

Review and Perspectives for Effective Solutions to Grand Challenges of Energy and Fuels Technologies via Novel Deep Eutectic Solvents

Mert Atilhan* and Santiago Aparicio*

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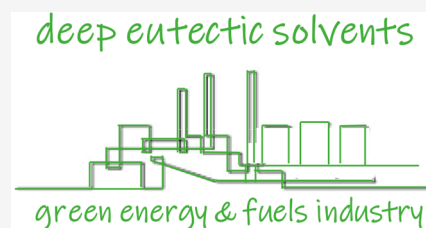
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ABSTRACT: Sustainable technologies applied to energy-related applications should develop a pivotal role over the next decades. Therefore, the development of new materials for old processes has merged as a central research line lately. Deep eutectic solvents (DESs) have been recently considered alternative and economic task-specific solvents for many chemical and environmental processes. The low-cost production of DESs production from natural sources and their tunable properties, such as neat null toxicity and biodegradability, make these solvents suitable candidates for various processes within the green chemistry framework. Considering the millions of possible DES combinations yet to be explored, a detailed review of DES research's current status that can elaborate on the structure–property relationship is an essential task to identify the missing links and strong points on DES research. Thus, this review work focuses on the recent research efforts on the utilization of DES on chemical processes, with the purpose of elucidation on gas capture/separation, fuel desulfurization, biodiesel production, and water treatment processes and provides a deeper understanding on outstanding scientific questions and identifies promising new research directions that involve DESs.



1. INTRODUCTION

Deep eutectic solvents (DESs) are novel solvents that are unique in their physical properties.¹ Mostly, they are associated with their predecessor, ionic liquids (ILs). DESs are formed by the combinations of at least two compounds, leading to a large melting point depression upon formation of a eutectic mixture, mostly leading to mixtures that are liquid under ambient conditions. DESs show significant depressions in melting points,² in comparison to those of other competitive solvents with neat constituent compounds. DESs can be classified into five different categories, corresponding to the types of compounds that are mixed to form the eutectic mixture (Figure 1a).³ Types I, II, and IV involve metallic compounds and are mostly used in metal processing applications.⁴ Type V DESs have been recently proposed and involve the combination of molecular compounds instead of salts for the DESs formation.⁵ Therefore, most of the literature, specially for applications in the energy and fuels area, is focused on Type III DESs. Type III DESs are obtained with the combination of two counterpart compounds, namely, hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs).^{6,15} A prototypical example of Type II is the one formed by the combination of choline chloride (ChCl) as HBA with urea at HBD (Figure 1b). The ChCl:urea mixture, when combined in a 1:2 molar ratio, leads to a large melting point depression, forming a liquid mixture at ambient temperature (Figure 1b). The Type III DESs group is extended by the selection of proper HBA:HBD combinations in suitable molar ratios from various different groups, which increases the potential combinations that can yield DESs on a factorial basis.⁷

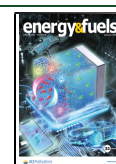
Given such flexibility in forming DESs among the many available combinations of HBA and HBD, they are often referred as designer solvents, task-specific,⁸ because they exhibit tunable physicochemical properties and provide alternative solutions to many industrial applications.^{9,10} Similarly, DESs are often referred as “green” solvents,¹¹ not only because they are associated with ILs, but they can also be formed with the inclusion of many other natural compounds, which results in nontoxic and biocompatible DESs.¹² Such DESs are often referenced as natural deep eutectic solvents (NADESs).¹³ There was a knowledge gap between the discovery of ILs and their actual recognition by the wider academic community. In contrast, with ILs, DESs and NADESs has been well-accepted by academia, since their potential for new chemical technologies has already been realized.¹⁴ Especially over the last 5 years, the volume of DES publications in academic journals has been increasing significantly and these publications cover various different applications of DESs (Figure 2).

Because of their low cost, suitable biodegradability, and low-toxicity designer solvent properties, they have been considered mostly in energy,¹⁶ environment,¹⁷ food processing,¹⁸ drug

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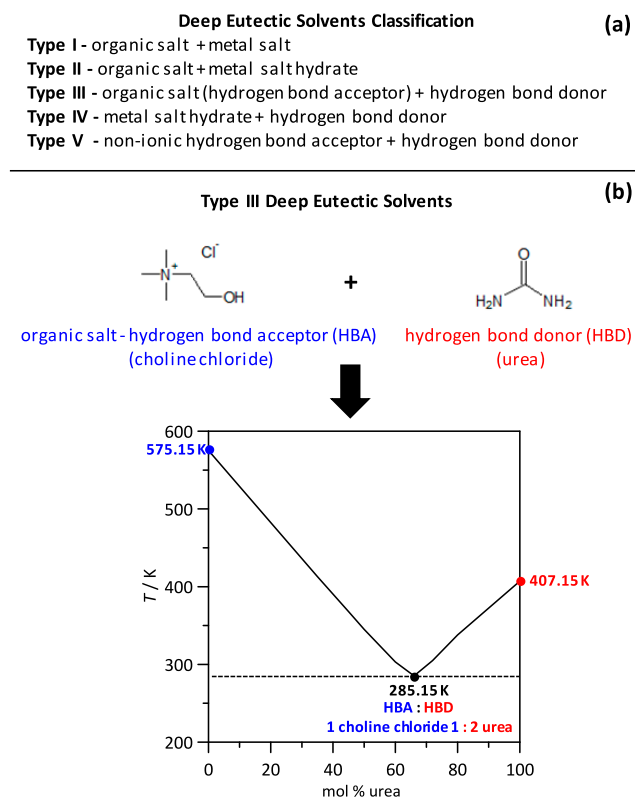


Figure 1. (a) Classification of DESs and (b) type III DES and the case of choline chloride:urea DES with the corresponding solid–liquid equilibria diagram.¹⁵

