–671. <https://doi.org/10.1039/D1AY01698A>.
83. Zhao, H.; Li, R.; Hu, J. Frequently used pesticides and their metabolites residues in apple and apple juice from markets across China: Occurrence and health risk assessment. *LWT* **2023**, *178*, 114610. <https://doi.org/10.1016/j.lwt.2023.114610>.
84. Tudi, M.; Daniel Ruan, H.; Wang, L.; Lyu, J.; Sadler, R.; Connell, D.; Chu, C.; Phung, D.T. Agriculture development, pesticide application and its impact on the environment. *Int. J. Environ. Res. Public Health* **2021**, *18*, 1112. <https://doi.org/10.3390/ijerph18031112>.
85. Rohani, M.F. Pesticides toxicity in fish: Histopathological and hemato-biochemical aspects—A review. *Emerg. Contam.* **2023**, *9*, 100234. <https://doi.org/10.1016/j.emcon.2023.100234>.
86. Song, X.; Li, F.; Yan, T.; Tian, F.; Ren, L.; Jiang, C.; Wang, Q.; Zhang, S. Research progress in the sample pretreatment techniques and advanced quick detection methods of pesticide residues. *Process Saf. Environ. Prot.* **2022**, *165*, 610–622. <https://doi.org/10.1016/j.psep.2022.07.047>.
87. Hejabri Kande, S.; Amini, S.; Ebrahimzadeh, H. Development of poly(vinyl alcohol)/chitosan/aloe vera gel electrospun composite nanofibers as a novel sorbent for thin-film micro-extraction of pesticides in water and food samples followed by HPLC-UV analysis. *New J. Chem.* **2022**, *46*, 2431–2440. <https://doi.org/10.1039/D1NJ05634D>.
88. Rykowska, I.; Ziembińska, J.; Nowak, I. Modern approaches in dispersive liquid-liquid microextraction (DLLME) based on ionic liquids: A review. *J. Mol. Liq.* **2018**, *259*, 319–339. <https://doi.org/10.1016/j.molliq.2018.03.043>.
89. Primel, E.G.; Caldas, S.S.; Marube, L.C.; Escarrone, A.L.V. An overview of advances in dispersive liquid-liquid microextraction for the extraction of pesticides and emerging contaminants from environmental samples. *Trends Environ. Anal. Chem.* **2017**, *14*, 1–18. <https://doi.org/10.1016/j.teac.2017.03.001>.
90. Toh, S.L.I.; McFarlane, J.; Tsouris, C.; DePaoli, D.W.; Luo, H.; Dai, S. Room-temperature ionic liquids in liquid-liquid extraction: Effects of solubility in aqueous solutions on surface properties. *Solvent Extr. Ion Exch.* **2006**, *24*, 33–56. <https://doi.org/10.1080/07366290500388400>.
91. Himani, Pratap Singh Raman, A.; Babu Singh, M.; Jain, P.; Chaudhary, P.; Bahadur, I.; Lal, K.; Kumar, V.; Singh, P. An update on synthesis, properties, applications and toxicity of the ILs. *J. Mol. Liq.* **2022**, *364*, 119989. <https://doi.org/10.1016/j.molliq.2022.119989>.
92. Yang, J.; Fan, C.; Tang, G.; Zhang, W.; Dong, H.; Liang, Y.; Wang, Y.; Zou, M.; Cao, Y. Relationship between the structure of ionic liquid and its enrichment ability to trace fungicides from an environmental water sample. *J. Agric. Food Chem.* **2018**, *66*, 9418–9425. <https://doi.org/10.1021/acs.jafc.8b03244>.
93. Eyckens, D.J.; Henderson, L.C. A Review of Solvate Ionic Liquids: Physical Parameters and Synthetic Applications. *Front. Chem.* **2019**, *7*, 263. <https://doi.org/10.3389/fchem.2019.00263>.
94. Li, C.; Begum, A.; Xue, J. Analytical methods to analyze pesticides and herbicides. *Water Environ. Res.* **2020**, *92*, 1770–1785. <https://doi.org/10.1002/wer.1431>.
95. Clark, K.D.; Trujillo-Rodríguez, M.J.; Anderson, J.L. Advances in the analysis of biological samples using ionic liquids. *Anal. Bioanal. Chem.* **2018**, *410*, 4567–4573. <https://doi.org/10.1007/s00216-018-0898-9>.
