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Advances in ionic liquid recycling for lignocellulosic biomass pretreatment

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Ionic liquids (ILs) are promising solvents for the pretreatment of lignocellulosic biomass due to their ability to disrupt cellulose, hemicellulose, and lignin structures. However, large-scale implementation requires the development of efficient recovery and recycling methods. This review provides a comprehensive analysis of the recyclability potential of ILs used in biomass pretreatment, emphasizing their mechanisms, recent innovations, and ongoing challenges. We begin by discussing the structural diversity and tunability of ILs, which underlie their effectiveness in biomass deconstruction. The distinct roles of IL anions and cations in dissolving specific biomass components are systematically presented and compared. Advances in IL recycling techniques, including antisolvent precipitation methods, membrane separation, and distillation, are critically examined, with attention to how mechanistic insights can inform the design of more efficient and selective recovery strategies. Despite progress, significant challenges remain to scaling up IL-based biomass processing, including high cost, environmental concerns, and impact of biomass-derived impurities (*e.g.*, lignin residues, sugars, proteins) on IL purity and functionality after reuse. We also review the applicability of different ILs based on life cycle assessments and techno-economic analyses. Lastly, we identify critical research gaps and propose future directions, including the design and development of next-generation ILs with improved recyclability, reduced toxicity, and enhanced economic viability for industrial-scale applications.

Green foundation

1. We discuss recent advances in the design of ionic liquids with properties that allow for their recycling in a biorefinery setting. We also provide examples of recovery techniques with the potential for reducing the cost and environmental impact of using ionic liquids at large scales.
2. Efficient and sustainable biomass pretreatment is one of the biggest bottlenecks to produce bioproducts. Given the growing push towards decarbonizing the chemical and energy sectors, this topic may be relevant to researchers, policymakers and industries aiming to transition towards circular and bio-based economies.
3. Future efforts in this field will focus on developing biomass conversion processes that are cost-effective and scalable. This review contributes to that goal by summarizing the state of the art and providing a systematic assessment of the unique advantages, challenges and opportunities of using recyclable ionic liquids as biomass pretreatment solvents.

1. Introduction

1.1. Lignocellulosic biomass: importance and challenges

The increasing demand for reliable and affordable energy has prompted a global shift towards exploring alternative energy sources to meet rising global energy requirements.[1–5] Although renewable energy constituted ~12% of the U.S. primary energy consumption in 2021, fossil fuels including petroleum, natural gas, and coal still dominated with ~79% of the energy mix.[6] Lignocellulosic biomass, the most abundant renewable feedstock on earth (*i.e.*, 100 × 10^8 MT produced each year all over the world),[7–9] is particularly promising for biofuel production due to its substantial energy content in the form of cellulose (~40–50 wt%), hemicellulose (~15–30 wt%), and lignin (~16–33 wt%) (see Fig. 1).[10–12] These structural biopolymers, primarily cellulose and hemicellulose, are composed of fermentable sugars like glucose and xylose, essential for biofuel production.[11] In the U.S., biomass-derived energy sources, including waste biomass (~4%), biofuels (~19%), and

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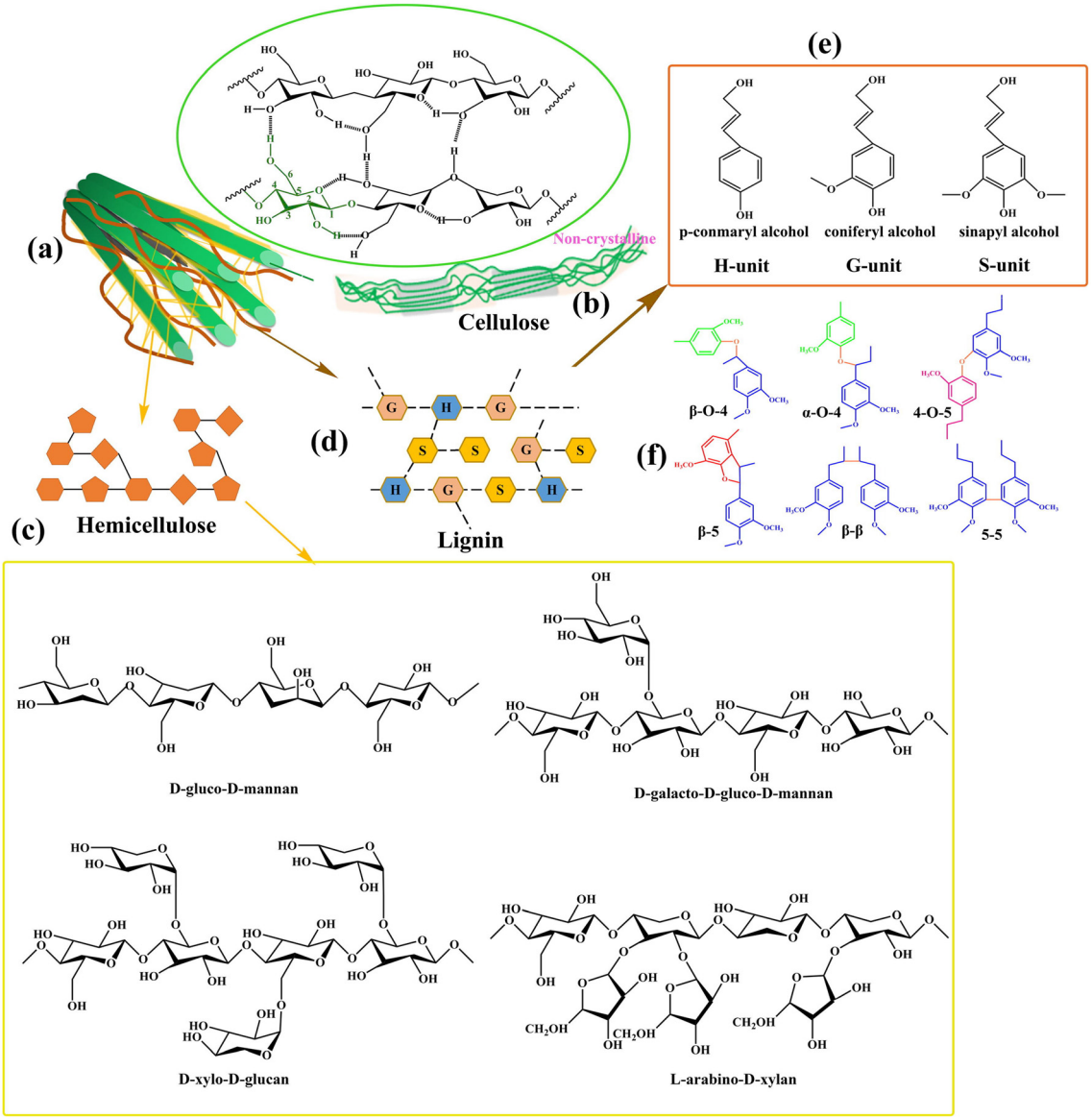

Fig. 1 Representation of the structure of lignocellulosic biomass. Panels: (a) cellulose microfiber; (b) macromolecular polymer with linear configuration; (c) hemicellulose; (d) lignin; (e) constitutional units of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S); (f) prevalent C–C and C–O bonds found in lignin. Adapted from ref. 18. Copyright 2022, Elsevier.

wood (~17%), contributed to ~40% of renewable energy production in 2021.[6,13] However, the crosslinked structure of lignocellulosic biomass, stabilized by covalent and hydrogen bonds, poses a significant challenge to enzymatic and microbial degradation.[6] Advanced pretreatment methods are thus critical to deconstructing this complex matrix, improving accessibility to cellulose and hemicellulose, and reducing the inhibitory effects of lignin on enzymatic hydrolysis.[14–17] Recent advancements in physicochemical pretreatment strategies have demonstrated considerable potential to enhance the efficiency of lignocellulosic biomass conversion, facilitating commercially viable biofuel/biochemical production.[6,16,18–20]

1.2. Rise of ionic liquids in biomass processing

Ionic liquids (ILs) have revolutionized modern chemistry since their first discovery by Paul Walden in 1914, who synthesized ethyl ammonium nitrate (EAN), a low-melting-point salt that functioned as an electrolyte.[21,22] These organic salts are liquid at temperatures below 100 °C (ref. 23–26) and composed of highly tunable organic cation and organic or inorganic anion combinations, allowing their properties to be customized for specific applications.[18,23] The exceptional characteristics of ILs such as low volatility, high thermal and chemical stability, strong solvation capacity, broad electrochemical windows, and recyclability have propelled their adoption across diverse

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fields, including catalysis, electrochemistry, material extraction, gas separation, and biomass pretreatment.[27–32] Their negligible vapor pressure initially earned them the label of "green solvents",[33] but this classification remains contested due to concerns over toxicity, biodegradability, energy-intensive production, and multi-step synthesis.[34,35] One of the most important and transformative applications of ILs is in the pretreatment of lignocellulosic biomass, which addresses the challenge of biomass recalcitrance caused by the intricate assembly of cellulose, hemicellulose, and lignin.[36,37] ILs such as 1-butyl-3-methylimidazolium chloride [BMIM]Cl and 1-ethyl-3-methylimidazolium acetate [EMIM][CH_3COO] have demonstrated remarkable efficiency in de-crystallizing cellulose and enhancing enzymatic saccharification, enabling high digestibility under mild conditions.[38–40] The development of cost-effective protic ionic liquids (PILs), including triethylammonium hydrogen sulfate [TEA][HSO_4], has further advanced biomass processing by achieving selective lignin removal while preserving cellulose integrity, even under hydrous conditions, with high recyclability and reduced costs.[34,41–45] More recently, superbase ionic liquids (SILs) have emerged as game changers, particularly in the IONCELL-F process for fiber spinning, producing cellulose-based fibers with mechanical properties that exceed those of commercial viscose fibers.[29–31]

Despite their potential, the widespread industrial implementation of ILs faces significant challenges, including their high production costs primarily due to energy-intensive recovery and purification processes, inhibitory effects on enzymatic processes, potential environmental toxicity, and scalability issues.[34,46] Additionally, life cycle assessments (LCA) and techno economic analyses (TEA) have revealed that, despite their advantages, ILs can have a higher eco-toxicity impact than conventional solvents unless efficient recovery and recycling strategies are implemented.[46,47] To address these limitations researchers have responded by proposing innovative recovery techniques involving integrated TEA-based and sustainability-focused frameworks. Research on IL-based biorefining processes like the Ionosolv technology underscore their transformative potential while emphasizing the need for continued research to optimize economic and environmental performance.[36,48–50]

It is worth noting that ILs remained relatively unnoticed until the early 21st century when researchers and chemical companies recognized their exceptional properties compared to conventional solvents. Since then, there has been a growing interest in developing diverse applications for ILs. The number of science citation index (SCI) publications on ILs has risen exponentially, from just a few in 1996 to over 5000 by 2018, surpassing the annual growth rates of many other popular scientific fields.[51,52] Additionally, their practical applications are expanding, as highlighted by Morton and Hamer's patent analysis, which shows an increasing variety of uses for ILs.[53] The rapid rise in the use of ILs for bioenergy purposes (Fig. 2) reflects their significant promise in advancing green chemistry, driving sustainable technologies, and enabling applications in biomass valorization and beyond.

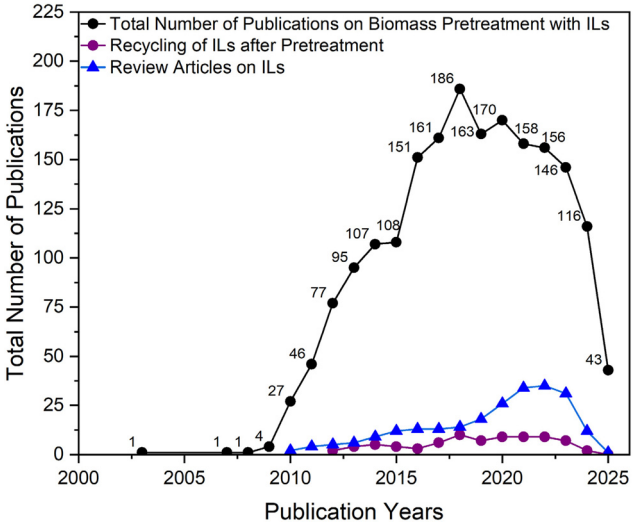

Fig. 2 Trend in the number of publications involving ILs for biomass pretreatment (black line), IL recycling after pretreatment (violet), and review articles on ILs (blue) over the past two decades.

Over the past decade, several review articles have explored the role of ILs in biomass processing, primarily focusing on their role in biomass deconstruction by enabling lignin separation and enhancing enzymatic hydrolysis (Table 1).[50,54–58] However, a comprehensive discussion of ionic liquid mechanisms, recyclability, and sustainability has not been published to date. Specifically, there is a critical need to consolidate insights on the dissolution mechanisms of cellulose, hemicellulose, and lignin, the role of anions and cations in biomass deconstruction, and the implications of biomass-derived impurities on the functionality of the recovered ILs. Additionally, the optimization of recycling techniques such as water- and salt-based methods, membrane-based systems, and co-solvent approaches and their economic and environmental implications require a critical assessment to understand the key challenges that remain to be addressed.[16,59,60]

1.3. Scope of the review

This review presents a systematic overview of the current state of research on ILs in biomass conversion with a specific emphasis on newer developments that enable their recyclability (Fig. 3). We begin by introducing the mechanisms of IL interactions with biomass in section 2, focusing on their structural characteristics and dissolution mechanisms. Section 3 presents advances in recycling techniques for ILs, followed by a detailed analysis of recyclability challenges in section 4. Section 5 discusses the sustainability and toxicity of recycled ILs, emphasizing their life cycle assessment and techno-economic analysis, identifying potential trade-offs and risks. Particular attention is paid to the limitations of IL recycling at industrial scales, including cost constraints, environmental impact and market adoption barriers. This review concludes by outlining key challenges and future perspectives in section 6, aiming to guide the development of next-generation ILs and

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Table 1 Key review articles on ILs used in biorefining over the past decades

Author (s)	Review article	Key issue(s) discussed	Year
Annegret Stark[54]	Ionic liquids in the biorefinery: a critical assessment of their potential	Potential of ionic liquids in an integrated biorefinery system for biomass processing, discussing both the benefits and potential risks	2011
Azmat Mehmood Asim *et al.*[55]	Acidic ionic liquids: promising and cost-effective solvents for processing of lignocellulosic biomass	Cost-effectiveness of acidic ionic liquids, challenges in recycling and environmental impact	2019
Florence J. V. Gschwend *et al.*[61]	Quantitative glucose release from softwood after pretreatment with low-cost ionic liquids	High glucose yield from softwood using low-cost ionic liquids	2019
Nana Yamaki *et al.*[62]	Thermal hazard analysis of a biomass pretreatment process using ionic liquids	Thermal safety concerns in using ionic liquids in industrial processes	2019
Zeba Usmania *et al.*[56]	Ionic liquid-based pretreatment of lignocellulosic biomass for enhanced bioconversion	Enhanced bioconversion using ionic liquid pretreatment, focus on green chemistry	2020
Niloofar Nasirpour *et al.*[51]	Ionic liquids: promising compounds for sustainable chemical processes and applications	Sustainability of ionic liquids in chemical processes, industrial scale application	2020
Isa Hasanov *et al.*[57]	The role of ionic liquids in the lignin separation from lignocellulosic biomass	Efficient lignin separation using protic ionic liquids	2020
Rajagopal Malolan *et al.*[58]	Green ionic liquids and deep eutectic solvents for desulphurization, denitrification, biomass, biodiesel, bioethanol and hydrogen fuels: a review	Green ionic liquids as viable solutions for fuel processing and bioethanol production	2021
Hakim Hebal *et al.*[63]	Activity and stability of hyperthermostable cellulases and xylanases in ionic liquids	Enzyme stability in ionic liquids for biomass degradation	2021
Kuan Shiong Khoo *et al.*[50]	How does ionic liquid play a role in sustainability of biomass processing?	Sustainability and techno-economic challenges in using ionic liquids for biomass processing	2021
Jinxu Zhang *et al.*[64]	Recent developments in ionic liquid pretreatment of lignocellulosic biomass for enhanced bioconversion	Technological hurdles in ionic liquid pretreatment processes with a focus on biocompatibility	2021
Xiaoqi Lin *et al.*[18]	Review on development of ionic liquids in lignocellulosic biomass refining	Summarizes the role of ionic liquids in pretreatment of lignocellulosic biomass and highlights challenges in achieving sustainable conversion	2022
Xiaofang Liu *et al.*[65]	The development of novel ionic liquid-based solid catalysts and the conversion of 5-hydroxymethylfurfural from lignocellulosic biomass	Focus on novel IL-based solid catalysts for the conversion of lignocellulosic biomass to platform chemicals like HMF	2022
Jikai Zhao, Juhee Lee, Donghai Wang[16]	A critical review on water overconsumption in lignocellulosic biomass pretreatment for ethanol production through enzymic hydrolysis and fermentation	Water overconsumption during biomass pretreatment for ethanol production, need for water-efficient methods in industrial processing	2023
Mohammad Eqbalpour *et al.*[66]	A comprehensive review on how ionic liquids enhance the pyrolysis of cellulose, lignin, and lignocellulose toward a circular economy	Role of ILs in enhancing the pyrolysis of cellulose, lignin, and lignocellulose for circular economy and sustainable energy applications	2023
Nazife Isik Haykir *et al.*[35]	Applications of ionic liquids for the biochemical transformation of lignocellulosic biomass into biofuels and biochemicals: a critical review	Reviews the role of ILs in biofuel and biochemical production, emphasizing technical and economic challenges	2023
Francieli Colussi *et al.*[10]	Challenges in using ionic liquids for cellulosic ethanol production	Challenges in pretreating lignocellulosic biomass with ionic liquids for cellulosic ethanol production, including cost and process efficiency	2023
Paul Wolski *et al.*[67]	Factors that influence the activity of biomass-degrading enzymes in the presence of ionic liquids: a review	Examines the interaction of ionic liquids with biomass-degrading enzymes, with a focus on the stability and activity of these enzymes	2023
Ting He *et al.*[60]	Latest advances in ionic liquids promoted synthesis and application of advanced biomass materials	Discusses advances in using ILs to produce advanced biomass-based materials, highlighting their application as solvents and modifiers	2023
Ruolin Li[59]	Recent advances in biomass pretreatment using biphasic solvent systems	Biphasic solvent systems, including ILs, for efficient fractionation of biomass and enhancing enzymatic hydrolysis	2023
A. S. Norfarhana *et al.*[68]	Revolutionizing lignocellulosic biomass: a review of harnessing the power of ionic liquids for sustainable utilization and extraction	Focus on ILs for fractionating lignocellulosic biomass, highlighting green and sustainable methods for cellulose, hemicellulose, and lignin extraction	2024
Kosuke Kuroda[69]	Bioethanol fermentation in the presence of ionic liquids: mini review	Challenges of microbial fermentation in the presence of toxic ionic liquids, need for low-toxicity ILs and IL-resistant microorganisms	2024
Pedro Verdía Barbará *et al.*[70]	Recent advances in the use of ionic liquids and deep eutectic solvents for lignocellulosic biorefineries and biobased chemical and material production	Current state of lignocellulosic biomass processing using ILs and DESs, focusing on pretreatment chemistry, process flows, and product streams, followed by sustainability assessments and key technological challenges	2025

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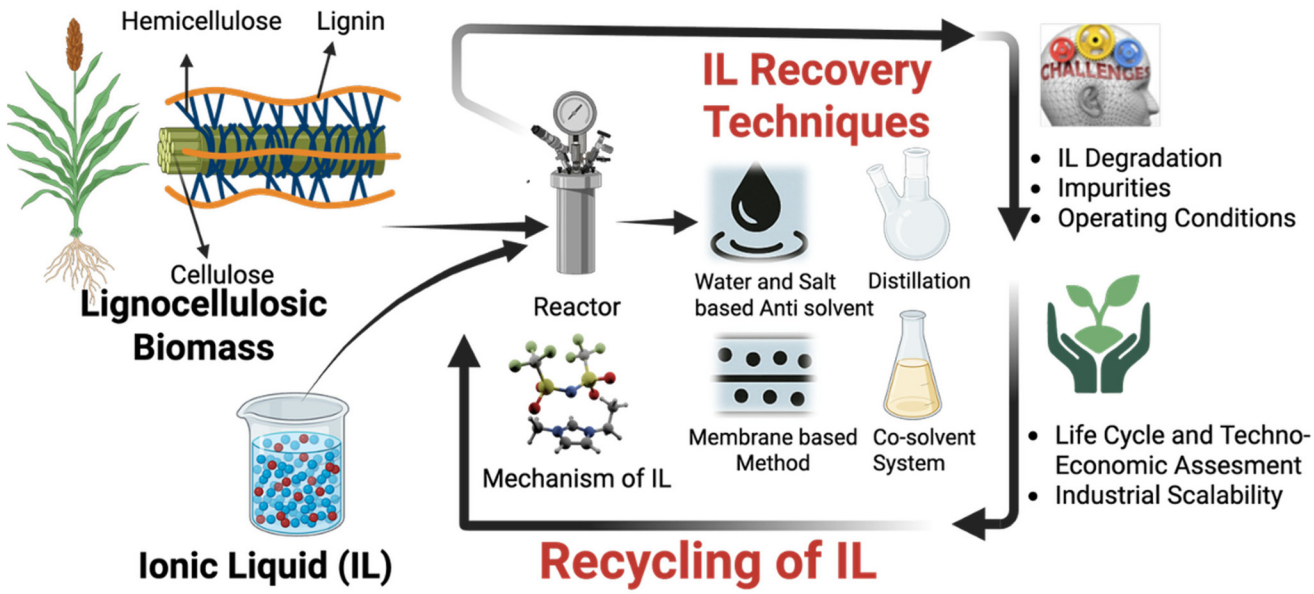

Fig. 3 Conceptual overview of ionic liquid recycling in lignocellulosic biomass pretreatment.

integrated recovery strategies that align with industrial scalability.

