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Review

Advances of Imidazolium Ionic Liquids for the Extraction of Phytochemicals from Plants

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Abstract: In this review, we present the research from 2013 to 2022 about the character of ionic liquids, the categories of phytochemicals, and the reasons for selecting imidazolium ionic liquids for phytochemical extraction. Then we introduce the structural formulae of the imidazolium ionic liquids commonly used in the extraction of phytochemicals, the methods used to prepare imidazolium ionic liquids, and a comprehensive introduction of how imidazolium ionic liquids are applied to extract phytochemicals from plants. Importantly, we discuss the strategies for studying the extraction mechanisms of imidazolium ionic liquids to extract phytochemicals, and the recovery methods regarding imidazolium ionic liquids and their recyclability are analyzed. Then the toxicity in imidazolium ionic liquids is pointed out. Finally, the challenges and prospects of extracting phytochemicals by imidazolium ionic liquids are summarized, and they are expected to provide some references for researchers.

Keywords: imidazolium ionic liquids; extraction; phytochemicals; plants

Citation: Gong, J.; Liang, C.; Majeed, Z.; Tian, M.; Zhao, C.; Luo, M.; Li, C. Advances of Imidazolium Ionic Liquids for the Extraction of Phytochemicals from Plants. *Separations* **2023**, *10*, 151. https://doi.org/10.3390/separations10030151

Academic Editors: Gavino Sanna and Rosaria Costa

Received: 11 January 2023
Revised: 3 February 2023
Accepted: 21 February 2023
Published: 23 February 2023

1. Introduction

Ionic liquids (ILs) belong to liquid molten salts that possess glass transition or melting points under 100 °C and are made up of wholly organic cations, as well as inorganic or organic anions [1]. As alternative solvents, ILs are appreciated for their excellent and distinctive properties, which include low vapor pressure, high thermal stability, low volatility, non-combustibility, favorable solubility in polar and non-polar chemicals, a wide electrochemical (conductivity) window, etc. [2–5]. These outstanding features led to their various applications within chemistry, analysis, electrochemistry, advanced materials, and environmental protection [6–10]. They are especially popular in the extraction and separation field [1].

The development history of ionic liquids is summarized in Figure 1A. The first use of ethyl ammonium nitrate [$EtNH_3$][NO_3] (m.p.12 °C) was introduced in 1914 [11]. Nearly 40 years later, F.H. Hurley and T.P. Wiler first synthesized ionic liquids in liquid state, at ambient temperature, which consists of a 1-ethylpyridinium bromide–aluminum chloride ([C_2py]Br-$AlCl_3$) mixture (molar ratio 2:1), in 1951 [12]. Subsequently, Osteryong and Wilkes et al. successfully produced room-temperature chloroaluminates for the first time in 1979 that they utilized to explore the role of 1-butylpyridinium chloride–aluminum chloride ([C_4py]-$AlCl_3$) in solute electrochemistry [13]. In 1992, Wilkes and Zavorotko synthesized [Bmim][BF_4], which exhibits strong water resistance, as well as stability, indicating that the development of ionic liquids has reached a new stage, and the research on imidazolium ionic liquids is developing gradually [14]. At present, there is more and more research on ionic liquids, and there exist more and more articles about ionic liquids. Using data collected from articles that were published between 2013 and 2022, trends in the amount of research documents on ionic liquids published by the Web of Science are summarized in Figure 1B. There appears to be an overall upward trend in the number of articles from 2013 to 2020, with the number tending to the maximum in 2020. Although the number of research documents decreases from 2021 to 2022, it is still more than that from 2013 to 2015. Nevertheless, the number of articles on studying ionic liquids is still sufficient each year, which shows that more and more researchers are taking part in this emerging field, with ample outcomes [15].

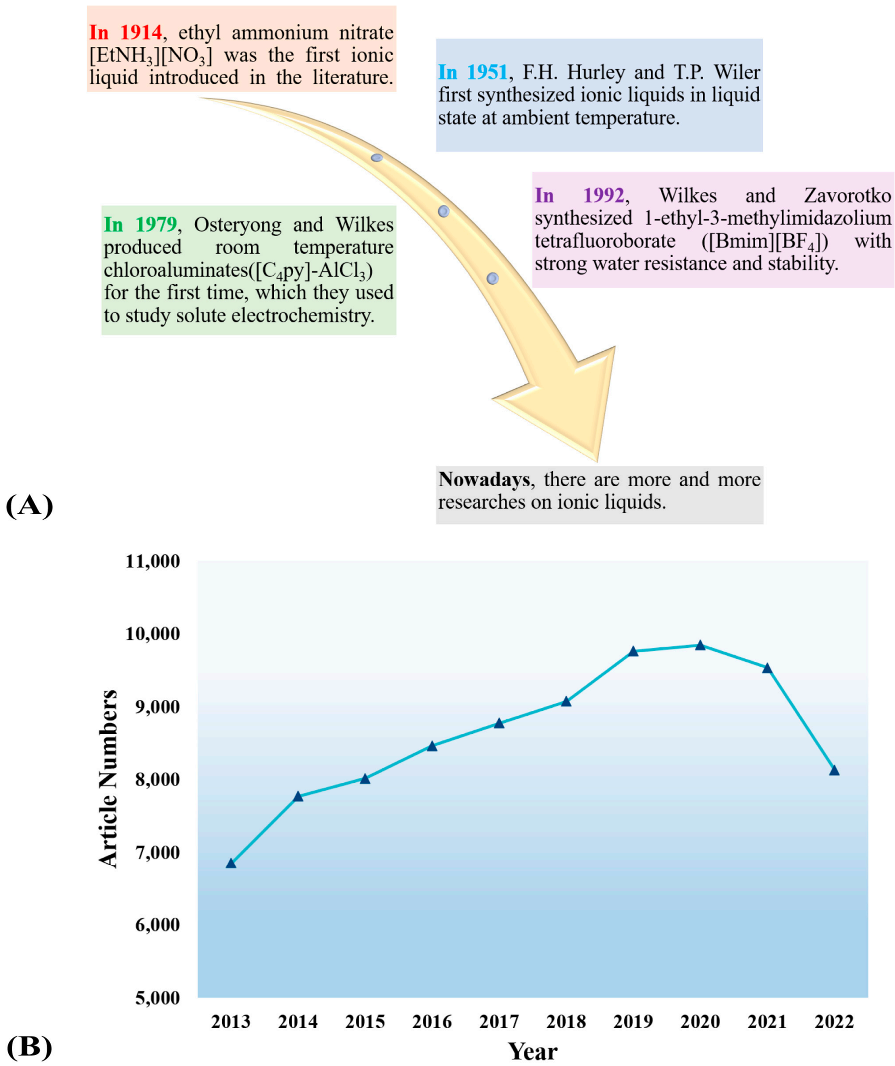


Figure 1. (**A**) Development history of ionic liquids. (**B**) Trends in the amount of academic documents on ionic liquids published from 2013 to 2022 (data based on Web of Science search, using the keyword "ionic liquids").

Phytochemicals are non-nutrient bioactive compounds obtained from plants, as the products of secondary metabolism [16]. Phytochemicals are bioactive compounds that can be classified as flavonoids, alkaloids, terpenoids, quinones, polysaccharides, phenols, glycosides, phenylpropanoids, etc. [17]. Phytochemicals have a variety of bioactivities, including anticancer, immunostimulatory, antioxidant, neuroprotective, hepatoprotective, etc. Meanwhile, their bioactivities currently lead to widespread use in pharmaceutical, food, textiles, cosmetics industries, and optical sensing applications [18–20]. At present, organic solvents are used to extract phytochemicals from plants. Although these solvents have been produced industrially, they continue to have various disadvantages, such as as poor extraction efficiency, high energy consumption, high time consumption, and the use of harmful organic solvents, which pollute the environment [21]. Therefore, the construction and selection of alternative extraction solvents has been a popular study subject for researchers in this field. Ionic liquids possess some distinctive advantages when used in extraction, such as their adjustable structure that could distinguish them from the extraction limitation of volatile organic solvents and their low vapor pressure, low nucleophilicity, good extractability for organic compounds and metal ions, etc. [6,22–24]. Among them, imidazolium ionic liquids are the most frequently used when extracting phytochemicals. Because imidazolium ionic liquids have good solubility for cellulose, their anions and cations especially can form complex structures with cellulose during the dissolution that can break the hydrogen bonding between cellulose molecules that makes up the majority of plant cell walls, allowing the extracts to be better dissolved out of the cell wall so that it can improve the extraction yield. However, cellulose is soluble in the majority of organic solvents and water [25–28]. Therefore, the trait of imidazolium ionic liquids offers an innovative idea for the extraction of phytochemicals from plants. After consulting some of the literature related to the extraction of phytochemicals, we found some of the same phytochemicals extracted by traditional solvents and imidazolium ionic liquids. Then we compared the results of phytochemicals extracted by organic solvents and imidazolium ionic liquids (Table 1). Imidazolium ionic liquids possess a better extraction yield than organic solvents. This may be attributed to the multiple interactions between imidazolium ionic liquids and phytochemicals that can facilitate extraction.

Table 1. Comparison between traditional solvents and imidazolium ionic liquids.

Plants	Extraction Solvents	Extraction Results	Ref.
Angelica gigas Nakai (*A. gigas*)	[Bmim][BF_4]	Decursin's yield was 43.32 mg/g, decursinol angelate's yield was 17.87 mg/g	[29]
Angelica gigas Nakai (AGN)	60% EtOH	Decursin's yield was 29.80 mg/g, decursinol angelate's yield was 13.55 mg/g	[30]
Anoectochilus roxburghii (Wall.) Lindl. (*A. roxburghii*)	[C_4mim][PF_6]	Rutin's enrichment factor was 32, the extraction efficiency was 71.8%	[31]
Amaranth (*Amaranthus* spp.)	Water and ethanol	Rutin's yields extracted from amaranth were 35.3 mg/kg (defatted seeds) and 41.1 mg/kg (non-defatted seeds)	[32]
Grape	[C_4mim][Br]	Anthocyanin's yield was 15.9 ± 0.1 mg/g	[33]
Purple-fleshed sweet potato (PSP)	80% Methanol	Anthocyanin's yield was 245.3 mg/100 g	[34]
Orange	[Bmim][Cl]	Carotenoid's yield was 32.08 ± 2.05 μg/g	[35]
Acerola	Acetone	Carotenoid's yield was 7.88 ± 0.59 μg/g	[36]
Glycyrrhiza uralensis	[Bmim][Br]	Isoliquiritigenin's yield was 0.665 mg/g	[37]
Licorice (*Glycyrrhiza glabra*)	Glycerol/water mixtures	Isoliquiritigenin's yield was 6.23 ± 0.16 μg/mL	[38]

In this work, we comprehensively summarized related research for extracting phytochemicals from plants by imidazolium ionic liquids. In detail, the first part of this work is an exhaustive introduction to imidazolium ionic liquids, including structural formula and preparation methods. The use of imidazolium ionic liquids in the extraction of phytochemicals from plants is next discussed and summarized. Then we emphasize the importance of extraction mechanisms, recovery methods, and reuse of imidazolium ionic liquids. Subsequently, the problem of toxicity in imidazolium ionic liquids is proposed. Finally, the existing challenges and outlooks of imidazolium ionic liquids are analyzed, which are expected to provide references for extracting phytochemicals efficiently from plants.

