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Integrated COSMO-RS screening and experimental validation of choline chloride-based deep eutectic solvents for sustainable polyurethane depolymerization

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ABSTRACT

Polyurethane (PU) waste has become a serious environmental issue, which has increased the demand for more sustainable and efficient recycling methods. Among these, deep eutectic solvents (DESs) have gained attention as green solvents for PU depolymerization because of their environmentally friendly properties. In this study, a computational screening method based on performance and sustainability indices was used to study the suitability of 10 choline chloride (ChCl)-based DESs for this purpose. This assessment combined the performance index from the Conductor-like Screening Model for Real Solvents (COSMO-RS) with the sustainability index from the Analytical GREENness (AGREE) metric and biodegradability values. Both indices were evaluated for the selected DESs by assigning a 55% weighting to the sustainability index and 45% to the performance index to emphasize the sustainability factor alongside performance. This method allowed for a more balanced assessment of depolymerization efficiency and environmental impact. The computational results showed that amide-based DESs, especially ChCl-Urea, demonstrated better solvation performance, with selectivity and capacity values of 0.741 and 1.718, respectively. Based on the screening results, ChCl-Urea and ChCl-Glycerol were selected as the most promising candidates because both DESs exhibited favorable solvation performance, lower toxicity, and improved biodegradability compared to the other systems studied. Experimental validation performed at 170 °C for 480 min supported the computational predictions: ChCl-Urea achieved complete (100%) PU degradation, whereas ChCl-Glycerol showed only a 29.87% degradation efficiency. The superior performance of ChCl-Urea was associated with its strong cooperative hydrogen-bonding interactions, which promoted the activation and cleavage of PU carbamate linkages. Overall, this study demonstrates that integrating computational prediction with sustainability evaluation can provide a practical and reliable approach for selecting greener solvents for advanced PU recycling applications.

Keywords: *COSMO-RS Predictive Modeling, Analytical GREENness (AGREE), Multi-Criteria Decision Analysis (MCDA), Deep eutectic solvents, polymer depolymerization*

1. INTRODUCTION

The rapid increase in the production and use of polymer materials has resulted in a large amount of polymer waste, with polyurethane (PU) becoming one of the most difficult materials to manage. PU has a highly crosslinked and complex chemical structure, which gives it excellent durability and allows its extensive application in foams, elastomers, coatings, and adhesives [1]. However, this durability also makes PU difficult to recycle. Common disposal methods such as landfilling and incineration can cause environmental problems, including slow degradation, greenhouse gas emissions, and the release of toxic compounds [2]. Several chemical recycling methods for PU have been reported, including glycolysis, hydrolysis, aminolysis, and alcoholysis, which commonly use solvents such as ethylene glycol, diethylene glycol, methanol, DMF, THF, and DMSO [3], [4]. However, these solvents have disadvantages, including toxicity, volatility, and a high energy demand during processing.

Consequently, deep eutectic solvents (DESs) have gained attention as greener alternatives due to their low toxicity, high biodegradability, and tunable properties. Therefore, DESs show potential as solvents for environmentally friendly and efficient recycling methods in the PU depolymerization process. DESs are commonly prepared by mixing a hydrogen bond acceptor (HBA) with a hydrogen bond donor (HBD), producing a eutectic mixture with altered physical and chemical properties [5]. DESs have received increasing attention because they provide several advantages, including good solubilization ability and tunable physicochemical properties. These characteristics make DESs suitable for various chemical and material processing applications, particularly in environmentally friendly recycling processes.

Previous studies reported that DESs are capable of dissolving, swelling, and degrading polymer materials such as PU under relatively mild operating conditions [6]. The strong hydrogen-bonding interactions present in DES systems can interact with the urethane bonds in PU, which helps promote bond cleavage and depolymerization of the polymer structure [7]. However, DESs can be prepared using many different combinations of HBAs and HBDs, resulting in a very large number of possible solvent formulations. Because of this, experimental screening of all possible DES candidates is costly and time-consuming.

Although several studies have explored the use of DESs for polymer degradation, most investigations have relied on conventional trial-and-error experimental methods without combining computational prediction and sustainability analysis in a single integrated approach. Existing studies also tend to emphasize degradation efficiency while giving less consideration to environmental aspects such as biodegradability, toxicity, and the overall sustainability of DES systems. In addition, detailed studies on the screening of ChCl-based DESs for PU degradation using integrated thermodynamic modeling, sustainability evaluation, and experimental validation are still limited. This situation creates a gap between theoretical predictions and practical applications. To overcome this issue, computational screening methods using the Conductor-like Screening Model for Real Solvents (COSMO-RS) can provide an efficient alternative. COSMO-RS applies quantum chemical calculations to estimate important properties such as solubility, vapor pressure, and activity coefficients. Through the analysis of molecular surface charge density and intermolecular interactions, COSMO-RS can predict the theoretical performance of DESs without requiring extensive laboratory experiments.