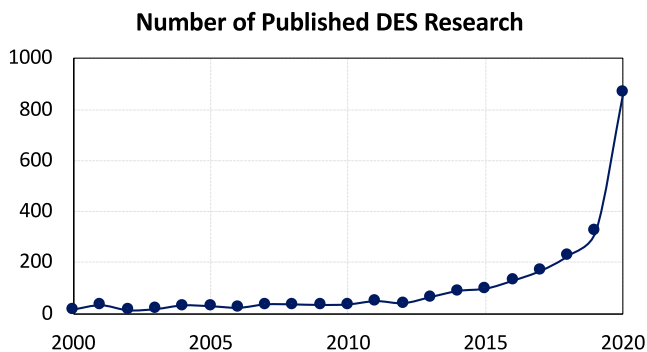


Figure 2. Number of published papers related with DESs research. [Source: Scopus database.]

delivery,¹⁹ catalysts in organic reactions,²⁰ polymer science,²¹ or metallurgy.²² In the case of DESs application for the fossil fuels industry, emphasis on specific processes such as fuel desulfurization, gas capture, and separation, has probed their suitability.²³ Over the past few years, DESs and NADESs have been considered for further complicated applications, such as biodiesel production,²⁴ biomedical and pharmaceutical applications,²⁵ power systems and battery technologies,²⁶ biomass processing,²⁷ nanomaterials synthesis,²⁸ and water treatment.²⁹ Gas capture and separation, water treatment, fuel conditioning and desulfurization processes are the most widely utilized chemical process and fuels industries; in addition, to obtain effective and sustainable outcomes from such classical processes, more innovative approaches are essential to complement the existing ones. Thus, discovery, development and deployment of

DESs in these areas has been studied widely in recent years, which forms the main motivation of this Review.

2. DES UTILIZATION IN CHALLENGING ENERGY AND FUELS PROCESSES

2.1. Toxic Gas Emission Management. DESs have been proposed for adsorption, capturing, and separation of toxic gases from gas mixtures in different sources. Three main groups of gases are considered in this work: (i) carbon compounds (CO_2), (ii) sulfur compounds (H_2S and SO_2), and (iii) nitrogen compounds (NO_x and NH_3).³⁰

2.1.1. CO_2 Capture. The management of CO_2 emissions has a pivotal role into the framework of sustainable technologies and fuels. The current levels of atmospheric CO_2 concentrations, with anthropogenic origin from fossil fuels burning for energy production require the development of suitable carbon capture technologies.³¹ The use of liquid sorbents has been considered as one of the most feasible approaches for post-combustion CO_2 capture from flue gases.³² The use of amine-based liquid sorbents in the natural gas industry has led to the possible use of these compound for emissions treatment.³³ Nevertheless, problems rising from high evaporation rates, solvent degradation and corrosion problems have led to a search of alternative liquid sorbents.³⁴ Ionic liquids (ILs) have been considered as a promising approach for this purpose, considering the possibility of tuning and tailoring their properties using the large number of available compounds,³⁵ and, thus, the suitability of industrial-scale use of ILs has been probed.³⁶ Nevertheless, several problems have been reported,³⁷ which, to date, have hindered the industrial-scale application of ILs for CO_2 capturing purposes. DESs are considered to be closely related solvents to ILs, and, thus, a large number of studies have been reported for carbon capture purposes using different types of HBA/HBD combinations.^{38,39} The advantages of DESs over ILs for this operation stand on the possibility of developing low-cost, natural origin DESs, with suitable affinity for CO_2 at moderate cost.⁴⁰ Similarly, the environmental and toxicological impact of DESs is lower than that observed for ILs;⁴¹ thus, DESs can be applied for carbon capture applications, considering both techno-economical as well as environmental reasons.^{42,43}

The first stage for developing suitable DES for CO_2 capturing purposes stands on the accurate determination of absorption equilibria data in wide relevant pressure–temperature ranges, as required for post-combustion capture processes. The literature shows a large collection of experimental absorption isotherms for different HBA–HBD combinations, from which values for the Henry's law constant (K_H) were inferred Figure 3. The classical ChCl:urea 1:2 DES has been widely studied for CO_2 capture; the literature shows K_H values, on a molality basis, of ~ 1 MPa at 313.2 K, which confirms the suitable affinity of this DESs for CO_2 molecules (Figure 3a). Nevertheless, some literature data show larger K_H values, which show the need of reliable methods for the synthesis and characterization of DESs, as well as the possible presence of impurities. The effect of the type of considered HBD for ChCl-based DES is analyzed in Figure 3b, where the best results are obtained for urea, although reasonably good capturing ability may be inferred for other types of DESs, thus allowing a suitable selection of the HBD considering factors such as cost, thermophysical properties, or toxicity/biodegradability issues. Another relevant effect in the DES design for CO_2 capture stand on the HBA:HBD molar ratio, results in Figure 3c for ChCl-based DESs show that, in most cases, the increase of HBD content decreases the K_H values (i.e., increases affinity