2. Imidazolium Ionic Liquids

2.1. Structures of Imidazolium Ionic Liquids

After reviewing some of the literature, it was found that the ionic liquids currently used for the extraction of phytochemicals are mainly imidazolium ionic liquids. Their cations are mainly N,N-dialkylimidazole cations, along with the increasing cationic alkyl chain; anions are mainly Br^-, Cl^-, PF_6^-, BF_4^-, Tf_2N^-, Ac^-, etc. Table 2 illustrates their structure.

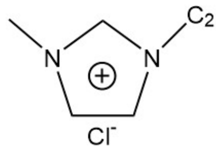
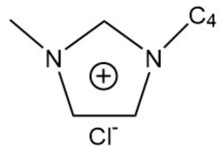
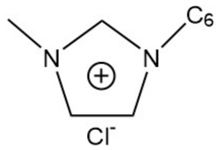
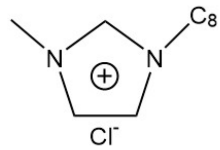
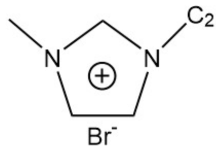
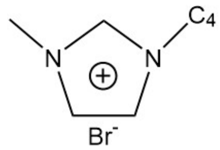
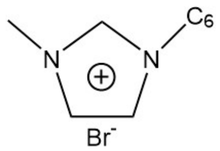
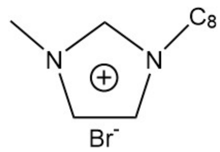
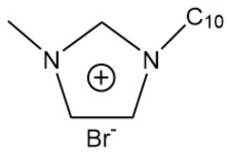
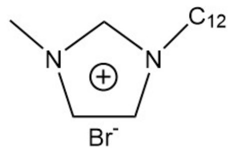
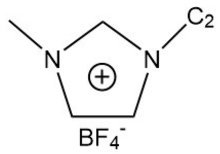
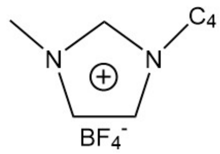
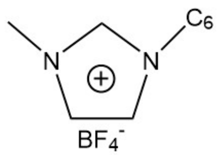
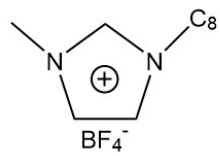
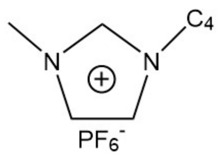
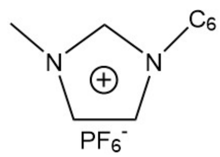
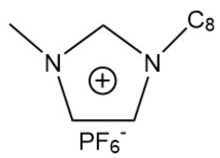
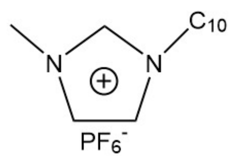
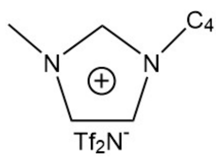
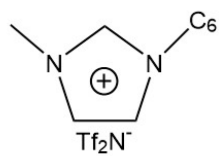
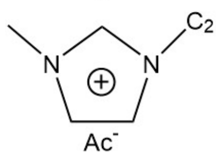
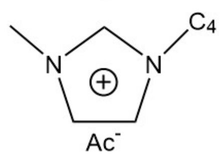
2.2. Preparation of Imidazolium Ionic Liquids

Before introducing the extraction of phytochemicals from plants by imidazolium ionic liquids, we first discuss how imidazolium ionic liquids are made by presenting the synthesis methods of conventional imidazolium ionic liquids and functional imidazolium ionic liquids.

2.2.1. Conventional Imidazolium Ionic Liquids

The 1,3-dialkyl imidazolium cation is the most investigated structure within the imidazolium ionic liquids previously studied [39]. Therefore, the conventional methods for the preparation of imidazolium ionic liquids are also related to 1,3-dialkyl imidazolium cations. In 2002, Jean-Marc et al. presented preliminary work for synthesizing some 1-butyl-3-methylimidazolium salts (BF_4, PF_6, CF_3SO_3, and BPh_4) with ultrasound assistance. Typically, two processes are required to create the 1-butyl-3-methylimidazolium salts. At first, the researchers performed the Menschutkin quaternization of 1-methylimidazole via butyl halide (bromide or chloride), and then anion was exchanged with ammonium salts, which is also called the Finkelstein reaction [40]. Simultaneously, Vasudevan et al. adopted an ultrasonic cleaning bath for synthesizing ambient-temperature ionic liquids; they prepared 1,3-dialkyl imidazolium halides and conducted more in-depth and comprehensive research than the method mentioned earlier. As shown in Figure 2A, the synthesis process was an effective reaction between 1-methyl imidazole and alkyl halides/terminal dihalides [41]. With further study of imidazolium ionic liquids, it is obvious that 1-butyl-3 methylimidazole chloride is the most widely utilized among them. Therefore, its preparation method is valuable. It involved taking the n-butyl chloride and slowly dropping it into the 1-methylimidazole solution at 25 °C, with 1-methylimidazole and n-butyl chloride mixed at a molar ratio of 1:1.2. The reaction lasted for 72 h, at 70 °C, with stirring. To get rid of the unreacted raw materials, the researchers used ethyl acetate to clean the mixture three times, followed by distillation at 70 °C, over 2 h, under reduced pressure; then [Bmim][Cl] was obtained, with a yield of 95% [42]. The synthetic reaction process is shown in Figure 2B. Additionally, there was progress in the synthesis of imidazolium ionic liquids for the extraction of phytochemicals. Li et al. produced [C_{12}mim][BF_4] and utilized it to extract echinacoside and acteoside from *Cistanche deserticola*, which showed exceptional extraction yields with echinacoside at 7.47 mg/g and acteoside at 3.56 mg/g. Figure 2C illustrates how the imidazolium ionic liquid was made [43].

Table 2. The chemical structures of the imidazolium ionic liquids used in the extraction of phytochemicals.

Ionic Liquid	Structure	Ionic Liquid	Structure
[Emim][Cl] ([C_2mim][Cl])		[Bmim][Cl] ([C_4mim][Cl])	
[Hmim][Cl] ([C_6mim][Cl])		[Omim][Cl] ([C_8mim][Cl])	
[Emim][Br] ([C_2mim][Br])		[Bmim][Br] ([C_4mim][Br])	
[Hmim][Br] ([C_6mim][Br])		[Omim][Br] ([C_8mim][Br])	
[Demim][Br] ([C_{10}mim][Br])		[Domim][Br] ([C_{12}mim][Br])	
[Emim][BF_4] ([C_2mim][BF_4])		[Bmim][BF_4] ([C_4mim][BF_4])	
[Hmim][BF_4] ([C_6mim][BF_4])		[Omim][BF_4] ([C_8mim][BF_4])	
[Bmim][PF_6] ([C_4mim][PF_6])		[Hmim][PF_6] ([C_6mim][PF_6])	
[Omim][PF_6] ([C_8mim][PF_6])		[Demim][PF_6] ([C_{10}mim][PF_6])	
[Bmim][Tf_2N] ([C_4mim][Tf_2N])		[Hmim][Tf_2N] ([C_6mim][Tf_2N])	
[Emim][Ac] ([C_2mim][Ac])		[Bmim][Ac] ([C_4mim][Ac])	

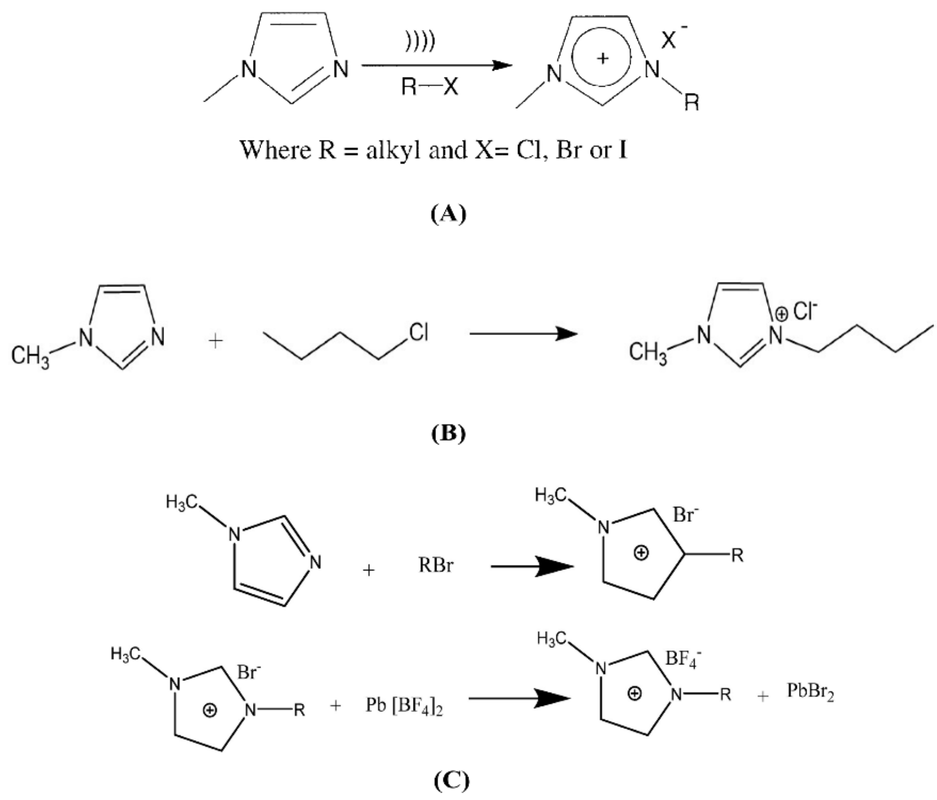


Figure 2. (**A**) An ultrasound-assisted preparation for a series of 1-alkyl-3-methylimidazolium halides. Republish from Ref. [41], Copyright (2002), with permission from American Chemical Society. (**B**) The preparation of [Bmim][Cl]. (**C**) Preparation reaction equations for [C_{10}mim][Br], [C_{12}mim][Br], [C_{14}mim][Br], [C_{10}mim][BF_4], [C_{12}mim][BF_4], and [C_{14}mim][BF_4] (R = decyl, dodecyl, or tetradecyl). Republished from Ref. [43], Copyright (2022), with permission from Elsevier.