Even though COSMO-RS is effective for predicting thermodynamic properties, the model does not directly evaluate environmental sustainability. Therefore, this study also employed the Analytical GREENness Calculator (AGREE) to assess the environmental performance of the DES candidates [8]. In addition, the biodegradability of the ChCl-based DESs was included as part of the sustainability evaluation to provide a more comprehensive assessment [9]. These sustainability parameters were combined with the COSMO-RS results to develop a solvent screening map for PU degradation.

In this work, ten commonly used ChCl-based DESs were screened to evaluate their potential for PU degradation. ChCl-based DESs were selected because of their environmentally friendly nature, low cost, easy availability, and strong hydrogen-bonding interactions that can improve PU solubility. By combining molecular-level performance predictions from COSMO-RS with sustainability assessments based on AGREE and biodegradability, this study aims to support the development of efficient and environmentally sustainable strategies for PU recycling through computational screening methods. The DES with the best overall performance was further validated experimentally to determine its degradation efficiency. The novelty of this study lies in the development of an integrated screening framework that combines COSMO-RS prediction, AGREE greenness assessment, biodegradability evaluation, and experimental validation for PU degradation. Compared to prior research that examined only degradation performance, this study also includes environmental sustainability in selecting the most appropriate DES. This work also develops a sustainability-weighted COSMO-RS screening map for PU degradation, a topic that has been rarely reported. The integration of computational analysis and experimental validation reduces the experimental workload and chemical consumption, thereby facilitating the development of more sustainable DESs for polymer recycling.

2. METHODOLOGY

The study is divided into two parts: computational screening and experimental method.

2.1. Computational screening of Deep eutectic solvent (DES) for PU degradation process

Deep eutectic systems (DESs) are characterized by the combination of an HBA and an HBD in specific molar ratios. In this study, ten commonly reported and readily available ChCl-based DESs were selected for screening based on their strong hydrogen-bonding capability, low toxicity, biodegradability, low cost, and prior applications in biomass dissolution and polymer solubilization, as shown in Table 1. Various classes of HBDs, such as amides, alcohols, organic acids, and polyols, were selected to study their effects on the solubilization behavior of PU. Different molar ratios were used because the HBA:HBD composition can affect the physicochemical properties of the DES, such as viscosity, hydrogen bonding, and solubility, which influence the interaction and degradation of PU. Therefore, the selected molar ratios were based on commonly reported stable DES formulations from previous studies to ensure proper DES formation and a consistent comparison. Water content was not explicitly considered in the COSMO-RS modeling, and all DES systems were treated as anhydrous mixtures to ensure a consistent comparison of intrinsic solvent–solute interactions. A representative PU linkage model compound was used in the computational analysis to simulate interactions between PU and the selected DES systems.

2.2. Performance index prediction using Conductor-like Screening Model for Real Solvent (COSMO-RS)

Performance index prediction for the ChCl-based DESs was conducted using COSMO-RS. In this study, the DES acted as the solvent and the PU acted as the solute. Predictions were based on the solubility of PU in the DES, utilizing Density Functional Theory (DFT) calculations and molecular interaction studies. This procedure consists of four steps: a) the molecular structures of the DES components, comprising the HBA and HBD, were optimized using TmoleX2024 software (Turbomole GmbH, Germany); b) thermodynamic parameters, such as the sigma profiles and σ-potentials of the DES and PU, were predicted using COSMO-RS software (SCM BV, Amsterdam); c) DES

performance was calculated based on the activity coefficient; and d) the performance index for each DES was evaluated and ranked. In the first step, all ChCl-based DES structures, along with the PU model compound, were manually constructed and optimized using the TURBOMOLE package. Geometry optimization was carried out in the gas phase using the B3LYP functional together with the def-TZVP basis set, while the COSMO solvation model was applied to obtain the surface screening charge densities. The optimized molecular structures were then used to generate COSMO files, which were later utilized in the COSMO-RS calculations. After that, the σ-profiles and σ-potentials of all DESs in the presence of PU were determined to study the surface charge distribution and intermolecular interaction behavior. This analysis allowed the evaluation of important interactions between the PU and DES components, including hydrogen bonding, electrostatic forces, and dispersive interactions. Based on the σ-profiles and σ-potentials analysis, COSMO-RS was used to predict thermodynamic properties related to PU solubility in all types of ChCl-based DESs. The activity coefficient at infinite dilution (y^{∞}) of the PU model compound in the DES systems was determined using Eq. (1) and served as the leading indicator of solubility behavior [10]. Additional thermodynamic parameters, such as the activity coefficient, selectivity, capacity, and performance index, were assessed to determine their potential.