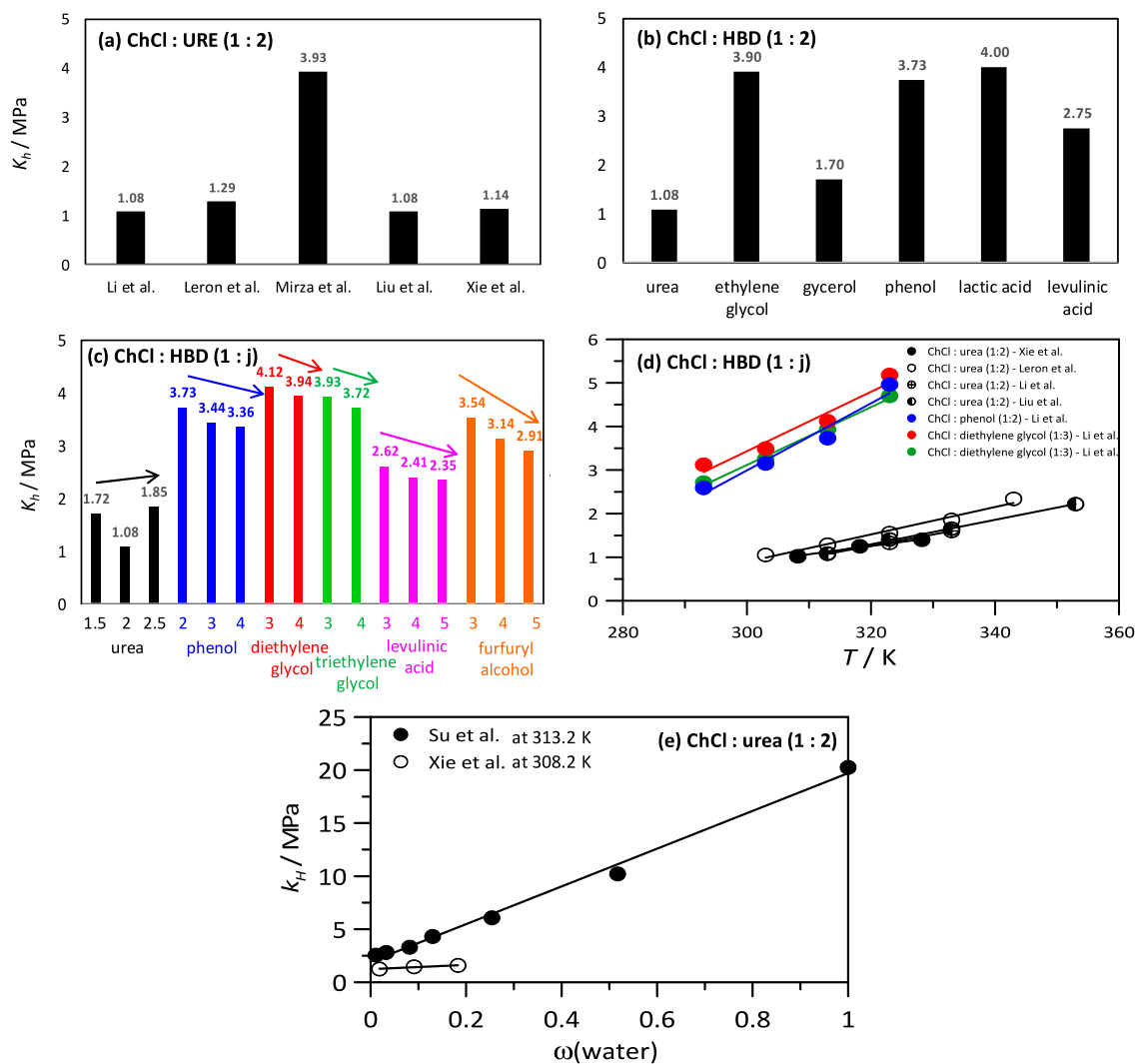


Figure 3. Henry's law constant (in molality basis), k_H , for the absorption of CO_2 in DESs considering different effects: (a) literature sources, (b) HBD type, (c) molar ratio, (d) temperature, and (e) water content. Results in panels (a)–(c) have been reported at 313.2 K. Data obtained from the available literature.^{45–55}

toward CO_2). The effect of temperature is analyzed in Figure 3d; an almost-linear increase of k_H is inferred for the studied DES (i.e., decreasing affinity for CO_2 molecules upon heating). Nevertheless, this decrease is moderate, e.g., in the case of ChCl:urea 1:2, the k_H value remains lower than 2 MPa for temperatures up to 353 K, thus allowing CO_2 capture from hot flue gases. The water content in DESs decreases CO_2 solubility but, at the same time, it decreases the viscosity of the fluid, which enhances heat and mass transfer.⁴⁴ The effect of water content on CO_2 solubility in ChCl:urea 1:2 is reported in Figure 3e, although a decrease in CO_2 solubility is inferred with increasing water content: for moderate water content, which will be the result of exposition of hydrophilic DESs to atmospheric water, the k_H values are still reasonably low to provide suitable CO_2 capture. Therefore, water content can be fine-tuned to balance CO_2 affinity as well as to provide suitable physicochemical properties such as low viscosity.

Beyond common DESs, mostly based on choline chloride as HBA, task-specific DESs have been designed to improve affinity for CO_2 molecules, as well as improving physical properties, e.g., lower viscosity, which may lead to feasible scaling up of these solvents at the industrial level. One approach considered for

improving DESs performance consists of the combined use of DESs + superbase (i.e., compounds with high protonic affinity) combinations. Pandey et al.⁵⁶ considered systems formed by classical DESs, choline chloride + urea, ethylene glycol, or monoethanolamine, in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) superbases. In the case of DESs leading to physical absorption of CO_2 , those with urea or ethylene glycol, the presence of the superbases leads to a remarkable increase in capturing ability, whereas for chemisorption cases (HBDs such as monoethanolamine), the superbase is not required. In the case of choline chloride:urea (1:2) at 60 °C, the CO_2 amount absorbed is 5.1 mg CO_2 /g sorbent, whereas upon the addition of DBN superbase, it increases to 33.4 mg CO_2 /g sorbent, with analogous results for ethylene glycol as HBD. Jiang et al.⁵⁷ considered DBN:2-imidazolidone, or DBN:1,3-dimethylurea or DBN:dimethylurea DESs, also reporting an improvement of capturing ability, especially for 2-imidazolidone. Additional relevant studies considering superbases were reported by Zhang et al.⁵⁸ (considering DBN) and Yan et al.⁵⁹ (considering DBU in superbase ILs mixed with ethylene glycol for DES development)