2.2.2. Functional Imidazolium Ionic Liquids

Because of the special physicochemical properties of ionic liquids, they are referred to as 'designer solvents', and cations and anions can be modulated to generate them in order to meet a specific requirement [44]. With the continuous improvement of ionic liquid extraction, the demand for the use of imidazolium ionic liquids is also increasing. As a result, researchers have become more involved in designing functional imidazolium ionic liquids to meet the needs of extracting phytochemicals from plants. Subsequently, it is about the preparation of magnetic ionic liquid, porous ionic liquid, and molecularly imprinted ionic liquid. To extract flavonoids from tree peony, Chen et al. created magnetic silicone particles loaded with ionic liquid (Fe_3O_4@SiO_2@IL). The findings demonstrated that flavonoids' purity has improved obviously [45]. They first synthesized Fe_3O_4 particles and then mixed them with 1-vinyl imidazole and tetraethoxysilane (TEOS) to obtain Fe_3O_4@SiO_2 particles, followed by the addition of vinyl triethoxysilane (VTES) to obtain Fe_3O_4@SiO_2@VTES particles; they were then reacted with various types of imidazolium ionic liquids ([VEim][Br], [VBim][Br], [VHim][Br], [VOim][Br], and [VDim][Br]) to finally obtain Fe_3O_4@SiO_2@IL particles. The preparation process of IL particles is shown in Figure 3A. Moreover, Zhao et al. developed a new poly(ionic liquid)-functionalized magnetic material (PILs@mSiO_2@nSiO_2@Fe_3O_4) for the enrichment of eight pyrethroids in apples [46]. Only one minute was required for the extraction process, thus greatly reducing extraction time. The preparation procedure of PILs@mSiO_2@nSiO_2@Fe_3O_4 is shown in Figure 3B. In addition, the phenolic compounds in fruit juice were extracted with a novel approach that used 3,4-dihydroxybenzenepropanoic acid for the template molecule, as well as 1-ally-3-vinylimidazolium chloride for the functional monomer to create poly(ionic liquid)-based molecularly imprinted polymers [47]. The method displayed high selectivity, exceptional sensitivity, and environmental friendliness compared with other approaches. By preparing functional imidazolium ionic liquids, it was revealed that they have several merits in comparison to conventional solvents applied for phytochemical extraction, such as a faster and more efficient extraction process, along with better purity. It serves as a reference for designing functional imidazolium ionic liquids that are utilized to extract phytochemicals. However, to develop functional imidazolium ionic liquids for extraction, it is essential to comprehend how the functional groups of functional imidazolium ionic liquids interact with the target chemicals, as well as to further explore the extraction mechanism.

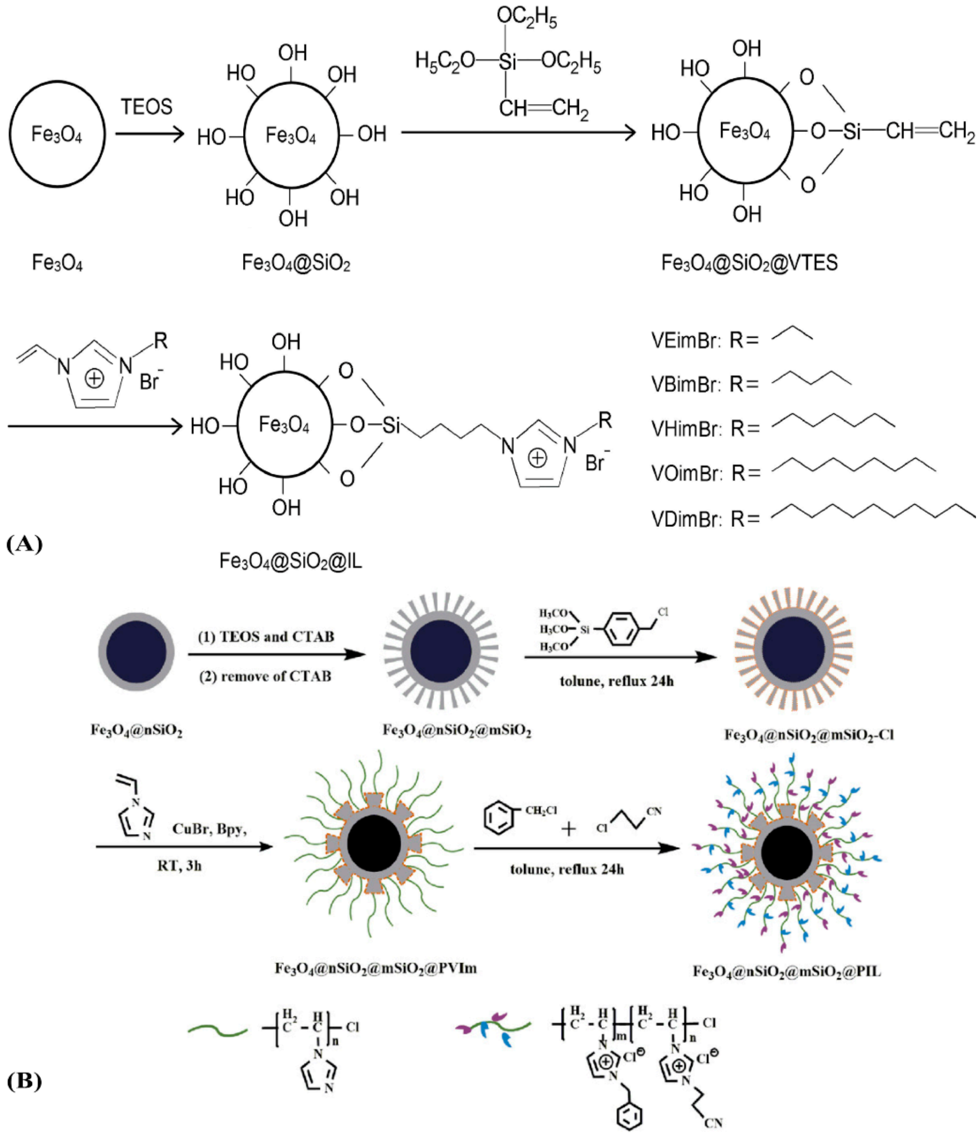


Figure 3. (**A**) Preparation procedure of $Fe_3O_4@SiO_2@IL$ particles. Republished from Ref. [45], Copyright (2020), with permission from Elsevier. (**B**) Synthesis of $PILs@mSiO_2@nSiO_2@Fe_3O_4$. Republished from Ref. [46], Copyright (2019), with permission from Wiley.

3. Extraction of Phytochemicals from Plants by Imidazolium Ionic Liquids

The reason that imidazolium ionic liquids can enhance the extraction efficiency of phytochemicals from plants is that imidazolium ionic liquids and the extracted groups can generate hydrogen bonding, electrostatic interactions, and other intermolecular forces to achieve extraction [48]. In addition, ionic liquids composed of imidazolium could efficiently dissolve cellulose. Meanwhile, the essential component of the cell wall is cellulose, which makes the extracted material better dissolve out of the cell wall, thus improving the extraction performance [28]. There is some research on extracting phytochemicals such as flavonoids, alkaloids, terpenoids, quinones, polysaccharides, phenols, glycosides, phenylpropanoids, organic acids, and others by imidazolium ionic liquids (as summarized in Table 3) which showed that imidazolium ionic liquids as extractants have exceptional extraction efficiency on many phytochemicals in plants. Additionally, there are several means that could assist with the imidazolium ionic liquids' extraction.

Table 3. Extraction of phytochemicals by imidazolium ionic liquids.

Category	Bioactive Compounds	Plants	Ionic Liquids	Methods *	Ref.
Flavonoids	Taxifolin	*Larix gmelinii*	$[C_4mim][Br]$	MAE	[49]
	Dihydroquercetin	*Larix gmelinii*	$[C_2mim][Br]$	Homogenate-ultrasound synergistic technique	[50]
	Isoflavones	*Radix Puerariae*	[Bmim][Br]	MAE	[51]
	Rutin, hyperoside, hesperidin	*Sorbus tianschanica*	$[C_6mim][BF_4]$	MAE	[52]
	Flavonoids	*Apocynum venetum* L.	$[C_4mim][N(CN)_2]$	UAE	[53]
	Amentoflavone, hinokiflavone	*Selaginella sinensis*	$[C_6mim][BF_4]$	MAE	[54]
	Isoangustone A, licoisoflavanone, licoricidin, glabridin	Licorice	$[C_8mim][BF_4]$	UAE	[55]
Alkaloids	Berberine, palmatine, jatrorrhizine	*Phellodendron amurense* Rupr.	[Bmim][Br]	UAE	[56]
	Aconitum alkaloids	*Aconitum carmichaeli* (Fuzi)	$[C_6mim][Br]$	Aqueous two-phase system	[57]
	Pronuciferine, N-nornuciferine, nuciferine, roemerine	Lotus	$[C_4mim][BF_4]$	Aqueous two-phase system	[58]
	Protopine, allocryptopine, sanguinarine, chelerythrine, dihydrochelerythrine, dihydrosanguinarine	*Macleaya cordata*	$[C_6mim][BF_4]$	UAE	[59]
	Sinomenine	*Sinomenium acutum*	$[C_2OHmim]FeCl_4$	UAE	[60]
	Berberine, palmatine, jatrorrhizine, magnoflorine, phellodendrine	*Phellodendron amurense* Rupr	$[C_4mim][OAc]$	UAE	[61]
	Liensinine, isoliensinine, neferine, O-demethyl nuciferine, nuciferine	Lotus	$[C_{12}mim][Br]$	Ionic-liquid-assisted mechanochemical extraction	[62]