96. Zhang, R.; Tan, Z.; Zhao, J.; Wen, Y.; Fan, S.; Liu, C. Determination of pyrethroid residues in herbal tea using temperature-controlled ionic liquid dispersive liquid-liquid microextraction by high performance liquid chromatography. *Sci. Rep.* **2020**, *10*, 4709. <https://doi.org/10.1038/s41598-020-61755-z>.

97. Ötles, S.; Aliment, C.K.J.A.S.P.T. Solid-phase extraction (SPE): Principles and applications in food samples. *Acta Sci. Pol. Technol. Aliment.* **2016**, *15*, 5–15.
98. Hashemi, B.; Zohrabi, P.; Shamsipur, M. Recent developments and applications of different sorbents for SPE and SPME from biological samples. *Talanta* **2018**, *187*, 337–347. <https://doi.org/10.1016/j.talanta.2018.05.053>.
99. Vidal, L.; Riekkola, M.-L.; Canals, A. Ionic liquid-modified materials for solid-phase extraction and separation: A review. *Anal. Chim. Acta* **2012**, *715*, 19–41. <https://doi.org/10.1016/j.aca.2011.11.050>.
100. Shi, M.-Z.; Yu, Y.-L.; Zhu, S.-C.; Yang, J.; Cao, J. Latest development of matrix solid phase dispersion extraction and microextraction for natural products from 2015–2021. *Sep. Purif. Rev.* **2023**, *52*, 262–282. <https://doi.org/10.1080/15422119.2022.2094274>.
101. Faraji, M. Recent analytical applications of magnetic nanoparticles *Nanochem. Res.* **2016**, *1*, 264–290. <https://doi.org/10.7508/ncr.2016.02.014>.
102. Varona, M.; Eor, P.; Ferreira Neto, L.C.; Merib, J.; Anderson, J.L. Metal-containing and magnetic ionic liquids in analytical extractions and gas separations. *TrAC Trends Anal. Chem.* **2021**, *140*, 116275. <https://doi.org/10.1016/j.trac.2021.116275>.
103. Chatzimitakos, T.G.; Pierson, S.A.; Anderson, J.L.; Stalikas, C.D. Enhanced magnetic ionic liquid-based dispersive liquid-liquid microextraction of triazines and sulfonamides through a one-pot, pH-modulated approach. *J. Chromatogr. A* **2018**, *1571*, 47–54. <https://doi.org/10.1016/j.chroma.2018.08.013>.
104. Ventura, S.P.M.; e Silva, F.A.; Quental, M.V.; Mondal, D.; Freire, M.G.; Coutinho, J.A.P. Ionic-liquid-mediated extraction and separation processes for bioactive compounds: Past, present, and future trends. *Chem. Rev.* **2017**, *117*, 6984–7052. <https://doi.org/10.1021/acs.chemrev.6b00550>.
105. Chatzimitakos, T.; Anagnostou, P.; Constantinou, I.; Dakidi, K.; Stalikas, C. Magnetic ionic liquids in sample preparation: Recent advances and future trends. *Separations* **2021**, *8*, 153.
106. Zulfiqar, S.; Rafique, U.; Javed Akhtar, M. Removal of pirimicarb from agricultural waste water using cellulose acetate–modified ionic liquid membrane. *Environ. Sci. Pollut. Res.* **2019**, *26*, 15795–15802. <https://doi.org/10.1007/s11356-019-04681-6>.
107. Fang, G.; Chen, J.; Wang, J.; He, J.; Wang, S. N-Methylimidazolium ionic liquid-functionalized silica as a sorbent for selective solid-phase extraction of 12 sulfonylurea herbicides in environmental water and soil samples. *J. Chromatogr. A* **2010**, *1217*, 1567–1574. <https://doi.org/10.1016/j.chroma.2010.01.010>.
108. Clark, K.D.; Nacham, O.; Purslow, J.A.; Pierson, S.A.; Anderson, J.L. Magnetic ionic liquids in analytical chemistry: A review. *Anal. Chim. Acta* **2016**, *934*, 9–21. <https://doi.org/10.1016/j.aca.2016.06.011>.
109. Pernak, J.; Niemczak, M.; Rzemieniecki, T.; Marcinkowska, K.; Praczyk, T. Dicationic herbicidal ionic liquids comprising two active ingredients exhibiting different modes of action. *J. Agric. Food Chem.* **2022**, *70*, 2545–2553. <https://doi.org/10.1021/acs.jafc.1c07750>.