$$y_i = \exp\left(\frac{u_i - u_i^i}{RT}\right) \quad (1)$$

where the μ_i^i is the potential of pure compound *i* in the reference state. The capacity, C_{AB}^{∞} is determined by inverting the activity coefficient and can be defined as the volume of solvent needed to extract a solute from the solution, as calculated in Eq. (2):

$$C_{AB}^{\infty} = \frac{1}{y_A^{\infty}} \quad (2)$$

The selectivity, $S_{A,B}^{\infty}$ was defined as the ratio of the amount of solute in the DES-rich phase to the amount in the aqueous phase, where subscripts 1 and 2 refer to the solvent and solute, respectively, as calculated using Eq. (3):

$$S_{A,B}^{\infty} = \frac{y_B^{\infty}}{y_A^{\infty}} \quad (3)$$

The performance index, PI, is the product of selectivity and capacity at infinite dilution, calculated using Eq. (4):

$$PI = S_{A,B}^{\infty} \times C_{A,B}^{\infty} \quad (4)$$

Finally, the performance index of each DES toward PU degradation was evaluated and rated using a numerical rating scale from 1 (low) to 10 (high).

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Table 1. ChCl-based DESs with their respective molar ratios.

HBA	HBD	Molar Ratio	DES
Choline Chloride	Urea	1:2	ChCl - Urea
Choline Chloride	Levulinic acid	1:2	ChCl - Lev
Choline Chloride	Glycerol	1:2	ChCl - Gly
Choline Chloride	Acetamide	1:2	ChCl - Ace
Choline Chloride	Ethylene glycol	1:2	ChCl - EG
Choline Chloride	1,4-butanediol	1:4	ChCl - But
Choline Chloride	Malonic acid	1:1	ChCl - MalA
Choline Chloride	Malic acid	1:1	ChCl - MA
Choline Chloride	Oxalic acid	1:1	ChCl - QA
Choline Chloride	Triethylene glycol	1:4	ChCl - TEG

2.3. Sustainability index prediction based Analytical GREENness Calculator (AGREE) and Biodegradability value

The sustainability index was calculated based on the greenness assessment and biodegradability values. The greenness assessment was conducted using the Analytical GREENness Calculator (AGREE) proposed by PenaPereira et al. [8]. Although AGREE was originally developed for analytical methodology evaluation, its principles were adapted in this study to comparatively assess the sustainability of the DES systems and the degradation process. The AGREE scale evaluates performance based on 12 elements: 1) Pretreatment/extraction [11]; 2.) Minimum amount and number of samples required; 3) The device location relative to the analysis site to reduce analysis time; 4) Number of steps involved in the analytical procedure; 5) Application of automated and miniaturized instruments. 6.) Circumventing derivation; 7.) Waste produced during the process; 8.) The analysis duration for each analytes; 9.) Energy consumption; 10.) Reagent originality; 11.) Toxicity of the reagent; 12.) Safety of the operator. The AGREE scale evaluates performance based on these 12 elements, rating each criterion as shown in Figure 1. The AGREE tool was employed as a semi-quantitative sustainability assessment approach for the comparative screening of DES systems rather than as a conventional analytical method evaluation.

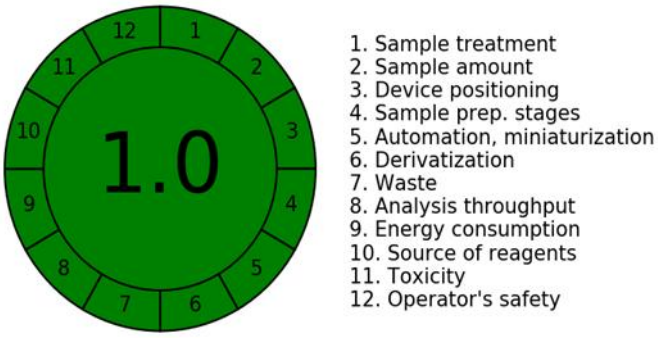

Figure 1. Ideal greenness assessment criteria as proposed by the AGREE method [6].

As shown in Figure 1, the green color code and values approaching 1.0 indicate a high degree of greenness, with 1.0 representing the ideal condition. The AGREE prediction considers that eliminating sample preparation reduces environmental and operator hazards, thereby promoting greenness. This index accounts for sample positioning, including online, offline, at-line, and remote sensing modes. Additionally, the sustainability index incorporates the biodegradability percentage of each ChCl-based DES to ensure that the chosen solvent is green and sustainable. The biodegradability data (28 days) used in this study were obtained from Ferreira et al. (2022) [9], and the DESs were ranked accordingly. Finally, the sustainability index was calculated using an equal weighting of the AGREE score and biodegradability.

2.4. In Silico Solvent Screening Map

The relationship between the performance and sustainability indices was plotted using an in silico solvent screening map. A weighting of 55% on the sustainability index is utilized to align with Green Chemistry Principle No. 4 for designing safer chemicals. This weighting ensures that environmental and safety criteria act as the primary filter, preventing the selection of high-performing but hazardous solvents that would be non-compliant with emerging regulations.

