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Current Opinion in
Green and Sustainable Chemistry

Purifying cellulose from major waste streams using ionic liquids and deep eutectic solvents

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Abstract

Cellulose is the main component in woody plant parts and a commodity industrial product, whose importance is set to increase as fossil hydrocarbons are phased out. Cellulose provided after a prior application can help secure stable, sustainable and cost-effective supplies of cellulosic glucose or cellulose fibers; however, the previous life poses additional challenges. Here, we discuss recent research efforts in recycling cellulose from waste biomass using ionic liquids and deep eutectic solvents, promising designer solvents for biopolymer separations. The review identifies large cellulosic waste streams that are not paper and cardboard waste, promising processing approaches employing ionic liquids and deep eutectic solvents to purify the waste cellulose, and discusses the opportunities and challenges in finding applications for the recovered cellulose. While the field of cellulosic waste recycling is relatively new, and hence decontamination and purification processes are at an early stage of development, further development has substantial potential to promote a more circular economy for cellulose.

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Current Opinion in Green and Sustainable Chemistry 2023, **41:**100783

This review comes from a themed issue on **Chemical conversion of biomass (2022)**

Edited by **Katalin Barta** and **Maxim Galkin**

Available online 16 February 2023

For complete overview of the section, please refer the article collection - Chemical conversion of biomass (2022)

https://doi.org/10.1016/j.cogsc.2023.100783

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Keywords

Cellulose recycling, Wood waste, Sludge, Textile waste, Ionic liquids, Deep eutectic solvents, Circular economy, Low-cost glucose.

Introduction

Waste cellulose

A sustainable economy must be based on affordable and renewable supplies of raw materials [1]. Maximizing the value of waste streams has been highlighted as a top priority for the manufacturing sector to meet the Sustainable Development Goals, as defined by the United Nations [2]. To support this, the landfilling of recyclable waste or its use as an energy vector may be restricted in the future, which will incentivize the valorization of waste streams [3]. In the last few years, the discovery and application of ionic liquids (ILs) and deep eutectic solvents (DESs) have resulted in improved chemistry due to their tunable solvent properties, which are usually different from established molecular solvents; some processes have reached commercial deployment. Here, we are reviewing the application of these designer solvents to the purification of cellulose waste streams. An imbalance in favor of ILs over DESs reflects the state of the bibliography, a consequence of research with ILs starting earlier.

Cellulose is a suitable raw material for sustainable manufacturing due to its abundance (180 billion tons are biosynthesized annually) [4], useful material properties, and biodegradability [5*]. Cellulose is a linear polymer of glucose connected by β-1,4-glycosidic bonds. The individual cellulose chains are stacked in a crystalline lattice, creating cellulose fibrils. The order and fibrillar arrangement provide relatively high tensile strength and stiffness, while its elemental composition (carbon, oxygen, and hydrogen) makes it lightweight, which is important for material applications such as paper and packaging. Cellulose can also be hydrolyzed to glucose, which can be used as a feed for industrial fermentation processes that produce food and beverages, pharmaceuticals, and commodity chemicals, for example, ethanol, butanol, acetic acid, lactic acid, or hydrogen [5*].

Sources of *primary cellulose* are plants specifically cultivated for cellulose fiber production, such as cotton grown for textile fibers (~26 million tons *per annum*) [6–9]. Pine, spruce, and eucalyptus are grown to supply pulp mills (~180 million tons of wood cellulose produced *per annum*) [10]. *Secondary cellulose* derives from by-products of crop growing, such as straws and leaves left in the field after harvesting [7]. *Tertiary cellulose* sources (Figure 1) are waste streams from sectors such as construction and demolition, textile manufacturing, wastewater treatment, and industrial processing of agricultural products, such as beer brewing, lipid extraction from oil crops, and sugar extraction from sugar crops [7,11–13]. These waste streams generally have