110. Davis, J.H.; Forrester, K.J.; Merrigan, T. Novel organic ionic liquids (OILs) incorporating cations derived from the antifungal drug miconazole. *Tetrahedron Lett.* **1998**, *39*, 8955–8958. [https://doi.org/10.1016/S0040-4039\(98\)02070-X](https://doi.org/10.1016/S0040-4039(98)02070-X).
111. Walden, P.J.B.A.I.S. Molecular weights and electrical conductivity of several fused salts. *Bull. Acad. Imper. Sci.* **1914**, *8*, 405–422.
112. Pernak, J.; Sobaszkiewicz, K.; Mirska, I. Anti-microbial activities of ionic liquids. *Green Chem.* **2003**, *5*, 52–56. <https://doi.org/10.1039/B207543C>.
113. Chrzanowski, Ł.; Stasiewicz, M.; Owsianiak, M.; Szulc, A.; Piotrowska-Cyplik, A.; Olejnik-Schmidt, A.K.; Wyrwas, B. Biodegradation of diesel fuel by a microbial consortium in the presence of 1-alkoxymethyl-2-methyl-5-hydroxypyridinium chloride homologues. *Biodegradation* **2009**, *20*, 661–671. <https://doi.org/10.1007/s10532-009-9253-3>.
114. Bica, K.; Cooke, L.R.; Nugent, P.; Rijkssen, C.; Rogers, R.D. Toxic on purpose: Ionic liquid fungicides as combinatorial crop protecting agents. *Green Chem.* **2011**, *13*, 2344–2346. <https://doi.org/10.1039/C1GC15170C>.
115. Pernak, J.; Syguda, A.; Janiszewska, D.; Materna, K.; Praczyk, T. Ionic liquids with herbicidal anions. *Tetrahedron* **2011**, *67*, 4838–4844. <https://doi.org/10.1016/j.tet.2011.05.016>.
116. Pernak, J.; Wasiński, K.; Praczyk, T.; Nawrot, J.; Cieniecka-Rosłonkiewicz, A.; Walkiewicz, F.; Materna, K. Sweet ionic liquids-cyclamates: Synthesis, properties, and application as feeding deterrents. *Sci. China Chem.* **2012**, *55*, 1532–1541. <https://doi.org/10.1007/s11426-012-4631-9>.
117. Lewandowski, P.; Kukawka, R.; Pospieszny, H.; Smiglak, M. Bifunctional quaternary ammonium salts based on benzo[1,2,3]thiadiazole-7-carboxylate as plant systemic acquired resistance inducers. *New J. Chem.* **2014**, *38*, 1372–1375. <https://doi.org/10.1039/C3NJ01613G>.
118. Wilms, W.; Woźniak-Karczewska, M.; Niemczak, M.; Parus, A.; Frankowski, R.; Wolko, Ł.; Czarny, J.; Piotrowska-Cyplik, A.; Zgoła-Grześkowiak, A.; Heipieper, H.J.; et al. 2,4-D versus 2,4-D based ionic liquids: Effect of cation on herbicide biodegradation, tfdA genes abundance and microbiome changes during soil bioaugmentation. *J. Hazard. Mater.* **2023**, *452*, 131209. <https://doi.org/10.1016/j.jhazmat.2023.131209>.
119. Ławniczak, Ł.; Syguda, A.; Borkowski, A.; Cyplik, P.; Marcinkowska, K.; Wolko, Ł.; Praczyk, T.; Chrzanowski, Ł.; Pernak, J. Influence of oligomeric herbicidal ionic liquids with MCPA and Dicamba anions on the community structure of autochthonic bacteria present in agricultural soil. *Sci. Total Environ.* **2016**, *563*–564, 247–255. <https://doi.org/10.1016/j.scitotenv.2016.04.109>.
120. Parus, A.; Zdebelak, O.; Ciesielski, T.; Szumski, R.; Woźniak-Karczewska, M.; Framski, G.; Baranowski, D.; Niemczak, M.; Zembrzaska, J.; Cajthaml, T.; et al. Can ionic liquids exist in the soil environment? Effect of quaternary ammonium cations on glyphosate sorption, mobility and toxicity in the selected herbicidal ionic liquids. *J. Mol. Liq.* **2023**, *370*, 120981. <https://doi.org/10.1016/j.molliq.2022.120981>.

121. Parus, A.; Homa, J.; Radoński, D.; Framski, G.; Woźniak-Karczewska, M.; Syguda, A.; Ławniczak, Ł.; Chrzanowski, Ł. Novel esterquat-based herbicidal ionic liquids incorporating MCPA and MCPP for simultaneous stimulation of maize growth and fighting cornflower. *Ecotoxicol. Environ. Saf.* **2021**, *208*, 111595. <https://doi.org/10.1016/j.ecoenv.2020.111595>.