2.5. Experimental Polyurethane (PU) degradation using Deep Eutectic solvent (DES)

2.5.1. Materials

The best-performing DESs were selected for experimental degradation. Choline chloride, urea, and glycerol (≥ 99%) were purchased from Sigma-Aldrich, Germany. Acetone was obtained from HMBG Chemical, Germany. The solvent used for NMR was deuterated dimethyl sulfoxide (DMSO-d6), which was obtained from Sigma-Aldrich, Germany. The thermoplastic polyurethane (TPU) pellets, specifically High Flow TPU 9392 with a hardness of 90A, were obtained from Revlogi Materials Solutions Sdn Bhd.

2.5.2. DES preparation

The DESs, ChCl-Urea (1:2) and ChCl-Gly (1:2), were prepared using a heating and stirring method. The HBA and HBD components were stirred at 65°C to –80°C and 500 rpm for 1 h until a clear and homogeneous liquid was formed [12].

2.5.3. PU degradation in DESs

The degradation of PU was conducted using thermal treatment techniques. This screening process serves as a benchmark for PU degradation across different DESs. ChCl-Urea and ChCl-Gly were used as the DESs. The standard procedure involved adding 5 g of PU elastomer and 50 g of DES solvent into a 500 mL beaker. The degradation process was carried out at 170°C and 500 rpm for 480 min. A temperature of 170°C was chosen to promote PU depolymerization while minimizing solvent degradation and side reactions, and a duration of 480 min was selected to ensure adequate contact time for a comparative evaluation of the degradation efficiency of the screened DES systems under atmospheric conditions without the use of an inert gas atmosphere. Figure 2 illustrates the experimental setup for the process.

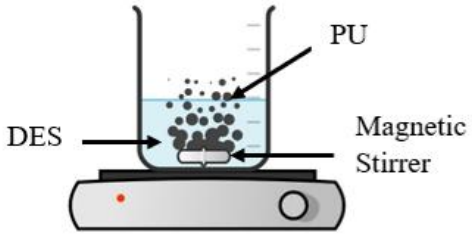

Figure 2. Experimental setup for PU degradation [7].

After degradation, the samples were subjected to a post-treatment process to calculate the degradation efficiency and recover the DES. During post-treatment, the mixture was filtered to separate unreacted PU from the DES and the degradation products. The DES was recovered using a rotary evaporator at 60°C and 100 Pa to remove water. Additionally, washing steps using water and acetone were performed on the remaining PU residue to remove residual DES and degradation products prior to drying and weighing to determine the final weight of the unreacted PU. Eq. (1) was used to calculate the degradation rate of PU.

$$\text{Degradation rate} = \frac{W_o - W_3}{W_o} \times 100\% \quad (1)$$

where Wo is the initial weight of PU and W_3 as unreacted PU.

3. RESULTS AND DISCUSSION

3.1. Performance index (PI) prediction using Conductor-like Screening Model for Real Solvent (COSMO-RS).

The performance index was predicted using the COSMO-RS method. COSMO-RS predicted the DES performance based on the probability distribution function and charge distribution calculated based σ-profiles value as shown in Figure 3.

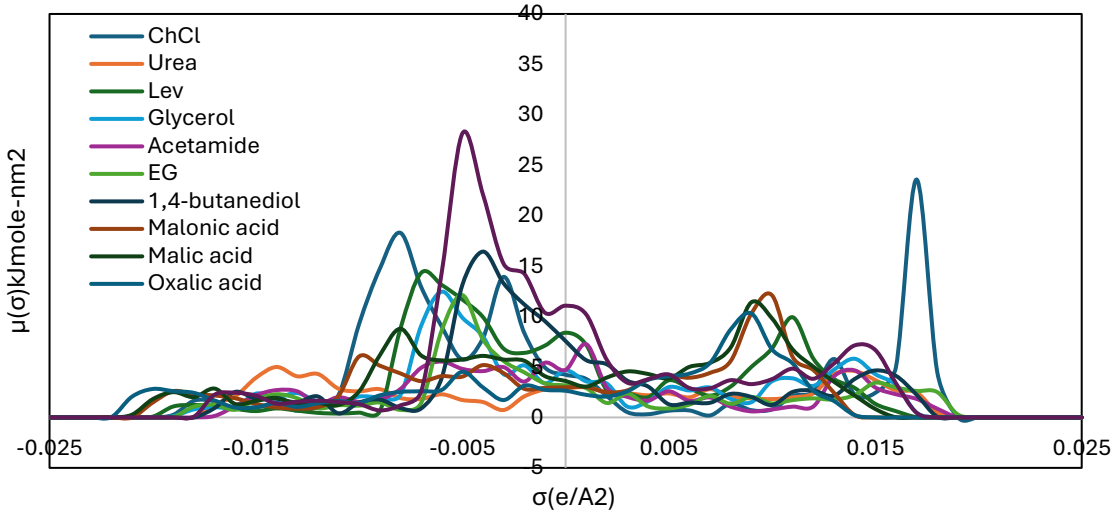

Figure 3. σ-profile of all components in the DES compositions.