2. Mechanisms of ionic liquids interaction with biomass

ILs interact with biomass mainly through hydrogen bonding and various non-covalent interactions (*i.e.*, π-stacking, hydrophobic interactions), facilitating the dissolution and transformation of biomass components into valuable chemicals and fuels.[71,72] The dissolution mechanism involves breaking down the complex, and rigid structure of biomass, making it more amenable to subsequent conversion. This section explores the underlying mechanism of ILs–biomass interactions, examining the influence of IL structure, key factors affecting dissolution of biomass components (*i.e.*, cellulose, hemicellulose and lignin), and distinct role of anions and cations.

2.1. Structure and characteristics

ILs are a unique class of compounds composed entirely of ions, typically consisting of a bulky organic cation and a smaller, either inorganic or organic anion.[21,72,73] The diversity of possible cation–anion combinations is vast, with estimates suggesting >10^{18} potential combinations, allowing for the customization of ILs for specific properties and applications.[74] Due to their vast structural and functional diversity, the classification of ILs is essential. Hajipour and Rafiee (2015)[75] categorized ILs into eleven distinct classes based on their properties including neutral, acidic, basic, functionalized, protic, chiral, supported, bio-ionic, polymerized, energetic, and those containing amphoteric anions. An alternative approach proposed by Buszewska-Forajta *et al.* (2018)[76] classifies ILs according to the nature of their constituent cations and anions including imidazolium, pyridinium, piperidinium, quinolinium, morpholinium, pyrrolidinium, and their alkyl derivatives, as well as tetraalkyl ammonium, phosphonium, and trialkyl sulfonium.[77]

Protic and aprotic ILs are synthesized by substituting heteroatoms in the cation with protons or alkyl groups, respectively. Protic ILs, which are formed *via* proton transfer from a Brønsted acid to a Brønsted base, are characterized by extensive hydrogen-bonding networks due to the presence of proton donor and acceptor groups. In contrast, aprotic ILs lack this extensive hydrogen-bonding capability, differentiating them from their protic counterparts.[78,79] However, the basic structure of ILs involves an asymmetry between the cation and anion, where the cation is generally a large, organic molecule (*e.g.*, imidazolium, pyridinium), and the anion ranges from simple halides (*i.e.*, Cl^-, Br^-) to complex fluorinated structures like bis(trifluoromethylsulfonyl)imide $[Tf_2N]^-$.[80,81]

This asymmetry reduces the effective coulombic interactions between the ions, lowering the lattice energy and enabling these salts to remain liquid at temperatures below 100 °C, distinguishing them from conventional salts.[73] The cationic component often features alkyl chains or aromatic groups that can influence the physicochemical properties of the ILs. For instance, imidazolium-based cations are known for their tunable solubility and thermal stability. The anion, on the other hand, plays a significant role in determining properties like hydrophilicity, polarity, and overall ionic strength.[82–84] The structure of ILs is influenced by the electrostatic attractions and steric packing, which contribute to their liquid-like ordering. This ordering is evident in the pair correlation functions observed in molecular dynamics simu-

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lations.[85] The presence of a pre-peak in the static structure factor indicates a geometric effect from the packing of alkyl chains, highlighting the importance of the molecular structure in determining the properties of ILs.[85]

The interaction between ions, including the magnitude of attraction and conformational flexibility, play crucial roles in determining the transport properties and stability of ILs[86] while computational methods such as molecular dynamics simulations are essential for understanding these interactions and the resulting liquid structures. Studies using molecular dynamics simulations and X-ray scattering have shown that ILs have distinct pair correlation functions, indicating specific spatial arrangements of ions within the liquid.[85,87] The structural organization of ILs can change with temperature, as seen in phase transition from solid to liquid phase which is often studied using techniques like X-ray diffraction and Raman spectroscopy.[88] However, the choice of ions directly impacts the physical and chemical properties of IL, such as viscosity, conductivity and solubility. However, ILs are classified into three generations which are typically based on the evolution in design, functionality and application focus, as depicted in Fig. 4.

First generation ILs have unique physical properties and are focused on simple ionic salts (*e.g.*, chloroaluminate based with simple cations like imidazolium or pyridinium) used mainly in electrochemistry (*e.g.*, electrolytes in batteries) but highly sensitive to moisture, air instability and corrosiveness. Second generation ILs are more stable and less reactive, which have been designed to overcome the limitation of the first generation and expand their application as green solvents.[89] The third generation of ILs introduced task specific functionalities tailored for targeted applications (*e.g.*, biomass processing, catalysis, CO_2 capture) and enhanced functionalities (*i.e.*, pharmaceutical synthesis, and electrochemical devices).

While third generation ILs offer task specific functionalities, they often rely on synthetic, non-renewable, and sometimes toxic components, which can lead to ecological concerns during disposal or accidental release. Additionally, the limited biodegradability of many existing ILs constrains their applications where environmental safety is paramount, such as biomedicine and environmental remediation.[73] Therefore, to address those concerns and fill the shortcomings of previous generations of ILs, significant efforts should be directed towards developing a new class of ILs with enhanced biodegradability, non-toxicity, and renewable sourcing features. This involves employing natural and renewable components such as amino acids, carbohydrates, and organic acids, moving away from synthetic, halogenated compounds that can pose serious environmental and health risks.

2.2. Ionic liquid-based dissolution mechanisms for lignocellulose components

The dissolution mechanisms of cellulose, hemicellulose and lignin are complex processes influenced by the chemical structure of these biopolymers and the solvents used. Each component of lignocellulosic biomass has unique interactions with solvents, which are crucial for their effective dissolution and subsequent processing. The following sections detail the mechanisms for each component based on the available knowledge and our expertise in the deconstruction of biomass.

2.2.1. Dissolution mechanism of cellulose. The sustainable valorization of biomass critically depends on the efficient deconstruction of its major structural component, cellulose. However, cellulose is inherently resistant to dissolution due to its extensive intra-and intermolecular hydrogen bonding, high crystallinity, and van der Waals interactions. The dissolution mechanism of cellulose during biomass pretreatment involves breaking down the rigid structure of cellulose to make it more accessible for efficient conversion into value added products such as biofuels and biochemicals.[90,91] The detail of cellulose existence in lignocellulosic biomass is shown in Fig. 5 and analytical and computational tools used for cellulose dissolution are presented in Table 2.

To disrupt this robust network of cellulose, several ILs have been used as solvents[91–95] to enable homogenous processing under relatively mild conditions (>150 °C). The dissolution of cellulose in ILs primarily hinges on their ability to disrupt the dense hydrogen-bonding that stabilizes the cellulose structure. This disruption is facilitated by the ILs anion, which acts as a strong hydrogen bond acceptor, forming interactions with the hydroxyl groups on cellulose chains. Swatloski *et al.*[38] first demonstrated that 1-butyl-3-methylimidazolium chloride [BMIM]Cl could dissolve cellulose by breaking these hydrogen bonds, highlighting the critical role of small, basic anions such as (Cl^-) and (CH_3COO^-) in the dissolution process. Subsequent research reinforced that the anion's basicity and size are pivotal. For instance, [EMIM][CH_3COO] exhibits superior dissolution capability (up to 16 wt%) due to acetate's strong hydrogen bond acceptor nature and the reduced viscosity compared to halide-based ILs.[96] Notably, anions such as acetate (CH_3COO^-) and chloride (Cl^-) play a crucial role by forming strong hydrogen bonds with the hydroxyl groups of cellulose, thereby destabilizing the crystalline structure. Concurrently, the cation also contributes by influencing viscosity and steric accessibility; imidazolium-based cations bearing acidic protons enhance solubility by interacting with cellulose's oxygen atoms. For example, 1-ethyl-3-methylimidazolium [EMIM]$^+$ interacts with the hydrophobic surfaces of cellulose fibrils, preventing reaggregation and promoting solvation. This synergistic action facilitates the separation of cellulose chains and enhances enzymatic accessibility.[92,93,95]

Mechanistically, the dissolution process is believed to occur by the formation of complexes between IL anions and cellulose hydroxyl groups, weakening the extensive hydrogen bonding within and between cellulose chains, followed by polymer chain separation and solvation by the IL medium. Some studies suggest that co-solvents like DMSO can further accelerate dissolution by reducing viscosity and improving mass transfer, although care must be taken to ensure sufficient anion availability.[97,98] In terms of structural transitions, ILs can convert crystalline cellulose I into cellulose II or amorphous cellulose, enhancing accessibility for further chemical

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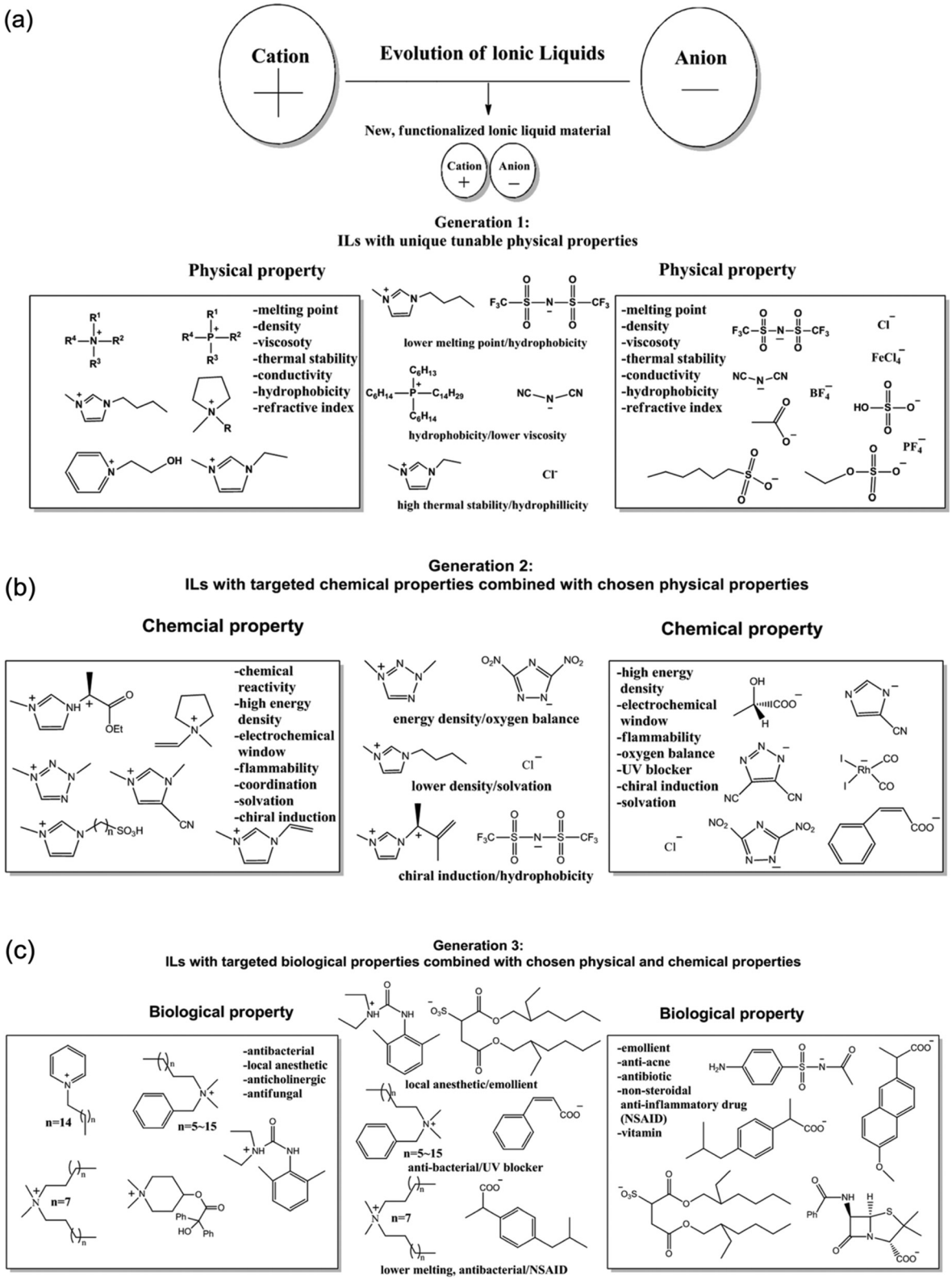

Fig. 4 Properties of ILs and examples of corresponding chemical structures employed over the generations. Panels: (a) first generation; (b) second generation; (c) third generation. Adapted from ref. 73. Copyright 2020, Universal Wiser.

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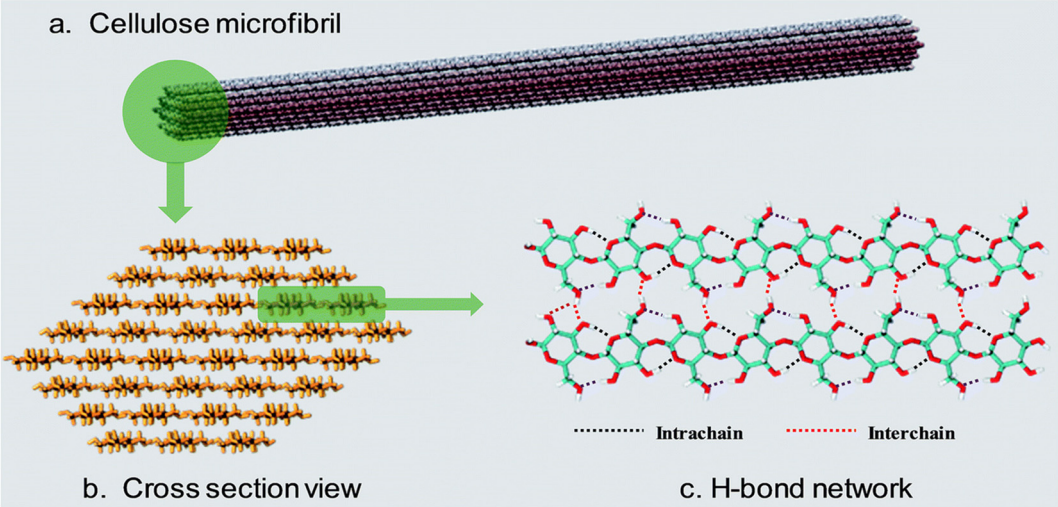

Fig. 5 Structural feature of cellulose: (a) general form of cellulose (*i.e.*, cellulose microfibril); (b) cross-section view of 36 chain cellulose elementary microfibril; (c) H-bond network between cellulose chains. Adapted from ref. 92. Copyright 2017, Royal Society of Chemistry.

Table 2 Analytical and computational techniques used for cellulose dissolution[91,93,95,99,100]

Techniques	Description	Insights
Molecular dynamics (MD) simulation	Computational studies analyzing solute–solvent interaction at molecular levels	Visualize anion and cation interactions with cellulose surface
Nuclear magnetic resonance (NMR)	Monitors changes in chemical environments during cellulose dissolution	Identifies hydrogen bonding disruption and chemical shifts
Fourier transform infrared spectroscopy (FTIR)	Track changes in functional groups and hydrogen bonding networks	Indicates disruption of crystalline hydrogen bonds
Scanning electron microscopy (SEM)	Visualize surface morphology of cellulose before and after dissolution	Shows structural changes and fibril disintegration
X-ray diffraction (XRD)	Measures crystallinity index changes during pretreatment	Evaluates reduction in cellulose crystallinity
Raman spectroscopy	Identifies molecular vibrations and interaction	Highlights structural transformations in cellulose
Thermal analysis (DSC, TGA)	Examines thermal stability and phase transition during dissolution	Provides insights into thermal effects on cellulose crystallinity

or enzymatic transformation. Przypis *et al.*[93] highlights that crystalline to amorphous conversion is essential for increasing cellulose reactivity and solubility. Moreover, the ability of ILs to dissolve cellulose without derivatization under mild conditions, positions them as promising solvents.

Despite its potential, the high viscosity of certain ILs, cost of production, and challenges in recyclability limit scalability, necessitating further research to optimize processes and materials. Additionally, developing cost-effective, biodegradable ILs with high recyclability remains a priority.[92,93] Addressing these challenges could revolutionize biomass pretreatment by enabling more efficient, sustainable, and economically viable processes. Future research should focus on optimizing solvent systems, understanding solvent–cellulose interactions at the molecular level, and integrating dissolution studies with downstream conversion processes. These approaches would enhance the feasibility of cellulose-based biorefineries, paving the way for widespread adoption of renewable bioresources.[92,93]

2.2.2. Dissolution mechanism of hemicellulose. Hemicellulose is an amorphous and heterogenous polysaccharide containing a branched chain of sugar monomers such as xylose, mannose, galactose, glucose, arabinose and in some extent uronic acids (*i.e.*, glucuronic acid) and acetyl groups, reflecting to its structural diversity. However, the exact composition and structure of hemicellulose vary significantly between plant species, tissues and even developmental stages. For instance, hardwoods predominately contain xylan, softwoods are rich in glucomannans, and grasses have a mix of xylan and arabinans.[93,101] A general structure of hemicellulose is presented in Fig. 6.

Chemically, hemicellulose is more soluble in alkaline solutions than cellulose and can be partially solubilized under mild pretreatment conditions. However, the variability influences the choice of pretreatment methods and conversion strategies in biomass processing. The dissolution of hemicellulose, a fundamental step in converting biomass into value-added products, is governed by the intricate interplay of chemical and physical processes that deconstruct the hemicellulose matrix. To date, various pretreatment methods (see Table 3) have been employed to deconstruct the hemicellulose in biomass.