122. Zhu, J.; Ding, G.; Liu, Y.; Wang, B.; Zhang, W.; Guo, M.; Geng, Q.; Cao, Y. Ionic liquid forms of clopyralid with increased efficacy against weeds and reduced leaching from soils. *Chem. Eng. J.* **2015**, *279*, 472–477. <https://doi.org/10.1016/j.cej.2015.05.025>.
123. Pernak, J.; Kaczmarek, D.K.; Rzemieniecki, T.; Niemczak, M.; Chrzanowski, Ł.; Praczyk, T. Dicamba-based herbicides: Herbicidal ionic liquids versus commercial forms. *J. Agric. Food Chem.* **2020**, *68*, 4588–4594. <https://doi.org/10.1021/acs.jafc.0c00632>.
124. Parus, A.; Lisiecka, N.; Zembrzuska, J.; Framski, G.; Woźniak-Karczewska, M.; Niemczak, M. Evaluation of the influence of different cations on the mobility and performance of dicamba-based ionic liquids. *J. Environ. Chem. Eng.* **2022**, *10*, 108397. <https://doi.org/10.1016/j.jece.2022.108397>.
125. Marcinkowska, K.; Praczyk, T.; Niemczak, M.; Rzemieniecki, T.; Kaczmarek, D.K.; Łacka, A.; Pernak, J. Herbicidal ionic liquids containing double or triple anions as a new potential tool for weed control including herbicide-resistant biotypes. *Crop Prot.* **2023**, *169*, 106238. <https://doi.org/10.1016/j.cropro.2023.106238>.
126. Wang, W.; Zhu, J.; Tang, G.; Huo, H.; Zhang, W.; Liang, Y.; Dong, H.; Yang, J.; Cao, Y. Novel herbicide ionic liquids based on nicosulfuron with increased efficacy. *New J. Chem.* **2019**, *43*, 827–833. <https://doi.org/10.1039/C8NJ05903A>.
127. Wilms, W.; Woźniak-Karczewska, M.; Syguda, A.; Niemczak, M.; Ławniczak, Ł.; Pernak, J.; Rogers, R.D.; Chrzanowski, Ł. Herbicidal ionic liquids: A promising future for old herbicides? Review on synthesis, toxicity, biodegradation, and efficacy studies. *J. Agric. Food Chem.* **2020**, *68*, 10456–10488. <https://doi.org/10.1021/acs.jafc.0c02894>.
128. Pernak, J.; Giszter, R.; Biedziak, A.; Niemczak, M.; Olszewski, R.; Marcinkowska, K.; Praczyk, T. Alkyl(C16, C18, C22)trimethylammonium-based herbicidal ionic liquids. *J. Agric. Food Chem.* **2017**, *65*, 260–269. <https://doi.org/10.1021/acs.jafc.6b04528>.
129. Cojocar, O.A.; Shamshina, J.L.; Gurau, G.; Syguda, A.; Praczyk, T.; Pernak, J.; Rogers, R.D. Ionic liquid forms of the herbicide dicamba with increased efficacy and reduced volatility. *Green Chem.* **2013**, *15*, 2110–2120. <https://doi.org/10.1039/C3GC37143C>.
130. Pernak, J.; Niemczak, M.; Shamshina, J.L.; Gurau, G.; Głowacki, G.; Praczyk, T.; Marcinkowska, K.; Rogers, R.D. Metsulfuron-methyl-based herbicidal ionic liquids. *J. Agric. Food Chem.* **2015**, *63*, 3357–3366. <https://doi.org/10.1021/jf505782p>.
131. Niemczak, M.; Rzemieniecki, T.; Biedziak, A.; Marcinkowska, K.; Pernak, J. Synthesis and structure–property relationships in herbicidal ionic liquids and their double salts. *ChemPlusChem* **2018**, *83*, 529–541. <https://doi.org/10.1002/cplu.201800251>.
132. Choudhary, H.; Pernak, J.; Shamshina, J.L.; Niemczak, M.; Giszter, R.; Chrzanowski, Ł.; Praczyk, T.; Marcinkowska, K.; Cojocar, O.A.; Rogers, R.D. Two herbicides in a single compound: Double salt herbicidal ionic liquids exemplified with glyphosate, dicamba, and MCPA. *ACS Sustain. Chem. Eng.* **2017**, *5*, 6261–6273. <https://doi.org/10.1021/acssuschemeng.7b01224>.