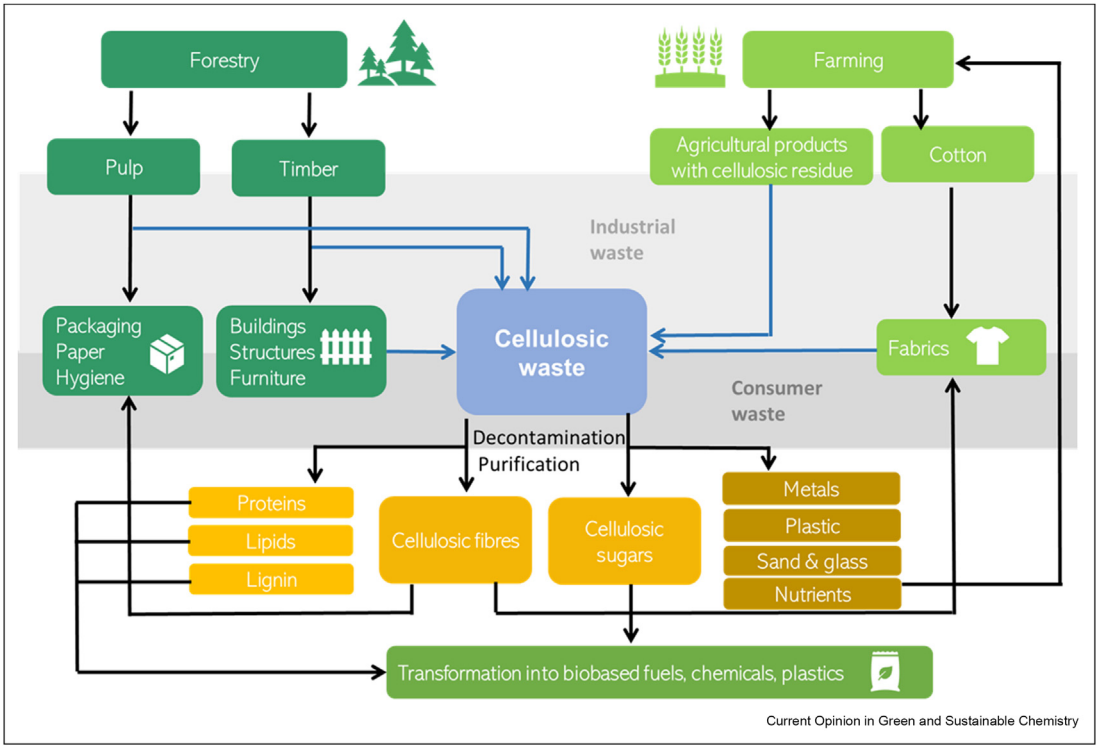
Abbreviations

[BMIm][$MeSO_4$] 1-Butyl-3-methylimidazolium methyl sulfate
[Ch][OAc] Choline acetate
[Ch]Cl:urea Choline chloride:urea
[DBNH][OAc] 1,5-Diazabicyclo[4.3.0]non-5-enium acetate
[DMBA][HSO_4] *N,N*-Dimethylbutylammonium hydrogen sulfate
[EMIm][OAc] 1-Ethyl-3-methylimidazolium acetate
[HMIm][HSO_4] 1-Methylimidazolium hydrogen sulfate
[HMIm]Cl 1-Methylimidazolium chloride
Na[OAc]:urea Sodium acetate:urea
[$P(CH_2OH)_4$]Cl Tetrakis(hydroxymethyl)phosphonium chloride
[TEA][HSO_4] Triethylammonium hydrogen sulfate
[TEA][$MeSO_3$] Triethylammonium methanesulfonate
[TEBA]Cl:la Triethylbenzylammonium chloride:lactic acid
BSG Brewers' spent grains
CCA Chromated copper arsenic
DES(s) Deep eutectic solvent(s)
HBD(s) HBD(s) Hydrogen Bond Donor(s)
IL(s) Ionic liquid(s)
LCA Life cycle assessment
OPEFB(s) Palm oil empty fruit bunch(es)
PAHs Polycyclic aromatic hydrocarbons
PET Poly(ethylene terephthalate)
Zn[$Ac]_2$:be Zinc acetate:betaine