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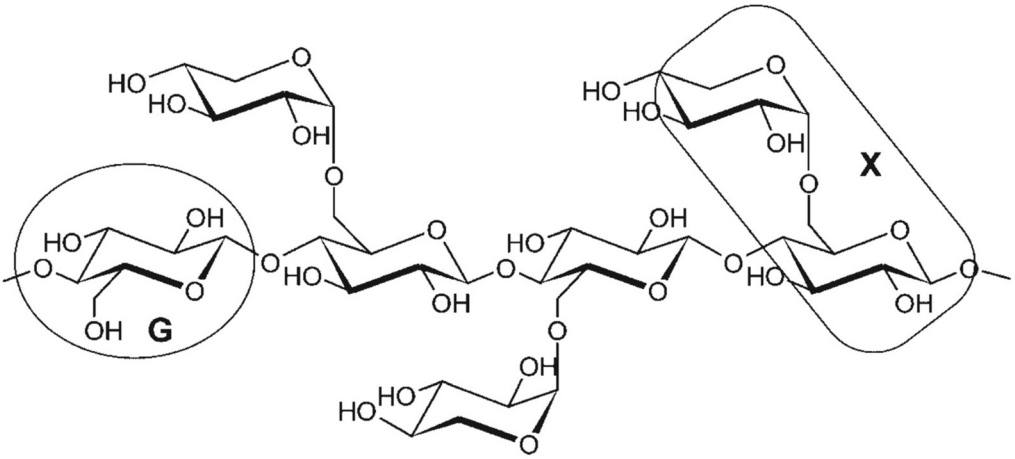

Fig. 6 Primary structure of D-xylo–D-glucan. Adapted from the ref. 102. Copyright 2006, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Table 3 Pretreatment techniques for hemicellulose deconstruction

Method	Key mechanism	Efficiency (%)	Environmental impact	Ref.
Oxidative torrefaction	Thermal decomposition, furan release	Moderate	Moderate	103
Hydrothermal pretreatment	Hot water hydrolysis	81.59	Low	104
Surfactant-assisted hydrolysis	Surface tension reduction	54.70	Low to moderate	105
Ionic liquid pretreatment	Hydrogen bond disruption	High	Low	101
Acidic electrolyzed water	Selective cleavage with $FeCl_3$	98.64	Low	106

Oxidative torrefaction thermally decomposes hemicellulose under controlled oxygen conditions, generating volatile compounds like furans and acids,[103] while hydrothermal pretreatment employs liquid hot water to hydrolyze hemicellulose, achieving dissolution rates up to 81.59% under optimized conditions.[104] Surfactant-assisted acid hydrolysis enhances dissolution by reducing surface tension and promoting ion diffusion, as demonstrated by increased hemicellulose removal from poplar wood chips.[105]

IL pretreatments disrupt the hydrogen bonding network in hemicellulose through the interaction of IL anions, achieving efficient dissolution with the added benefit of solvent recovery.[101] Zhao *et al.*[101] studied the dissolution of hemicellulose in ILs using computational methods, specifically the Conductor-like Screening Model for Real Solvents (COSMO-RS) to accurately predict the solubility of hemicellulose in ILs. Six hemicellulose models were evaluated (see Fig. 7), with the mid-dimer xylan chain (MDXC) emerging as the most suitable due to its alignment with experimental solubility data. A total of 1368 ILs were screened, emphasizing the role of hydrogen bonding, particularly the anion's acceptor capacity, in enhancing hemicellulose solubility. Smaller anions with strong hydrogen-bonding capabilities, such as chloride and acetate, were found to be most effective. Additionally, the study revealed that longer alkyl chains on cations negatively impact dissolution. The s-profile, a COSMO-RS-derived property, was used to analyze molecular interactions, providing insights into solubility patterns and enabling high-throughput screening of ILs. The findings highlight the potential of ILs as green solvents for hemicellulose dissolution, paving the way for improved lignocellulosic biomass processing.

The MDXC (mid-dimer xylan chain) model displayed balanced charge interactions, making it most representative of hemicellulose behavior in solution, which is crucial as accurate charge distribution predicts the molecular interactions, especially hydrogen bonding, with ILs. Acidic and catalytic pretreatments, such as $FeCl_3$ coupled with acidic electrolyzed water, selectively remove hemicellulose while preserving cellulose and lignin, reaching a remarkable 98.64% removal rate in poplar wood.[106] While each method demonstrates distinct advantages, their integration into sustainable biorefinery frameworks remains a critical avenue for advancing hemicellulose valorization while minimizing environmental impacts.

2.2.3. Dissolution mechanism of lignin. The dissolution mechanism of lignin involves complex interactions between lignin's molecular structure and various solvent systems. Lignin, a natural aromatic biopolymer, composed of both aliphatic and aromatic fragments, is notoriously difficult to dissolve due to its complex and heterogenous structure (see Fig. 8). Its primary building blocks are the monolignols: *p*-coumaryl, coniferyl, and sinapyl alcohols.[93,107] The composition of these precursors varies depending on the lignin source; for instance, softwood lignin (~24–33%) predominantly consists of coniferyl alcohol, while hardwood lignin (~19–28%) is rich in both coniferyl and sinapyl alcohols. Grass lignin

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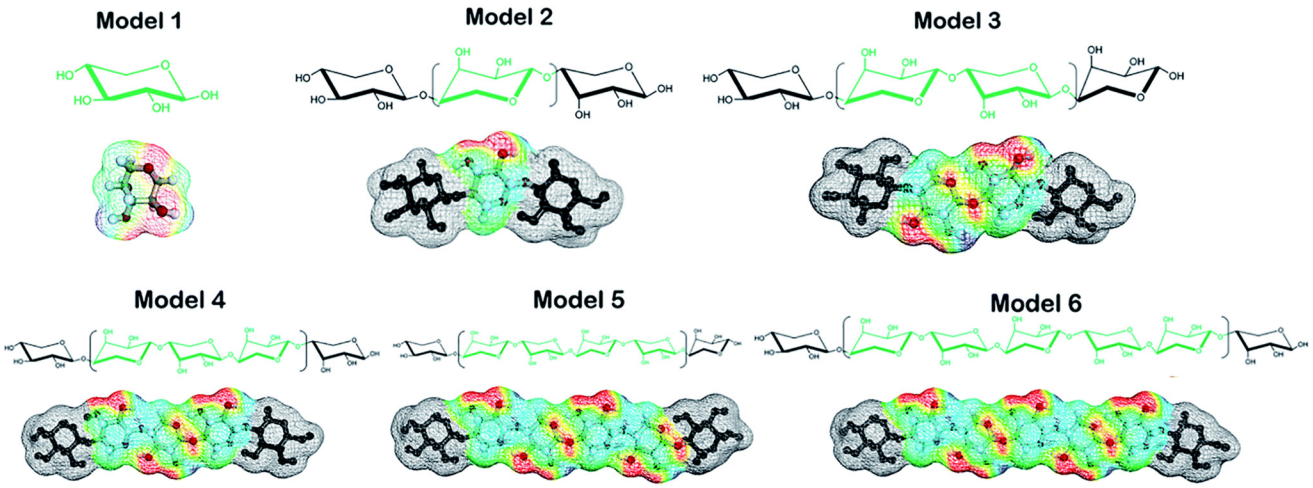

Fig. 7 COSMO-RS charge surfaces of six hemicellulose models: Model 1: xylan; Model 2: mid-monomer of xylan chain; Model 3: mid-dimer of xylan chain; Model 4: mid-trimer of xylan chain; Model 5: mid-tetramer of xylan chain; Model 6: mid-pentamer of xylan chain. (Red zones indicate a positive surface charge, yellow and green zones indicate almost neutral charges, navy blue designate negative surface charge.) Adapted from the ref. 101. Copyright 2022, Royal Society of Chemistry.

(~15–25%), in contrast, includes significant amounts of *p*-coumaryl alcohol.[93,107] These monomers are interconnected by ether (C–O–C) and carbon–carbon (C–C) bonds.

Within biomass, lignin forms a structural matrix with polysaccharides, contributing to the mechanical strength of plant tissues and enhancing their resistance to chemical and enzymatic degradation.[93,108,109] Recent studies have explored different solvent systems, including ILs, deep eutectic solvents (DESs), and other innovative approaches, to understand and enhance lignin dissolution. These studies reveal that the dissolution process is primarily driven by specific interactions such as hydrogen bonding, π–π stacking, and electrostatic interactions between lignin and the solvent components. DESs, such as those composed of choline chloride and lactic acid, are effective in dissolving lignin due to their ability to form hydrogen bonds with lignin molecules. The addition of co-solvents like ethylene glycol or γ-valerolactone (GVL) enhances these interactions by altering hydrogen bond strength and electrostatic potential, leading to improved lignin separation and dissolution efficiency.

Zhang *et al.* (2024)[110] explores novel ternary DESs combining choline chloride, lactic acid, and additives like ethylene glycol or GVL for lignin dissolution. These DESs showed enhanced delignification efficiency, retaining lignin's structural integrity while reducing molecular weight heterogeneity and improving antioxidant properties. Liu *et al.* (2020)[109] investigates alkali lignin dissolution using lactic acid–choline chloride DES. The mechanism involves lignin depolymerization through β-O-4 bond cleavage, facilitated by lactic acid's acidity and interactions between lignin phenolic groups and choline chloride. They explored the role of temperature in modifying the molecular weight distribution and structure of lignin, offering insights for valuable applications. ILs are known for their ability to dissolve lignin through a combination of hydrogen bonding and π-stacking interactions. The anion–cation pairs in ILs play a crucial role, with anions forming strong hydrogen bonds with lignin, while cations engage in π-stacking interactions.[111,112] Zhang *et al.* (2017)[111] employed Density Functional Theory (DFT) to elucidate the molecular mechanisms underlying lignin dissolution in imidazolium-based ILs. They identified hydrogen bonding between anions (chloride and acetate) and lignin as the dominant interaction driving dissolution, with anions preferentially binding to hydroxyl groups on lignin's β-O-4 model structure. Cations play a complementary role through π-stacking interactions with aromatic lignin units. These findings highlight the potential of engineering IL components to optimize specific interactions, paving the way for more effective lignin solubilization strategies.

Wang *et al.* (2017)[112] investigated lignin dissolution in ILs, emphasizing hydrogen bonding by anions (*e.g.*, chloride, acetate) and π-stacking by cations and demonstrate the interplay between lignin structure and IL components, offering insights to optimize ILs for enhanced lignin solubility and sustainable biorefinery processes. In another example, Mohan *et al.* (2023)[113] integrated multiscale molecular simulations and the COSMO-RS model to systematically screen 5670 ILs for lignin dissolution efficiency (see Fig. 9). By analyzing key thermodynamic parameters, such as activity coefficients and excess enthalpy, they discovered ILs containing acetate, glycinate, and lysinate anions paired with tetraalkylammonium and pyridinium cations as optimal.

Xue *et al.* (2016)[114] studied binary solvent systems, particularly those utilizing GVL combined with co-solvents such as water or ILs, exhibit exceptional efficiency in lignin dissolution. The solubility of lignin in these systems is primarily influenced by the hydrogen bond basicity of the solvent, which varies depending on the type of lignin and solvent

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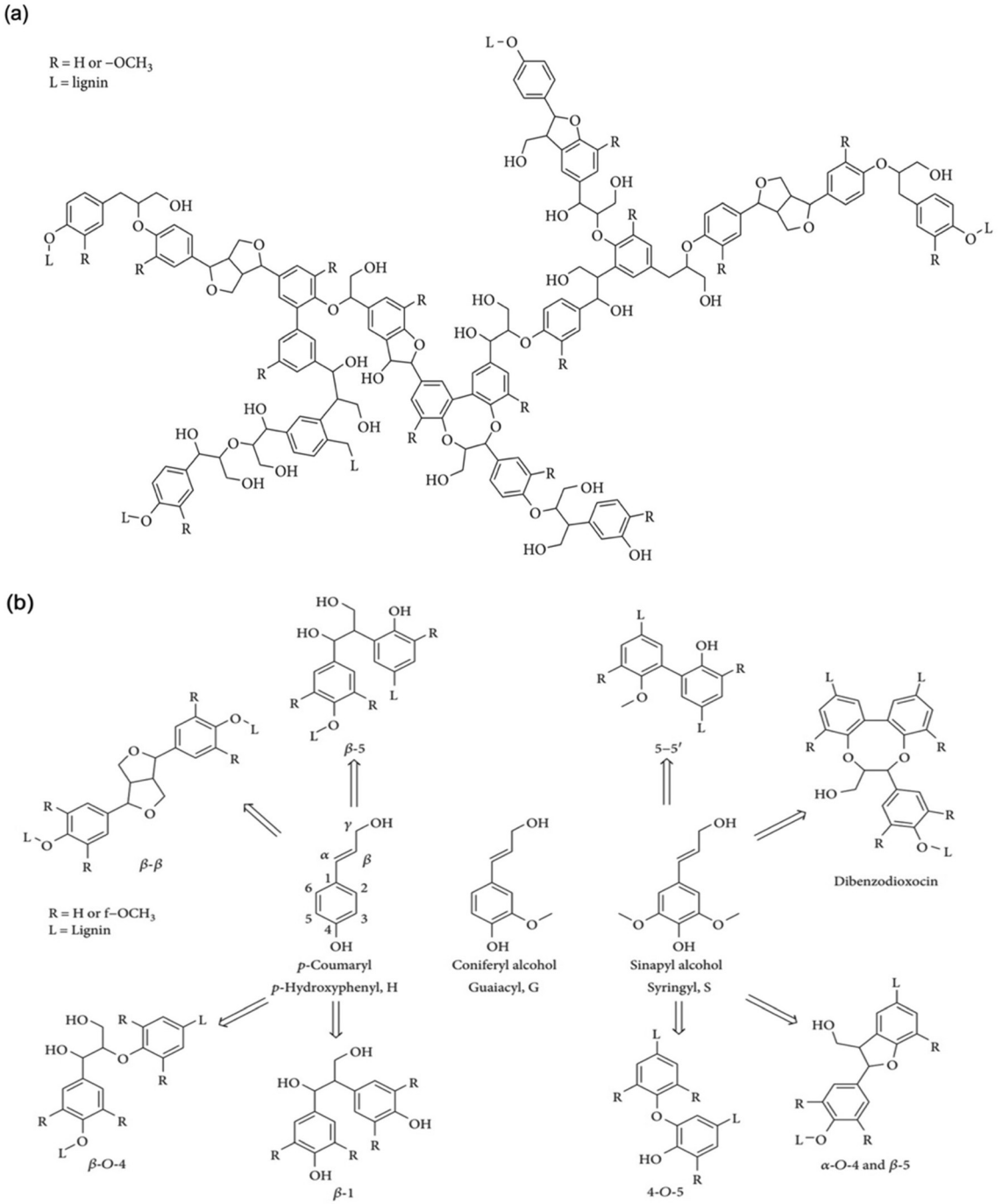

Fig. 8 Typical structure and interactions of lignin. Panels: (a) structure of lignin; (b) linkages of lignin. Adapted from ref. 107. Copyright 2017, Hindawi.

employed.[114] GVL–water mixtures, for example, demonstrate a remarkable ability to dissolve dealkaline lignin (DAL) through enhanced hydrogen bonding interactions, maintaining lignin's structural integrity while enabling sustainable delignification under mild conditions. Additionally, the inclusion of water in these systems significantly enhances the cleavage of intermolecular linkages within lignin, thereby facilitating its dissolution and depolymerization.[115]

2.3. Role of anions and cations in biomass deconstruction

The dissolution of lignocellulosic biomass in ILs is driven by the coordinated action of anions and cations, each playing a specific role in overcoming biomass recalcitrance. Anions primarily disrupt the hydrogen bonding network within cellulose and lignin, with their hydrogen bond basicity being a critical factor.[116,117] For instance, acetate (CH_3COO^-) and chloride (Cl^-)

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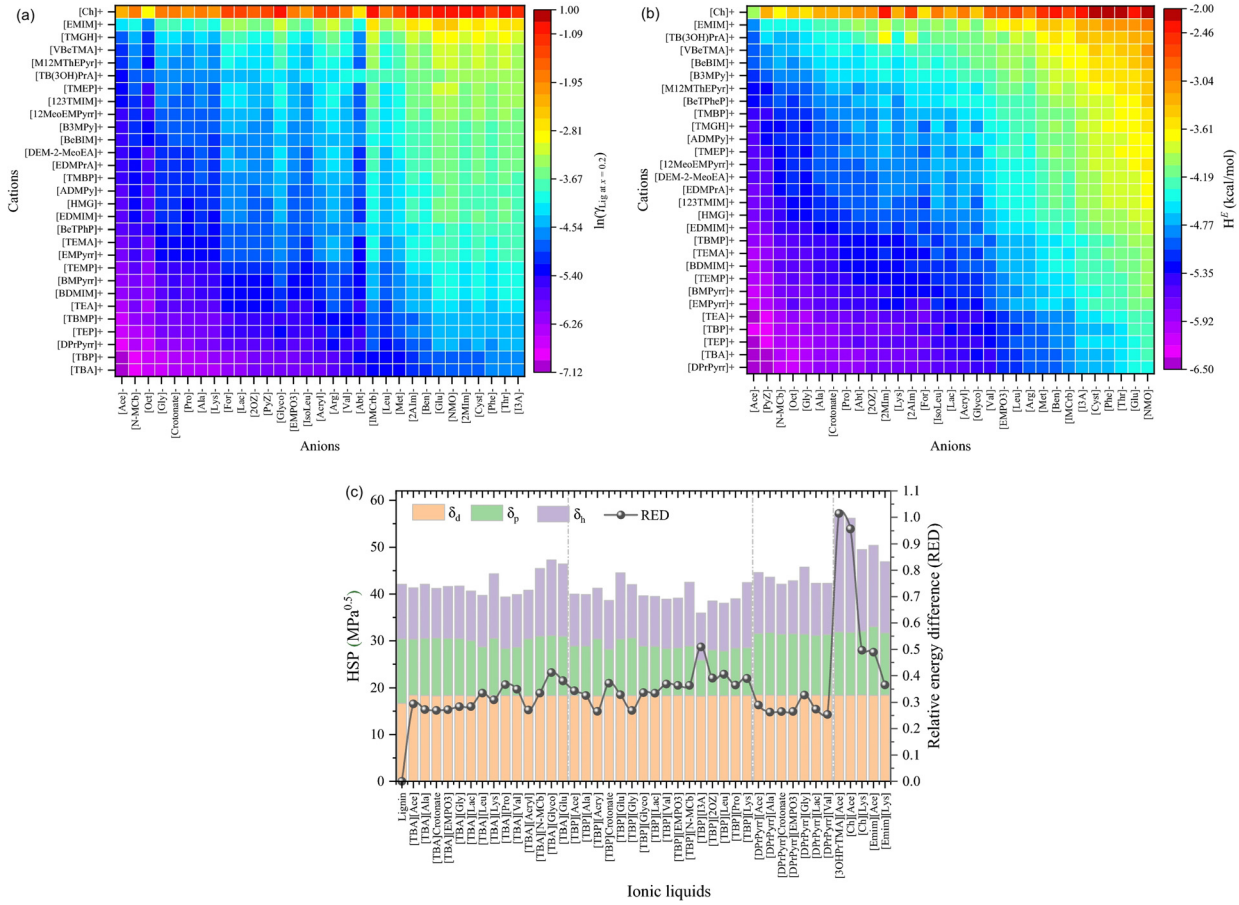

Fig. 9 Graphical representation of the lignin activity coefficient, enthalpy and solubility parameters by the COSMO-RS model. Panels: (a) logarithmic activity coefficients (ln(γ)) of lignin in different ILs at 363.15 K; (b) excess enthalpy, HE (kcal mol^{-1}) of lignin; (c) the COSMO-RS-based predicted Hansen Solubility Parameters of ILs. COSMO quick tool version 1.7 is used to predict the HSP of ILs. Adapted from ref. 113. Copyright 2023, Springer Nature.

anions are highly effective in breaking cellulose microfibrils, enhancing dissolution rates.[118] Specific anions, such as amino acid–based variants, are particularly suited for delignification while preserving polysaccharides, making them ideal for subsequent enzymatic hydrolysis.[119] Conversely, aromatic and hydroxyl-containing anions are less effective, as they may stabilize lignin's structure rather than breaking it apart. While acetate and chloride anions are widely used and effective, the choice of anion can be tailored to specific biomass types and desired outcomes. For instance, anions may offer better solubility for certain biomass types, while amino acid–based anions provide enhanced delignification. The selection of anions should consider the specific interactions and hydrogen-bonding capabilities required for efficient biomass dissolution.[116,118]

Cations, though secondary in direct interaction with biomass, modulate the physical properties of ILs, including viscosity and steric effects, which indirectly influence dissolution efficiency. Imidazolium-based cations like [EMIM]$^+$ (1-ethyl-3-methylimidazolium) and [AMIM]$^+$ (1-allyl-3-methylimidazolium) are widely used, as their unsaturated structures reduce steric hindrance, enhancing biomass solubility.[92,116] For example, ILs such as [EMIM][CH_3COO] effectively disrupt cellulose crystallinity, while [AMIM][HCOO] demonstrates superior biomass solubility due to stronger anion–polymer interactions.[116,119] Schutt *et al.* (2016)[120] revealed that cations can influence the activity of enzymes used in biomass processing. As a consequence, modifications to the cation structure, such as adding oxygen atoms, can improve mass transport properties and reduce enzyme deactivation, thereby enhancing the overall efficiency of biomass deconstruction.[120]

Innovative systems combining multiple ions, such as cholinium and lysinate or acetate mixtures, exhibit synergistic effects that enhance cellulose dissolution.[92] It has been revealed that the combination of ions enhance both solubility and enzymatic hydrolysis while maintaining biocompatibility for downstream processing.[121]

Although the role of anions and cations in biomass deconstruction is well-documented, challenges remain in optimizing these interactions for large scale/industrial applications. The cost and recyclability of ILs, as well as their impact on the properties of recovered materials, are critical factors that need to be addressed for commercial viability.[122,123] Additionally, the presence of water in IL systems can reduce their solvating power, although additives like lithium chloride can mitigate

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this effect.[124] These insights highlight the complexity and potential of ILs in biomass processing, suggesting avenues for future research and development.