Table 3. *Cont.*

Category	Bioactive Compounds	Plants	Ionic Liquids	Methods *	Ref.
Terpenoids	Ganoderic acid	*Ganoderma lucidum*	$[C_4mim][Cl]$	-	[63]
	Paeoniflorin	*Paeonia suffruticosa* Andr.	$[C_4mim][Br]$	MAE	[64]
	Ionone, linalool oxide pyranoid, linalool oxide furanoid	*Osmanthus fragrans* var. aurantiacus	$[C_2mim][(MeO)(H)PO_2]$	Maceration	[65]
	Morroniside, sweroside, loganin, cornuside	*Fructus Corni*	$[Domim][HSO_4]$	Maceration	[66]
	Cynaropicrin	*Cynara cardunculus* L.	1-alkyl-3-methylimidazolium chloride	-	[67]
	Limonene, β-pinene, 1r-α-pinene, limonene oxide, linalool, β-citral, (R)-(+)-citronellal, eremophilene, geranial, α-citral	*Citrus sinensis*	$[C_2mim][OAc]$, $[C_4mim][Cl]$	MAE	[68]
Quinones	Physcion, chrysophanol, emodin, rhein, aloe–emodin	Rhubarb	[Bmim][Br]	UMAE	[69]
	Physcion, chrysophanol, emodin, rhein, aloe–emodin	*Aloe vera* L.	$[C_4mim][BF_4]$	Aqueous two-phase system	[70]
	Miltirone, tanshinone IIA, cryptotanshinone	*Salvia miltiorrhiza* Bunge	$[C_8mim][PF_6]$	Ultrahigh-pressure-assisted extraction	[71]
	Physcion, chrysophanol, emodin, aloe–emodin	*Rheum palmatum* L.	$[C_8mim][BF_4]$	MAE	[72]
	Rhein and emodin	*Rheum palmatum* L.	$[BHim][MeSO_3]$	MAE	[73]
	Physcion, chrysophanol, emodin, rhein, aloe–emodin	*Polygonum multiflorum*	$[C_4Bmi][p\text{-}TSA]$	UAE	[74]
Polysaccharides	Aloe polysaccharides	*Aloe vera* L.	$[Bmim][BF_4]$	Aqueous two-phase system	[75]
	Polysaccharides	*Japanese Cedar*	1-(3-methoxypropyl)-3-methyl imidazolium ethyl ethylphosphonate	-	[76]
	Ginger polysaccharides	Ginger (*Zingiber officinale Roscoe*)	$[C_4mim][BF_4]$	UAE	[77]
	Arabinogalactan	*Larix gmelinii*	$[C_2mim][Br]$	Homogenate-ultrasound synergistic technique	[50]
	Bamboo polysaccharides	Bamboo	$[Bmim][PF_6]$	UMAE	[78]

Table 3. *Cont.*

Category	Bioactive Compounds	Plants	Ionic Liquids	Methods *	Ref.
Phenols	Aspidinol, aspidin PB, dryofragin, aspidin BB	*Dryopteris fragrans*.	$[C_8mim][Br]$	MAE	[79]
	Polyphenolics	*Peperomia pellucida* (L.) Kunth (*P. Pellucida*)	$[Bmim][BF_4]$	MAE	[80]
	Catechins	*Camellia sinensis* (Linn.) O. Kuntze	$[C_3mim]FeCl_4$	UAE	[81]
	Polyphenols	*Carya cathayensis* Sarg	$[C_4C_1im][BF_4]$	UAE	[82]
Glycosides	Glycosides salicin, hyperin	Populus	$[C_4mim][BF_4]$	MAE	[83]
	Verbascoside	Rehmannia	[Bemim][Cl]	MAE	[84]
	Triterpenoid saponins, glycyrrhizin	Licorice	$[C_4mim][BF_4]$	UAE	[85]
	Oxypaeoniflorin, albiflorin, paeonin, paeoniflorin, benzoylpaeoniflorin	*Paeonia suffruticosa* (*P. suffruticosa*)	$[C_8mim][Br]$	-	[86]
	Syringin, oleuropein	*Syringa reticulata* subsp. amurensis	$[C_4mim][Br]$	UAE	[87]
Phenylpropanoids	Cajanol	*Cajanus cajan* (L.) Millsp (Pigeon pea)	$[C_4mim][Br]$	MAE	[88]
	Coumarins	*Cortex fraxini*	$[C_4mim][Br]$	UMAE	[89]
	Lignans	Schisandra	$[C_4mim][BF_4]$	UAE	[90]
	Psoralen	*Ficus carica* L.	[Bmim]Br–citric acid mixture	Aqueous two-phase system	[91]
	Psoralen and isopsoralen	*Psoralea corylifolia*	$[C_{10}mim][Br]$	UAE	[92]
Organic acids	Gallic acid, ellagic acid	*Eucalyptus camaldulensis*	$[C_4mim][BF_4]$	MAE	[93]
	Aristolochic acid	*Pinellia Tenore*	IM-BIM@Sil (imidazolium chloride–butylimidazolium chloride immobilized silica)	-	[94]
	Gallic acid, malic acid, ellagic acid, tannic acid, chlorogenic acid, quercetin	Oak galls (*Quercus* sp.)	$[Bmim][Tf_2N]$	Ultrasonic-probe-assisted extraction	[95]
Others	Diterpenoid lactone-andrographolide	*Andrographis paniculata*	[Bmim][Cl]	MAE	[96]
	Carotenoids	Orange	[Bmim][Cl]	UAE	[35]
	Corilagin	*Phyllanthus*	[Bmim][Br]	-	[97]

* MAE, microwave-assisted extraction; UAE, ultrasound-assisted extraction; UMAE, ultrasound- and microwave-assisted extraction.

3.1. Flavonoids

Flavonoids belong to a class of significant compounds with numerous biological functions that are present throughout nature. Their molecules contain mostly ketone groups, and most of them have the basic skeleton of C_6-C_3-C_6 [98]. Imidazolium ionic liquid can be used to extract taxifolin, dihydroquercetin, isoflavones, rutin, hyperoside, hesperidin, flavonoids, amentoflavone, hinokiflavone, isoangustone A, licoisoflavanone, licoricidin, and glabridin [49–55]. Their extraction results are superb, especially the extraction of dihydroquercetin from Larix gmelinii by [C_2mim][Br], as it showed a higher extraction yield (53.09 ± 2.24 mg/g) with lower energy and time consumption versus the conventional extraction method. In addition, studies showed that the cationic alkyl chain lengths of most imidazolium ionic liquids were between C_2 and C_8, and mononuclear anions were mostly used as anions when extracting flavonoids, thus indicating that such types of imidazolium ionic liquids are more suitable for extracting flavonoids.

3.2. Alkaloids

Alkaloids are a kind of non-primary metabolites existing in biological organisms, most of which contain one or more carbon ring with nitrogen atoms bound in the ring [98]. Many kinds of alkaloids are extracted based on imidazolium ionic liquids, such as berberine, palmatine, jatrorrhizine, aconitum alkaloids, pronuciferine, N-nornuciferine, nuciferine, roemerine, protopine, allocryptopine, sanguinarine, chelerythrine, dihydrochelerythrine, dihydrosanguinarine, sinomenine, berberine, palmatine, jatrorrhizine, magnoflorine, phellodendrine, liensinine, isoliensinine, neferine, and O-demethyl nuciferine [56–62]. The extraction of alkaloids by imidazolium ionic liquid has achieved excellent outcomes. The poor water solubility of isoquinoline alkaloids and the high viscosity of the ionic liquid were addressed by Peng et al. in a way that may effectively guarantee the yield and quality of the alkaloids that are extracted. The ionic liquid they used was [C_4mim][OAc] [61]. In addition, a method for the simultaneous extraction and enrichment of alkaloids in lotus leaves by using a mechanochemical extraction approach supported by ionic liquids was proposed, and it also provided a reference for more efficient extraction with imidazolium ionic liquid [62].

3.3. Terpenoids

Terpenoids are a group of phytochemicals in huge quantities and complex structural types in nature; most of them have the molecular formula of $(C_5H_8)_n$ [99]. Imidazolium ionic liquids can extract ganoderic acid, paeoniflorin, ionone, linalool oxide pyranoid, linalool oxide, furanoid, morroniside, sweroside, loganin, cornuside, cynaropicrin, limonene, β-pinene, 1r-α-pinene, limonene oxide, linalool, β-citral, (R)-(+)-citronellal, eremophilene, geranial, and α-citral [63–68]. Research showed that their extraction yields were improved by imidazolium ionic liquids. In particular, when using the cation alkyl chain [Bmim] for extraction of ganoderic acid, paeoniflorin, limonene, β-pinene, 1r-α-pinene, limonene oxide, linalool, β-citral, (R)-(+)-citronellal, eremophilene, geranial, and α-citral, higher extraction efficiencies were obtained. It is possible that imidazolium ionic liquids with side-chain alkyl chain length of four carbons typically have a moderate viscosity and mass transfer effect [100].

3.4. Quinones

The class of phytochemicals known as quinones, which have a quinone structure, is primarily split into four categories: benzoquinone, naphthoquinone, phenanthrenequinone, and anthraquinone. Quinones play an important role in nature due to their extensive biological activities. Some studies on the extraction of physcion, chrysophanol, emodin, rhein, aloe-emodin, miltirone, tanshinone IIA, and cryptotanshinone by imidazolium ionic liquids were described [69–74]. According to research, we can extract some of the same phytochemicals from plants such as physcion, chrysophanol, emodin, rhein, and aloe–emodin from Rhubarb, *Aloe vera* L., and *Polygonum multiflorum*, respectively. The type of cation they used was [C_4mim], which had high efficiency and good selectivity. The physcion, chrysophanol, emodin, and aloe–emodin can also be extracted from *Rheum palmatum* L. by [C_8mim][BF_4]. The studies indicate that imidazolium ionic liquids are appropriate to use to extract these phytochemicals.

3.5. Polysaccharides

Through the polymerization of more than ten monosaccharide molecules using large-molecular-weight glycosidic linkages, polysaccharides are created. Phytochemicals such as aloe polysaccharides, polysaccharides of Japanese Cedar, ginger polysaccharides, arabinogalactan, and bamboo polysaccharides can all be extracted by imidazolium ionic liquids [50,75–78]. Using imidazolium ionic liquids, all have exceptional extraction results compared with traditional solvents. We can take bamboo polysaccharides as an example. As we all know, bamboo and its sap are one of the raw materials for industrial production; bamboo also is a functional food. Jiang et al. developed ionic-liquid-involved membranes with solvent-free for extracting bamboo polysaccharides. According to the results, the system's benefits were mild conditions, ease of use, environmental friendliness, and simple continual phytochemical enrichment, which showed a possibility for the extraction of bamboo polysaccharides by modified imidazolium ionic liquid.