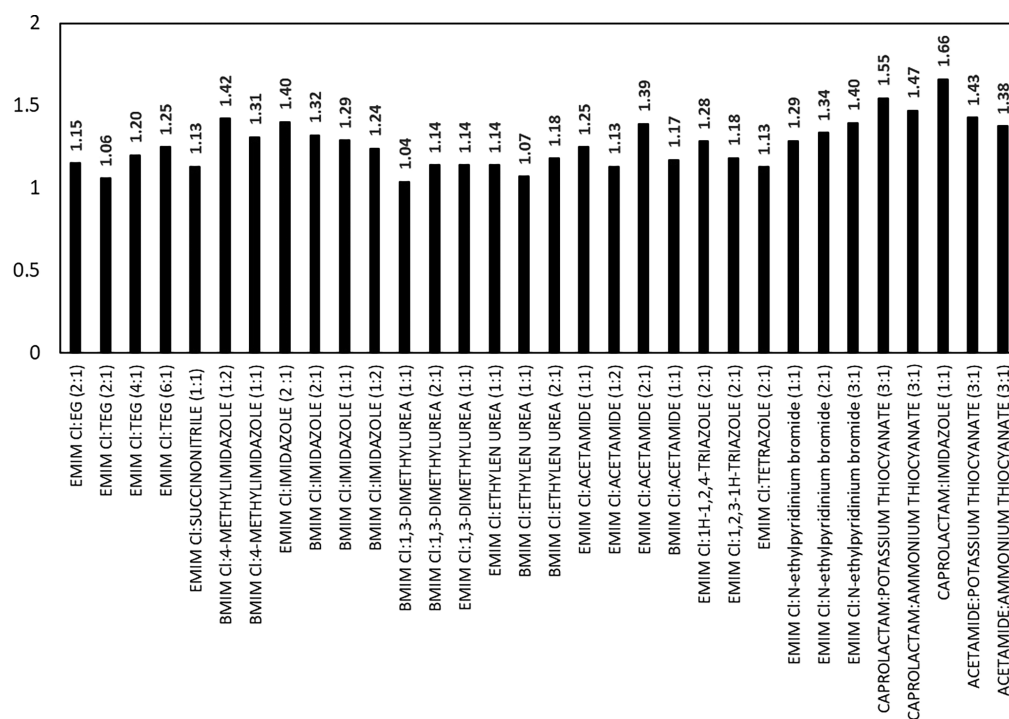


Figure 4. Experimental solubility data for SO₂ in selected DESs. Data taken from the available literature.^{84,85,88–95}

showing in all the cases reversible and efficient CO₂ adsorption, as confirmed by the analysis reported by Liu et al.⁶⁰ Nevertheless, these superbase-based DESs systems may present problems related to the increase of viscosity upon CO₂ capture, the poor performance of desorption cycles, with only 23% release of captured CO₂ upon heating to 60 °C.⁵⁶ Similarly, that of superbase–DESs has been questioned in the literature,⁶¹ considering the poor thermal stability of superbases in certain solvents, as well as the extreme sensitivity of superbases toward water,⁶² which would require special conditions from their preparation and handling hindering scaling up.

Additional modifications of DESs formulation have considered the use of amine-based DESs, thus evolving from physical to chemical absorption. Hsu et al.⁶³ considered aqueous mixtures of choline chloride:urea (1:2) with monoethanolamine (MEA) showing a 2–3-fold increase in CO₂ absorption, in comparison with DES in the absence of MEA. *N*-methyldiethanolamine solutions in choline chloride:ethylene glycol DES were studied by Mahi et al.,⁶⁴ who reported large capturing ability for the solutions. Adeyemi et al.⁶⁵ incorporated MEA as HBD into the DESs (as well as other amines) using choline chloride as HBA; these amine-based DESs shown are ~3 times larger than that observed for MEA–water solutions and 16 times larger than for conventional DESs (e.g., choline chloride:glycerol). These results were confirmed by Li et al.,⁶⁶ who also reported high solvent stability, as well as short adsorption times. Additional amine-functionalized DESs were reported by Sarmad et al.⁶⁷ considering choline chloride as the HBA and different amines (ethanol amine, diethanolamine, methyldiethanol amine, amino ethyl piperazine, and piperazine) as HBDs; these authors did not report a remarkable increase of CO₂ solubility, when compared with non-amine-based DESs, the values being in the range of those for choline chloride:urea compounds, which is not in agreement with other experimental studies. Similarly, all of the amine-based DES reported by Sarmad et al.⁶⁷ showed a large increase of viscosity upon CO₂

capture. Haider et al.⁶⁸ considered DESs based on several ammonium chloride or bromide as HBA and 2-methylamino ethanol or 2-ethylaminoethanol as HBDs, showing larger CO₂ solubilities than for other amine-based DESs or ILs, but, in this case, having lower solubilities than those observed for MEA aqueous solutions, in contrast with the results from Mahi et al.⁶⁴ Haider et al.⁶⁸ also confirmed the large viscosity increase upon CO₂ absorption. Therefore, the main advantages of using amine-based DESs, or amines in DESs solutions, stand on the large capturing ability, a decrease in the evaporation of amine solvent, lower corrosion, and a decrease in solvent regeneration costs. Trivedi et al.⁶⁹ analyzed monoethanolamine hydrochloride:ethylenediamine DES, confirming the high CO₂ uptake ability. Similarly, these authors confirmed the lower solvent regeneration costs, because of lower heat of absorption, when compared with an aqueous alkanol amine solution; thus, together with the null volatility upon sorption–desorption cycles and the decrease in corrosion rates, by the hydrogen bonding protecting the main functional groups, it is confirmed that alkanol amine-based DESs are advantageous over traditional amine solutions. Nevertheless, it should be remarked that the large viscosity upon CO₂ capture and the slower absorption processes, in comparison with physical absorption, may lead to difficulties for the scaling up of these materials. Closely related azolide-based DESs, with ethylene glycol, were reported by Cui et al.⁷⁰

The modification of DES through the inclusion of additives has also been considered by Chemat et al.,⁷¹ using *L*-arginine for choline chloride:glycerol DES, showing the enhancement of CO₂ solubility by *L*-arginine addition. The Henry constant (in molality basis) for ChCl:glycerol (1:2), being 1.1835 MPa, decreases to 0.4435 MPa upon the addition of *L*-arginine at a ratio of 1:2:0.2.