3. Advances in recycling techniques for ILs

Over the past decades, researchers have dedicated significant effort to developing sustainable recovery strategies such as vacuum distillation, membrane separations, extraction, and adsorption methods, each customized to the distinct physicochemical properties of ILs.[125] Recent studies have also reviewed advancements in recycling and recovery techniques for ILs, providing insights on state-of-the-art methodologies and their applications.[126,127]

Despite these advancements, challenges persist, such as scalability and cost-efficiency, highlighting the need for integrated recycling approaches that combine multiple techniques. We envision a simplified framework for selecting a suitable IL recovery method subsequent to biomass pretreatment as a decision-making scenario, based on current knowledge (Fig. 10). These efforts not only support the circular economy but also ensure the sustainable use of ILs in green chemistry and beyond. The following section will systematically articulate recent advancements of recycling techniques applied to ILs.

3.1. Water- and salt-based antisolvent methods

Water- and salt-based antisolvent methods are pivotal for the recovery of ILs from aqueous mixtures, ensuring their sustainable reuse in diverse industrial applications. These techniques exploit the interaction between ILs, water, and salts to induce phase separation, thereby facilitating efficient recovery while reducing energy consumption and waste generation. Among the prominent methods, electrodialysis, aqueous biphasic systems (ABS), and antisolvent crystallization (ASC) stand out due to their scalability, environmental compatibility, and adaptability to different industrial requirements. Electrodialysis employs ion exchange membranes to separate ionic species and water from ILs, enhancing solvent purity and recycling efficiency.[128] This technique has been effectively demonstrated in systems involving ethanol recovery for lithium-ion battery recycling, requiring an energy input of 60–200 kWh per cubic meter of ethanol processed, making it a viable alternative to distillation, which is energy-intensive.[128] Fig. 11 illustrates process comparison, operational setup, and a cyclic process flowchart, emphasizing the energy efficiency and scalability of this method.

ABS employs salts such as Na_2CO_3 or $MgSO_4$ to create two immiscible aqueous phases, with ILs preferentially partitioning into the IL-rich phase. This method is particularly effective in recovering ILs from complex matrices such as plant extracts, achieving nearly quantitative recovery rates when the salt type and concentration are optimized.[129,130] Similarly, ASC utilizes the addition of antisolvents like methanol to selectively precipitate salts from aqueous IL solutions. This approach enables the separation of inorganic salts from saline effluents or IL mixtures, offering a green and cost-effective solution. For instance, ASC has been used to recover sodium sulfate from saline effluents, with a focus on solvent recovery to minimize environmental impact.[131]

Despite their advantages, these methods face challenges such as membrane fouling in electrodialysis, salt solubility limitations in ABS, and solvent loss in ASC. Hybrid approaches combining these techniques have shown promise in addressing these limitations. For example, integrating ABS with electrodialysis enhances IL recovery efficiency while reducing energy consumption.[128,131] Another advanced hybrid design

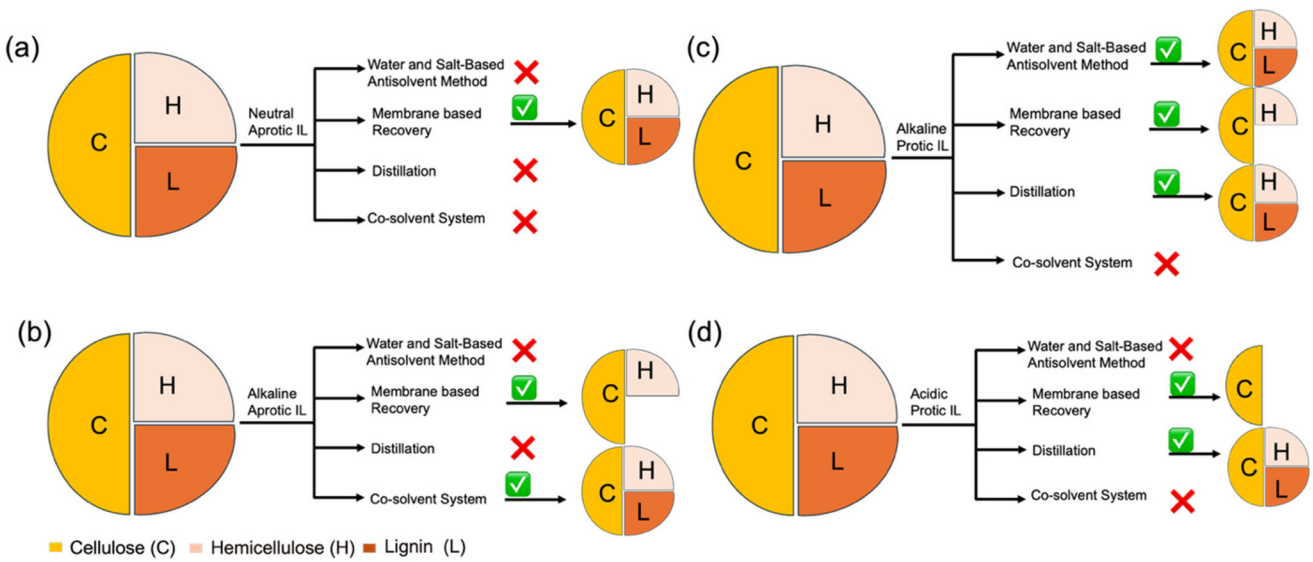

Fig. 10 Main categories of ILs in biomass pretreatment and related recycling techniques. Panels: (a) scenario-1; (b) scenario-2; (c) scenario-3; (d) scenario-4.

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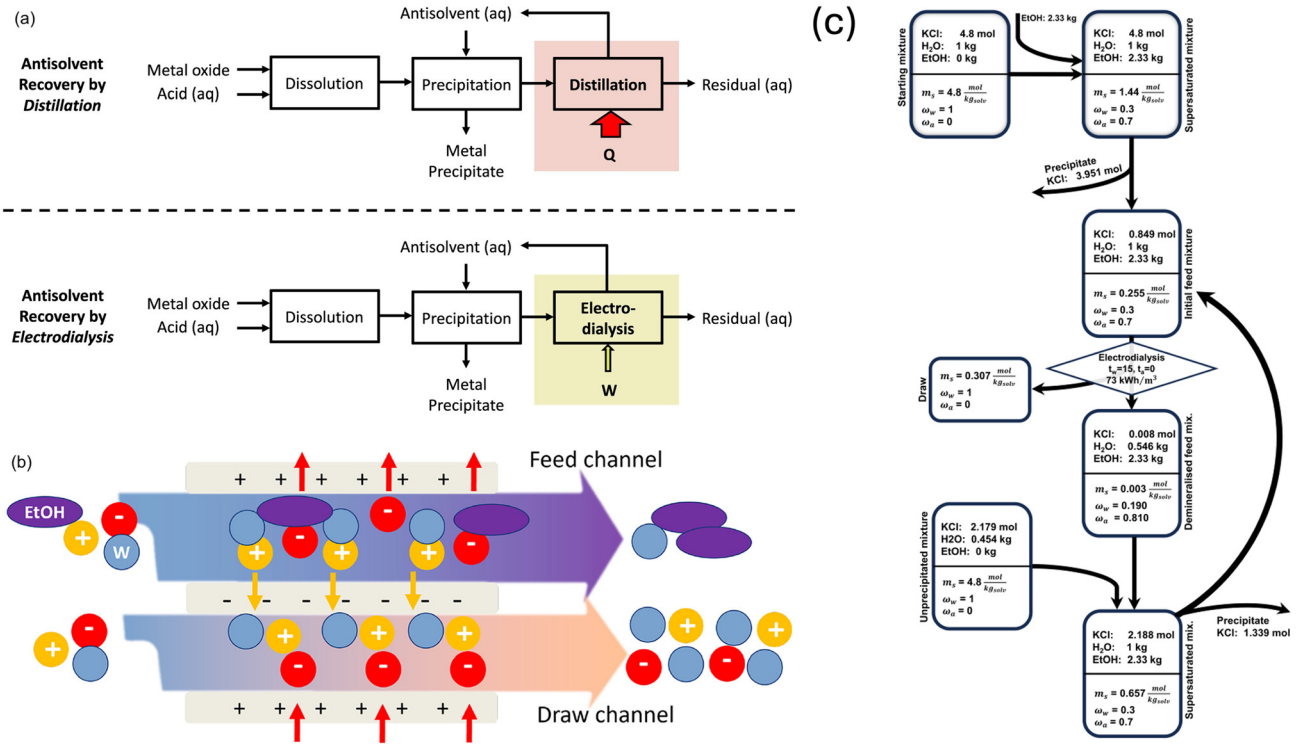

Fig. 11 IL recovery process comparison, operational setup, and a cyclic process flowchart. Panels: (a) options for antisolvent recovery and associated utilities. Recovery by distillation requires a heat duty, *Q*, while the electrodialysis process requires electrical work, *W*. (b) A concept that uses electrodialysis for antisolvent recovery. The sketch illustrates a section of an electrodialysis cell, where a mixture of antisolvent, water and salt enter in the feed channel and salt, and water enters in the draw channel. The two feed channels are separated by cation-exchange membrane and anion-exchange membranes. (c) Flowchart detailing the compositions of an example cyclic process involving antisolvent recycling by electrodialysis. Adapted from ref. 128. Copyright 2024, Elsevier.

merges aqueous two-phase extraction, membrane separation, and distillation to recover hydrophilic ILs from dilute aqueous solutions, achieving substantial reductions in both total annual costs and energy consumption compared to standalone distillation processes.[132] Additionally, incorporating salting-out agents like $(NH_4)_2SO_4$ significantly boosts process efficiency, achieving energy savings of up to 91% in certain scenarios.[132] Table 4 summarizes the key features of these methods, highlighting their energy efficiency, advantages, and challenges. Continued research into the thermodynamic properties of ILs in aqueous systems and the development of advanced materials for membranes and solvents can further optimize these processes, aligning them with green chemistry principles and fostering their broader adoption.

This review underscores the transformative potential of water- and salt-based recovery strategies in advancing sustainable industrial applications. Exploring hybrid methodologies and refining process conditions hold the key to unlocking their full potential.[128,129,131] While these methods offer promising solutions for the recovery of ILs and salts, several challenges remain. The selection of appropriate antisolvents and salts is crucial for optimizing recovery efficiency and minimizing environmental impact. Additionally, the integration of these methods into existing industrial processes requires careful consideration of economic and technical feasibility. Further research is needed to address these challenges and develop more robust and scalable recovery systems.

3.2. Membrane-based recycling: pervaporation and hollow fiber systems

Membrane-based recycling of ILs using pervaporation and hollow fiber systems is a promising approach for efficient separation and recovery processes. Pervaporation, a membrane separation process, is particularly effective for separating vola-

Table 4 Comparative analysis of water- and salt-based antisolvent methods for IL recovery[128,130,131]

Method	Energy efficiency	Key advantages	Challenges
Electrodialysis	60–200 kWh m^{-3}	High selectivity, low energy use	Membrane fouling and cost
ABS	High (near complete)	Simultaneous IL and solute recovery	Salt concentration dependency
ASC	Moderate	Selective salt recovery, green process	Solvent loss, antisolvent recycling challenges

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tile solutes from non-volatile solvents, making it suitable for IL dehydration and recovery.[133,134] Hollow fiber membranes, known for their high surface area-to-volume ratio, enhance the efficiency of pervaporation systems. This synthesis explores the application of these technologies in IL recycling, highlighting their advantages and potential challenges. It is worth noting that a recent review by Khoo *et al.* (2024)[126] extensively covered ILs recovery techniques by membrane separation with a particular focus on reverse osmosis and nanofiltration therefore these techniques are not discussed in detail in this review.

Pervaporation offers exceptional efficiency and selectivity for IL recovery. For instance, the dehydration and recycling of 1-ethyl-3-methylimidazolium acetate [EMIM][CH_3COO] from aqueous solutions achieved a remarkable separation factor of 1500, recovering over 99.9 wt% of the IL. Compared to other methods, pervaporation exhibited the highest IL recovery (>99 wt%) and negligible losses (0.02–0.04 wt%) compared to vacuum distillation and electrodialysis, which showed higher IL losses and lower final IL concentrations, as shown in Table 5. These results highlight the superior efficiency and selectivity of pervaporation for IL dehydration. This capability underscores its potential to improve the economics of biorefineries by reducing IL losses and operational costs.[135]

Membrane materials, particularly polydimethylsiloxane (PDMS), have demonstrated stable flux and effective separation performance over extended periods. For example, PDMS membranes were successfully used to recover ILs from methanol, showing increased flux with rising temperatures but reduced flux at higher IL concentrations. These findings illustrate the critical influence of operational parameters on process efficiency.[136] Nafion™ membranes have also proven effective, especially for water removal from IL solutions, achieving significant fluxes for both water and solvents like *N*-methyl-2-pyrrolidone (NMP), further highlighting the versatility of pervaporation in handling various IL–solvent systems.[137] Huang and Fedkiw (2016)[137] explored the application of Nafion membranes for water removal from IL solutions through pervaporation. By optimizing operational parameters, they effectively reduced water content from 1.0 wt% to 0.5 wt%. Among the tested membranes, the XL membrane exhibited the highest performance, achieving a water flux of 10 mg h^{-1} cm^{-2} at 100 °C. Their findings revealed a significant increase in water and solvent flux with temperature, with water flux peaking at 7–10 mg h^{-1} cm^{-2}. However, selectivity slightly declined above 90 °C. Additionally, gas-sweep rates influenced performance, with higher rates improving water flux (up to 10.4 mg h^{-1} cm^{-2}) but reducing selectivity due to increased solvent permeation, as shown in Fig. 12.

To address membrane swelling and stability challenges, support layers were introduced, ensuring mechanical reliability and consistent operation. These results confirm the feasibility of Nafion membranes for efficient IL recovery, combining high performance with robust thermal and mechanical stability.

However, hollow fiber membranes offer unique advantages in pervaporation processes due to their high surface area-to-volume ratio. They have been extensively used for separating water–organic and organic–water mixtures, and even for applications like water desalination.[138] An innovative application includes the concentration of glycerol using hollow fiber pervaporation membranes, which significantly reduces energy consumption compared to distillation while preserving product quality by operating at lower temperatures. This capability highlights their energy efficiency and product safety advantages.[139] The dynamic cross-flow coating method for hollow fiber membranes creates defect-free selective layers, enhancing pervaporation for alcohol–water separation with a separation factor of 6.4.[139] PDMS/PVDF hollow fiber membranes have shown exceptional potential for phenol recovery from coal chemical wastewater. In pilot-scale experiments, these membranes achieved a phenol removal efficiency of 72% under optimal conditions: 70 °C, 150 L h^{-1} flow rate, 5 kPa membrane pressure, and a 0.3 gas–water ratio, within a 6-hour cycle. Moreover, the system demonstrated long-term operational stability, maintaining over 60% efficiency for 120 hours.[140] The use of PDMS/PVDF hollow fiber composite membranes in such processes has shown high removal efficiency and stable operation over extended periods, proving their suitability for industrial wastewater treatment.[140,141] Jie *et al.* (2014)[140] demonstrated phenol removal efficiency increases with time and temperature due to enhanced molecular energy, but prolonged high temperatures may compromise membrane integrity. Higher flow rates reduce concentration polarization and improve efficiency, while lower membrane pressures promote phenol permeation at the risk of fouling. The system demonstrated stability over 120 hours with consistent removal efficiency exceeding 60%. These results underscore the system's potential for energy-efficient and scalable phenol recovery in industrial wastewater treatment applications.

However, there are challenges to the widespread adoption of these systems. Table 6 summarizes key insights and applications of pervaporation and hollow fiber membrane systems for ionic liquid recycling. Membrane stability under varying operational conditions, such as temperature and pH, is essential for ensuring long-term performance. The choice of membrane material significantly impacts the durability and efficiency of the process. Moreover, economic viability remains a key consideration, as the initial investment and operational costs associated with these systems must be justified through

Table 5 Efficient dehydration and recovery of ionic liquid after lignocellulosic processing using pervaporation[135]

Techniques	IL : H_2O (w/w)	t/P (h kPa^{-1})	Final IL concentration (wt%) (°C)	IL loss (wt%)
PV	20 : 80	4/~12	>99 (@100)	0.02–0.04
ED	10 : 90	4/—	45 (@20)	7.0
VD	20 : 80	4/10	90 (@100)	0.1
VD	53 : 47	13.8	69 (@80)	0.15
PV	53 : 47	13.8	69 (@80)	0.03

PV: pervaporation, VD: vacuum distillation, ED: electrodialysis.

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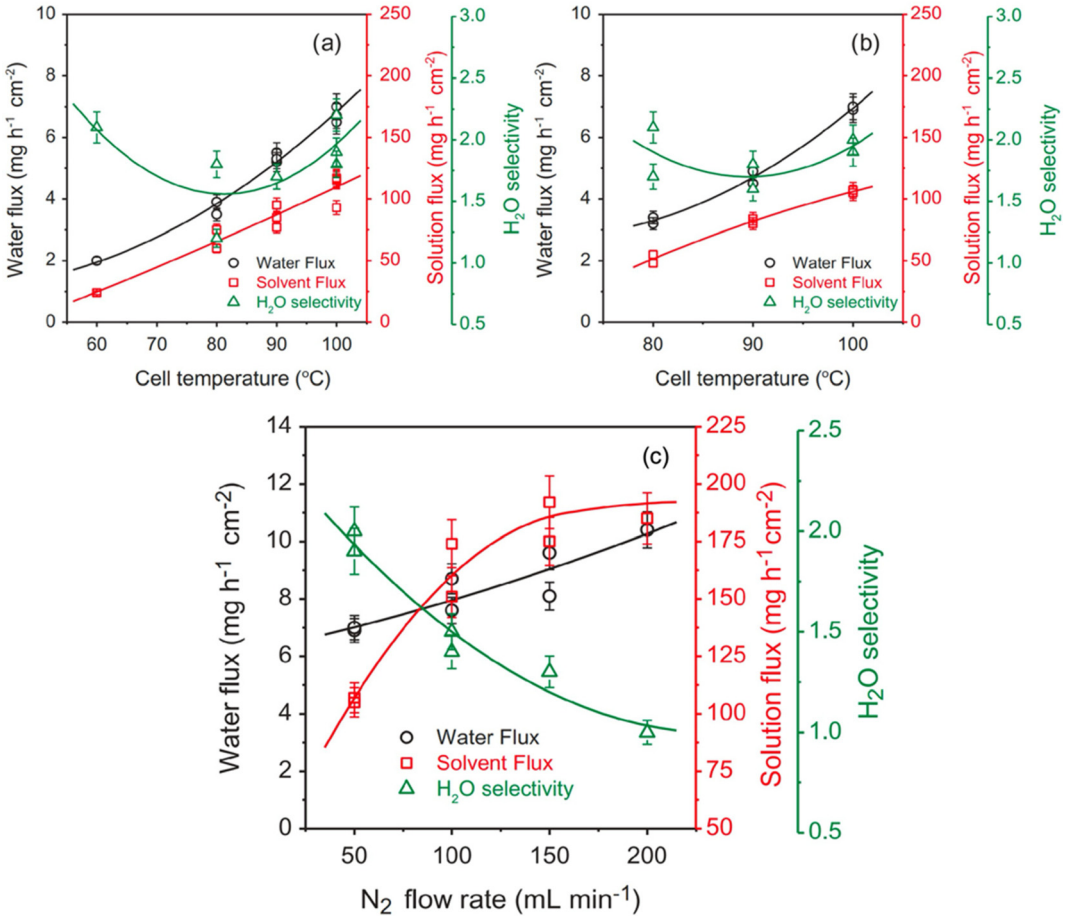

Fig. 12 Effect of temperature and gas as-sweep rate on pervaporation. Panels: effect of temperature on pervaporation results with liquid and gas flow rates of 5 and 50 mL min^{-1}, respectively: (a) XL membrane; (b) Gore A membranes; (c) effect of gas-sweep rate on pervaporation rates: Gore A membrane with metal grid at 100 °C. Adapted from ref. 137. Copyright 2016, Taylor & Francis.