3.6. Phenols

Phenols widely exist in nature, with their structures containing hydroxyl, most of which have an aroma. Some phenols were extracted by imidazolium ionic liquids, including aspidinol, aspidin PB, dryofragin, and aspidin BB from Dryopteris fragrans.; polyphenolics from *Peperomia pellucida* (L.) Kunth; catechins from Camellia sinensis; and polyphenols from *Carya cathayensis* Sarg [79–82]. Their extraction results were good. For example, Li et al. proposed that the extraction efficiencies by using [C_8mim][Br]-based surfactant with microwave-assisted extraction for four phloroglucinols increased from 1.5% to 40.4% compared to other methods [79]. Islamudin et al. optimized the process with imidazolium ionic liquid [Bmim][BF_4] to extract polyphenolic contents from *Peperomia pellucida* (L) kunth. A magnetic ionic liquid was presented to extract polyphenols from tea leaves, and it provided a new method for improvement based on imidazolium ionic liquid to extract phytochemicals [80]. Correspondingly, the Nanobubbles (NBs)-assisted ionic liquid [C_4C_1im][BF_4] to extract polyphenols from *Carya cathayensis* Sarg was reported [82].

3.7. Glycosides

Glycosides belong to a kind of compound formed by the condensation and dehydration of sugars or sugar derivatives with non-sugar parts through hemiacetal hydroxyl or hemiacetal ketone hydroxyl groups on their end carbon. Glycosides such as glycosides salicin, hyperin, verbascoside, triterpenoid saponins, glycyrrhizin, oxypaeoniflorin, albiflorin, paeonin, paeoniflorin, benzoylpaeoniflorin, syringing, and oleuropein were extracted by imidazolium ionic liquids with terrific extraction effects [83–87]. A new method for removing triterpenoid saponins from licorice by using in situ alkaline aqueous biphasic systems was developed [85]. A novel reinforced cloud point extraction using imidazolium ionic liquid was utilized to extract five monoterpene glycosides from the flower of *Paeonia suffruticosa* [86].

3.8. Phenylpropanoids

Phenylpropanoids refer to a class of phytochemicals containing one or more C_6-C_3 units in their structures [101]. Some studies on the extraction of cajanol, coumarins, lignans, psoralen, and isopsoralen were described [88–92]. Their extraction results were satisfactory. The studies indicate that the [C_4mim][Br] is usually used to extract phenylpropanoids, and it can efficiently improve the extraction efficiency. Moreover, for the extraction of psoralen from fig leaves, Wang et al. suggested using a [Bmim][Br]–citric acid mixture, which exhibited enhanced extraction efficiency. In comparison to [Bmim][Br]–water, ethanol–citric acid, and ethanol, it was demonstrated that the extraction yield of psoralen from [Bmim][Br]–citric acid mixture was 1.45-, 2.45-, and 3.68-times greater, respectively. It provides a reference for the application of an imidazolium ionic-liquid-pH-based aqueous two-phase system for extraction [91]. From the phenylpropanoids in Table 4, we can see that the common anion of imidazolium ionic liquids used for the extraction is Br^-, and this may be because the Br^- and the extract are prone to produce stronger multiple interactions, including π–π, hydrogen bonding, etc., which can increase the interaction between the carboxyl and carbonyl groups of the structure of the extract and the Br-, thus promoting the extraction [102].

3.9. Organic Acids

Organic acids are a class of compounds that contain carboxyl groups in their molecular structure. Research on the extraction of gallic acid, ellagic acid, aristolochic acid, malic acid, tannic acid, chlorogenic acid, and quercetin was performed [93–95]. Compared with conventional extraction solvents, their extraction outcomes were ample by using imidazolium ionic liquid. Fang et al. used imidazolium-chloride–butylimidazolium-chloride-immobilized silica (IM-BIM@Sil) to extract aristolochic acid from plants, the extraction yield they acquired was 16.69 mg/g of aristolochic acid, which provides the possibility for more extraction methods based on imidazolium ionic liquid [94].

3.10. Others

We also summarize the research on other phytochemicals with extracting by imidazolium ionic liquids, such as the diterpenoid lactone andrographolide, carotenoids, and corilagin [35,96,97]. The type of cation they used was [Bmim], which showed excellent extraction results. For example, Meenu et al. used [Bmim][Cl] with microwave-assisted extraction to extract the diterpenoid lactone andrographolide from Andrographis paniculate; the yield of andrographolide was increased obviously [96]. A method using imidazolium ionic liquid [Bmim][Cl] with ultrasonic-assisted to extract carotenoids from orange peel was also proposed, resulting in a better extraction yield compared with the yield by acetone extraction [35]. Hou et al. used [Bmim][Br] for the extraction of corilagin from Phyllanthus; the yield of corilagin they obtained had a purity of 86.49% [97].

3.11. Factors Affecting the Extraction Results by Imidazolium Ionic Liquids

The structure of imidazolium ionic liquids is intimately related to their physicochemical properties and the effectiveness of phytochemical extraction. The conventional classification of ionic liquids is predicated upon their anions and cations. According to the structure of anions, ionic liquids can be divided into two types: one is mononuclear anions, such as Cl^-, Br^-, F^-, $PF_6{}^-$, $BF_4{}^-$, etc.; the other is polynuclear anions, such as $Al_3Cl_{10}{}^-$, $Cu_2C_{13}{}^-$, $Fe_2C_7{}^-$, etc. Meanwhile, cations are mainly divided into imidazolium, pyrrolidinium, pyridinium, and quaternary ammonium, phosphonium [21]. Among multifarious organic cations, imidazolium ions are the widely used [103]. In order to improve the extraction effects of imidazolium ionic liquids, the choice of anion species and the length of the carbon chain must be carefully taken into consideration. The extraction mechanism is mainly based on the interactions between imidazolium ionic liquids and target components. The stronger the interaction, the higher the extraction yield.

3.11.1. Effect of the Type of Anions

Studies on the effect of anion species on extraction have been conducted. The hydrophobic ionic liquids of 1-butyl-3-hexylimidazolium with diverse anions ($[ClO_4]^-$, $[BF_4]^-$, $[PF_6]^-$, $[CF_3SO_3]^-$, and $[NTf_2]^-$) were produced in a sequence, which was used for assessing the effect of different anionic types of imidazolium ionic liquids on the extraction results of gramine and quinine [104]. According to the study, the interactions between two alkaloids and the imidazolium ionic liquids contain a hydrophobic interaction, hydrogen bonding interaction, and steric effect, but their extraction capacity mainly relies on how well anions form hydrogen bonds. It was confirmed that $[C_4C_{10}im][CF_3SO_3]$ is the best extractant to extract gramine and quinine, probably because the F and O in $[CF_3SO_3]$ can establish hydrogen bonding with the proton in the −NH group of gramine or the −OH group of quinine, thus contributing to the extraction.

Li et al. selected 1-alkyl-3-methylimidazolium ionic liquids with various anions ($[BF_4]^-$, $[PF_6]^-$, $[OAc]^-$, and $[NTf_2]^-$) for the extraction of glabridin [105]. After comparing their extraction efficiencies, different anions were found to have different extraction efficiency of glabridin, which was ranked from highest to lowest as $[NTf_2]^-$, $[OAc]^-$, $[BF_4]^-$, and $[PF_6]^-$. The extraction efficiency of $[C_4mim][NTf_2]$ was the best, at 95.72%. It may be attributed to the $[NTf_2]^-$, as it can provide more atoms to generate hydrogen bonding with the hydroxyl group of glabridin [106,107]. Therefore, the primary interaction between the anions of imidazolium ionic liquids and glabridin is hydrogen bonding, and this influences the ability of imidazolium ionic liquids to extract glabridin.

Zhang et al. adopted some 1-alkyl-3-methylimidazolium ionic liquids for studying how anions affected the extraction of salidroside and tyrosol from *Rhodiola*, which might influence the extraction yields of target compounds [108]. They compared the extraction yield of 1-butyl-3-methylimidazolium ionic liquids with four anions ($[Cl]^-$, $[Br]^-$, $[BF_4]^-$, and $[PF_6]^-$). The findings revealed that the water solubility of the imidazolium ionic liquids is important for the extraction process, and the polarity of the imidazolium ionic liquids can be altered with the change of anions, all of which affect their extraction efficiencies.

In conclusion, the polarity of the anion in imidazolium ionic liquids, as well as hydrogen-bonding interactions between anions and target compounds, may influence how effectively phytochemicals are extracted by imidazolium ionic liquids.

3.11.2. Effect of the Alkyl Chain Length of Cations

In addition to the influence of the type of anions on the extraction of phytochemicals, the change in the length of the alkyl chain on the cation can also have a significant effect on extraction. Some 1-alkyl-3-methylimidazolium cations ($[C_4mim]^+$, $[C_6mim]^+$, and $[C_8mim]^+$) on the extraction of glabridin have been studied, and the results showed that the extraction efficiency of glabridin increased with the range of alkyl chain length from C_4 to C_6 and decreased with the change of alkyl chain length from C_6 to C_8 [105]. Imidazolium ionic liquids with $[C_6mim]^+$ had the optimal extraction performance for glabridin at 88.23%. The reason for the phenomenon may be due to the hydrophobic interaction between the cation of the imidazolium ionic liquid and the glabridin increases with increasing the length of the alkyl chain, so the extraction efficiency is enhanced. However, as the alkyl chain length continues to increase, the steric impact also rises. It may decrease the hydrophobic interaction and lower the extraction efficiency.

Ji et al. used some $[C_{12}mim][BF_4]$, $[C_{10}mim][BF_4]$, $[C_8mim][BF_4]$, $[C_6mim][BF_4]$, $[C_4mim][BF_4]$, and $[C_2mim][BF_4]$ to extract prenylated flavonoids from licorice when comparing their extraction efficiency [55]. It was revealed that, as the alkyl chain length is raised from ethyl to octyl, their extraction efficiency steadily increases. This may be due to their increased hydrogen bond acidity and hydrophobicity, increasing hydrogen bonding interaction, and hydrophobic interaction with the target components. However, the extraction efficiency decreases when the alkyl chain length changes from octyl to dodecyl, which may be owing to the increase in their viscosity. As a result, $[C_8mim]^+$ turned out to be the most effective cation for obtaining prenylated flavonoids.

Wang et al. used three ionic liquids with diverse alkyl chain lengths ([Omim][Br], [Bmim][Br], and [Hmim][Br]) to extract alkaloids from *Phellodendron amurense Rupr* [56]. The results demonstrated that extracting with [Bmim][Br] produced the highest yield. It was found that the extraction yield decreases as the alkyl chain length of imidazolium ionic liquids increases; this may be attributed to these alkaloids being hydrophilic and the fact that the imidazolium ionic liquids with short alkyl chain also have better hydrophilicity, so they are more conducive to the solubilization of alkaloids, thus contributing to the extraction yield.

Qin et al. selected $[Bmim][PF_6]$, $[Hmim][PF_6]$, and $[Omim][PF_6]$ for the extraction of five hydrophilic phenolic compounds from figs [109]. According to the study, the imidazolium ionic liquid extraction yield declines as the alkyl chain length increases, and better extraction yield is obtained when utilizing $[Bmim][PF_6]$ as the extraction solvent. The phenomenon may be owing to the fact that, with the increase in the length of the alkyl chain, the hydrophilicity of the imidazolium ionic liquids is reduced, as well as the increase in viscosity of the imidazolium ionic liquids, thus leading to the decrease in extraction yield.