low value, and may be spread on fields, burned for energy, or landfilled, resulting in the loss of resources and often incurring costs to the industry producing the waste. Since feedstock pricing accounts for > 50% of production costs for commodity chemicals, valorising tertiary cellulose can reduce cellulose production cost and waste disposal costs, while expanding the reservoir of sustainable cellulose available to the economy[14]. An established recycling supply chain exists for paper and cardboard, a model that should be transferred to other cellulosic waste streams.

One challenge in utilizing tertiary cellulose is that it typically occurs in a matrix of other constituents. Depending on the source, the constituents can be biopolymers and biomolecules (*e.g.* lignin, hemicellulose, protein, and lipids) [15], as well as material or chemical contaminants (*e.g.* plastic, sand, resins, paints, or preservatives). The matrix makes tertiary cellulose waste streams distinct from recycled paper and board and requires innovative processes for achieving decontamination and purification of the cellulose [16]. Another challenge, shared with wastepaper recycling, is that cellulose fibers get damaged and shortened during use or the recycling process, resulting in downcycling (lower value applications) [17]. Reinforcing with higher-quality cellulose (recycled or fresh) can extend the life span, but hydrolysis of low-quality fibers to low-

Figure 1



Origins of tertiary cellulose and constituents that may be isolated alongside the recovered cellulose.

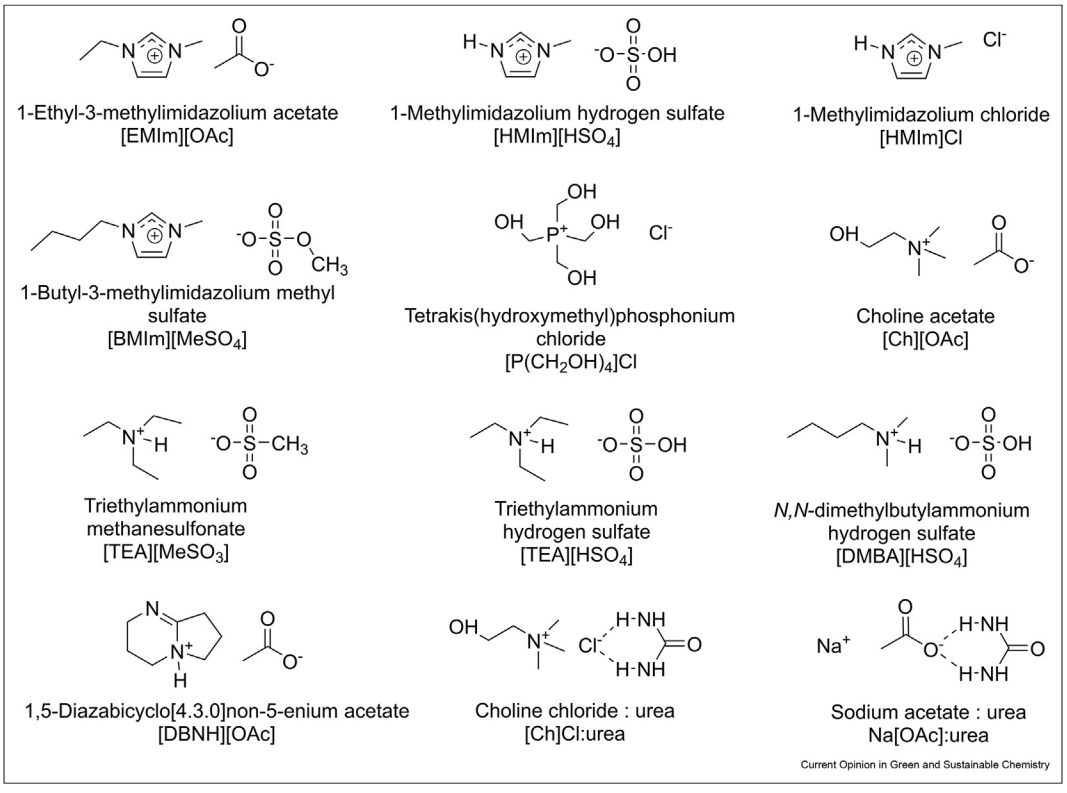
cost glucose is an emerging alternative to disposal or incineration.