Table 6 Key observations of pervaporation and hollow fiber membrane systems for ionic liquid recycling

Aspect	Key observations	Ref.
Pervaporation efficiency	Highly selective and efficient for IL recovery, achieving a separation factor of 1500 and >99.9 wt% recovery for [EMIM][CH_3COO]	135
PDMS membranes	Stable flux and good separation performance for IL recovery from methanol; flux increases with temperature but decreases with IL concentration	136
Nafion membranes	Effective for water removal from IL solutions, achieving high flux for water and solvents like NMP	137
Hollow fiber membranes	High surface area enhances efficiency in water–organic and organic–water separations and desalination	138
Glycerol concentration	Reduces energy consumption compared to distillation, operating at lower temperatures to avoid glycerol decomposition	139
Phenol recovery	PDMS/PVDF membranes used in coal chemical wastewater for phenol recycling, achieving high efficiency and stable operation	140 and 141

comprehensive techno-economic analyses to validate their commercial feasibility.

In comparison to traditional separation methods, membrane-based recycling using pervaporation and hollow fiber systems offers distinct advantages in energy efficiency and selectivity. Addressing challenges such as membrane stability and economic feasibility will be crucial to fully realizing their potential in industrial applications. Continued development of robust and cost-effective membrane materials will be instrumental in advancing these technologies for IL recycling, paving the way for greener and more sustainable industrial processes.

3.3. Distillation for IL recovery

For volatile ILs, distillation has emerged as a critical technique for the recovery and recycling of ILs, particularly in industrial applications such as biomass pretreatment. This method offers significant advantages in terms of sustainability and

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economic feasibility. Despite the low vapor pressures of ILs, recent advancements in vacuum and molecular distillation techniques have enabled the efficient separation of ILs from volatile impurities and reaction by-products.[142,143] These methods leverage the high thermal stability and negligible volatility of ILs to achieve exceptional recovery rates. For example, vacuum evaporation of 1-butyl-3-methylimidazolium acetate [BMIM][CH_3COO] has shown high enzymatic hydrolysis efficiency (over 70%) after multiple cycles, retaining the ILs chemical structure with minimal lignin accumulation.[144] Similarly, molecular distillation at reduced pressures has successfully recovered [EMIM][CH_3COO] with over 90% yield and purity exceeding 95%, demonstrating its potential for industrial scalability.[145]

The effectiveness of distillation hinges on optimizing parameters such as temperature, pressure, and IL composition. Protic ionic liquids (PILs), such as ethanolamine acetate [EthA][CH_3COO], have demonstrated recovery rates exceeding 85% in vacuum distillation at the lab scale, achieving glucose and xylose yields of 73.6% and 51.4%, respectively, during biomass pretreatment,[146] as shown in Fig. 13. While these yields were lower than those from early separation, they were coupled with higher retention of lignin and hemicellulose, enabling potential downstream valorization. The trends in glucose and xylose release during saccharification are also depicted, highlighting the leveling off sugar yields after five days. This indicates the need for further optimization to improve the enzymatic hydrolysis step in the distillation process. These findings highlight distillation's ability to outperform traditional methods like water washing, which are often energy-intensive and generate toxic waste streams.[135] Further optimization has been observed in ILs like 1-ethylimidazolium chloride [EIM]Cl, which, when distilled at 200 °C under vacuum, achieved 93% recovery while maintaining structural integrity.[119] Distillation also offers the advantage of retaining IL structural integrity, enabling reuse and alignment with circular economy principles. For instance, the neutral compound distillation of [TMGH][CO_2ET] resulted in >99% recovery purity with negligible decomposition, emphasizing its robustness under thermal conditions.[147] Studies have demonstrated that distillation is particularly effective when integrated with complementary techniques. For example, combining distillation with membrane separation or desorption columns has enhanced recovery efficiency and reduced operational costs.[148]

Economic and environmental considerations are paramount for distillation's industrial adoption. Innovations such

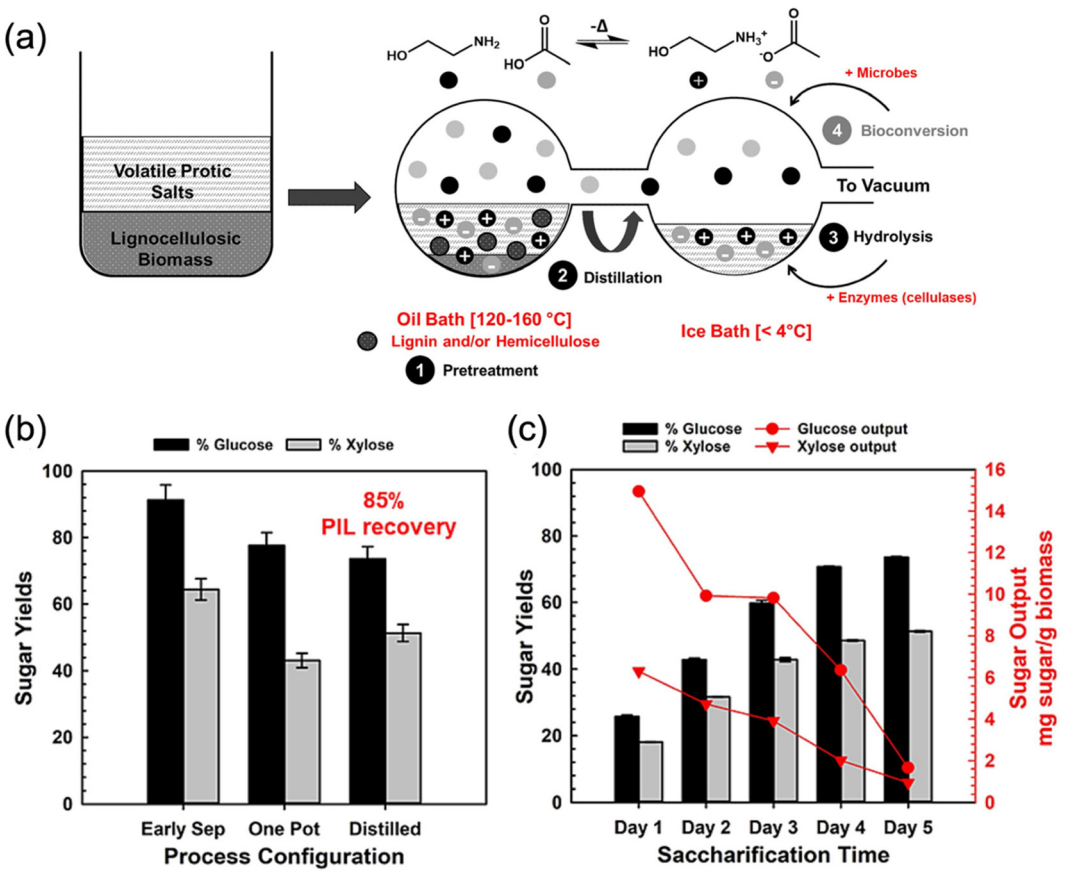

Fig. 13 Biomass pretreatment with distillable ILs. Panels: (a) process configuration; (b) comparative sugar yields from different methods of processing using ethanolamine acetate; (c) glucose and xylose yield *vs.* saccharification time for distillation recovery method using ethanolamine acetate. Adapted from ref. 146. Copyright 2024, Elsevier.

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as agitated thin-film evaporators have enhanced energy efficiency, achieving consistent recovery rates above 90% for ILs like [MTBDH][CH_3COO].[149] Additionally, reducing vacuum requirements and modifying IL compositions such as employing lower-boiling-point alkanolamines have demonstrated potential to decrease energy consumption and improve economic feasibility.[150] Pilot-scale studies have validated these findings, with integrated distillation processes reducing reliance on water washing while achieving comparable sugar recovery rates in consolidated biorefinery designs.[146]

Despite its advantages, distillation faces challenges such as residual IL contamination in biomass and the generation of inhibitory by-products like furfurals and phenolics. Addressing these issues requires further optimization of process conditions and apparatus design. Nevertheless, the scalability and adaptability of distillation, particularly when coupled with advancements in apparatus design and process integration, underscore its viability as a cornerstone technology for IL recycling. Table 7 provides a detailed comparison of the performance of various ILs under different distillation conditions, illustrating the versatility and potential of this method for widespread industrial applications. However, distillation represents a robust and adaptable solution for IL recovery, balancing technical efficiency with environmental sustainability. Continued innovation in apparatus design, IL formulation, and process integration promises to enhance the viability of distillation, solidifying its role in sustainable IL recycling and industrial applications.

3.4. Co-solvent systems for enhanced recyclability of ILs

The use of co-solvent systems with ILs has been shown to enhance the recyclability and efficiency of various chemical processes. Co-solvents can address issues such as high viscosity and limited miscibility of ILs, thereby improving their performance in industrial applications. This approach is particularly beneficial in processes requiring catalyst recycling, solvent recovery, and enhanced reaction yields. The following sections explore different aspects of co-solvent systems for enhanced recyclability of ILs.

The development of co-solvent systems integrated with ILs marks a significant innovation in enhancing their recyclability and functional efficiency, addressing both environmental sustainability and industrial scalability. These systems mitigate the intrinsic limitations of ILs, such as high viscosity and restricted miscibility with non-polar reagents, by tailoring their properties for improved performance. For instance, the incorporation of water as a co-solvent in ILs, as demonstrated by Pugin *et al.* (2004),[151] enabled remarkable improvements in catalyst recyclability during enantioselective hydrogenation reactions. Using a multi-phase IL–water system, their method involved monitoring Rh content with ICP-MS to confirm minimal leaching and employing ferrocene-based ligands for high turnover and enantioselectivity. This IL–water combination not only achieved turnover numbers exceeding 10 000 but also minimized catalyst leaching to 0.9 ppm while enhancing enantioselectivity and activity. Such advancements underscore the superiority of IL–water systems over traditional IL–organic solvent combinations, particularly in reactions involving Rh-ferrocenyl-diphosphine catalysts. Tomar and Jain (2022)[154] investigates the versatility of co-solvent systems, emphasizing their ability to stabilize ILs and improve recovery rates in enzyme-catalyzed reactions, with experimental methods focusing on optimizing physicochemical conditions to ensure repeatability across cycles, contributing to the broader goals of green chemistry.

The synergy between ILs and co-solvents is particularly evident in applications like *N*-debenzylation reactions. Choi *et al.* (2010)[155] demonstrated how combining [BMIM][BF_4] with methanol not only enhanced reaction yields but also mitigated palladium leaching. Their method involved catalytic hydrogenation at room temperature and atmospheric hydrogen pressure for 16 hours using Pd/C catalysts. Dichloromethane proved effective in minimizing palladium leaching during extraction, enabling reuse of the ionic liquid phase for up to eight cycles with only a slight reduction in yield, followed by a significant decline. However, challenges such as diminishing yields after repeated cycles call for optimization strategies to extend the lifespan of these systems. Corley and Iacono (2019)[156]

Table 7 Summary of key findings of various ILs under different distillation conditions

Ils	Recovery method	Conditions	Recovery rate (%)	Observations	Ref.
[BMIM][CH_3COO]	Vacuum distillation	80 °C, 6 h, reduced pressure	>90	Minimal lignin accumulation; high stability	142 and 144
[EMIM][CH_3COO]	Molecular distillation	170 °C, 0.05 mbar, 4 h	>90	High purity (>95%); effective for cellulose	143 and 145
[EIM]Cl	Vacuum evaporation	200 °C, 1 h, vacuum	~93	Maintains acid : base ratio; no structural change	119
[TMGH][CO_2ET]	Neutral compound distillation	200 °C, 1.0 mmHg	>99	Regenerated with high purity; negligible decomposition	147
[MTBDH][CH_3COO]	Thin-film evaporator	61–82 °C, 17–20 mbar	~90	Consistent performance over five cycles	149
[EthA][CH_3COO]	Vacuum distillation	5–20 kPa, 140 °C, full vacuum	~85	High sugar yields; minor contamination	146
[EMIM][CH_3COO] + methanol/ethanol	Flash distillation	25–50 kPa, ~150 °C	~95	Effective recovery; requires vacuum conditions to avoid IL decomposition	152
Dialkylimidazolium-based ILs	Flash distillation	30–101 kPa, 120–180 °C	—	Challenges in achieving high purity due to viscosity and thermal sensitivity	153

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describes a method to recycle the ionic liquid [DMPIm][NTf_2] using a combined cation–anion exchange adsorption–desorption process with a 0.1 M NaCl : methanol (90 : 10 v/v) eluent. This approach enables simultaneous desorption of ionic liquid ions, separation from neutral impurities, and recovery of high-purity products with ~60% yield, followed by liquid–liquid extraction. While addressing challenges in recycling ILs with complex anions, the study does not explore scalability for industrial applications or the long-term stability and reusability of adsorbents, limiting its economic and environmental assessment.

In the realm of cellulose chemistry, Gericke *et al.* (2011)[157] showcased the role of polar co-solvents in reducing IL viscosity and enhancing miscibility with cellulose-dissolving ILs, leading to more efficient derivatization processes. Their study systematically evaluated 18 solvents and binary mixtures, employing solvatochromic parameters such as polarity, acidity, and basicity to assess miscibility and reaction outcomes. Despite these benefits, there remains a need for comprehensive evaluations of the long-term stability and reactivity of such systems under varying environmental conditions. Enhancing miscibility and phase behavior, Najdanovic-Visak *et al.* (2002)[158] study on ternary mixtures of ILs with water and ethanol revealed the potential of a 1 : 1 molar ratio in facilitating effective extraction and recovery processes. Accurate phase diagrams were obtained using laser light scattering techniques to detect cloud points, ensuring reliable data collection. However, the lack of detailed thermodynamic data continues to pose a barrier to process optimization.

The recyclability of superbase-derived ionic liquids (SILs) for cellulose processing has been comprehensively evaluated, focusing on [DBUH][CH_3OCH_2COO], [DBUH][$CH_3CH_2OCH_2COO$], and [AMIM]Cl. Among these, [DBUH][CH_3OCH_2COO] exhibited the highest thermal stability and recyclability, sustaining 10 recovery cycles with a recovery yield of 95–97%, compared to 5 cycles for [AMIM]Cl and 4 cycles for [DBUH][$CH_3CH_2OCH_2COO$]. Degradation mechanisms, depicted in Fig. 14a, highlight structural transitions affecting recyclability, while Fig. 14b demonstrates improved polymerization and crystallinity of regenerated cellulose processed with [DBUH][CH_3OCH_2COO]. These results establish [DBUH][CH_3OCH_2COO] as a superior, sustainable, and economically viable solvent for large-scale cellulose processing.[159] Another pivotal advancement in IL recyclability involves biphasic systems. Research by Bagherzadeh and Ghazali-Esfahani in (2012)[160] explored toluene as a co-solvent with molybdate-anion-based ILs, achieving over 99% conversion in sulfoxide reduction and retaining catalytic activity across eight cycles. The methodology included employing newly synthesized room-temperature ILs containing molybdate anions, with conversions monitored using GC-MS and catalyst stability verified through repeated reaction cycles.

While the results are promising, challenges such as substrate diversity and large-scale applicability persist. On a different front, Giacalone and Gruttadauria (2016)[161] introduced covalently supported IL phases, where ILs are immobilized on solid supports like silica and polystyrene. This approach not only simplifies separation and reuse but also improves catalytic performance by providing a stable environment for reactions. Methods focused on covalent attachment techniques and post-reaction recovery assessments to validate reusability. Similarly, IL–water mixtures demonstrated enhanced recyclability and catalytic efficiency, outperforming conventional organic solvents in multiple cycles of use. Their approach included systematic variations in water content to optimize catalyst separation and solvent recovery.[162]

Recent innovations in liquid–liquid extraction processes for IL recycling, such as those proposed by Pan *et al.* (2024),[163] have opened new pathways for industrial applications. By employing hydrophobic ILs as accommodating agents, this method facilitates the effective recovery of water-miscible ILs. Pan's experimental design involved biphasic slug flow and membrane separation techniques, with efficacy demonstrated through platinum nanoparticle synthesis. This technique has shown significant promise, although its environmental and economic impacts warrant further assessment. Deng *et al.* (2020)[164] discussed the integration of ILs and water in biphasic systems for enzymatic bio transformations, where the dual advantages of automatic purification and enzyme reuse significantly reduced waste and improved sustainability. Their method utilized a continuous-flow setup with compartmentalized spaces to streamline purification and recovery processes. Renewable co-solvents have also gained attention, particularly in lignin extraction. Yang *et al.* (2020)[165] identified how these co-solvents, by increasing hydrogen bonding, selectively remove lignin while maintaining the structural integrity of the ILs, thus enhancing recyclability and reducing environmental impact. Their experimental process combined ILs with renewable co-solvents under controlled thermal conditions to maximize lignin dissolution and recovery.

Economic and environmental implications remain at the forefront of discussions surrounding IL recyclability. Tomar and Jain (2022)[154] stressed that co-solvent systems reduce the dependency on fresh solvent inputs, aligning with sustainable industrial practices. However, the implementation of these systems on a commercial scale requires careful optimization to balance cost-effectiveness with technical efficacy. Guidelines proposed by Gericke *et al.* (2011)[157] for co-solvent selection-considering polarity, acidity, and basicity-serve as a roadmap for tailoring IL systems to specific applications. Giacalone and Gruttadauria (2016)[161] further emphasized that covalently supported IL phases contribute significantly to reducing solvent waste and lifecycle costs. Nonetheless, challenges such as the economic viability of co-solvent mixtures, potential environmental trade-offs, and the technical complexity of recycling processes highlight the need for continued research and innovation.

To address these challenges, future research should focus on developing advanced co-solvent systems with tunable properties to further enhance IL performance and recyclability. Machine learning and computational chemistry could be leveraged to predict optimal co-solvent combinations and reaction conditions, reducing experimental trial and error.