The negative impact of water content on the absorption ability of DESs was circumvented by the design of hydrophobic DESs. Gu et al.⁷² designed DES considering polyamine chloride and thymol, showing an absorption capacity of 0.09 g CO₂/g

DES, which is larger than observed for most of the DESs available in the literature. Additional hydrophobic DESs were designed in the literature based on ammonium–decanoic acid combinations,^{73,74} leading to excellent CO₂ absorption ability.

Although DESs have probed excellent performance in the liquid phase for the capturing of CO₂, additional studies have been reported considering DESs supported on different materials. A CO₂-phillic membrane developed from choline chloride:ethylene glycol DES confined into graphene oxide nanoslits was designed by Li et al.,⁷⁵ the reported results showed large changes in the DESs upon confinement, which led to outstanding separation performance, thereby forming a suitable membrane for CO₂ capture. Graphene oxide + DESs membranes were also developed by Mubasir et al.,⁷⁶ confirming suitable permeability, durability, and selectivity. Similarly, DESs confined in graphite or rutile,⁷⁷ nanoporous or mesoporous silica,^{78,79} laminated MXene,⁸⁰ metal organic frameworks,⁸¹ or immobilized on polymeric membranes,⁸² probed how the performance of DESs can be improved through interaction and confinement with suitable materials, thus allowing the development of membranes for CO₂ capture.

2.1.2. Sulfur and Nitrogen Compounds. The performance of DESs for capturing toxic sulfur gases (SO₂ and H₂S) and nitrogen (NO_x and NH₃) was recently analyzed by Chen et al.³⁰ The capturing ability for SO₂ is reviewed in Figure 4 for those DESs that are able to absorb amounts larger than 1 g SO₂ per g of DES. Although not included in Figure 4, reasonably large amounts of SO₂ may be captured using common DESs such as ChCl:urea (0.35 g SO₂/g DES), which may be improved using thiourea as HBD (0.88 g SO₂/g DES).⁸³ Results in Figure 4 show that the use of alkylimidazolium-based DESs led to SO₂ capture above 1 g SO₂/g DES;^{84,85} in fact, most of the available literature reporting larger absorbed amounts of SO₂ considers imidazolium-based DES. The increase of alkyl imidazolium amount into the DES formulation increases the amount of absorbed SO₂ (see Figure 4). Theoretical calculations reported by Atilhan et al.⁸⁶ showed the prevailing role of cation–SO₂ interactions for the DES performance, with imidazolium cations leading to large interaction energies with the SO₂ molecules, which would justify the suitable capturing ability of imidazolium-based DESs, as reported in Figure 4. Despite these suitable SO₂ capturing abilities for imidazolium-based DES, the poorer biodegradability, larger toxicity, and higher costs of these DESs, in comparison with ammonium-based ones, should be noted.^{41,87} DESs based on caprolactam and acetamide show SO₂ capturing abilities above 1.5 g per g of DES, which confirm their suitability for application on an industrial scale (Figure 4). Therefore, the reported literature shows SO₂ capturing abilities in the 0.2–1.7 g SO₂/g DES range³⁰ (Figure 4) for very different types of DESs, which are larger than those for CO₂, thus showing DES as a suitable platform for developing SO₂ capturing operations; thus, a suitable selection of DESs can be done considering both the capturing ability as well as suitable thermophysical properties, cost, and toxicological and biodegradability aspects. Nevertheless, studies considering non-imidazolium-based DESs are required, considering the scarcity of information for these systems and keeping in mind the technoeconomical and environmental problems involved with the use of imidazolium cations for the development of DESs.

In the case of the highly toxic H₂S, Figure 5 shows the most relevant literature results. ChCl:urea DES was studied by Liu et al.,⁴⁸ with $K_{\text{H}} = 3.57$ MPa (in mole fraction basis) for a 1:1.5 molar ratio, which shows suitable affinity of this DES for H₂S.

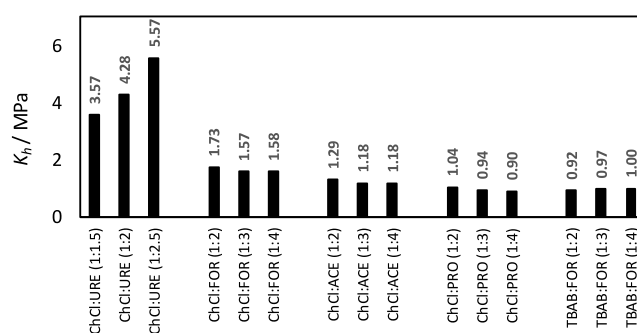


Figure 5. Henry's law constant (in molality basis), k_{H} , for the absorption of CO₂ in DESs.^{48,96} (Legend: TBAB, tetrabutylammonium bromide; FOR, formic acid; ACE, acetic acid; PRO, propanoic acid.) All data were obtained at 298.15 K, except for ChCl–URE, which were obtained at 313.15 K.