Ionic liquids and deep eutectic solvents in cellulosic feedstock processing

ILs are liquids composed of salts with a low melting point (typically below 100 °C) [18], while DESs are mixtures of pure compounds for which the eutectic point temperature is considerably below that of the ideal mixture. A common type of DES is a mixture of a hydrogen bond accepting salt and a hydrogen bond donor (HBD) molecule (Figure 2) [19], but DESs with two molecular components are also possible. Both ILs and DESs have high design flexibility, such as tuneable solvent polarity, coordination power, and catalytic activity [20]. ILs and DESs have emerged as designer solvents that are being explored and increasingly established in solvent-based applications [20], including the dissolution, fractionation, and purification of biopolymers [16*, 21–23]. A recent review on similarities and differences between ILs and DESs is available, with a specific view to cellulosic biomass processing, addressing topics, such as solvent cost and toxicity, thermal stability, vapor pressure, and polarity [24]*. While ILs and DESs were initially considered "green" solvents due to their low volatility compared to commonly used organic solvents, further research found that they have a wide toxicity range related to their chemical structures [25]. ILs and DESs may also have resource-heavy syntheses, especially in the case of ILs, and contain environmentally persistent constituents, for example, fluorinated anions. ILs tend to have a higher production cost compared to industrial molecular solvents [26], which was one of the drivers in developing a subclass of DES based on choline chloride ([Ch]Cl). The development of low-cost non-toxic DESs and ILs and reports of high solvent recycling rates, however, show that favourable economics and environmental impacts are possible [22,24]. For research purposes, the solvent can be initially designed by applying simple rules (e.g. short synthesis tree from commodity starting materials, short alkyl substituents on cation for low toxicity) to identify promising performance. This can be followed up with recycling studies and techno-economic and life cycle analysis (LCA) considering production, use, and end-of-life phases to confirm whether treatment with the selected IL or DES is indeed the preferrerd process for the cellulose containing waste, economically and environmentally [24,27–29].

ILs with certain design characteristics can swell and dissolve whole lignocellulosic biomass, including the cellulose fraction, which can be precipitated from the solutions using an antisolvent (*e.g.* water or alcohols), leading to a reduction and change of the crystalline ordering [22]. However, the separation of lignin and hemicellulose from cellulose is limited in this approach,

Figure 2



Chemical structures of selected ILs and DESs that have been employed in the valorization of cellulose containing waste streams.

as the fractions usually dissolve and precipitate together upon antisolvent addition. A different approach allows for the fractionation of lignocellulose by using certain ILs mixed with water. These mixtures dissolve the lignin and hemicellulose but leave a solid cellulose-rich pulp that can be separated by filtration and retains the natural cellulose I crystal structure [30]. Recently, a similar approach was used for the purification of cellulose contained in commercial Kraft cellulose pulp with DESs based on [Ch][OAc] with three different HBDs [31]. In this review, we discuss the use of ILs and DESs for the purification of cellulose from high volume tertiary waste streams that have an existing infrastructure for collection (Table 1). The chemical structure, full names, and common notations of selected ILs and DESs solvents relevant for the review are shown in Figure 2.