In this subsection, we learned that when extracting hydrophobic components, with increasing alkyl chain length of imidazolium ionic liquids, the hydrophobicity of imidazolium ionic liquids increases, and the extraction efficiency responsively increases. However, when the length of alkyl chain is too long, this may lead to an increase in viscosity, as well as an increase in the steric effect, which may weaken the hydrophobic interaction and reduce the extraction efficiency. For extracting hydrophilic components, with the increase in the alkyl chain length of imidazolium ionic liquids, the hydrophilicity of imidazolium ionic liquids decreases, and the extraction efficiency also decreases.

4. Extraction Mechanism

Imidazolium ionic liquids have diversity due to their ability to be generated by mixing various anions with imidazolium cation. Understanding the relationship among the imidazolium ionic liquids' structure, their physiochemical properties, the structure of the phytochemicals, and extraction efficiency is crucial when extracting a variety of phytochemicals by imidazolium ionic liquids. Consequently, it is essential to find the mechanism of how phytochemicals are extracted by using imidazolium ionic liquids. According to studies previously conducted, computer simulations, such as molecular simulation, molecular dynamics, etc., or experimental verifications are suitable approaches to reveal the extraction mechanism in phytochemicals. With the ongoing investigation of the extraction mechanism, there is a novel phenomenon regarding the use of computer simulation in conjunction with experiments. Research on the extraction mechanism involved in extracting phytochemicals via imidazolium ionic liquids is discussed in this part.

4.1. Extraction Mechanism by Computer Simulation

Based on computer simulation approaches, these have been performed on the mechanisms of extracting phytochemicals by imidazolium ionic liquids. The extraction mechanism of acteoside from *Cistanche tubulosa* by [C_4mim][BF_4] was demonstrated by Xu et al., using molecular simulation [110]. The molecular simulation has revealed that the extraction performance of acteoside through [C_4mim][BF_4] is related to the high polarity of [C_4mim][BF_4], and thus the ease of hydrogen bonding acceptors can be formed, as well as a wide range of interactions between them (including hydrogen bonding, van der Waals forces, and π–π stacking) that contribute to the extraction efficiency.

Shen et al. simultaneously extracted and saponified zeaxanthin from *Lycium barbarum* L. that utilized a composite solvent made up of ethanol, a variety of imidazolium ionic liquids, and inorganic bases. Response surface methodology (RSM), as well as single-factor experiments, found that [Hmim][OAc] was the imidazolium ionic liquid with the best extraction efficiency, and quantum chemical calculations were employed to investigate the extraction mechanism, which included atoms in molecules (AIMs), reduced density gradient (RDG) analysis, and density functional theory (DFT) [111]. According to quantum chemical calculations, the primary powers behind the efficient extraction of zeaxanthin by containing imidazolium ionic liquid solvents are hydrogen bonding and van der Waals interactions between zeaxanthin and imidazolium ionic liquids. Moreover, the strength of the interactions is correlated with the extraction efficiency. Additionally, the other element impacting the imidazolium-based ionic liquid's extraction efficiency is the sort of anion it contains.

Yuan et al. proposed a way for extracting podophyllotoxin from three Chinese herbal plants via imidazolium ionic liquids, along with microwave assistance. Three imidazolium ionic liquids, namely [Bmim][BF_4], [Demim][BF_4], and [Amim][BF_4], were observed to be the most useful extractants for *Dysosma versipellis*, *Sinopodophyllum hexandrum*, and *Diphylleia sinensis*, respectively. The dynamics analysis of these extractants' extraction mechanisms was explored [112]. The findings indicate that the type of herb medicines' components and how they interact in the herb medicines may be related to the dynamic analysis curve. However, further research needs to be performed to determine the precise interactions. Moreover, longer microwave times are not advantageous for the extraction of podophyllotoxin when imidazolium ionic liquids are adopted as solvents since the active compounds in these plants can be altered or destroyed at high temperatures for a long period of time.

Similarly, Bogdanov et al. studied the extraction mechanism for S-(+)-glaucine from *Glaucium flavum* Crantz by [C_4mim][Ace] [113]. Furthermore, they put forward a rational approach for the extraction mechanism, explaining each step of the extraction process in terms of interactions involving the solute and the solvent, substrate and the solvent, and substrate and the solvent. At the same time, the kinetic parameters exemplify that the higher yield of extraction by imidazolium ionic liquids is attributed to the hydrogen bonding interactions between [C_4mim][Ace] and cellulose that result in the destruction of the cells and changes in the permeability of the cell walls, ultimately leading to the division of the cells, thus making the extraction more favorable.

In conclusion, the diverse interactions between imidazolium ionic liquids and phytochemicals can be observed and properly analyzed using computer simulation to explore the extraction mechanism. Researchers have demonstrated that the hydrogen bonding interaction is mostly to influence the extraction efficiency.

4.2. Extraction Mechanism by Experiments

Based on the method that has been experimentally verified, including experimental characterization techniques, investigation of the experimental process, etc., the mechanism of phytochemical extraction via imidazolium ionic liquids has been studied. In order to extract baicalin, wogonoside, baicalein, and wogonin from *Scutellaria baicalensis*, Georgi, Zhang, et al. utilized several imidazolium ionic liquids as the extractant. In addition, they examined the *S. baicalensis* powders' microstructures before and after extraction, using scanning electron microscopy (SEM) to investigate the extraction mechanism [114]. It was discovered that imidazolium ionic liquids may enhance the extraction efficiency until the microstructure of the phytochemicals is destroyed, because the studied imidazolium ionic liquids, such as [C_8mim][Br], have the capacity to damage the cell wall by dissolving cellulose, allowing it to extract the targeted phytochemicals from the plant cells.

Liu et al. presented the method based on imidazolium ionic liquids to extract chlorogenic acid from *Eucommia ulmoides* with enzyme-assisted extraction, and they investigated the relationship between the usage of enzyme treatment in imidazolium ionic liquids and the extraction outcome [115]. As demonstrated by SEM, the untreated plant samples exhibit a distinct structural shape, but the treated samples show substantially altered cells and cell walls, exposing the target compounds to the extraction solution. This suggests that changes in plant structure after cellulase treatment in imidazolium ionic liquids strengthen the solvent's ability to enter the plant matrix, thereby accelerating the release of the target components from the cells. By lowering mass transfer barrier, it can result in more valid extraction.

Analogously, Ji et al. chose [C_4mim][Ac] for the extraction of triterpenoid saponins and flavonoid glycosides from licorice, and they investigated the extraction mechanism by SEM characterization techniques [116]. It was observed that the [C_4mim][Ac] treated materials' structures completely broke down, making it simpler to extract triterpenoid saponins and flavonoid glycosides from these samples, using imidazolium ionic liquids. Moreover, the extraction yields of these phytochemicals are markedly increased when [C_4mim][Ac] is utilized as the extractant because it allows for better access to the target compounds in plants and enhances the solvation of the imidazolium ionic liquids to the target compounds.

Fan et al. developed a microwave-assisted method based on imidazolium ionic liquids for extracting verbascoside from *Rehmannia* root and explored the mechanism through several experiments in the extraction process [84]. According to the experimental data, the hydrophobicity and hydrogen bonding of imidazolium ionic liquids, the π–π stacking between imidazolium ionic liquids and verbascoside, and the steric hindrance effect are the factors which influence the extraction efficiency. Moreover, the findings of the research indicate that [Bemim][Cl] has the best extraction capacity because verbascoside and [Bemim][Cl] have a higher π–π stacking interaction.

In this section, it is revealed that the experimental verification of the extraction mechanism between imidazolium ionic liquids and phytochemicals mostly entails the employment of SEM characterization and to comprehend the extraction process by observing microstructural changes or to make inferences about probable extraction processes from the results of a range of experiments; thus, experimental verification methods frequently require more evidence to support their results.

4.3. Extraction Mechanism by Computer Simulation Combination with Experiments

The strategy using a combination of computer simulation and experiments has been carried out for the in-depth investigation and exploration of the extraction mechanism. For the extraction of flavonoids from Tartary buckwheat, Feng et al. created a unique three-phase system, using [C_4mim][Br], the deep eutectic solvent, and the raw material. Then kinetic and thermodynamic mechanisms were employed to investigate the system's extraction mechanism. Spectral characterization was also utilized to establish the efficacy of the described approach [117]. The two-stage extraction process can be monitored and predicted thanks to the analysis of extraction kinetics, which also demonstrates that Fick's second diffusion rule could apply in the extraction. Additionally, it is shown that the two-stage extraction is spontaneous. Meanwhile, it reveals that higher temperatures make the system simpler to extract them, and the extraction process is a heat absorption process. In addition, the extraction of flavonoids using 70% ethanol solution and using this system are compared. It reveals that the spectra of flavonoids extracted by the two ways are practically similar. However, the extraction mechanism of this method should still be explored in more depth to determine the interactions between them and the factors affecting the extraction efficiency.

Shi et al. extracted essential oil from *Forsythiae fructus* by using microwave-assisted imidazolium ionic liquids, together with hydrogenated distillation. They explored the extraction mechanism to improve the output and applied SEM characterization to verify the presumed mechanism [118]. By using cellobiose as the model molecule, DFT is utilized to explore the mechanism. Electrostatic potential (ESP) plots and general interaction properties function (GIPF) are employed to investigate the interactions between [C_4mim][Br] and the cell wall after the structure has been optimized. The findings indicate that [C_4mim][Br] can successfully induce cellulose breakdown, and the Br^- can effectively interact with cellulose in negative ESP areas. Moreover, because the extraction is involved with the microwave aided, microwave energy can be quickly converted into heat. As a result, the solution inside the cells heats up more quickly and produces steam, increasing the internal pressure inside the cells and possibly causing the cell walls to become more permeable or even rupturing them. Therefore, it speeds up the internal components' diffusion, which improves the effectiveness of essential oil extraction. This can be confirmed by SEM inspection of the morphology of the plant surface.