Based on Figure 3, the tendencies of ChCI as an HBA can be evaluated for each of its HBDs. COSMO-RS analysis of the σ-profiles shows that ChCl exhibits distinct positive and negative σ-peaks, reflecting its ionic nature and strong HBA capability. Urea and acetamide display broad negative σ-regions due to their amide groups, indicating strong hydrogen-bond donation and favorable complementarity with ChCl, which explains their strong performance. The overlap between the positive σ-region of ChCl and the negative σ-region of amide-based HBDs promotes extensive hydrogen-bonding networks, enhancing solvent affinity toward the polar urethane linkages in PU. These interactions weaken intermolecular forces near the urethane bonds, facilitate polymer swelling, and improve solvent penetration. In addition, the presence of several hydrogen-bonding sites in amide-based DESs helps stabilize degraded PU fragments in the solvent phase, promoting dissolution and degradation. Polyol-based HBDs, including glycerol and EG, show moderate σ-distributions and intermediate performance, while organic acids exhibit sharp negative σ-peaks and strong acidity but less balanced interactions, resulting in localized rather than uniform solvation. These observations indicate that effective PU degradation requires high selectivity and sufficient capacity to dissolve and stabilize degraded fragments. Therefore, DESs with balanced σ-profile overlap generally demonstrate stronger interactions and better overall performance. Based on the σ-profiles, the activity coefficients of the HBA, HBD, and PU were calculated and used to determine the capacity, selectivity, and performance index (PI) of the studied DESs. These parameters provide molecular-level insights into the solvation behavior and degradation efficiency of the DES systems, as summarized in Table 2.

Table 2. Summary of the capacity, selectivity, and performance index (PI) predicted using COSMO-RS equations for the studied DESs.

DES	Capacity	Selectivity	PI	PI rank
ChCl - Urea	1.718	0.741	1.273	10
ChCl - Lev	0.185	0.933	0.172	4
ChCl - Gly	0.898	0.872	0.783	8
ChCl - Ace	1.053	0.875	0.921	9
ChCl - EG	0.655	0.868	0.569	7
ChCl - But	0.574	0.777	0.446	5
ChCl - MalA	0.007	2.364	0.017	3
ChCl - MA	0.009	1.723	0.015	2
ChCl - OA	0.000	4.819	0.000	1
ChCl - TEG	0.596	0.772	0.460	6

Among the evaluated DESs, ChCl-Urea showed the highest PI value of 1.273, followed by ChCl-Ace (0.921) and ChCl-Gly (0.783). This indicates that these systems have better solvation ability, with a good balance between selectivity and capacity. The high activity coefficients obtained for both solvent and solute suggest favorable molecular interactions, which support effective solute partitioning during PU degradation [13], [14]. The enhanced performance of ChCl-Urea and ChCl-Ace can be attributed to improved polarity alignment and increased hydrogen-bonding density between the DES components and the polar urethane groups in PU. DESs prepared with organic acids, such as OA, MA, and MalA, exhibited very low solute activity coefficients and capacities. As a result, their PI values were close to zero, even though some of them showed high selectivity. For example, ChCl-OA showed the highest selectivity value of 4.819, but its PI was 0.000 due to its poor ability to dissolve the target solute. This behavior may be associated with localized molecular interactions and steric hindrance effects that reduce the uniform solvation of PU chains. These findings indicate that selectivity alone cannot fully describe solvent performance and must be considered together with solvent capacity.

The COSMO-RS calculations showed that DESs containing amide- or amino-based compounds, such as urea, acetamide, and glycerol, provide more balanced interactions between solvent and solute molecules. This behavior is mainly influenced by their strong hydrogen-bonding capability, which may assist in stabilizing intermediate compounds formed during the degradation process [15]. In comparison, polyol-based DESs, such as EG and TEG, exhibited moderate performance. Acid-based DESs, despite having high polarity, showed weaker compatibility with the solute system. Among the DESs studied, ChCl-Lev displayed relatively high selectivity, with a value of 0.933, but showed a low capacity of 0.185, resulting in a moderate performance index (PI) value of 0.172. This finding suggests that Lev-based DESs may interact selectively with certain solutes, but their overall effectiveness is still limited due to insufficient solubilization capability.

3.2. Sustainability index based on AGREE and Biodegradability

The sustainability index in this study consisted of two major components: the greenness assessment index and biodegradability values. The greenness level of each DES was evaluated using the AGREE metric, producing scores in a narrow range between 0.57 and 0.59, as presented in Table 3. The small variation in the scores indicates that all studied DESs generally follow Green Analytical Chemistry principles. This result also shows that DES systems are commonly associated with environmentally friendly characteristics, indicating their overall suitability as greener solvent options.

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Table 3. Summary of the sustainability index values based on AGREE and biodegradability for the studied DESs.