Cellulose purification for major cellulose-containing waste streams

By-products of processing of agricultural products

Tertiary cellulose from food processing is typically contained in stalks, husks, and hulls which are left after the edible part has been processed. Examples include sugarcane bagasse, corn cobs, rice husks, oil palm empty fruit bunches (OPEFBs), brewer's spent grains (BSG), and spent coffee beans. While usually not containing toxic contaminants, biogenic fractions other than cellulose or less desirable portions (*e.g.* pith from sugarcane bagasse) need to be removed for further use of the cellulose. Some agro-industrial products also contain concerning concentrations of heavy metals, for example, rice husks can contain hazardous levels of mercury [40]. Most studies investigating IL and DES based purification of cellulose from food processing residues focus on generating glucose for fermentation. Literature reports cellulosic bioethanol, levulinic acid, and ethyl levulinate production [19,32,34,36,41–44].

Sugarcane bagasse, the residue obtained after extracting sucrose for food or bioethanol production, consists of two major fractions, a fraction called fibers (~65%) and a fraction called pith (~30%). It is often disposed of by incineration, and some mills capture the resulting (bio)energy for use in the plant and export to the electricity grid. Bagasse can be a source of cellulose fibers, if the soil (de-rocking), shorter pith fibers, and the silica-containing ash are removed, which is done mechanically before alkaline pulping to remove the lignin and part of the hemicellulose [41,45]. Bagasse can also be a source of cellulosic glucose if the cellulose can be made accessible to hydrolytic enzymes. As an example, high glucose yields were obtained from whole sugarcane bagasse and depithed bagasse after fractionation with the protic IL [TEA][HSO_4] followed by enzymatic saccharification of the cellulose pulp [41]. Glucose yields from the pith fraction were similar to depithed bagasse, suggesting that either the pith fraction could be used for glucose production or whole bagasse without mechanical separation [41]. DESs composed of lactic acid and the hydrogen bond acceptors [Ch]Cl or triethylbenzylammonium chloride [TEBA]Cl result in high lignin removal and can yield highly digestible cellulose [46,47]. The authors mention that additional or different purification would be needed for the production of materials from the cellulose.

The production of cellulosic glucose from oil palm empty fruit bunches has been reported with different ILs and DESs, including [TEA][$MeSO_3$], [TEA][HSO_4], [HMIm][HSO_4], [DMBA][HSO_4], [Ch][OAc], and [Ch]Cl:urea [36,48–52]. A recent study suggests that dewaxing OPEFBs with an organic solvent mixture before IL treatment was beneficial with certain ILs but not others [53].

BSGs are a major agro-industrial by-product that has a significant protein content (20–30%) and, because of this, is used as low-value animal feed for ruminants. There are few studies on using the cellulose fraction.

Table 1

Annual production and composition of major tertiary cellulose sources.

	Waste stream	Annual production (million tons/year)	Cellulose content	Matrix of the cellulose (excluding moisture)	Origin
Agro-industrial waste	Sugarcane bagasse	~600 (global) [32]	~45% [33]	Lignin, hemicellulose, ash	Residue from sucrose (sugar) production in sugar mills
	Brewer's and distiller's spent grains	~7.8 (global)[a] [34,35]	17% [35]	Protein, lipids, hemicellulose, lignin	Solid residue from breweries and distilleries
	Oil palm empty fruit bunches	~80 (global) [32]	~50% [32]* [36]	Lignin, hemicellulose, lipids (fats)	Waste residue from palm oil extraction
Industrial & municipal waste	Municipal & industrial sludges	~13 (Europe)[a] [37]	20–50% [38]	Protein, lipids, sand, metals	Wastewater treatment plants, wood pulp mills
	Waste timber	~55 (Europe) [39]	28–50% [16,21]	Lignin, hemicellulose, metals, glass, stones, plastic	Off-cuts from manufacturing, old furniture, buildings, wooden structures

[a] Dry weight basis, assuming 38.6 million tons of wet BSG and a moisture content of 80%.