133. Szymaniak, D.; Maćkowiak, A.; Ciarka, K.; Praczyk, T.; Marcinkowska, K.; Pernak, J. Synthesis and characterization of double-salt herbicidal ionic liquids comprising both 4-chloro-2-methylphenoxyacetate and trans-cinnamate Anions. *ChemPlusChem* **2020**, *85*, 2281–2289. <https://doi.org/10.1002/cplu.202000546>.
134. Islam, M.M.; Barik, S.; Preeyanka, N.; Sarkar, M. Interaction of lysozyme with monocationic and dicationic ionic liquids: Toward finding a suitable medium for biomacromolecules. *J. Phys. Chem. B* **2020**, *124*, 961–973. <https://doi.org/10.1021/acs.jpcc.9b10270>.
135. Niu, J.; Zhang, Z.; Tang, J.; Tang, G.; Yang, J.; Wang, W.; Huo, H.; Jiang, N.; Li, J.; Cao, Y. Dicationic ionic liquids of herbicide 2,4-dichlorophenoxyacetic acid with reduced negative effects on environment. *J. Agric. Food Chem.* **2018**, *66*, 10362–10368. <https://doi.org/10.1021/acs.jafc.8b02584>.
136. Chatel, G.; Pereira, J.F.B.; Debbeti, V.; Wang, H.; Rogers, R.D. Mixing ionic liquids—“simple mixtures” or “double salts”? *Green Chem.* **2014**, *16*, 2051–2083. <https://doi.org/10.1039/C3GC41389F>.
137. Shamshina, J.L.; Kelley, S.P.; Gurau, G.; Rogers, R.D. Chemistry: Develop ionic liquid drugs. *Nature* **2015**, *528*, 188–189. <https://doi.org/10.1038/528188a>.
138. Rzemieniecki, T.; Wojcieszak, M.; Materna, K.; Praczyk, T.; Pernak, J. Synthetic auxin-based double salt ionic liquids as herbicides with improved physicochemical properties and biological activity. *J. Mol. Liq.* **2021**, *334*, 116452. <https://doi.org/10.1016/j.molliq.2021.116452>.
139. Lagator, M.; Vogwill, T.; Mead, A.; Colegrave, N.; Neve, P. Herbicide mixtures at high doses slow the evolution of resistance in experimentally evolving populations of *chlamydomonas reinhardtii*. *New Phytol.* **2013**, *198*, 938–945. <https://doi.org/10.1111/nph.12195>.
140. Powles, S.B.; Yu, Q. Evolution in action: Plants resistant to herbicides. *Annu. Rev. Plant Biol.* **2010**, *61*, 317–347. <https://doi.org/10.1146/annurev-arplant-042809-112119>.
141. Marcinkowska, K.; Praczyk, T.; Gawlak, M.; Niemczak, M.; Pernak, J. Efficacy of herbicidal ionic liquids and choline salt based on 2,4-D. *Crop Prot.* **2017**, *98*, 85–93. <https://doi.org/10.1016/j.cropro.2017.03.011>.
142. Pernak, J.; Markiewicz, B.; Zgoła-Grześkowiak, A.; Chrzanowski, Ł.; Gwiazdowski, R.; Marcinkowska, K.; Praczyk, T. Ionic liquids with dual pesticidal function. *RSC Adv.* **2014**, *4*, 39751–39754. <https://doi.org/10.1039/C4RA04816D>.
143. Pernak, J.; Niemczak, M.; Materna, K.; Marcinkowska, K.; Praczyk, T. Ionic liquids as herbicides and plant growth regulators. *Tetrahedron* **2013**, *69*, 4665–4669. <https://doi.org/10.1016/j.tet.2013.03.097>.
144. Kukawka, R.; Spychalski, M.; Stróżyk, E.; Byzia, E.; Zajac, A.; Kaczyński, P.; Łozowicka, B.; Pospieszny, H.; Smiglak, M. Synthesis, characterization and biological activity of bifunctional ionic liquids based on dodine ion. *Pest Manag. Sci.* **2022**, *78*, 446–455. <https://doi.org/10.1002/ps.6639>.

145. Ciarka, K.; Olszewski, R.; Praczyk, T.; Pernak, J. Synthesis and characterization of herbicidal ionic liquids based on (4-chloro-2-methylphenoxy)acetate and phenoxyethylammonium. *Chem. Pap.* **2021**, *75*, 3607–3615. <https://doi.org/10.1007/s11696-021-01610-1>.