The increasing amount of URE in the DES leads to a decrease in absorbed H₂S, which can be justified considering that H₂S molecules develop hydrogen bonding with ChCl and interactions with the URE HBD are minor.⁴⁸ Therefore, the cation–H₂S interactions via hydrogen bonding are pivotal for the design of suitable DESs for H₂S absorption. In the case of ChCl-based DES with organic acids as HBDs (formic, acetic or propionic acids), results in Figure 5 show larger solubilities than for URE, which may be justified considering the stronger Lewis acid character of the HBD and, thus, the possibility of interacting with the absorbed H₂S also via the considered HBD. In this case, the effect of HBA:HBD molar ratio is very minor, compared to URE systems, and the H₂S solubility even increases with HBD (organic acid) content. Similarly, the replacement of ChCl as HBA by TBAB (tetrabutylammonium bromide) leads to larger H₂S solubilities. Therefore, the interaction of the H₂S molecules with the DES is justified by the formation of hydrogen bonding;⁴⁸ thus, the stronger the hydrogen bonding, the larger the capturing ability of the DES. Wu et al.⁹⁶ considered alkylammonium bromide-based DESs leading to K_{H} values of <1 MPa, which are lower than those for choline chloride-based ones, although the mechanism of H₂S capture stands on the development of strong hydrogen bonding in both cases. Therefore, DESs, even common ones such as choline chloride ones, can be used for developing H₂S capture operations.

The capturing of NO_x (NO₂ and NO) has also been considered, although the available experimental and theoretical information is very scarce. For the case of NO₂, theoretical studies probed the affinity for NO₂ of choline chloride-based DESs,⁹⁷ especially when thiourea is considered as HBD, which is developed through charge–dipole interactions; thus, these DESs could be used for NO₂ capture operations. Chen et al.⁹⁸ determined experimentally the NO₂ absorption in choline chloride:glycerol or choline chloride:ethylene glycol (see Figure 6), showing values in the 0.36–0.55 g NO₂/g DES range, with larger absorption for ethylene glycol at the 1:4 ratio, the obtained K_{H} values are lower than those for commercial sorbents and are in the range of studied ILs.⁹⁹ In the case of increasing amounts of HBD in the DES, the NO₂ solubility is also increased (see Figure 6), which is justified considering the stronger NO₂–HBD interaction when compared with that for ChCl,⁹⁷ thus improvements of NO₂ solubility in DES may be achieved by the selection of suitable HBDs strongly interacting with the gas molecules.

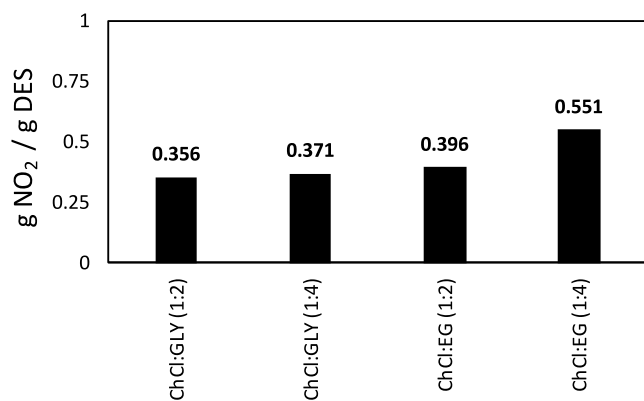


Figure 6. Experimental solubility data for SO₂ in selected DESs. Data taken from the available literature.⁹⁸

In the case of NO, several DESs were probed to be suitable for capturing this gas. Sun et al.¹⁰⁰ studied 1,3-dimethylthiourea-based DESs showing excellent performance with up to 4.25 mol NO per mol DES. Zhang et al.¹⁰¹ considered azole-based DESs with NO solubility of up to 2.1 mol NO per mol of DES, with the main advantage of these DESs standing on their low viscosity, which even decreases upon NO absorption. Amine-based DESs were considered by Wu et al.¹⁰² with an absorption capacity of up to 0.33 g NO per g DES at 303 K. Atilhan et al.¹⁰³ reported theoretical studies on NO solubility in arginine-based NADES probing large DES-NO affinities, thus considering NADES as a suitable alternative for NO absorption. Nevertheless, the scarcity of experimental and theoretical information requires specific design of DESs with properties tailored for NO absorption.

Finally, DES ability for absorption of NH₃ has been considered with a large number of DESs being studied.³⁰ DESs with largest absorption abilities are reported in Figure 7. Common ChCl-based DES are not suitable for NH₃ absorption

purposes, e.g., ChCl:urea 1:2 absorbs 0.01 g per g of DES.¹⁰⁴ In contrast, complex DESs including ChCl and two types of HBDs have been reported showing large NH₃ solubility (see Figure 7). Choline chloride-based DES with resorcinol/glycerol as HBDs, thus leading to absorption of up to 0.13 g NH₃ per g DES at 313 K, which considering the natural origin of the DES, low cost and biodegradability justify the possible use of these DESs for NH₃ absorption operations. Similarly, ChCl:tetrazole:EG DES shows 0.17 g NH₃ per g DES at 313 K. Therefore, a large NH₃ capturing ability has also been reported for choline chloride-based DESs considering many different types of HBDs,¹⁰⁵ although developing complex DES formulations through the selection of suitable HBDs in selected molar ratios. Moreover, DESs based on other compounds such as amine-based ones¹⁰⁶ or azole-based ones¹⁰⁷ (Figure 7) also lead to large solubilities for NH₃. Therefore, DESs are also suitable platforms for developing NH₃ absorption operations, even considering simple choline chloride-based DESs, thus being advantageous over traditional solvents or ILs.^{30,104}

2.2. Fuel Desulfurization Process. Sulfur compounds in fuels are a large environmental problem, because they are converted to SO_x¹¹² which may lead to acid rain, and sulfate particular matter, which has been strongly correlated with severe public health problems.¹¹³ Similarly, sulfur compounds poison catalytic devices used in vehicles for treating exhaust gases.¹¹⁴ Other undesired effects of these compounds stand on corrosion results in combustion engines and refining devices, which, together with poisoning of catalysts used for downstream and hydrocarbons upgrading, justify the large relevance of deep desulfurization processes for the petroleum industry.¹¹⁵ European Union regulations (Euro 5) limit the sulfur concentration in fuels to 10 ppm,¹¹⁶ and the USA regulations for diesel standard are limited to 10 ppm for gasoline or 15 ppm for diesel.¹¹⁷ Therefore, the desulfurization of fuels is a required operation in the petroleum industry for decreasing the