DES	A. AGREE metric		B. Biodegradability		Sustainability Index SI ($A \times B$)
	Value	Rank	Value (%) [7], [8]	Rank	
ChCl - Urea	0.59	10	97.1 ± 0.7	10	100
ChCl - Lev	0.57	9	74.2 ± 2.2	4	36
ChCl - Gly	0.59	10	95.9 ± 0.7	9	90
ChCl - Ace	0.59	10	89.5 ± 0.6	8	80
ChCl - EG	0.57	9	81.9 ± 0.6	7	63
ChCl - But	0.57	9	73.6 ± 0.9	3	27
ChCl - MalA	0.57	9	76.3 ± 1.3	5	45
ChCl - MA	0.57	9	79.4 ± 1.0	6	54
ChCl - OA	0.57	9	73.4 ± 1.5	2	18
ChCl - TEG	0.57	9	69.3 ± 0.5	1	9

The highest AGREE scores (0.59) were obtained for ChCl-Urea, ChCl-Gly, and ChCl-Ace. This shows that these solvents have better performance in terms of safety, lower toxicity, and a reduced use of volatile organic compounds. It also suggests that their overall environmental impact is lower, with fewer hazards, better biodegradability, and a lower risk of secondary pollution during preparation, usage, and disposal compared to traditional solvents. In addition, these DES systems are considered more favorable because of their ease of preparation, low vapor pressure, and non-toxic nature.

DES systems containing organic acids and diols, such as ChCl-EG, ChCl-But, ChCl-MalA, ChCl-MA, and ChCl-OA, showed slightly lower AGREE values, although they are still within a similar range. This small reduction can be explained by the hazard information reported in MSDSs, where some organic acids and diols are classified as irritant

or corrosive substances. Consequently, the health- and safety-related scores in AGREE were reduced, even though these DESs still provide overall environmental advantages.

Table 3 also shows that the biodegradability of the DESs was significantly influenced by the characteristics of the HBD. ChCl-Urea demonstrated the highest biodegradability at 97.1 ± 0.7%, followed by ChCl-Gly at 95.9 ± 0.7%. This high biodegradability is linked to the fact that urea and glycerol can be more easily broken down by biological systems due to their simple and accessible molecular structures [9]. This observation supports the findings of Xue-Dan Hou et al.,. [17], who reported that high biodegradability is related to the presence of the cholinium cation and functional groups such as primary amino or carboxyl groups that are readily degraded by microorganisms.

ChCl-Ace demonstrated significant biodegradability at 89.5 ± 0.6%, which is slightly lower than that of urea and glycerol. The observed reduction is likely linked to enhanced hydrogen-bonding interactions within the DES matrix, potentially limiting microbial accessibility. DESs consisting of polyols and organic acids, including ChCl-EG, ChCl-MA, and ChCl-MalA, demonstrated moderate biodegradability. This observation indicates that increased acidity and more robust ionic-hydrogen bonding networks could reduce biodegradation rates [18]. The lowest biodegradability values for ChCl-based DESs were recorded for ChCl-OA and ChCl-But, which is likely attributable to microbial inhibition by OA and decreased bioavailability linked to longer-chain diols. The lowest overall biodegradability was observed for ChCl-TEG, which can be attributed to the reduced transmembrane transport of long-chain compounds [8] . Compared to conventional solvents such as DMF and DMSO (which exhibit low biodegradability) and ethylene glycol (moderate biodegradability), ChCl-based DESs remain more environmentally favorable overall.

3.3. COSMO-RS Solvent Screening Map

Based on the computational data generated for the performance index (PI) and sustainability index (SI), their correlation was analyzed to identify the best DES for the PU degradation process. This metric is based on a composite score, with weightings of 55% for the SI and 45% for the PI. The analysis is shown in Table 4 below.

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Table 4. Matrix for the composite score analysis on the solvent screening map.

DES	PI rank (45%)	SI rank (55%)	Composite score (0.45 * PI + 0.55 * SI)
ChCl - Urea	10	10	10.00
ChCl - Lev	4	4	4.00
ChCl - Gly	8	9	8.55
ChCl - Ace	9	8	8.45
ChCl - EG	7	7	7.00
ChCl - But	5	3	3.90
ChCl - MalA	3	5	4.10
ChCl - MA	2	6	4.20
ChCl - OA	1	2	1.55
ChCl - TEG	6	1	3.25

Based on this analysis, the COSMO-RS solvent screening map was generated, as shown in Figure 4. The integrated sustainability–performance assessment of ChCl-based DESs provides a systematic basis for selecting suitable systems for PU degradation.

As shown in Figure 4, DESs located in the upper-right quadrant, specifically ChCl-Urea, ChCl-Gly, and ChCl-Ace, demonstrate both high performance and enhanced sustainability. Among these systems, ChCl-Urea demonstrates the most advantageous characteristics, attaining the highest performance index and sustainability metrics. This result demonstrates effective solvation and advantageous molecular interactions, aligning with the COSMO-RS predictions, along with elevated biodegradability and AGREE scores. The upper-left section of the map contains ChCl-EG and ChCl-TEG, which show good sustainability with moderate performance. These amine-based systems are more suitable for processes where environmental safety is prioritized over maximum performance. In simple terms, this means that the DESs are environmentally friendly, but their degradation capability is not as strong as that of other systems.