146. Syguda, A.; Wojcieszak, M.; Materna, K.; Woźniak-Karczewska, M.; Parus, A.; Ławniczak, Ł.; Chrzanowski, Ł. Double-action herbicidal ionic liquids based on dicamba esterquats with 4-CPA, 2,4-D, MCPA, MCPP, and clopyralid anions. *ACS Sustain. Chem. Eng.* **2020**, *8*, 14584–14594. <https://doi.org/10.1021/acssuschemeng.0c05603>.
147. Pernak, J.; Nawrot, J.; Kot, M.; Markiewicz, B.; Niemczak, M. Ionic liquids based stored product insect antifeedants. *RSC Adv.* **2013**, *3*, 25019–25029. <https://doi.org/10.1039/C3RA41716F>.
148. Markiewicz, B.; Sznajdrowska, A.; Chrzanowski, Ł.; Ławniczak, Ł.; Zgoła-Grześkowiak, A.; Kubiak, K.; Nawrot, J.; Pernak, J. Ionic liquids with a theophyllinate anion. *New J. Chem.* **2014**, *38*, 3146–3153. <https://doi.org/10.1039/C4NJ00463A>.
149. Pernak, J.; Łęgosz, B.; Walkiewicz, F.; Klejdysz, T.; Borkowski, A.; Chrzanowski, Ł. Ammonium ionic liquids with anions of natural origin. *RSC Adv.* **2015**, *5*, 65471–65480. <https://doi.org/10.1039/C5RA11710K>.
150. Klejdysz, T.; Łęgosz, B.; Czuryżkiewicz, D.; Czerniak, K.; Pernak, J. Biobased ionic liquids with abietate anion. *ACS Sustain. Chem. Eng.* **2016**, *4*, 6543–6550. <https://doi.org/10.1021/acssuschemeng.6b01381>.
151. Zhou, Y.; Wang, Q.; Wang, T.; Gao, H. Preparation and properties of multifunctional phenoxyacetate-based ionic liquids and their application in citrus bacteriostatic preservation. *New J. Chem.* **2022**, *46*, 22621–22632. <https://doi.org/10.1039/D2NJ03461A>.
152. Kaczmarek, D.K.; Pacholak, A.; Burlaga, N.; Wojcieszak, M.; Materna, K.; Kruska, D.; Dąbrowski, P.; Sobańska, K.; Kaczorek, E. Dicationic ionic liquids with an indole-3-butyrate anion—Plant growth stimulation and ecotoxicological evaluations. *ACS Sustain. Chem. Eng.* **2023**, *11*, 13282–13297. <https://doi.org/10.1021/acssuschemeng.3c02286>.
153. Tang, G.; Niu, J.; Tang, J.; Yang, J.; Zhou, Z.; Gao, Y.; Chen, X.; Tang, R.; Tian, Y.; Li, Y.; et al. Development of poly(ionic liquids) based on mepiquat chloride with improved rainfastness and long-lasting activity on growth regulation of cotton plant. *ACS Sustain. Chem. Eng.* **2020**, *8*, 14996–15004. <https://doi.org/10.1021/acssuschemeng.0c05419>.
154. Weigt, D.; Siatkowski, I.; Magaj, M.; Tomkowiak, A.; Nawracała, J. Impact of ionic liquids on induction of wheat microspore embryogenesis and plant regeneration. *Agronomy* **2020**, *10*, 839. <https://doi.org/10.3390/agronomy10060839>.
155. Pernak, J.; Feder-Kubis, J. Synthesis and properties of chiral ammonium-based ionic liquids. *Chemistry* **2005**, *11*, 4441–4449. <https://doi.org/10.1002/chem.200500026>.
156. Simões, M.; Pereira, A.R.; Simões, L.C.; Cagide, F.; Borges, F. Biofilm control by ionic liquids. *Drug Discov. Today* **2021**, *26*, 1340–1346. <https://doi.org/10.1016/j.drudis.2021.01.031>.
157. Venkata Nancharaiyah, Y.; Reddy, G.K.K.; Lalithamanasa, P.; Venugopalan, V.P. The ionic liquid 1-alkyl-3-methylimidazolium demonstrates comparable antimicrobial and antibiofilm behavior to a cationic surfactant. *Biofouling* **2012**, *28*, 1141–1149. <https://doi.org/10.1080/08927014.2012.736966>.