Similarly, Zhang et al. studied a method applying imidazolium ionic liquids based on microwave-assisted extraction for obtaining salidroside and tyrosol from Rhodiola. They investigated the extraction mechanism by the molecule's electrostatic potential (ESP) distributions and verified it by using SEM characterization. The ESP's eigenvalues and extraction yield were found to be correlated by theoretical and experimental studies [108]. They separately studied how the alkyl chain length on cation and anions influences the extraction by 1-alkyl-3-methylimidazolium ionic liquids. Salidroside and tyrosol are more easily solvated in imidazolium ionic liquids due to the interactions between cations and extracted molecules. ESP data also demonstrate a gradual decrease in the polarity of imidazolium ionic liquids with the increase of the alkyl chain, a more similar distribution of ESP to salidroside and tyrosol, and an increase in extraction yield (from ethyl to octyl). In addition, an analysis of the ESP data showed that the anions could markedly change the polarity of the imidazolium ionic liquids, thus affecting the extraction yield. Imidazolium ionic liquids containing Br^- are found to be less polar and more capable of dissolving cellulose, which facilitates the extraction. Particularly, the SEM characterization shows that the substances treated with imidazolium ionic solutions containing Br^- display many micropores on their surface. It suggests that the anions' primary function is to break down cellulose and damage the cell wall, which makes it possible for the target components to dissolve effectively inside the cells.

To extract and separate polysaccharides, phenols, and amino acids from bamboo juice in free of solvents, Jiang et al. established an imidazolium ionic liquid ([Bmim][PF_6])-involved "sandwich" membranes method [78]. Investigations are also conducted into the kinetics and molecular simulation in exploring the extraction and separation mechanism, and a series of characterization techniques are employed to confirm the experimental results. According to the results of the molecular simulation, these phytochemicals are able to electrostatically interact with the cation of [Bmim][PF_6] and then bind to it to form complexes of different strengths, with the stably bound components remaining in the ionic liquid phase and the unstable ones being removed by dialysis. Besides this, the hydrogen bonding between the phenols' hydroxyl H and the ionic liquid's anion and the hydrophobic interaction between the phenol and the imidazolium cation of [Bmim][PF_6] are the key causes of extracting phenols. The IR, UV–Vis, and TGA techniques were applied to characterize the products produced by this method and compare them to those produced by conventional methods. Their spectra were then utilized to confirm the structure of the produced products.

Luo et al. established an innovative solvent to extract phenolic acids and alkaloids from *Camptotheca acuminata* that was based on [Hmim][BF_4] [119]. Dissipative particle dynamics (DPD) is applied to simulate how this new solvent extracts the target compound; the DPD simulation reveals the generation of the solvent structure, as well as the target compound's migration path, demonstrating that the based [Hmim][BF_4] solvent's extraction mechanism is connected to the particular structure. According to the outcome of characterized ^{2}D NMR, the forces in the solvent and the target chemical are primarily van der Waals forces and C-H bonds. The interactions between the solvent and the target chemical, as well as enhancing the solubility, are aided by the solvent's unique structure, and the efficiency of the extraction is boosted by the higher solubility of the target chemical in the system.

After realizing the extraction mechanism using a combination of computer simulation and experiments, we noticed that the method has a significant advantage as a more convincing and accurate mechanism study, as well as a series of experiments to support the results of the mechanism. It increases the credibility and authenticity of the extraction mechanism and provides a more thorough simulation of the extraction mechanism, which includes simulating the interactions between imidazolium ionic liquids and phytochemicals or simulating the function of the imidazolium ionic liquids' structure. There is little doubt that using a combination of computer simulation and experiments for exploring extraction mechanisms will be a prominent subject of study in the future.

5. Recovery Methods and Reuse of Imidazolium Ionic Liquids

In the past decades, researchers devoted themselves to recycling and reusing imidazolium ionic liquids to solve the price problem and save costs. Therefore, the effective recovery of imidazolium ionic liquids is crucial to their industrial production. In addition, in the process of industrial application, it also had the possibility of mixing with other products, which also required the effective recovery of imidazolium ionic liquids. Some recovery methods are summarized as follows, including distillation, liquid–liquid extraction, adsorption, membrane separation, etc. [120–123].

5.1. Distillation

Distillation refers to the process of separating components by taking advantage of the difference in volatility of components in liquid mixtures. It has the gradient boiling and condensation, which is widely used in separating liquid mixtures [124]. Distillation of volatile solutes can be the first choice to recover and reuse imidazolium ionic liquids [125]. For example, imidazolium ionic liquids such as [C_2mim][OAc] and [C_2mim][SCN] were recovered from binary mixtures of ionic liquids and methanol or ethanol by distillation, using the correlation between the experimental data and the NRTL model; Aspen Plus was used to simulate the flash unit at different temperatures and pressures. The results showed that the system containing [C_2mim][SCN] obtained high ionic liquid purity, which can be satisfactorily recovered under a medium vacuum [126]. Jiao et al. used [C_2mim][OAc] with microwave-assistedto isolate the essential oil from Fructus forsythia seed through an azeotropic distillation of EtOH/H_2O; [C_2mim][OAc] was simply recovered, and it may be reused five times without further purifying but is black [120].

5.2. Liquid–Liquid Extraction

A technique for separating mixtures based on the different solubilities of each component in the solvent is called liquid–liquid extraction. This has proven to be an effective way to recover imidazolium ionic liquids. To extract the aconitum alkaloids from Aconitum Carmichaeli Debx, a method based on an ultrasound-assisted imidazolium ionic liquid aqueous two-phase system was proposed, which used [C_6mim][Br]. After extraction, the HCl aqueous solution containing 5% Tween-20 was utilized as the back-extractant to recover the ionic liquid [57]. Wang et al. used [Bmim][Br] to extract flavonoids from bamboo leaves of Phyllostachys heterocycle with ultrasonic-assisted extraction, and then they compared the recovery results of n-butanol, chloroform, and ethyl acetate as ideal solvents to recover products and ionic liquids; they found that n-butanol was the only one with good recovery of flavonoids and ionic liquids [121].

5.3. Adsorption

Adsorption has been considered a reliable and robust method to facilitate the recovery or removal of imidazolium ionic liquids [124]. Nowadays, there are a series of studies on adsorbents; taking ion exchange resins as an example, Li et al. prepared the [C_{12}mim][BF_4] and used it as an extractant for extracting echinacoside and acteoside from Cistanche deserticola Y. C. Ma. The reuse of the [C_{12}mim][BF_4] aqueous system was also developed, and they acquired solutions after resin adsorption and selected six resins, namely as AB-8, D-100, D-101, HPD-100, HPD-300, and DM-130, and compared their adsorption and desorption capacities. The recovery solution was used once more for the extraction experiment, which was carried out four times [43]. Ma et al. used the [C_4mim][Ac] to extract biphenyl cyclooctene lignans from *Schisandra Chinensis*; for the recovery of [C_4mim][Ac], they also employed a two-solid-phase recycling technique, using HPD 5000 macroporous resin and the SK1B strong acid ion-exchange resin [122].

5.4. Membrane Separation

A readily available and well-researched method is membrane separation, which needs less energy and fewer solvents, making it more suitable for industrial applications [120]. Due to its lower energy consumption and simple operation, membrane separation is used for recovering imidazolium ionic liquids. Pervaporation (PV) is a kind of membrane separation process with high selectivity. Sun et al. adopted the pervaporation for recycling [C_2mim][OAc], and they found that [C_2mim][OAc] can be recycled five times from an aqueous solution [123]. In addition, the permeate flux was found to improve with the increase of applied pressure when two nanofiltration membranes (NF90 and NF27) were used to concentrate [Amim][Cl], [C_4mim][Cl], and [C_4mim][BF_4]. NF90 can be used to concentrate [C_4mim][Cl] from its initial content of 5 wt% to 18.85 wt%, leading to a recovery of about 96% [127].

After realizing some methods for the recovery of imidazolium ionic liquids, we noticed that although these approaches have been successful in isolating and recovering imidazolium ionic liquids from the system, some of them are inefficient, and the recovered products may have low purity or high energy losses. The recovery of imidazolium ionic liquids should be further optimized in the future by choosing and developing combined recovery methods that take into account the features of imidazolium ionic liquids. Moreover, it is crucial to perform more extensive and in-depth research on recovery techniques, including the analysis of thermodynamics and kinetics in distillation and adsorption, the optimization of mass and heat transfer processes in liquid–liquid extraction, and the exploration of membrane deactivation and regeneration in membrane separation. Meanwhile, the research on some imidazolium ionic liquids with reusable times is summarized in Table 4 to serve as a guide for better imidazolium ionic liquid recovery and reuse.

Table 4. Recycle and reuse of imidazolium ionic liquids.

Types of Ionic Liquids	Reused Times	Ref.
$(ViIm)_2C_6(L\text{-}Pro)_2$	4	[128]
P[VEIm][Br], P[VEIm][BF_4], P[VEIm][PF_6],	4	[129]
[C_{12}mim][BF_4]	4	[43]
DSIMHS (include 1,3-Disulfonic acid imidazolium hydrogen sulfate)	4	[130]
[C_2mim][OAc]	5	[123]
[Msim][HSO_4]	5	[131]
[C_4mim][BF_4]	10	[132]
[Momim][PF_6]	14	[133]

6. Toxicity of Imidazolium Ionic Liquids

Considering their great thermal stability and minimal vapor pressure at ambient temperature, imidazolium ionic liquids were formerly considered to be environmentally friendly; there are a few studies that considered their toxicity at first [134]. However, with further study of imidazolium ionic liquids, some potential problems have gradually emerged. Imidazolium ionic liquids are unlikely to pollute the atmosphere due to their low volatility. Nevertheless, due to their being soluble in water, imidazolium ionic liquids may enter the environment through industrial wastewater, which heightens the latent danger to the aquatic ecosystem and the organisms that live there. In addition, imidazolium ionic liquids are also difficult to biodegrade because of their high viscosity and stability, thus allowing them to exist in this environment persistently [135]. Until now, the toxicity of imidazolium ionic liquids to diverse organisms, also with respect to bacteria, fungi, soil, and ecosystems, has been investigated, and Table 5 provides a summary of the toxicity in imidazolium ionic liquids. The information indicates that the type of anion and the alkyl chain length on the cation are relevant to the toxicity of imidazolium ionic liquids.

Table 5. Toxicity of imidazolium ionic liquids.