Extraction of the BSG protein with selected ILs and DESs has been investigated with the aim to produce a higher-value livestock feed or low-carbon protein for human nutrition [34,42]*. For these, it is very important that any residual solvent is food safe. DESs, such as [Na][OAc]:urea (1:2) and [Ch]Cl:urea (1:2), which are food safe, have been demonstrated for protein extraction from BSG [15]. However, issues with IL recycling have been reported when processing the protein-rich waste biomass [43].

The hemicellulose fraction can make up a high proportion of agricultural biomass and hence may become an important co-product of cellulose purification. It is typically rich in the pentose sugars xylose and arabinose and could be used for furfural production, a value-added bio-based chemical with a variety of current and potential industrial applications [54]. Acidic ILs have shown promise in generating high yields of furfural while purifying the cellulose fraction [55]. In addition, the removal of phenolic compounds with potential biological activity from OPEFB and coconut residues with DESs has been also reported [56], highlighting the potential of designer solvents to isolate value-added extracts from biomass waste.

Waste wood

Waste wood originates from industrial (off-cuts and sawdust) and postconsumer sources. The presence of toxic compounds often hinders reuse and recycling. The waste wood can contain heavy metals originating from preservatives added to protect from rot and insect infestation as chromated copper arsenic (CCA) formulations, which have been banned but are still present in installed structures [21]. Lead, zinc, cadmium, and titanium were also introduced as paints (serving as pigments or stabilizers). ILs (and potentially DESs) are uniquely placed to purify the cellulose and remove the metal contamination, due to their complexation ability.

It was recently reported that [HMIm]Cl water mixtures can remove 80–100% of the heavy metal content from CCA-treated wood and postconsumer waste wood, with simultaneous removal of 60–70% lignin and 90–100% hemicellulose, combining cellulose purification and decontamination in one step [16,57]. Enzymatic hydrolysis resulted in glucose yields of >90%. Furthermore, copper ions could be recovered as copper metal from the IL solution via electrodeposition, using the high conductivity and the electrochemical stability of the IL, showing the potential for a zero-waste process [57]*. The study notes that metal recovery should be performed before the lignin recovery stage; otherwise, metal ions would be sequestered by lignin during its precipitation. Decontamination and fractionation using the ILs [HMIm]Cl and [DMBA][HSO_4] showed similar performance on samples from a waste wood processing plant, as well as construction and demolition activities, including 84–96% extraction of heavy metals (Pb, Zn, Cu, Cr, Cd, As, Ni, and Ti) [16]. It has been also shown that varying the electrode potential can allow for separate recovery of individual metal species [57].

Wood preservatives can also consist of organic compounds, such as creosote, a mixture of ~85% of polycyclic aromatic hydrocarbons (PAHs) and ~15% of phenolics. The purification of creosote-treated waste wood with the IL [DMBA][HSO_4] achieved quantitative removal of PAHs and ~70% cellulosic glucose yield [21]*. Analysis of the product streams showed that the extracted PAHs co-precipitated with lignin, which has implications for the use of the lignin fraction [21].

IL-mediated synchronous cellulose purification and decontamination have also been combined with phytomining. *Miscanthus* biomass was deliberately contaminated during growth on a phytoremediation site. The harvested biomass was treated with [HMIm]Cl to strip away the heavy metal ions (mainly Pb) and the lignin, generating purified cellulosic glucose after enzymatic hydrolysis. This is a strong example of "regenerative circular economy" which can help reversing environmental damage that has already occurred [58]*.