158. Cybulski, J.; Wiśniewska, A.; Kulig-Adamiak, A.; Dąbrowski, Z.; Praczyk, T.; Michalczyk, A.; Walkiewicz, F.; Materna, K.; Pernak, J. Mandelate and proline ionic liquids: Synthesis, characterization, catalytic and biological activity. *Tetrahedron Lett.* **2011**, *52*, 1325–1328. <https://doi.org/10.1016/j.tetlet.2011.01.069>.
159. Ye, Q.; Gao, T.; Wan, F.; Yu, B.; Pei, X.; Zhou, F.; Xue, Q. Grafting poly(ionic liquid) brushes for anti-bacterial and anti-biofouling applications. *J. Mater. Chem.* **2012**, *22*, 13123–13131. <https://doi.org/10.1039/C2JM31527K>.
160. Fang, Z.; Zheng, X.; Li, L.; Qi, J.; Wu, W.; Lu, Y. Ionic liquids: Emerging antimicrobial agents. *Pharm. Res.* **2022**, *39*, 2391–2404. <https://doi.org/10.1007/s11095-022-03336-5>.
161. Kaczmarek, D.K.; Gwiazdowska, D.; Juś, K.; Klejdysz, T.; Wojcieszak, M.; Materna, K.; Pernak, J. Glycine betaine-based ionic liquids and their influence on bacteria, fungi, insects and plants. *New J. Chem.* **2021**, *45*, 6344–6355. <https://doi.org/10.1039/D1NJ00498K>.
162. Cybulski, J.; Wiśniewska, A.; Kulig-Adamiak, A.; Lewicka, L.; Cieniecka-Rosłonkiewicz, A.; Kita, K.; Fojutowski, A.; Nawrot, J.; Materna, K.; Pernak, J. Long-alkyl-chain ouaternary ammonium lactate based ionic liquids. *Chemistry* **2008**, *14*, 9305–9311. <https://doi.org/10.1002/chem.200800973>.
163. Piotrowska, A.; Syguda, A.; Wyrwas, B.; Chrzanowski, Ł.; Heipieper, H.J. Toxicity evaluation of selected ammonium-based ionic liquid forms with MCPP and dicamba moieties on *Pseudomonas putida*. *Chemosphere* **2017**, *167*, 114–119. <https://doi.org/10.1016/j.chemosphere.2016.09.140>.
164. Markiewicz, M.; Lewandowski, P.; Szychalski, M.; Kukawka, R.; Feder-Kubis, J.; Beil, S.; Smiglak, M.; Stolte, S. New bifunctional ionic liquid-based plant systemic acquired resistance (SAR) inducers with an improved environmental hazard profile. *Green Chem.* **2021**, *23*, 5138–5149. <https://doi.org/10.1039/D1GC00107H>.
165. Stasiewicz, M.; Fojutowski, A.; Kropacz, A.; Pernak, J. 1-Alkoxyethyl-X-dimethylaminopyridinium-base ionic liquids in wood preservation. *Holzforschung* **2008**, *62*, 309–317. <https://doi.org/10.1515/HF.2008.028>.
166. Zabielska-Matejuk, J.; Stangierska, A.; Kot, M. New ammonium- and 1,2,4-triazolium-based ionic liquids for wood preservation. *J. Wood Chem. Technol.* **2015**, *35*, 178–192. <https://doi.org/10.1080/02773813.2014.909852>.
167. Zeier, J. Metabolic regulation of systemic acquired resistance. *Curr. Opin. Plant Biol.* **2021**, *62*, 102050. <https://doi.org/10.1016/j.pbi.2021.102050>.
168. Kouzai, Y.; Noutoshi, Y.; Inoue, K.; Shimizu, M.; Onda, Y.; Mochida, K. Benzothiadiazole, a plant defense inducer, negatively regulates sheath blight resistance in *Brachypodium distachyon*. *Sci. Rep.* **2018**, *8*, 17358. <https://doi.org/10.1038/s41598-018-35790-w>.

169. Smiglak, M.; Hines, C.C.; Wilson, T.B.; Singh, S.; Vincek, A.S.; Kirichenko, K.; Katritzky, A.R.; Rogers, R.D. Ionic Liquids Based on Azolate Anions. *Chem.-Eur. J.* **2010**, *16*, 1572–1584. <https://doi.org/10.1002/chem.200901418>.
170. Kukawka, R.; Czerwoniec, P.; Lewandowski, P.; Pospieszny, H.; Smiglak, M. New ionic liquids based on systemic acquired resistance inducers combined with the phytotoxicity reducing cholinium cation. *New J. Chem.* **2018**, *42*, 11984–11990. <https://doi.org/10.1039/C8NJ00778K>.