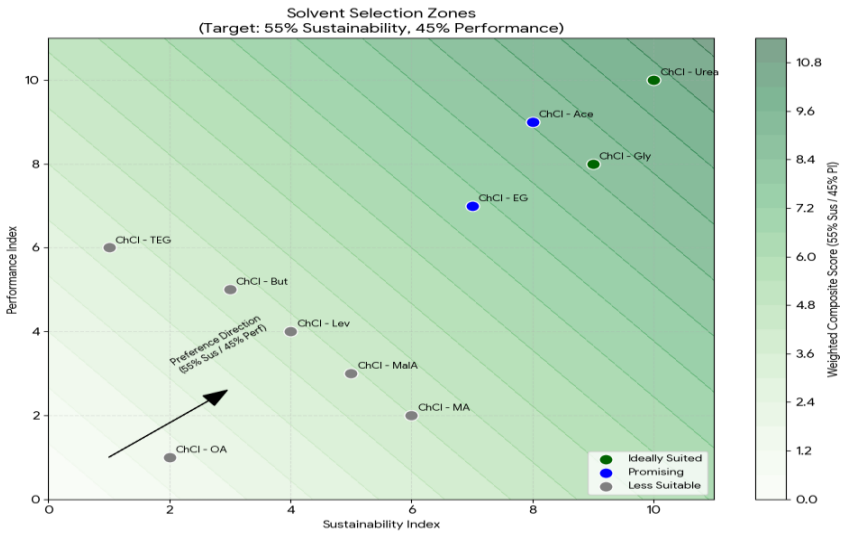

Figure 4. COSMO-RS solvent screening map for PU degradation.

These polyol-based DESs are more environmentally friendly, but their ability to dissolve or interact with the solute is lower than that of amide-based systems. On the other hand, DESs located in the lower-left area of the evaluation map, such as ChCl-OA and ChCl-But, show low performance and low sustainability values. Even though ChCl-OA has high selectivity based on the COSMO-RS results, its low solvation capacity and poor biodegradability make it less suitable for practical applications. This shows that selectivity alone cannot be used as the sole factor to judge solvent quality. In addition, no DES was found in the lower-right quadrant, which indicates that, in this study, systems with high performance also tend to have favorable environmental properties.

The quadrant analysis shows that using only one factor is not enough when selecting a DES for sustainable processes; it is necessary to consider several criteria simultaneously. From the results, ChCl-Urea and ChCl-Gly were identified as the best solvents because they show good performance while maintaining environmental sustainability. Overall, this study shows that choosing a suitable solvent should not depend on a single parameter. A proper evaluation needs to include thermodynamic behavior, environmental impact, the feasibility of solvent recovery, and molecular-level interactions to make a reliable decision.

3.4. PU degradation in the DESs

Based on the computational screening results, the most promising DESs, ChCl-Urea and ChCl-Gly, were prepared and evaluated experimentally for PU degradation at 170°C for 480 min. Among them, ChCl-Urea showed the highest degradation performance, with 100% conversion of PU, which was supported by the complete disappearance of solid PU as shown in Figure 5. In contrast, ChCl-Gly showed a much lower degradation efficiency, exhibiting only 29.87% degradation. These results suggest that the chemical nature of the HBD in the DES plays an important role in the PU degradation process. In particular, a stronger hydrogen-bonding capability helps improve the breakdown of the polymer structure [16].

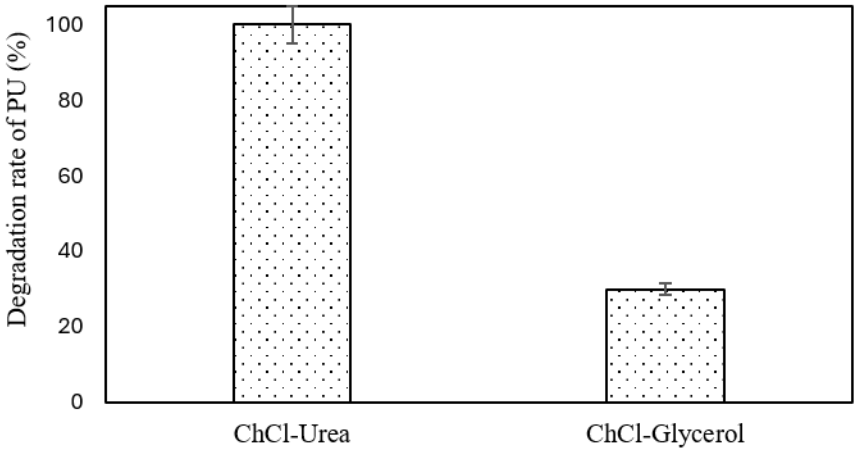

Figure 5. Degradation rate of ChCl-Urea and ChCl-Gly at 170°C for 480 min.