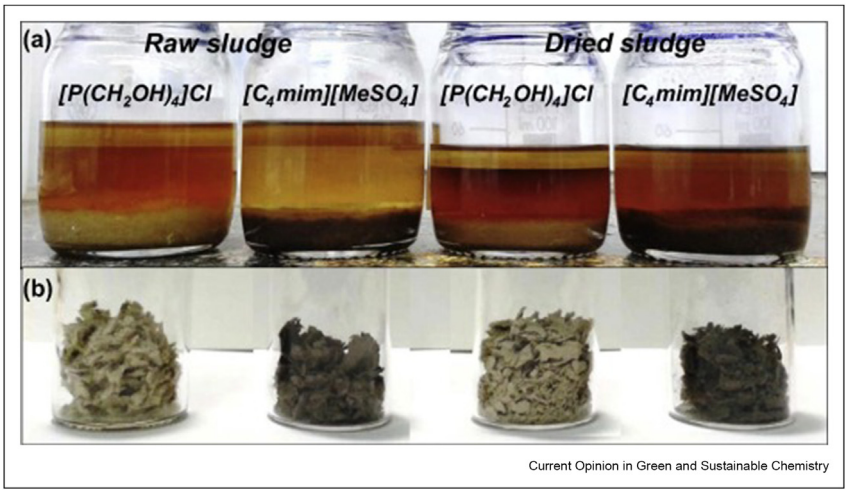
Municipal and industrial sludges

Certain wet slurries contain biogenic substances, such as cellulose, protein, lipids, and inorganic materials (minerals and heavy metals) [59], for example, sludges from municipal wastewater and industrial wastewater treatment, including from pulp and paper mills. Sludge composition is variable and depends on the sludge source. Municipal wastewater sludges can contain heavy metals originating from cleaning products, fertilizers, pharmaceuticals, and corrosion of sewer systems [60]. The heavy metals cause difficulties with the traditional destination of municipal sludges, spreading on agricultural land to enrich the soil [61–63].

The ability of ILs to dissolve biopolymers alongside metallic and polyaromatic contaminants means they are promising media for decontaminating and purifying cellulose-rich sludges [38,64]. Recently, the combination of lipid extraction and heavy metal removal from an industrial sludge was demonstrated by Abouelela et al. using the IL [HMim]Cl [37]. One of the isolated fractions was rich in cellulose (40%) and protein (44%) while the second fraction mainly consisted oflipids (>80%).

Lipid extraction from wet municipal and paper mill sludges has been the target of several studies, with the cellulose-rich streams regarded as side products [59*,64–66]. Olkiewicz et al. used the ILs [BMIm][$MeSO_4$] and [$P(CH_2OH)_4$]Cl to facilitate the

Figure 3



Use of two ILs in the separation of lipids from municipal sludge. It was found that sludge drying was not needed to obtain good lipid recovery in the hydrophobic top phase [64].

separation of lipids from the cellulose-rich solid (Figure 3) [64]. A reduction of protein and ash content was also observed, which was studied in more detail by a recent study employing ILs and DESs [67]. $[P(CH_2OH)_4]Cl$ was also used as one among several solvents to extract cellulose from dried sludge for acid-catalyzed conversion into levulinic acid, but with limited success [59]*.

Other cellulosic wastes

Cellulose is an important polymer in the textile industry, one of the most environmentally damaging industries [68]. Cellulose is the polymer in farmed cotton and wood-derived fabrics, such as viscose and lyocell. Designer solvents could play a role in deriving more value from damaged textiles that cannot be reused. Recent efforts have been successful in dissolving cellulose from postconsumer textile waste blends of polyester and cotton cellulose using the protic IL [DBNH][OAc], which dissolves cellulose selectively [8,69]. These studies found that dry-jet wet spinning of dissolved waste cellulose dissolved in [DBNH][OAc] can give textile grade cellulose fibers with better mechanical properties than virgin cotton fibers [8]*, showing the promise of ILs in cellulose fiber recycling. It has been also shown that the cotton fraction could be converted into microcrystalline cellulose with 69% yield, recovering 99% of the poly(ethylene terephthalate) (PET) using an acidic DES based on [Ch]Cl and *p*-toluenesulfonic acid [70]. Another study took a different approach, converting the PET to monomers using ethylene glycol and the DES $[Betaine]Zn[OAc]_2$ with a 82% yield, while recovering 95% of the waste cotton in polymeric form [71]. The mechanical properties of the cotton were not tested.