171. Md Moshikur, R.; Chowdhury, M.R.; Moniruzzaman, M.; Goto, M. Biocompatible ionic liquids and their applications in pharmaceuticals. *Green Chem.* **2020**, *22*, 8116–8139. <https://doi.org/10.1039/D0GC02387F>.
172. Curreri, A.M.; Mitragotri, S.; Tanner, E.E.L. Recent advances in ionic liquids in biomedicine. *Adv. Sci.* **2021**, *8*, 2004819. <https://doi.org/10.1002/advs.202004819>.
173. Yang, J.; Zhou, Z.; Liang, Y.; Tang, J.; Gao, Y.; Niu, J.; Dong, H.; Tang, R.; Tang, G.; Cao, Y. Sustainable preparation of microcapsules with desirable stability and bioactivity using phosphonium ionic liquid as a functional additive. *ACS Sustain. Chem. Eng.* **2020**, *8*, 13440–13448. <https://doi.org/10.1021/acssuschemeng.0c04245>.
174. Zhang, W.; Guo, Y.; Yang, J.; Tang, G.; Zhang, J.; Cao, Y. Prodrug based on ionic liquids for dual-triggered release of thiabendazole. *ACS Omega* **2023**, *8*, 3484–3492. <https://doi.org/10.1021/acsomega.2c07511>.
175. Steudte, S.; Bemowsky, S.; Mahrova, M.; Bottin-Weber, U.; Tojo-Suarez, E.; Stepnowski, P.; Stolte, S. Toxicity and biodegradability of dicationic ionic liquids. *RSC Adv.* **2014**, *4*, 5198–5205. <https://doi.org/10.1039/C3RA45675G>.
176. Reid, J.E.S.J.; Prydderch, H.; Spulak, M.; Shimizu, S.; Walker, A.J.; Gathergood, N. Green profiling of aprotic versus protic ionic liquids: Synthesis and microbial toxicity of analogous structures. *Sustain. Chem. Pharm.* **2018**, *7*, 17–26. <https://doi.org/10.1016/j.scp.2017.11.001>.
177. Butucel, E.; Balta, I.; Ahmadi, M.; Dumitrescu, G.; Morariu, F.; Pet, I.; Stef, L.; Corcionivoschi, N. Biocides as biomedicines against foodborne pathogenic bacteria. *Biomedicines* **2022**, *10*, 379. <https://doi.org/10.3390/biomedicines10020379>.
178. Zajac, A.; Kukawka, R.; Pawlowska-Zygarowicz, A.; Stolarska, O.; Smiglak, M. Ionic liquids as bioactive chemical tools for use in agriculture and the preservation of agricultural products. *Green Chem.* **2018**, *20*, 4764–4789. <https://doi.org/10.1039/C8GC01424H>.
179. Hernández, A.F.; Gil, F.; Lacasaña, M. Toxicological interactions of pesticide mixtures: An update. *Arch. Toxicol.* **2017**, *91*, 3211–3223. <https://doi.org/10.1007/s00204-017-2043-5>.
180. Stasiewicz, M.; Mulkiewicz, E.; Tomczak-Wandzel, R.; Kumirska, J.; Siedlecka, E.M.; Gołebiowski, M.; Gajdus, J.; Czerwicka, M.; Stepnowski, P. Assessing toxicity and biodegradation of novel, environmentally benign ionic liquids (1-alkoxymethyl-3-hydroxypyridinium chloride, saccharinate and acesulfamates) on cellular and molecular level. *Ecotoxicol. Environ. Saf.* **2008**, *71*, 157–165. <https://doi.org/10.1016/j.ecoenv.2007.08.011>.
181. Pernak, J.; Niemczak, M.; Giszter, R.; Shamshina, J.L.; Gurau, G.; Cojocar, O.A.; Praczyk, T.; Marcinkowska, K.; Rogers, R.D. Glyphosate-based herbicidal ionic liquids with increased efficacy. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2845–2851. <https://doi.org/10.1021/sc500612y>.
182. Woźniak-Karczewska, M.; Parus, A.; Ciesielski, T.; Trzebny, A.; Szumski, R.; Wilms, W.; Homa, J.; Framski, G.; Baranowski, D.; Frankowski, R.; et al. Effect of cation sorption on 2, 4-D mobility of herbicidal ionic liquids in agricultural soil combined with diversity of the bacterial community. *ACS Sustain. Chem. Eng.* **2022**, *10*, 12559–12568. <https://doi.org/10.1021/acssuschemeng.2c02665>.

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