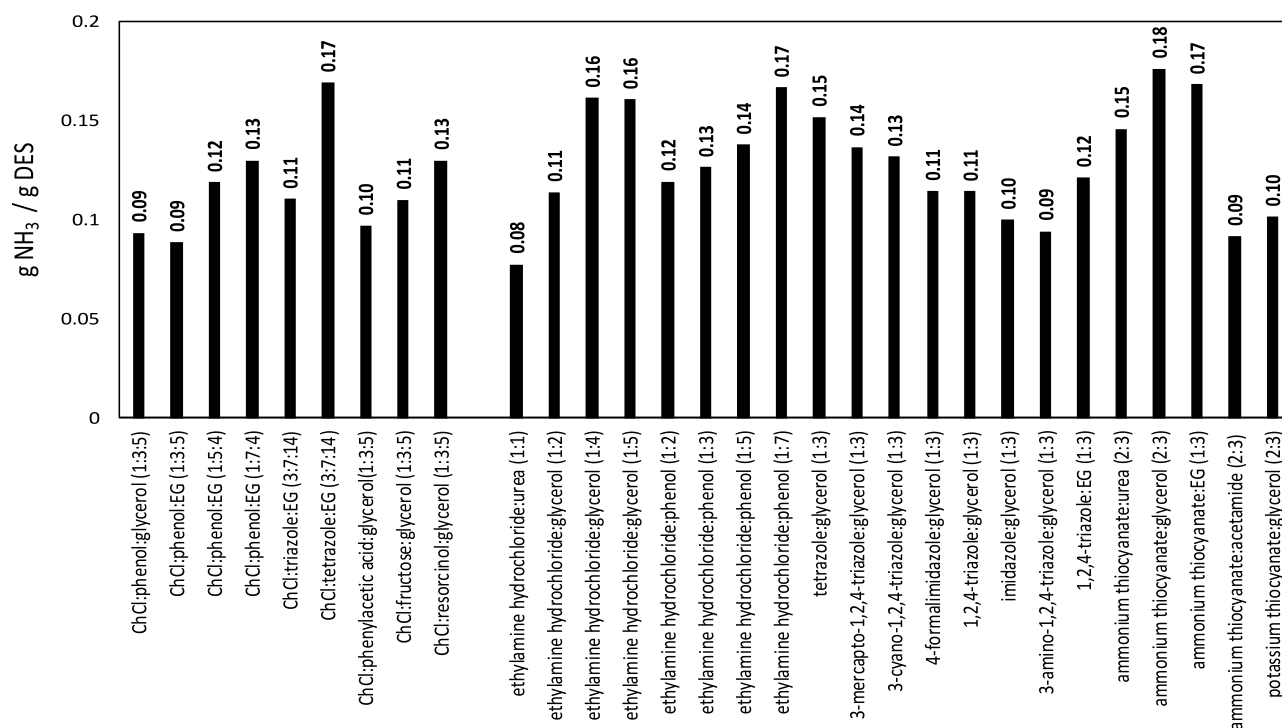


Figure 7. Experimental solubility data for NH₃ in selected DESs. Data taken from the available literature.^{104,106–111}

environmental impact of fossil fuels combustion and assuring the performance of fossil-fuels-related operations.

The available main technologies for fuels desulfurization are hydrodesulfurization technology (HDS), and oxidative, adsorption, biological, and solvent extraction.¹¹⁸ HDS is the most used technology for desulfurization processes on an industrial scale,¹¹⁹ but although being effective for aliphatic hydrocarbon sulfur removal, it shows problems for the deep removal of polycyclic organic sulfides such as thiophene (TP), benzothiophene (BT), dibenzothiophene (DBT), and their derivatives.¹²⁰ Similarly, operational conditions for HDS lead to a substantial increase of the desulfurization costs. Therefore, new technologies are required among those extractive desulfurization can be considered as suitable option, because of its low costs and high desulfurization efficiency.¹²¹ Nevertheless, the selection of solvents is required to ensure the suitability of the technology, for the use of organic solvents, because of their volatility, toxicity, and low biodegradability issues.¹²² Therefore, new solvents have been explored to fulfill requirements of ultradeep desulfurization by extraction at low cost with suitable environmental properties. Among these group of new solvents, ILs,^{123,124} as well as DESs,^{125–127} have attracted great attention in the literature. ILs have been successfully studied for desulfurization processes and showed a high extractive ability for many different types of sulfur compounds; nevertheless, some concerns rising from their cost and the difficulties for scaling-up the processes, as well as concerns on their environmental fate,^{128,129} have attracted more interest to DESs as alternative solvents for extractive desulfurization.

The literature shows different types of DESs that have been considered for extractive desulfurization purposes. Cheng et al.¹³⁰ developed a screening procedure based on the COSMO-RS method using DBT and *n*-octane as model oil. A large effect of HBA and HBD components of the DESs is inferred, showing tetrabutylphosphonium bromide:dimethylformamide (1:3), leading to the highest performance with the sulfur content reduced from 500 ppm to 9.8 ppm after three extraction cycles with the desulfurization ratio of the first cycle being 82.1%, similarly showing facile solvent recycling. Although Cheng et al.¹³⁰ showed lower performance for ChCl-based DESs, in comparison with other HBAs such as alkylammonium or alkylphosphonium, several studies have considered ChCl-DES for desulfurization purposes, mainly because it is among the lowest-cost HBAs. The most relevant DES for desulfurization purposes are summarized in Figure 8. Makos et al.¹³¹ reported extraction of thiophenes using ChCl and aromatic HBDs, showing a 99.99% removal in three stages extraction using ChCl:phenol (1:4) DES, with the techno-economic analysis showing excellent performance at a low cost. Other HBDs have been considered using ChCl as HBA, such as glycerol,¹³² organic acids,¹³³ and FeCl₃,¹³⁴ or even forming extractive nanofluids when combined with nanoparticles.¹³⁵ Most of these ChCl-based DESs have been proven to have suitable extractive ability, stability, and recyclability, thus confirming this type of DESs as a platform for developing solvents for sulfur extraction at moderate cost. Additional families of DESs have been considered in the literature beyond the ChCl type, e.g., based on polyethylene glycol,¹³⁶ alkylammonium bromide,¹³⁷ or alkylimidazolium,^{89,138} with most of the cases reporting deep desulfuration (sulfur content <10 ppm) in 3–5 extraction cycles. In the case of tetrabutylammonium chloride (TBAC)-based DESs, results in Figure 8 show lower performance than ChCl-based ones. Similarly, the easy procedure for regenerating the