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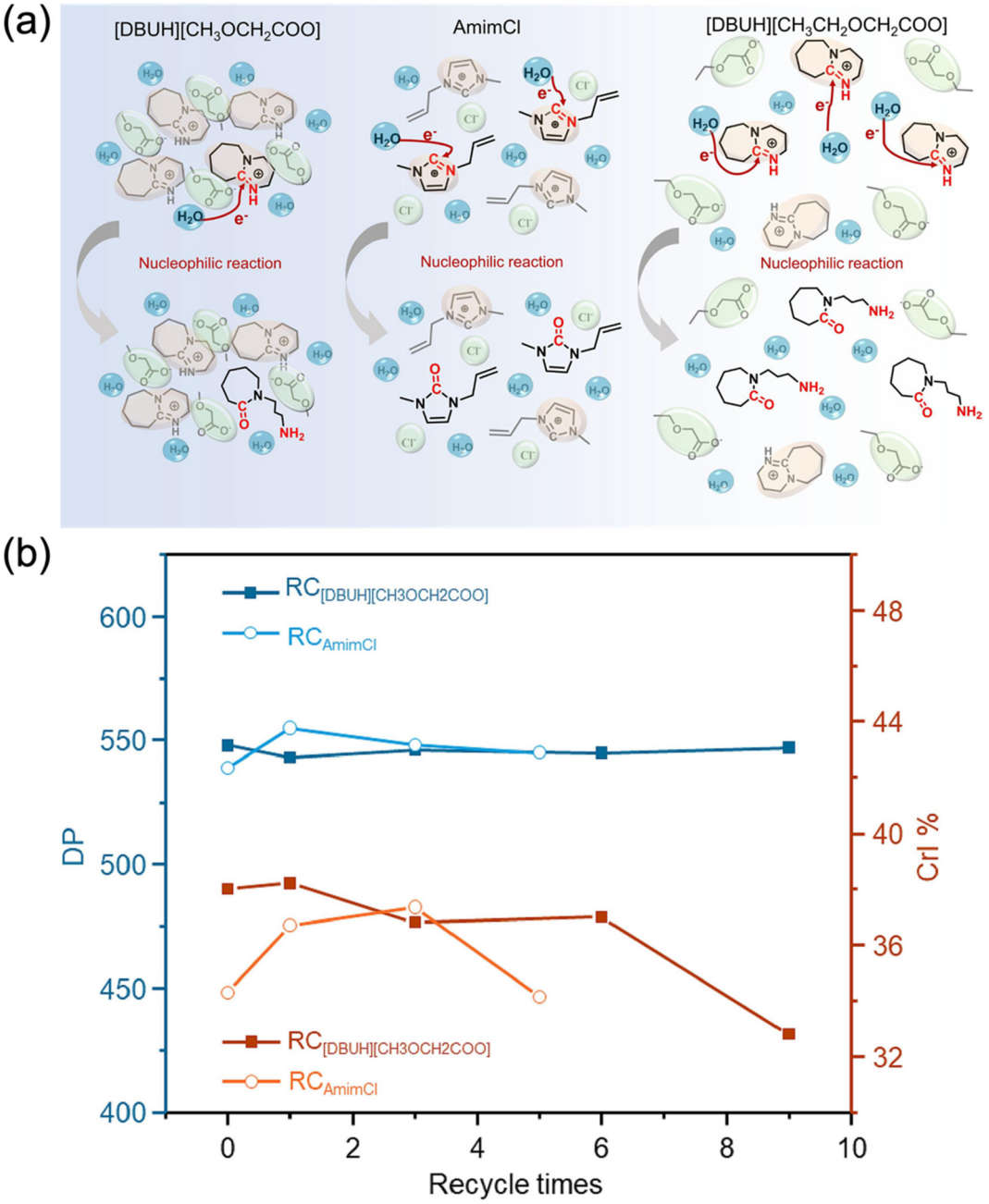

Fig. 14 Degradation mechanisms of ILs and their impact on the degree of polymerization and crystallinity of regenerated cellulose. Panels: (a) degradation mechanism of [DBUH][CH_3OCH_2COO], [AMIM]Cl, and [DBUH][$CH_3CH_2OCH_2COO$] in the recycling process; (b) degree of polymerization and crystallinity index of RC obtained from fresh and recycled [DBUH][CH_3OCH_2COO] and [AMIM]Cl. Adapted from ref. 159. Copyright 2023, Elsevier.

Additionally, exploring hybrid co-solvent systems that combine the strengths of multiple solvents could improve stability and reduce viscosity while maintaining recyclability. For large-scale applications, modular reactor designs that integrate continuous flow processes could streamline IL recovery and reduce costs. Furthermore, advancing greener synthesis routes for ILs and co-solvents, along with detailed life-cycle assessments, would ensure their environmental impact is minimized.

4. Challenges in IL recyclability

4.1. Factors affecting ionic liquid recovery

The recovery of ILs is critical for their sustainable application, primarily due to their high synthesis cost and environmental concerns. Recovery efficiency is influenced by a wide range of factors, encompassing the chosen recovery methods, the physical and chemical properties of ILs, operational parameters,

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and the complexity of the system in which ILs are employed. Understanding these factors allows for the optimization of recovery strategies, ensuring economic and environmental sustainability. These sections detail the key factors affecting ionic liquid recovery.

4.1.1. Recovery methods. Recovery techniques for ILs include distillation, extraction, adsorption, membrane separation, aqueous two-phase systems (ATPS), and crystallization. Distillation, particularly under vacuum, is effective for thermally stable ILs, offering high recovery efficiency but requiring significant energy input.[142,156] Adsorption and membrane separation are advantageous for selective recovery, though their efficiency depends on the adsorbent material and membrane characteristics.[156,166] ATPS induced by salts or gases, such as carbon dioxide, is particularly promising due to its simplicity and reduced environmental impact.[166]

4.1.2. Structure of ILs. The molecular structure of ILs, including the type of cation and anion pair, strongly influences recovery efficiency. Hydrophobicity, viscosity, and solubility of the ILs are key factors. ILs with longer alkyl chains exhibit increased hydrophobic interactions, which can enhance extraction processes.[71,167,168] ILs with shorter alkyl chains and more aromatic rings have been found to be more efficient in certain applications, such as oil recovery, which can also affect their recovery process.[169] Additionally, the anion type affects the thermal stability and separation behavior, impacting recovery efficiency during distillation or crystallization.[156]

4.1.3. Operational conditions. Parameters such as temperature, pressure, salinity and pH significantly affect the recovery process. Elevated temperatures reduce viscosity and surface tension, facilitating better separation in liquid–liquid extraction systems.[168] ATPS methods are highly sensitive to temperature, with specific ILs forming distinct phases under controlled thermal conditions. pH adjustments can also enhance the interaction between ILs and target compounds, improving recovery.[166,168] In applications like enhanced oil recovery, the salinity and pH of the solution can affect the performance and recovery of ILs. High salinity can enhance the surface activity of ILs, which may influence their recovery efficiency.[170]

4.1.4. Nature of the system. The complexity of the medium, including the presence of impurities or solvents, necessitates tailored recovery strategies. For instance, systems containing organic impurities may require ion-exchange processes combined with liquid–liquid extraction for effective IL recovery.[156] Similarly, the compatibility of ILs with solvents or salts can dictate the choice of recovery method.[166]

4.1.5. Economic and environmental considerations. Sustainable recovery processes must balance cost and environmental impact. Techniques such as CO_2-induced ATPS are not only cost-effective but also eco-friendly, regenerating ILs under mild conditions without toxic byproducts.[166,167] Recycling strategies focusing on less toxic ILs further minimize environmental risks.[167,171] Additionally, the integration of recovery methods into industrial processes requires careful techno-economic analyses to ensure viability.[135]

A detailed summary of the influencing factors is listed in Table 8. However, the recovery of ILs requires an integrated approach that combines advanced recovery technologies, a deep understanding of ILs chemistry, and environmentally sustainable practices. As the process is influenced by a complex interplay of structural, operational, and economic factors, making it essential to tailor recovery strategies to the specific properties of ILs and the requirements of the system. Innovations in materials and processes, along with system-specific optimizations, hold the potential to significantly improve recovery efficiency and facilitate broader industrial adoption of ILs. Furthermore, cutting-edge research into eco-friendly technologies, such as CO_2-induced phase separations, continues to enhance the sustainability of IL applications, enabling high recovery efficiency with minimal environmental impact.

4.2. Biomass-derived impurities affecting recyclability of ILs

The recyclability of ILs in biomass processing is heavily influenced by impurities originating from the biomass itself, such as lignin, sugars, proteins, and inorganic residues.[172–175] These impurities not only affect the purity and functionality of ILs during recycling but also pose significant challenges to their recovery and reuse in subsequent processing cycles. As a

Table 8 Factors influencing IL recovery

Influencing factors	Impacts	Examples	Ref
Recovery method	Determines efficiency, purity, and feasibility	Distillation for thermal stability; ATPS for aqueous systems	142, 156 and 166
Cation structure	Hydrophobicity and tunability influence recovery methods	Longer alkyl chains enhance hydrophobic extraction	167 and 168
Anion type	Stability and solubility impact separation behavior	$[BF_4^-]$, $[Tf_2N^-]$ affect crystallization and extraction efficiency	166 and 168
Temperature	Reduces viscosity and enhances separation	High temperatures improve distillation and ATPS efficiency	167 and 168
Pressure	Facilitates specialized recovery techniques	High-pressure CO_2-based ATPS for IL separation	166
System impurities	Complexity necessitates tailored approaches	Ion-exchange for organic impurities; ATPS for aqueous separations	156 and 167
Economic/ environmental	Balances cost and ecological impact	CO_2-induced ATPS as a cost-effective and eco-friendly recovery method	166, 167 and 171

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result, the economic and environmental viability of IL-based biomass processing is directly impacted. Addressing these challenges requires a comprehensive understanding of the impurities and their effects, which has led to the development of various strategies aimed at enhancing the separation and purification processes for ILs to improve their recyclability.

The presence of these impurities can significantly reduce the purity and functionality of recycled ILs. For instance, a study demonstrated that impurities such as lignin and sugars could lead to a decrease in the efficiency of IL recycling, necessitating additional purification steps.[173,176] Although there has been significant focus on the recovery rate of ILs, there is a lack of comprehensive analysis regarding the purity and functionality of the recovered ILs after multiple recycling runs. This indicates a need for further research to evaluate how the recycling process affects the chemical properties and effectiveness of ILs in enzymatic hydrolysis.[177]

The efficiency of IL recycling is often measured by the recovery yield and purity of the ILs. Impurities can lower the recovery yield and require more complex separation techniques, such as aqueous two-phase systems or pervaporation, to achieve high purity levels.[135,173] Although previous studies have shown varying effects of lignin on pretreatment efficiency, the specific impact of lignin accumulation in the recycled IL solutions on the pretreatment of different biomass types remains unclear and warrants additional research.[177]

The presence of impurities can increase the cost of recycling the IL due to the need for additional purification steps. This can affect the overall economic viability of using ILs in biomass processing, as the cost of ILs is a significant factor in the process economics. Although some research[174,175] demonstrates a significant reduction in the cost of ionic liquid pretreatment, it lacks a comprehensive economic analysis comparing the cost-effectiveness of this method against other pretreatment technologies, which could provide insights into its practical application in large-scale biorefineries.

While impurities pose challenges to the recyclability of ILs, advancements in separation and purification technologies offer potential solutions. Techniques such as phase separation, the use of adjuvants, and optimized recycling processes can help mitigate the impact of impurities and improve the efficiency of IL recycling. These developments are crucial for making IL-based biomass processing more sustainable and economically viable.

4.2.1. Types of biomass-derived impurities affecting recyclability of ILs

4.2.1.1. Lignin. Lignin is a major impurity that affects IL recyclability.[172] Its recalcitrant nature and solubility in ILs make it difficult to separate during recycling processes.[57,177] Lignin contamination can lead to decreased performance of ILs in subsequent cycles, as observed in the extraction of lignin from biomass using methylsulphate 1-butyl-3-methylimidazolium IL, where contamination appeared after third cycles. In the fourth cycle, there was noticeable contamination of the lignin with the ionic liquid, leading to a significant decrease in the extraction performance.[178,179] Born-Oppenheimer quantum molecular dynamics calculations were performed using the BIOVIA 2016 Materials Studio program under varying pressure and temperature conditions with the micro canonical assemblies NVE and NVT, revealing insights into the molecular interactions between the ILs and lignin dimers. Research findings revealed that the interaction between lignin dimers derived from coniferyl alcohol (*i.e.*, containing the characteristic β-O-4 bond) and certain ILs (*i.e.*, cations: [$EMIM^{++}$], [$BMIM^{++}$], and [$HMIM^{++}$], while the anions are [BF_4^-], [CH_3COO^-], and (Cl^-)) is favorable, while for other ILs there is a significant destabilization of the lignin–IL interaction.[179] However, they did not delve into the specific molecular mechanisms behind these interactions, leaving a research gap in understanding the underlying factors influencing the outcomes.

4.2.1.2. Sugars. Sugars derived from the hydrolysis of polysaccharides are another significant impurity. They are soluble in ILs and can complicate the recycling process. The presence of sugars can lead to the formation of by-products such as furfural resin or humin, which need to be separated from the ILs to maintain their efficiency.[57,180] A study conducted by Yu *et al.* (2012)[176] demonstrate that using $CrCl_3$ and $CrCl_3{\cdot}6H_2O$ as catalysts in the ionic liquid [BMIM]Cl allows for the one-pot conversion of lignin and sugars, resulting in the production of furfural resin or humin, which can be effectively separated from the ionic liquid after the reactions. The research indicates that when the reactions are catalyzed by $CrCl_3{\cdot}6H_2O$ at high temperatures (≥170 °C), nearly all lignin and sugars are converted to humin, significantly enhancing the efficiency of recycling the ionic liquid (see Fig. 15). However, this study does not explore the potential effects of varying concentrations of these catalysts on the efficiency of lignin and sugar conversion, which could provide insights into optimizing the process.

4.2.1.3. Inorganic residues and proteins. Inorganic residues, such as bicarbonate ions (HCO_3^-), ammonium sulfate $(NH_4)_2SO_4$, minerals and enzyme proteins can also be present as impurities. These impurities can complicate the separation and recovery processes of ILs from enzymatic hydrolysates, posing challenges for large-scale biomass processing.[173,174,181] Feng *et al.* (2016)[173] employs an aqueous two-phase/reverse micelle (APTs/RM) process for the recycling and simultaneous purification of ILs from enzymatic hydrolysate mixtures. This method effectively separates the IL from impurities such as lignin, bicarbonate, ammonium sulfate, and enzyme proteins, achieving a recovery yield of 92.3% and a purity of 99.1%. Additionally, the study compares the APTs/RM process with other recovery methods, including direct recovery methods and alumina column methods. The direct recovery method involves adding anti-solvents to extract IL, while the alumina column method separates sugars and IL but is time-consuming and costly, making them less suitable for large-scale applications compared to the APTs/RM process.[173] Another study demonstrated that the pretreatment of rice straw using a mixture of 40% 1-ethyl-3-methylimidazolium chloride [EMIM]Cl, 53% water, and 7% K_2CO_3 at 110 °C for 1 hour resulted in

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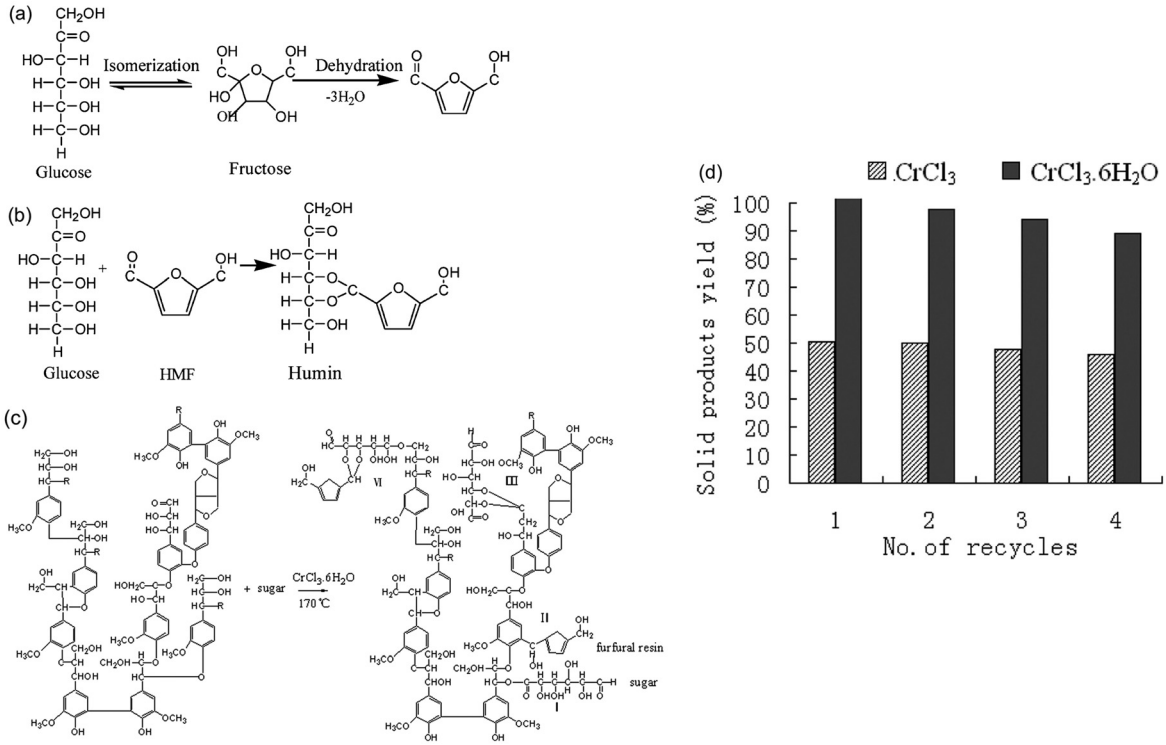

Fig. 15 Conversion of glucose in IL, lignin conversion and use of ILs as catalyst. Panels: (a) glucose was converted to HMF; (b) HMF condenses with glucose to form sugar-derived humin; (c) possible formation pathway of lignin-derived humin; (d) successive use of IL and catalyst. Conditions: 277 mg of lignin and 342 mg of sugars were added into 5 g of IL and reacted at 170 °C for 2 h. The catalyst was 10 mol% to IL. Adapted from ref. 176. Copyright 2012, American Chemical Society.

a significant removal of lignin (93.70%) and a high sugar yield (92.07%), indicating enhanced susceptibility to enzymatic hydrolysis of lignocellulosic biomass. The research found that increasing the concentration of K_2CO_3 to more than 30% led to the formation of a [EMIM]Cl–K_2CO_3 aqueous biphasic system at room temperature, which allowed for a recovery rate of 94.32% of [EMIM]Cl, suggesting that the addition of inorganic salts can effectively reduce the cost of ionic liquid pretreatment while maintaining enzymatic efficiency. However, this research does not explore the long-term effects of repeated use of these inorganic salts on the efficiency of the pretreatment process or the enzymatic hydrolysis over multiple cycles.[174]

4.3. Technical challenges of ILs for industrial scale-up

The recycling of ILs for industrial scale-up presents several limitations, primarily due to the complex nature of these substances and the challenges associated with their recovery and reuse. While ILs are touted for their potential as green solvents, their recyclability is crucial for their economic and environmental viability in large-scale applications. The transition from laboratory to industrial scale involves overcoming significant hurdles related to the separation, purification, and cost-effectiveness of ILs.

It is worth mentioning that most IL pretreatment studies to date have been performed in batch mode with extended residence times. However, evidence from related pretreatment technologies demonstrates that continuous systems can achieve short residence times and scalable throughputs. For instance, continuous hydrothermal pretreatment of wheat straw at 195 °C for 9–12 min resulted in >90% cellulose recovery and ethanol yields approaching 93% of the theoretical maximum, while sorghum bagasse processed at 180 °C for 10 min achieved glucose and xylose yields of 82.6% and 70.8%, respectively.[182] Pilot-scale steam pretreatment of wood chips at 215 °C with a residence time of 7 min and a throughput of 39 kg h^{-1} produced liquors containing >30 g L^{-1} glucose and solids with up to 88% glucan hydrolysis yield, and continuous steam explosion of wheat straw at 178 °C for 6 min enabled enzymatic recovery of more than half of the glucose and 46% of the initial xylose in the liquor. Likewise, continuous tubular reactors with extruder feeding and residence-time control, and twin-screw extrusion platforms integrating staged autohydrolysis and alkaline delignification at 210–220 °C, have demonstrated residual lignin contents of ~2% and ~80% glucose recovery.[183]

Emerging designs such as continuous ultrasound baths (5 L, 40/80/120 kHz, 260 W) further illustrate mass-transfer intensification strategies transferable to IL pretreatment.[184] Collectively, these studies highlight that reducing residence times from hours to minutes is technically feasible, and adapting such strategies to IL systems will require careful control of residence-time distributions in viscous slurries, extruder-based

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solid handling, ultrasound-assisted mixing, and energy-integrated solvent recovery. Representative continuous pretreatment studies are summarized in Table 9.