Conclusions

ILs and DESs have promise in the valorization of cellulose containing waste due to their vast design space, which can be used to achieve recovery of cellulose-enriched fractions from complex biopolymer matrices. Advantages of these designer solvents are potential for high biopolymer solubility (which can be tuned selectively), an ability to design for selective depolymerization of polymers in polymer blends and composites, and an ability to extract charged pollutants, including dyes and heavy metal ions [29].

Our review shows that most studies to date aim to valorize cellulose-containing waste by producing cellulosic glucose for industrial fermentations or chemical transformation. Studies that prepare recycled cellulose for material applications (*e.g.* cellulose-based packaging, dispersants, textile fibers, nanocellulose, and fibrillated cellulose) are less common. Purified tertiary cellulose should be characterized for its material properties, especially fiber dimensions, crystallinity, and molar weight, enabling comparisons with cellulose from conventional pulping and paper and board recycling [72]. Collaboration between researchers with expertise in IL and DES design and use and those in the cellulose materials community can provide the additional data. Valorization of co-fractions (*e.g.* lignin, protein, hemicellulose, lipids, and metals) has been investigated in some studies, and will be needed to improve the profitability of scaled processes, which is important despite the attractive low cost of the relevant waste feedstocks.

While performance is important, aspects that need to be considered in the design of decontamination and purification methods are solvent recyclability, toxicity, and approximate scaled manufacturing costs, and data gaps

should be closed at the earliest opportunity. Recent techno-economic studies and existing commercial scale IL based processes demonstrate that IL-based processes can be profitable, challenging the view that ILs are generally too costly [73]. It should be noted that every solvent and every separation step will add process cost and environmental impacts; hence, there should be as few as possible to achieve the goal of a sufficiently purified cellulose. As promising approaches emerge, techno-economic modeling and life cycle assessment (LCA) for the recovery of purified cellulose and comparison with conventionally produced cellulose or cellulosic glucose production are needed, which will demonstrate quantitatively the cost of equipment and (replacement) solvent, energy consumption, and multi-dimensional potential impacts on the environment at scale [24].

Despite these challenges, the valorization of cellulose from municipal and industrial waste streams will be an important contributor to a fossil-free, resource-efficient economy. Investing in the development of waste cellulose purification using ionic liquids and deep eutectic solvents will ensure that the best processes delivering the highest product quality can be discovered.

CRediT author statement

Pedro Verdía Barbará: conceptualization, writing - original draft, preparation, writing - review & editing, visualization. Aida Abouelela Rafat: conceptualization, writing - original draft, preparation, writing - review & editing, visualization. Jason P. Hallett: writing - review & editing, supervision, project administration, funding acquisition. Agnieszka Brandt-Talbot: conceptualization, writing - review & editing, visualization, project administration, funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Agnieszka Brandt-Talbot reports financial support and administrative support were provided by Imperial College London. Agnieszka Brandt-Talbot reports a relationship with Lixea Ou that includes: board membership, consulting or advisory, and equity or stocks. Agnieszka Brandt-Talbot has patent #WO2017/085516 licensed to Lixea best to use without, as the company has a group structure and patents will be transferred to another branch. Jason Hallett reports financial support and administrative support were provided by Imperial College London. Jason Hallett reports a relationship with Lixea Ou that includes: board membership, consulting or advisory, and equity or stocks. Jason Hallett has patent ##WO2017/085516 licensed to Lixea.

Data availability

No data was used for the research described in the article.

Acknowledgements

We would like to thank the EPSRC for its financial support via the SuperGen Bioenergy Hub project (EP/S000771/1) and the BBSRC for its financial support via the "WasteWood2Paper" project (POC08-Nov20 Hallett-04).

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