Ionic Liquids	Affected Organisms/System	Toxicity Estimated Parameters	Observations	Ref.
[Emim], [Bmim], [Hmim], [Omim], [Dmim] with [Cl]	*Oocystis submarina*, *C. vulgaris*, *Cyclotella meneghiniana*, *Geitlerinema amphibium*	Growth inhibition [I%] under different salinities [PSU] (8, 16, 24, 32)	The toxicity of ILs was impacted by rising salinity. Algal growth was less inhibited at higher salinities.	[136]
$[C_n mim][NO_3]$ (*n* = 2, 4, 6, 8, 10, 12)	*C. vulgaris*, *Daphnia magna*.	The 50% effect concentration (EC_{50}), EC_{50} (mg L^{-1}) 24, 48, 72, 96 h	The toxicity of the studied ILs in test organisms enhanced with alkyl chain length improved.	[137]
$[C_8 mim][Br]$	Brocarded carp (*Cyprinus carpio* L.)	The determination of 50 percent lethal concentration (LC_{50})	After 7 days of $[C_8 mim][Br]$ treatment, 300 mg L^{-1} of $[C_8 mim][Br]$ caused some damage to brocaded carp.	[138]
$[C_6 mim][Br]$	*Daphnia magna (D. magna)*	Survival rate (%), malformation rate of offspring	The results showed that $[C_6 mim][Br]$ could lead to the abnormal development and reproduction of Daphnia magna.	[139]
[Bmim], [Hmim], [Omim], [Dmim] with [Cl]; [Bmim], [Hmim], [Omim], [Dmim] with $[BF_4]$; [Bmim], [Hmim], [Omim], [Dmim] with $[Tf_2N]$	*Vibrio fischeri* (*Photobacterium phosphoreum*)	The EC_{50} values	The findings indicated that toxicity enhanced with improving n-alkyl chain length; the ecotoxicity measured by respiration inhibition tests followed the order $[Tf_2N]^-$ > $[Cl]^-$ > $[BF_4]^-$.	[140]
[Emim], [Bmim], [Dmim] with $[BF_4]$; [Emim], [Bmim], [Dmim] with [Cl]	Mammalian cells	The number of viable cells (mammalian cells were dealt with the ILs, and surviving cells were recorded 48 h posttreatment)	The cycle and death of cells indicated that the effect is strongly dependent on the hydrophobic strength of ionic liquids.	[141]
1-butyl-3-methylimidazolium series and 1-(propoxycarbonyl) methyl-3-methylimidazole series	*D. magna*, *Photobacterium phosphoreum*	The EC_{50} values (μM) 24 h; The IC_{50} values (μM) 24 h	In two bioassays, the analyzed dialkylimidazolium ionic liquids were more toxic than conventional organic solvents.	[142]
$[C_n mim]$, *n* = 4, 5, 7, 10 with $[BF_4]$, $[PF_6]$, [Br], $[Tf_2N]$.	The fish CCO cell line	The EC_{50} values (mM) 72h	The results demonstrated a relationship between anion type, alkyl chain length, and the cytotoxicity of the ionic liquids in CCO cells; the EC_{50} values indicated imidazolium ionic liquids have moderate-to-high toxicity.	[143]
$[C_4 mim][BF_4]$, $[C_4 mim][CH_3CO_2]$, $[C_4 mim][Br]$, $[C_7 mim][Br]$, $[C_{10} mim][Br]$	Barley (*Hordeum vulgare*)	Germination inhibition, shoot-height and root-length inhibition, and EC_{50} values	The inhibitory effect was decided by the concentration and chemical structure of ionic liquids and the toxic order of them was $[C_{10} mim][Br]$ > $[C_7 mim][Br]$ > $[C_4 mim][Br]$ > $[C_4 mim][CH_3CO_2]$ > $[C_4 mim][BF_4]$.	[144]
$[C_n mim][Cl]$ (*n* = 2, 4, 6, 8 and 10)	*Escherichia coli* (EPEC), *Staphylococcus aureus* (MRSA)	Mortality and minimal bactericidal concentration (MBC)	There is no proof that ILs with side chains shorter than 16 interact with the cell membrane. It appeared that ILs with side-chain lengths below 16 affect bacterial cellular proteins.	[145]
1 octyl 3 methylimidazolium (M8OI)	Soils	The M8OI toxicity database in cultured mammalian cells, in experimental animal studies, and in environmental impact model indicators	It has the potential to cause an autoimmune liver disease	[146]
($[C_n mim][NO_3]$ (*n* = 4, 6, 8, 10, and 12)	Earthworms (*Eisenia fetida*)	Reactive oxygen species (ROS) levels after 14 and 28 days of exposure	The toxicity of tested imidazolium ionic liquids was $[C_{10} mim][NO_3]$ < $[C_{12} mim][NO_3]$ < $[C_4 mim][NO_3]$ < $[C_6 mim][NO_3]$ < $[C_8 mim][NO_3]$.	[147]
$[C_6 mim][Br]$, $[C_6 mim][NO_3]$, $[C_6 mim][PF_4]$	*Vicia faba*	The EC_{50} values	The toxic of the three ionic liquids was $[C_6 mim][NO_3]$ < $[C_6 mim][Br]$ < $[C_6 mim][BF_4]$.	[148]

7. Discussion

After exploring the application of extracting phytochemicals by imidazolium ionic liquids, diverse challenges for their future applications were discussed by summarizing the cost, recycling and reuse, high viscosity, and toxicity, as shown in Figure 4.

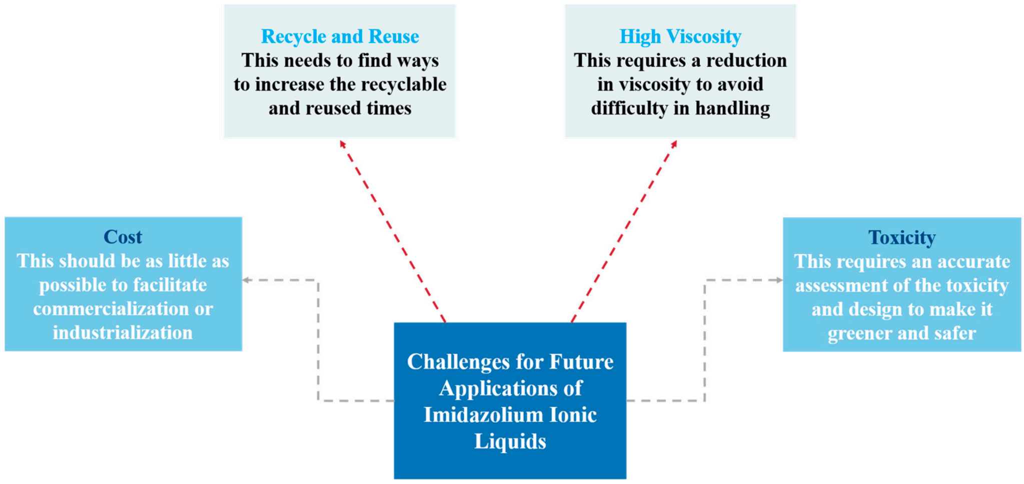


Figure 4. Overview of challenges for future applications in imidazolium ionic liquids.

Although using imidazolium ionic liquids as extractants has shown the advantages of their extraction, the extraction of phytochemicals by imidazolium ionic liquids is still in the laboratory stage. The major obstacle to the industrialization of the extraction of phytochemicals based on imidazolium ionic liquid is mainly the high cost of this reagent. The latest development of imidazolium ionic liquids showed that the cost of extraction can be reduced by using cheaper raw materials and increasing the reused times of the recovered imidazolium ionic liquid for the subsequent extraction.

When it comes to increasing the recyclable and reusable times of the recovered imidazolium ionic liquid, it is crucial to first select the appropriate structure of the imidazolium ionic liquid for extraction and use a suitable and matching method for its recovery, the choice of which depends on the structural characteristics of the imidazolium ionic liquid selected. In addition, there is a way of combining imidazolium ionic liquids with other materials to form new types of materials, such as polyionic liquids, which could increase their recyclable and reused times.

When using imidazolium ionic liquids to extract phytochemicals, the high viscosity of imidazolium ionic liquids may make it difficult to treat them in the extraction process, and the utilization of imidazolium ionic liquids as extractants in various extraction processes often requires a low viscosity to acquire high extraction yields, so the problem of how to reduce the viscosity of imidazolium ionic liquid also needs to be addressed by researchers. Some studies showed that the viscosity of $[C_4mim][Cl]$ can be decreased by introducing DMA, DMF, DMSO, and PYR into the reaction process, among which DMF had the greatest influence on the viscosity of imidazolium ionic liquids [149]. In addition, we can also refer to some methods for preparing low-viscosity imidazolium ionic liquids and choose low-viscosity imidazolium ionic liquids to use.

To meet the demand of green chemistry, as well as to address the potential toxicity in imidazolium ionic liquids, the toxicity of imidazolium ionic liquids must first be assessed to verify their safety. However, the study of toxicity mechanisms and assessment is still in its infancy, and it is a promising research direction for the future. There is a method for reducing the toxicity of imidazolium ionic liquids by the addition of polar functional groups to alkyl side chains [142]. However, the use of toxic imidazolium ionic liquids should be avoided from the beginning, and this requires the selection of natural sources as raw materials for the synthesis in the creation of imidazolium ionic liquids. The replacement of the cations or anions in imidazolium ionic liquids with natural sources has been carried out, such as using oleic acid in vegetable oils, glycine, and lysine in meat and dairy products; and choline generated from soybeans, eggs, and peanuts [150]. Moreover, some bio-derived ionic liquids and choline amino acid ionic liquids were developed. Meanwhile, since biocompatible ionic liquids are ecologically and biologically friendly ionic liquids, biocompatible ionic liquids can also be used to replace highly toxic ionic liquids [151–153]. In the future, the application of imidazolium ionic liquids may be expanded by developing natural and low-toxicity imidazolium ionic liquids.

8. Conclusions

The better extraction efficiency of imidazolium ionic liquids in extracting phytochemicals suggests that they are more suitable as extractants compared with traditional solvents. However, in order to make imidazolium ionic liquids play a more important role in the future, it is necessary to solve various problems related to the usage of imidazolium ionic liquids, including toxicity, cost, and viscosity. Researchers especially still need to make efforts in studying the extraction by imidazolium ionic liquids for developing greener phytochemical extractants. Furthermore, a novel future research strategy combining computer simulation and experiments is recommended in order to more thoroughly explore the extraction mechanisms between phytochemicals and imidazolium ionic liquids, which also aid in recognizing the connection among the structure of imidazolium ionic liquids, their physicochemical features, phytochemicals' structure, and the extraction efficiency.

Author Contributions: Data curation, writing—original draft preparation, and investigation, J.G. and C.L. (Chunyu Liang); writing—review and editing, Z.M.; visualization and investigation, M.T.; formal analysis, C.Z.; conceptualization and supervision, C.L. (Chunying Li); supervision and project administration, M.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Fundamental Research Fund for Central Universities (2572022DP06); the Research Foundation for Distinguished Scholars of Hainan Tropical Ocean University (RHDRC202107); the Natural Science Foundation of Heilongjiang Province (LH2022C004), the Key Research; the Development project of Heilongjiang Province (JD22A008 and 2022ZX02C11); the Higher Education Discipline Innovation Project (the 111 Project), China (B20088).

Conflicts of Interest: The authors declare no conflict of interest.

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