In addition to reactor configuration, the high viscosity of ILs and their strong interactions with biomass limit mass transfer, reduce solids loading, and make scale-up challenging.[51] The viscosities of ILs are typically 1–3 orders of magnitude higher than conventional organic solvents, with values ranging from 4.8 to 1110 mPa s^{-1} (ref. 186) depending on the ion pairing, which hinders diffusion-controlled processes such as enzymatic hydrolysis and biomass fractionation.[187] These rheological properties restrict mixing and heat transfer, thereby slowing biomass fractionation and contributing to the excessive solvent requirements often reported in batch studies. Several approaches have been implemented to mitigate these effects. For example, co-solvent addition (*e.g.*, water or volatile organics) can significantly reduce viscosity without compromising pretreatment efficiency, while rational design of low-viscosity ILs, including protic and bio-derived ILs, offers another promising pathway.[34,188] Process-intensification methods such as ultrasound, microwave irradiation, and mechanical shear can enhance mixing and diffusion, accelerating lignocellulose dissolution. Furthermore, continuous configurations such as twin-screw extrusion inherently improve mass transfer by applying shear and mixing forces, and continuous ultrasound devices with defined flow control demonstrate additional opportunities to intensify diffusivity in viscous media. Collectively, these strategies offer effective means to alleviate viscosity-related mass transfer limitations and facilitate the scalable application of IL pretreatment.

Another significant challenge in current IL pretreatment methods is the requirement for large solvent-to-biomass ratios in batch operations. Such high IL loadings are typically necessary to ensure complete wetting and swelling of biomass fibers, uniform mixing in viscous solutions, and effective lignin disruption. Although this approach is widely utilized in laboratory studies, industrial adoption will require strategies to overcome the challenge of high solvent consumption. Several strategies have been explored to address this limitation, including high-solids loading (≥20–30 wt%) to reduce solvent use, co-solvent systems to lower viscosity and improve mass transfer, and solvent recycling to minimize the need for fresh IL. In addition, continuous platforms such as twin-screw extrusion can reduce solvent requirements by promoting mixing and solvent penetration at lower IL-to-biomass ratios. These advances indicate that solvent demand, though a major bottleneck, can be alleviated through a combination of solvent engineering, process intensification, and continuous reactor design.

The recycling of ILs involves complex processes to separate and purify the solvents from impurities and other substances. However, the recovery and regeneration of ILs are essential for their sustainable use in industrial processes, particularly in refining and chemical production. ILs recovery methods commonly include distillation, liquid–liquid extraction, and stripping, alongside emerging techniques like membrane separation and solubility-switchable ILs. Each method provides unique advantages and limitations. Distillation, a prominent method, involves separating ILs based on the volatility of components. Earle *et al.* (2006)[189] demonstrated the distillation of

Table 9 Continuous pretreatment studies demonstrating feasibility of short residence times and scalable operation, summarized from the ref. 182–185

Approach	Feedstock	Conditions	Throughput	Outcomes
Review of pretreatment fundamentals	General lignocellulosic materials	Survey of physical (milling, extrusion), chemical (dilute acid, alkali, organosolv), physicochemical (steam explosion, AFEX), and IL pretreatments	—	Identifies scale-up challenges; steam explosion typically 160–240 °C, seconds–minutes; dilute acid ~1–5 wt% H_2SO_4, 120–200 °C; AFEX 60–100 °C, 15–30 min; IL pretreatments noted as emerging but limited by viscosity and recovery
Continuous tubular reactor (CTR) with residence-time control	Wheat straw, corn stover	Autohydrolysis in CTR; dynamic model with RT control; PI controller implemented	Pilot-scale; continuous flow	RT control validated at 5–20 min target residence times; experimental deviations reduced to <2% with controller; demonstrated stable throughput of lignocellulosic slurry
Continuous pretreatment–hydrolysis–fermentation train	Organic residues (*e.g.*, corn stover, food residues)	Hydrothermal pretreatment (170–200 °C, 5–15 min) integrated with enzymatic hydrolysis and microbial fermentation	Conceptual to pilot scale	Demonstrated continuous production of lactic acid and succinic acid; glucose recovery up to 79% (w/w) after wet-disk milling; ethanol fermentation reached 93% of theoretical yield in wheat straw case study
Continuous ultrasound bath (intensification module)	General biomass slurries	CAD-designed bath; 5 L capacity, operated at 75–80% fill; ultrasound at 40, 80, 120 kHz; 260 W power	Flow-controlled; sampling port included	Enhanced lignin removal (up to 79–88%) in fiber-based residues; FEA modeling confirmed uniform cavitation field; enables real-time sampling and continuous operation

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imidazolium-based ILs at 200–300 °C under vacuum conditions (0.001 mbar), achieving low decomposition rates and high regeneration efficiency. However, the requirement of ultra-low pressures and high energy consumption hinders industrial-scale application.[189] Vacuum distillation has shown promise in removing high-boiling-point compounds like dibenzothiophene (DBT) from ILs but struggles with larger molecules such as carbazole (b.p. 354 °C). Techniques involving the distillation of volatile components from non-volatile ILs are better suited for practical applications.[190]

Liquid–liquid extraction is another practical method, particularly using water or organic solvents. For instance, Gao *et al.* (2018)[191] illustrated the regeneration of hydrophilic ILs (*i.e.*, 1-methyl-3-(4-sulfonic acid butyl)) imidazole *p*-toluenesulfonic acid [$(CH_2)_4SO_3HMIm$][Tos] through water extraction, maintaining desulfurization efficiency across five cycles with minimal performance decline (*i.e.*, 43.6% to 41.2%). However, the use of volatile organic compounds (VOCs) as solvents raises environmental and cost concerns. Cross-contamination and additional equipment needs further complicate this process.[142] Stripping methods, utilizing gaseous agents like nitrogen or steam, have shown high regeneration efficiencies. Liu *et al.*[192] demonstrated nitrogen stripping for hydroxyl ammonium ILs, achieving over 95% efficiency within five cycles. Steam stripping, as applied by Hardacre *et al.*, effectively removed reaction byproducts but remains challenging for large-scale applications due to equipment and operational complexities.

Emerging techniques like rotary evaporation, crystallization, membrane regeneration, and force field-based methods offer additional pathways for IL recovery. Rotary evaporation, demonstrated by Yao *et al.*,[193] achieved efficient recycling of [C_4mim][BF_4] with good extraction performance. However, crystallization, while delivering high purity, remains energy-intensive and suitable only for small-scale applications. Membrane regeneration provides high selectivity and lower energy demand but suffers from fouling and low throughput. Advanced innovations such as solubility-switchable ILs (see Fig. 16), described by Kamimura *et al.*,[194] represent promising solutions for scalable IL recovery. These ILs enable efficient phase separation and recovery under controlled conditions but require further development for industrial adoption. Similarly, continuous microfluidic processes, as explored by Pan *et al.*, (2023)[195] employs a continuous microfluidic process for the purification of metal-ion-loaded ILs, specifically utilizing inline analytical tools and a modified Nelder-Mead simplex algorithm for statistical optimization to determine the best operating conditions for ion extraction and phase separation. The process includes the extraction of Fe(III) ions from the ionic liquid [BMIM][NTf_2] into deionized water, followed by membrane separation of the ionic liquid and aqueous phases. While these processes improve separation efficiency, they remain costly and technically challenging.

Although many laboratory studies have demonstrated recycling of ionic liquids, they typically report a few recovery cycles that correspond to hours rather than months of operation, limiting their industrial relevance. A prominent case study is the ionoSolv process developed by Hallett and colleagues,[196–198] which employed distillation and antisolvent precipitation as primary recovery strategies for low-cost protic ionic liquids. At laboratory scale, solvent recycling was demonstrated for up to six consecutive cycles with stable performance. However, at pilot scale, this translated to only a few hours of continuous operation, underscoring the limitations of extrapolating from batch studies. To bridge this gap, the spin-out company Lixea[196–198] established a dedicated pilot plant, where solvent recovery and reuse were demonstrated for over one year of continuous operation while maintaining biomass fractionation efficiency and solvent integrity. This example highlights both the promise and the challenges of IL recycling: while recovery by distillation and antisolvent is technically feasible, long-term operation must address impurity accumulation, solvent losses, and energy costs. The ionoSolv case thus provides a critical benchmark, emphasizing that sus-

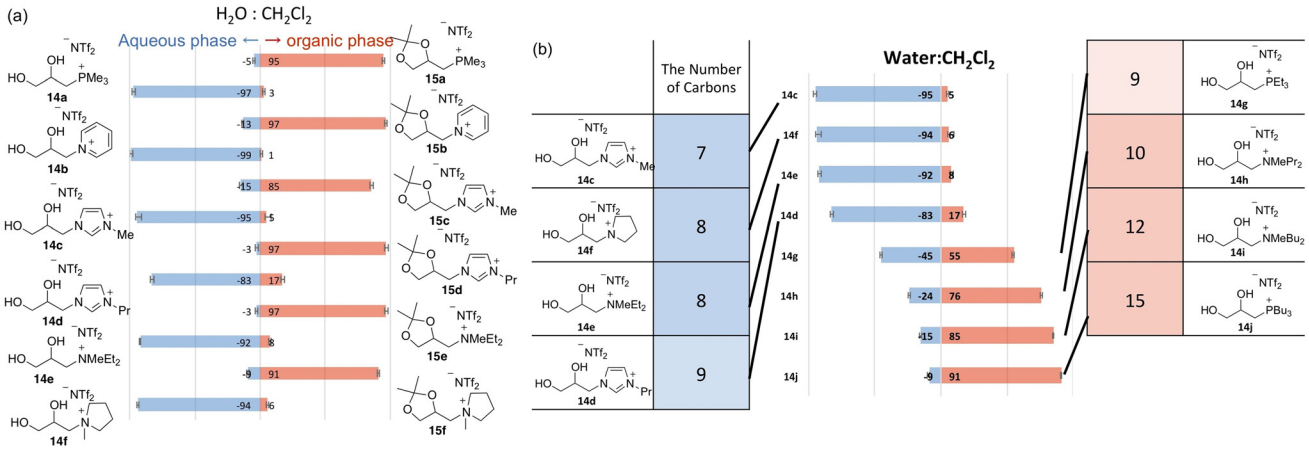

Fig. 16 Solubility-switchable ILs. Panels: (a) partition ratio of the solubility-switchable ILs in CH_2Cl_2–water system; (b) relationship between the number of carbon atoms in the cation and partition ratios in water–CH_2Cl_2 system. Adapted from ref. 194. Copyright 2023, The Chemical Society of Japan and Wiley-VCH GmbH.

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tainable IL implementation requires validation at pilot and demonstration scale, supported by techno-economic and life cycle assessments.

Despite advancements, challenges remain (*i.e.*, poor electrical conductivity) the degradation of ILs (*i.e.*, corrosive nature of some ILs, leading to degradation of cell components and contamination of the ILs), during electrochemical processes.[199] Impurities accumulating during use and their corrosive nature further complicate recycling efforts, necessitating additional purification steps.[199–201] These limitations underline the need for integrated approaches combining efficient, scalable regeneration methods with innovations in IL design.

4.4. Sustainability and economic limitation

The broader adoption of ILs in industrial applications is hindered by several interlinked economic, environmental and regulatory constraints that challenge their sustainability and commercialization. The industrial implementation of ILs in refinery processes faces significant economic challenges, primarily due to their high costs relative to traditional solvents,[202] which can exceed $800 per kg,[203] far surpassing that of conventional solvents like *n*-methyl-pyrrolidone (NMP) widely used in extractive desulfurization,[204] rendering many large-scale implementations economically unfeasible.[205] This cost disparity is influenced by the cation and anion combinations in ILs, as well as the lack of established bulk pricing. Although high purchase costs impede large-scale adoption, these challenges can be mitigated through efficient recovery and multi-cycle use, process integration and solvent minimization. Diluting ILs with inexpensive co-solvents like water-offers a practical means of reducing consumption in processes such as biomass pretreatment, thereby lowering the overall process cost.

In addition to solvent recovery, energy consumption is a critical parameter influencing both the economic and environmental performance of pretreatment. Conventional processes such as steam explosion are relatively energy efficient, consuming ~1.3 kg of steam and 0.31–0.47 kWh of electricity per kg dry biomass, equivalent to 2–4 MJ kg^{-1} of biomass.[206] Recent innovations, including fluidized-bed detoxification systems operating at 70 °C and 150 kg h^{-1} throughput, have demonstrated further reductions in energy demand by minimizing additional steam requirements while simultaneously improving ethanol yields by 14% compared to conventional washing.[207] In contrast, batch IL pretreatments often require higher energy inputs due to large solvent loadings and extended heating. A recent techno-economic assessment of butylamine depots identified solvent loading as a major driver of both cost and energy demand, where high ratios (850 g kg^{-1} slurry) substantially increased heating requirements.[208] Lowering the solvent concentration to 5 wt% (59 g kg^{-1} slurry) reduced sugar production costs by ~33% and decreased energy input, while solvent recovery efficiencies of 93–99% *via* thin-film drying and distillation further lowered net energy demand.[208] These findings suggest that with optimized solvent loading, efficient recovery, and integration into continuous processes, IL pretreatment could achieve energy performance comparable to or better than established methods such as dilute acid[209–211] and AFEX.[212,213]

Despite these encouraging outcomes, detailed systematic energy analyses of IL pretreatment and solvent recycling are still limited in the literature. Most reported studies are confined to laboratory studies, with little evaluation across different IL families, recovery methods, or process scales. This gap prevents a clear understanding of trade-offs and hinders meaningful comparisons with conventional technologies. Future research should therefore prioritize detailed energy benchmarking of IL processes, explicitly linking solvent recovery efficiency, process configuration, and scale-up with overall energy performance, to establish their true competitiveness against established fractionation methods.

The transition of ILs from laboratory-scale to industrial applications has catalyzed advancements in production, driving down costs per kilogram through economies of scale.[203] Such reductions are already enabling the integration of IL-based technologies in alkylation processes, with several companies leading scale-up efforts. However, much of the current research focuses on maximizing IL removal efficiency in applications like desulfurization and denitrogenation. Greater emphasis is needed on optimizing entire processes, conducting comprehensive economic analyses, and enhancing IL regeneration.[214] Innovations such as IL immobilization and ultrasound-assisted methods offer promising avenues for overcoming mass transfer limitations, reducing operational costs, and enhancing industrial feasibility.[215,216] Research highlights the need for economic optimization to facilitate IL adoption. Ahmed *et al.* (2020)[217] emphasize that the high costs of production and recycling limit the commercialization of IL technologies. Scaling up IL technologies poses further challenges, as large volumes complicate recycling, increasing energy and resource demands.[205] Techniques like distillation, extraction, and membrane separation require significant investments in energy and equipment, offsetting potential benefits.[156] Additionally, the synthesis of ILs often relies on costly raw materials and intricate processes, making them less competitive than conventional solvents.[201,218] Pan *et al.* (2023)[195] further highlight the transition from technical feasibility to commercial viability, emphasizing the importance of scaling production while minimizing associated costs.

Achieving economic viability for IL technologies requires holistic advancements in synthesis, recycling, and process efficiency. For instance, enhancing IL immobilization can minimize material requirements and simplify regeneration processes. Additionally, alternative methods such as ultrasound irradiation show potential to mitigate mass transfer limitations, providing a pathway toward broader industrial adoption. Future research should focus on cost-effective recycling strategies, mass production techniques, and the development of integrated IL-based systems that leverage the unique properties of these solvents while addressing their economic limitations.

However, from an environmental perspective, ILs are not without concerns. Although their negligible vapor pressure

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reduces air emissions, many exhibit toxicity and poor biodegradability. They can enter the environment through waste streams from refineries, solvents used during IL regeneration, or traces left in treated products. This has led to growing concern about their ecotoxicity and biodegradability, necessitating research into their environmental fate and safe disposal methods.

A number of studies have demonstrated varying degrees of toxicity and biodegradability among ILs. For example, Thuy Pham *et al.* (2010)[219] examined the toxicity of ammonium, pyridinium, and imidazolium-based ILs, concluding that ammonium ILs are the least toxic, while increasing aromatic nitrogen atoms significantly heightens toxicity. In terms of biodegradability, pyridinium-based ILs outperform imidazolium-based ILs, with structural modifications, such as the inclusion of ester groups in the side chains, significantly reducing toxicity and enhancing enzymatic degradation potential.[220,221] Moreover, the length of alkyl side chains influences IL behavior, where chains of 6 to 8 carbon atoms are more biodegradable, though longer chains may inadvertently increase toxicity.[220]

The choice of anions also plays a pivotal role. While some anions, like alkylsulfates, exhibit favorable biodegradability, others, such as fluorinated anions, present challenges due to their hydrolytic instability and harmful decomposition products, like hydrofluoric acid.[222,223] The combination of cationic and anionic components must be carefully optimized to maximize efficiency in applications like desulfurization, denitrogenation, and alkylation, while minimizing environmental risks. For example, pyridinium- and imidazolium-based ILs containing anions like tetrafluoroborate [BF_4], hexafluorophosphate [PF_6], and nitrate [NO_3] have shown desulfurization efficiencies above 90% in advanced extraction methods.[155] However, nitrate anions pose hazards due to their explosive nature, and tetrachloroferrate [$FeCl_4$] anions have been shown to be toxic to marine organisms.[219,224]

Addressing these concerns requires robust recycling and regeneration strategies. Innovative techniques such as electrochemical leaching and electrodeposition have been developed to recover valuable materials like platinum from spent fuel cell electrodes, using chloride-based ILs under mild conditions without harmful gas emissions.[225] These approaches represent a shift away from traditional pyro-hydrometallurgical processes, which are less environmentally friendly. However, inefficiencies in recycling can lead to significant waste generation, including the loss of ILs and secondary waste streams, which undermine the sustainability of IL-based processes.[167,226] Furthermore, regulatory hurdles related to toxicity and poor biodegradability often increase the economic burden of implementing IL technologies.[33] Fig. 17 illustrates a

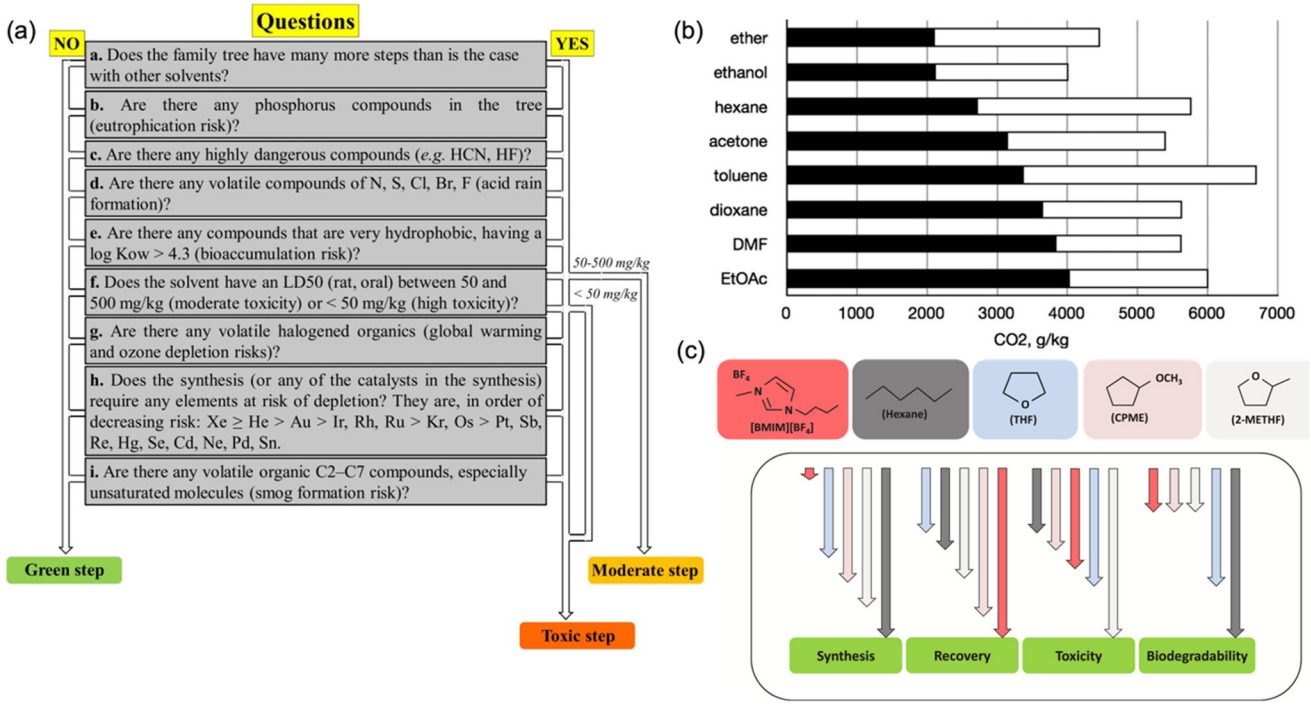

Fig. 17 Analytical framework of questions aimed at evaluating the environmental friendliness of a solvent's synthesis process. Panels: (a) questions related to the synthesis steps of a given solvent regarding some environmental issues that allow a general comparison between solvents, adapted from the ref. 33 and 227. Copyright 2022, Elsevier; Copyright 2011, Royal Society of Chemistry. (b) Greenhouse gas emissions resulting from the energy consumed during manufacture (solid bars, assuming 0.042 g CO_2 emissions per kJ) and from the eventual oxidation or incineration (hollow bars) of 1 kg of solvent, adapted from ref. 227 and 228. Copyright 2011, Royal Society of Chemistry (c) comparison between [BMIM][BF_4] and fossil-based solvents (hexane and THF) and organic-based green solvents (CPME and 2-METHF), in relation to synthesis, recovery, toxicity and biodegradability. Note: The larger the arrow, the greener the solvent, adapted from ref. 33. Copyright 2022, Elsevier.