Hydrogen-bonding interactions in DESs are important because they can selectively activate certain chemical bonds in PU. In the ChCl-Urea system, the cooperative interactions among the chloride anion, choline cation, and urea molecules help activate the carbamate (urethane) linkages in PU. This process promotes chain breaking and leads to a more controlled degradation of the polymer structure [17]. The hydrogen bonds formed between the DES components and the PU help weaken the urethane bonds, making bond cleavage easier. Previous studies have also shown similar behavior, where urea-based DESs can dissolve complex polymers effectively due to strong interactions with functional groups such as carbonyl and amine groups [16].

In contrast, ChCl-Gly showed lower efficiency. This lower degradation rate can be related to the weaker acidity of glycerol and its weaker HBD capability compared to urea. Glycerol, frequently used as an HBD in green solvents, exhibits moderate polarity that may not adequately disrupt the hydrogen-bonding networks and urethane linkages in PU [18]. Based on the screening results, ChCl-Urea was selected for further studies of PU degradation due to its superior degradation performance and strong hydrogen-bonding interactions. The selection was primarily influenced by its capacity to facilitate effective carbamate bond activation via hydrogen-bonding interactions rather than solely by its physicochemical properties, making it an effective medium for PU depolymerization under the studied conditions.

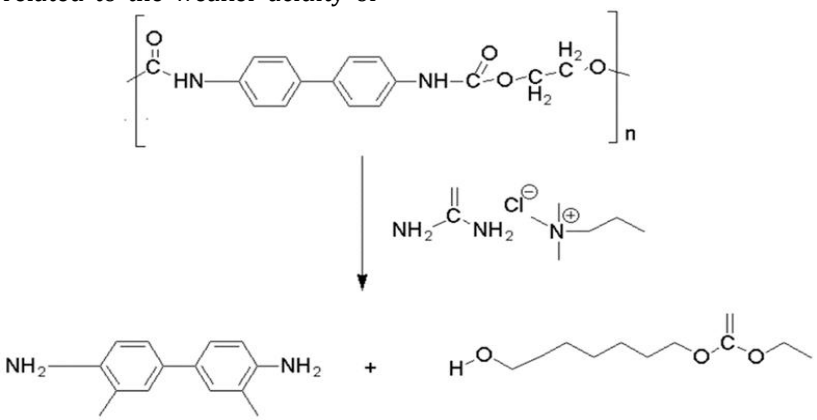

Figure 6. The degradation pathway of PU in ChCl-Urea.

Figure 6 shows the possible degradation pathway for the depolymerization of PU. The DES facilitates the degradation of PU through nucleophilic attack and hydrogen-bonding interactions. The chloride anion in ChCl, together with urea, forms robust hydrogen bonds with the carbonyl groups of the urethane linkages, increasing their susceptibility to nucleophilic cleavage [21]. The presence of protonated amines ($-NH_3^+$) in the degradation products signifies that the process occurs through a partial hydrolysis mechanism, in which urea aids in the cleavage of urethane bonds. The emergence of an aromatic diamine fragment indicates the degradation of the hard segment in PU. This signifies that the degradation process effectively cleaves the bonds connecting the diisocyanate-derived segments of the polymer. The presence of polyol degradation products, including hydroxyl (-OH) and carbonate (-COO-) functionalities, suggests that the soft segment of PU undergoes cleavage as well. The observed structures indicate the hydrolysis or aminolysis of ester and carbonate groups within the polymer backbone [22].

4. CONCLUSION

This study successfully demonstrated an integrated, multi-criteria screening framework to identify optimal DESs for the sustainable chemical recycling of PU. ChCl-Urea was identified as the best candidate from the selected 10 DESs based on the computational screening using performance prediction via COSMO-RS and sustainability assessments via AGREE metrics and biodegradability value. The experimental validation is strongly follow the this predictions where ChCl-Urea achieved an exceptional degradation efficiency of approximately 100% at 170°C over 480 mins, significantly outperforming ChCl-Gly (29.87%). The superior performance of this DES is attributed to the robust hydrogen-bonding network and cooperative interactions. This characteristic is effectively activated and cleave the carbamate linkages within the PU matrix. This research also highlights the optimal solvent selection must consider the multicriteria based on performance criteria and environmental sustainability. The study also show that the combined computational-to-experimental methodology established herein provides a highly efficient, rational design tool that can be broadly adapted to accelerate the discovery of green solvents for advanced polymer upcycling and circular economy applications. Future work should focus on process optimization, possible temperature and reduction times reduction through process intensification, DES recyclability, detailed mechanistic characterization for mechanism study of the degradation products, and pilot-scale validation to support industrial-scale implementation of DES-based polyurethane recycling.

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