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structured framework of questions designed to assess the environmental sustainability of solvent synthesis processes. It evaluates key aspects such as the incorporation of renewable feedstocks, energy efficiency, and waste minimization. The framework highlights the critical need to reduce the use of hazardous reagents and byproducts, ensuring that the synthesis process adheres to the principles of green chemistry.

When applied to ILs, this assessment reveals significant trade-offs between their advantageous properties and the environmental costs associated with their production. Notably, many ILs fail to satisfy these criteria due to the reliance on toxic chemicals, high energy demands, and substantial waste generation, prompting a reconsideration of their classification as environmentally friendly solvents. Despite these challenges, ILs remain a valuable tool in sustainable chemistry. To comprehend their full potential, researchers must prioritize the design of ILs with enhanced biodegradability and lower toxicity, while advancing recycling technologies to reduce environmental impact. By balancing performance, safety, and sustainability, ILs can play a transformative role in greener industrial applications.

5. Sustainability of recycled ILs

The economic and environmental feasibility of IL-based pretreatment depends heavily on efficient recycling. Although numerous studies have demonstrated recovery, the reported results often vary due to differences in IL families, biomass types, and process conditions. Among these strategies, antisolvent recovery is the most widely explored, achieving 80–95% recovery, however, it requires large water volumes that generate substantial waste streams, raising concerns about scalability and sustainability.[10,18,57] Distillation, in contrast, is effective for volatile and protic ILs, with >95% recovery demonstrated in pilot studies, particularly for amine-based distillable solvents. Nevertheless, its energy demand remains moderate to high.[50,68,121,196,197] Membrane separation offers lower energy demand and recovery efficiencies of 70–90%, though membrane fouling and stability challenges must be resolved before scale-up.[10,67] Similarly, co-solvent and hybrid IL–DES systems can achieve 80–90% recovery and reduce viscosity, but their toxicity and downstream separation complexity present additional trade-offs.[51,59]

A critical comparison (see Table 10) reveals that no single recycling strategy is universally optimal since they all present trade-offs between recovery efficiency, energy consumption, scalability, and environmental impact. Variations in solvent recovery efficiencies and recycling performance across ionic liquids, distillable solvents, and DESs (*e.g.*, imidazolium ILs, cholinium ILs, distillable solvents, DESs, *etc.*) highlight the need for standardized evaluation protocols to enable consistent and comparable assessments. Imidazolium-based ILs remain effective for biomass fractionation, but their high toxicity and costly recovery restrict broader applicability. Conversely, cholinium lysinate offers clear biocompatibility advantages, although its recovery remains challenging, suggesting that diluted cholinium lysinate formulations might be more practical and sustainable.[18,68,81] Distillable solvents such as ethanolamine and other amine-based IL analogues are particularly attractive, as they can be efficiently recovered by distillation and reused, representing a practical pathway toward sustainable recycling.[50,121] Looking forward, research should therefore prioritize the development of recyclable protic ILs and distillable solvent systems, alongside benchmarking against DESs and biphasic systems that offer inherent recyclability and reduced environmental burden.[51,59]

5.1. Life cycle assessment of recycled ILs

The life cycle assessment (LCA) of ILs is a critical tool for evaluating their environmental sustainability across various applications. ILs are often touted as green alternatives to traditional solvents due to their unique properties, such as low volatility and high thermal stability. However, a comprehensive LCA reveals a more nuanced picture, highlighting both the potential benefits and significant environmental challenges associated with their production, use, and disposal. This analysis explores the environmental impacts of ILs, focusing on their application in separation processes, CO_2 capture, and other industrial uses.

ILs have emerged as versatile compounds with potential applications across chemical and environmental processes, yet

Table 10 Comparison of ionic liquid recycling strategies in biomass pretreatment[10,18,50,51,57,59,67,68,125,126,146,196,197]

Recycling strategy	Recovery efficiency	Energy demand	Scalability	Environmental impact
Antisolvent	~80–95%	High	Limited by waste streams; lab-scale	Large aqueous waste, costly purification
Distillation (volatile and amine-based solvent)	>95% (volatile ILs)	Moderate–high	Pilot-scale demonstrated (volatile/protic ILs)	Lower waste, but heat intensive
Membrane separation	~70–80%	Low–moderate	Pilot-scale; fouling remains a barrier	Reduced waste; membrane disposal issues
Co-solvent/hybrid	~70–80%	Moderate	Emerging; potential with IL–DES systems	Co-solvent toxicity and separation challenges
Deep eutectic solvents	—	Low-moderate	Lab- to pilot-scale; viscosity a challenge	Biodegradable, low-cost, but lower pretreatment efficiency than ILs
Biphasic solvents	—	Low	Promising at pilot scale; solvent selection critical	Phase separation aids recovery; solvent cross-contamination risk

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their LCA underscores both opportunities and challenges in their sustainability. Although limited studies have studied LCA of ILs,[47,229–232] it is imperative to highlight these assessments to foster environmentally responsible processes and broader industrial adoption. Studies, such as Kralisch *et al.* (2005),[233] pioneered LCA analyses of ILs like 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) for reactions such as 1-octene metathesis, revealing that solvent-free reactions are not always ecologically advantageous. Their comparative analysis of energy requirements between biphasic and homogeneous reactions challenged the assumption that biphasic systems are inherently superior due to recycling ease.

Over the years, the environmental trade-offs of ILs compared to conventional solvents have been scrutinized. For instance, Zhang *et al.* (2008)[234] demonstrated that [BMIM][BF_4] poses greater environmental impacts than organic solvents like acetone in synthesizing cyclohexane. Similarly, Amado Alviz and Alvarez (2017)[235] found that [BMIM][Br] exhibited higher ecotoxicity in pharmaceutical synthesis compared to toluene. These findings highlight that despite ILs benefits in reducing emissions during use, their synthesis and recovery often offset ecological advantages. ILs roles in carbon capture have also been a focus, with Cuéllar-Franca *et al.* (2016)[236] advocating LCA for assessing ILs like [P66614][124Triz] against monoethanolamine (MEA). Farahipour and Karunanithi (2014)[237] revealed that [BMIM][CH_3COO] for carbon capture reduced greenhouse gas (GHG) emissions by only 50%, falling short of the 75% reduction with MEA. Likewise, Peterson (2013)[230] conducted a cradle-to-grave LCA on 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and trihexyl (tetradecyl)phosphonium 1,2,3-triazolide for CO_2 refrigerant systems and highlighted minimal environmental impacts from IL synthesis for CO_2 refrigerant systems, emphasizing the need for cradle-to-grave analyses. Righi *et al.* (2011)[238] compared [BMIM]Cl with NMMO/H_2O in cellulose dissolution, noting that while effective, IL processes contributed significantly to abiotic depletion and toxicity.

Huebschmann *et al.* (2011)[239] assessed simplified LCA combined with cost analysis for catalytic phenol and benzoyl chloride conversion using [BMIM]Cl, [MIM][$BuSO_3$], and [C_{18}MIM]Br, finding [MIM][$BuSO_3$] ecologically superior due to exothermic synthesis *versus* [C_{18}MIM]Br's energy-intensive process. While batch synthesis of [BMIM]Cl had low environmental impacts, continuous synthesis proved threefold ecologically advantageous. Mehrkesh and Karunanithi (2013)[240] reported higher environmental impacts for IL synthesis compared to TNT production, reinforcing concerns about ILs ecological burden.

Optimization of ILs through molecular design and synthesis route adjustments is essential for sustainable application. For example, Guo *et al.* (2023)[229] identified [BMIM][NTf_2] as a cost-effective, environmentally superior IL for methanol/dimethyl carbonate azeotrope separation, outperforming other ILs in thermodynamic efficiency and total annual cost. However, toxicity issues, as seen with [BMIM]Cl and [EMIM][TCB], underscore the need for molecular tailoring and advanced recovery technologies to mitigate impacts. Fig. 18 illustrates simplified synthesis routes, and compares production impacts, highlighting [BMIM][NTf_2]'s advantages. Energy-intensive production, as noted by de Jesus and Filho (2022),[33] remains a critical barrier, compounded by decomposition losses and high utility consumption during IL use. Recent studies emphasize IL synthesis complexities and their significant environmental impacts. Imidazolium-based ILs for methanol/dimethyl carbonate separation, for example, show high impacts due to energy-intensive production and the use of volatile carbon, nitrogen, sulfur, and halogen compounds.[33,229] While ILs reduce CO_2 capture emissions, challenges like thermal decomposition losses and additional electricity needs compromise their benefits. As global sensitivity analysis (GSA) analyses by Baaqel *et al.* (2023)[241] demonstrate, identifying environmental hotspots can guide greener designs.

The potential of ILs in natural gas dehydration and other separations remains tempered by their poor biodegradability and long-term toxicity. Comparisons with volatile organic solvents reveal that while ILs may reduce emissions during use, their overall ecological footprint including high impacts from synthesis and disposal often negates benefits. [BMIM][CH_3COO] showed a 50% global warming potential reduction compared to unabated processes but lagged behind MEA's 75% reduction.[237] Future pathways, integrating computational modeling and LCA, as suggested by Cuellar-Franca *et al.* (2016),[236] aim to align ILs with green chemistry principles, emphasizing biodegradability and resource efficiency. These efforts are critical in ensuring that IL innovations address environmental hotspots holistically, preventing burden shifts across the life cycle.

Although ILs like [BMIM][NTf_2] offer promising pathways for sustainable industrial applications, their environmental trade-offs necessitate further optimization. Through comprehensive LCA and targeted innovations, ILs can achieve a balance between functionality and sustainability, enabling greener chemical processes without unintended ecological costs.

5.2. Techno-economic analysis of ILs

Techno-economic analysis (TEA) has been instrumental for evaluating the feasibility and scalability of new processes, enabling researchers to identify technological barriers early in development and determine cost-driving factors.[242] It utilizes experimental or empirical data to perform process design and simulation, including mass and energy balances, to estimate key economic metrics such as capital investment, operational costs, and minimum selling price (MSP) for products in large-scale refineries.[243] Among various pretreatment technologies,[244–247] ILs pretreatment has emerged as a promising method for deconstructing lignocellulosic biomass; however, it faces substantial challenges related to high material costs, energy-intensive recovery processes, and limited solid loadings, which collectively hinder its commercial viability. Klein-Marcuschamer *et al.* (2011)[248] investigated economic factors affecting ethanol refineries, such as ionic liquid-to-biomass ratios, recycle rates, and IL costs, revealing that reducing IL consumption and leveraging lignin as a co-

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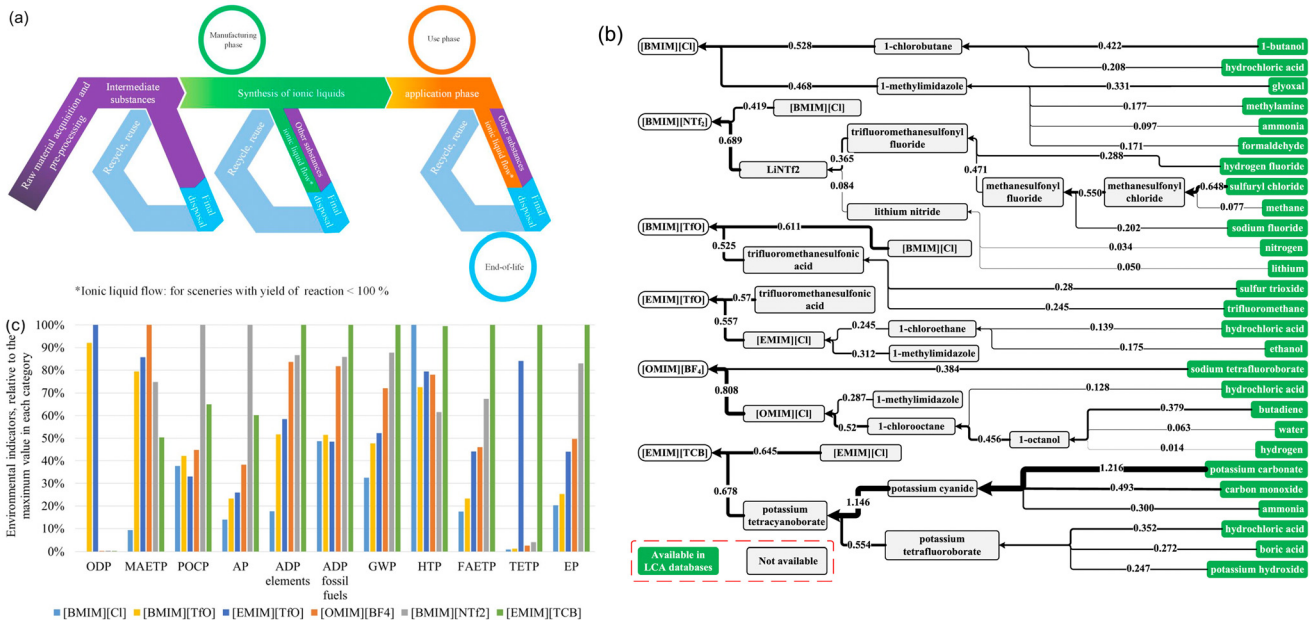

Fig. 18 Life cycle analysis of ILs. Panels: (a) life cycle perspective of ILs; adapted from ref. 47. Copyright 2019, Elsevier (b) life cycle trees for IL production; (c) comparison of life cycle impacts of the production of 1 kg of ILs, adapted from ref. 229. Copyright 2023, American Chemical Society.

product could significantly lower ethanol MSPs. Ovejero-Pérez *et al.* (2021)[249] explored washing strategies for recovering ILs like [EMIM][CH_3COO], demonstrating that minimal water use not only recovers ILs cost-effectively but also mitigates operating costs.

Similarly, Ferrari *et al.* (2021)[250] highlighted the importance of optimizing pretreatment conditions-solid loading and water content had greater impacts on energy consumption than temperature, underscoring the role of process parameters in economic outcomes. Innovations like ensiling biomass, as shown by Magurudeniya *et al.* (2021),[251] have reduced IL consumption by up to 50%, shortened hydrolysis times from 72 to 24 hours without compromising sugar yield, and allowed one-pot processes for biofuel production, leading to reduced production costs and environmental footprints. Similarly, biocompatible ILs like cholinium lysinate ([Ch][Lys]) have enabled one-pot processes that integrate pretreatment, enzymatic hydrolysis, and fermentation without requiring solid–liquid separation or detoxification steps, achieving ethanol MSPs as low as \$3 per gallon under ideal conditions.[252] A techno-economic analysis indicates that using recyclable ILs like [BMIM][NTf_2] can achieve costs competitive with traditional organic solvents like 1-octadecene (ODE).[202] However, high IL costs, ranging from \$20 to \$100 per kg, and cost-intensive recovery processes remain significant challenges.[196,253]

Industrial applications of IL pretreatment coupled with pyrolysis for co-producing biofuels and chemicals like furfural and levoglucosenone have shown potential to enhance economic returns through coproduct revenues and waste heat recovery, achieving MSPs of \$1640 per tonne and \$3590 per tonne, respectively.[254] Despite these advancements, challenges like IL toxicity, low biodegradability, and high viscosity continue to limit mixing efficiency and sustainability. To address these issues, current research is focusing on developing low-cost, biodegradable ILs such as choline-based derivatives and integrating advanced recovery technologies like distillation–filtration systems, which are critical for improving the economic and environmental feasibility of IL-based biorefineries.[249,254] Moving forward, greater attention should be paid towards valorization of lignin and other coproducts to offset production costs and enhance economic feasibility.

6. Challenges and perspectives

The use of ILs in lignocellulosic biomass pretreatment represents a promising strategy to overcome biomass recalcitrance and enable efficient biofuel and biochemical production. Despite notable advances over the past two decades, significant challenges remain in translating IL-based pretreatment to cost-competitive industrial-scale applications. We have identified the following key issues:

1. The molecular mechanisms underpinning biomass dissolution by ILs, particularly the role of specific anion–cation interactions, remain insufficiently underexplored. A deeper mechanistic insight, supported by advanced computational modeling and experimental studies, is critical to guide the rational design of more effective ILs.

2. The recovery and recycling of ILs are often energy-intensive, challenging the economic and environmental sustainability of the process. Existing recycling techniques such as distillation, membrane separation, and antisolvent precipitation

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methods face limitations in energy use, scalability, and the accumulation of biomass-derived impurities, which degrade IL performance over repeated cycles. This highlights the urgent need for more robust, energy-efficient, and cost-competitive recycling technologies.

3. The presence of impurities/biomass-derived components, including lignin fragments, sugars, and inorganic residues, introduces further complexity, affecting IL functionality, recyclability, and the quality of biomass-derived products. These impurities reduce the functional integrity of ILs during repeated cycles and increase the complexity of the recovery process. Standardized protocols for IL selection and optimization tailored to specific feedstocks and pretreatment conditions are lacking, limiting process reproducibility and scalability a challenge.

4. Despite being promoted as "green solvents", many ILs tend to inhibit enzyme activity and/or are toxic to microorganisms used in bioconversion processes. Additionally, concerns persist over the biodegradability and the environmental footprint of IL synthesis and disposal. Innovative biocompatible IL formulations and effective detoxification strategies are required to address this challenge.

5. The commercialization of IL-based biomass pretreatment is hindered by high upfront costs, competition with cheaper alternatives, and limited industrial collaboration. Limited data on life cycle impacts and techno-economic feasibility of IL-based processes restrict IL deployment at scale, requiring rigorous data modeling and systems analysis.

Despite these challenges, future advancements can pave the way for the sustainable and large-scale application of ILs in biomass pretreatment. Developing cost-effective and biodegradable ILs through iterative designs that integrate renewable and bio-derived components is a promising direction. Innovations in hybrid recycling techniques, combining methods such as distillation, membrane separation, and anti-solvent recovery, could enhance scalability and efficiency. Furthermore, standardizing IL optimization protocols, conducting comprehensive system analyses, and fostering collaboration among academia, industry, and policymakers will be critical for translating IL-based biomass processing from promising research to industrial reality.

Conflicts of interest

BAS has a financial interest in Illium Technologies, Caribou Biofuels, and Erg Bio. All other authors declare the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

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