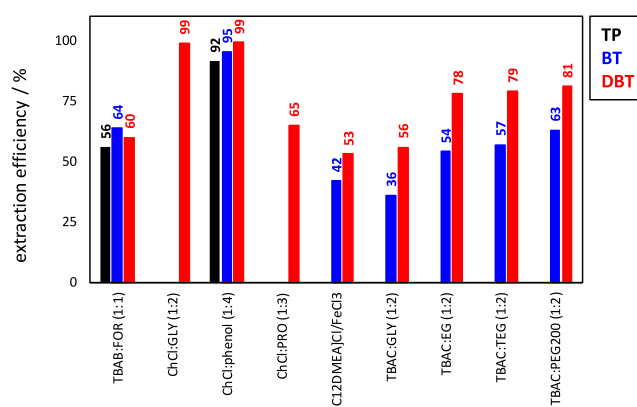


Figure 8. Extraction efficiency for sulfur compounds using selected DESs. All values reported for DES extractant:oil 1:1 ratio.^{125,131–133,136,139}

DESs is another factor favoring the industrial use of these solvents.

Regarding the factors controlling the DESs performance for desulfurization purposes, the large effect of viscosity has been shown, i.e., when HBA:HBA ratios lead to large variations of viscosity, those ratios with lower viscosity lead to large extractive ability.¹³¹ The effect of physical properties, HBA:HBD ratios, temperature, extractant volume, and other factors have been studied and optimized through response surface methodology¹³³ or central composite design.¹³¹

The molecular level roots determining the mechanism of DES–sulfur compounds interactions have been analyzed using different theoretical methods. Quantum chemistry calculations, using density functional theory (DFT), allowed to analyze the nature of intermolecular forces controlling sulfur compounds extraction. Wagle et al.¹⁴⁰ studied the interaction between aromatic sulfur compounds and choline chloride:urea or choline chloride:ethylene glycol 1:2 DESs, showing noncovalent interactions of the sulfur compounds with the cholinium and HBD compounds, whereas the chlorine anion is not interacting. Similarly, it is demonstrated that the DESs does not lead to hydrogen bonding with the aromatic sulfur compounds and the structure of the DES is not affected by the interaction with the sulfur compounds, with HBA:HBD hydrogen bonds without suffering any change.¹³¹ Classical molecular dynamics simulations were performed to study the behavior of alkylammonium chloride-based DESs including metal compounds, with regard to aromatic sulfur compounds; the reported simulations were allowed to infer the effect of composition and conditions on the effectiveness of extraction, determining how being close to ambient conditions improve the solvent–sulfur compounds interactions.¹⁴¹ Additional studies on ammonium-based DESs were reported proving the organosulfur compounds interactions with the alkylammonium cation, which leads to efficient extraction from model oils; similarly, the structuring of the DESs remained almost unchanged by the presence of the sulfur compounds.

2.3. Separation and Extraction Processes. DESs have been applied in the oil and gas industry for several relevant applications as alternative media for traditional operations. DESs have been successfully considered for separation and extraction operations relevant for the oil and gas industry, as summarized in Figure 9. Aromatic nitrogen compounds (basic six-membered rings, and nonbasic five-membered rings) are difficult to remove and the commonly applied hydrodenitrifi-

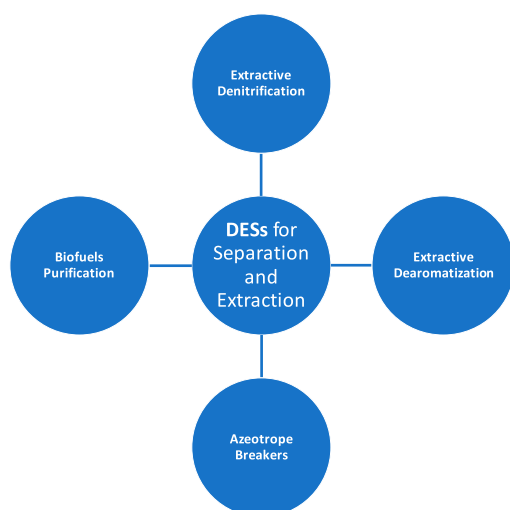


Figure 9. Main separation and extraction operations involving DESs.

cation operations requires harsh conditions, therefore extractive denitrification has been proposed in parallel to extractive desulfurization; thus, the use of DESs for extractive denitrification operations has been considered. Hizaddin et al.¹⁴² used the COSMO approach to predict the extractive denitrification ability of 94 different DESs, showing the prevailing role of hydrogen bonding as the driving force for the extraction of aromatic nitrogen compounds. Ammonium-based DESs, including choline chloride, showed the largest selectivity, whereas phosphonium-based ones showed the largest extractive capacity. The type of HBD has also a large effect on the nitrification ability whereas the HBA:HBD ratio has a minor effect. Experimental studies have probed the extractive denitrification of DES; Rogosic et al.¹⁴³ considered choline chloride:propylene glycol for the extractive denitrification of gasoline, using pyridine as a model compound, showing a 45% reduction in a single-step extraction. Extraction of NO₂ have also been probed using choline chloride-based DESs by Waite et al.,⁹⁷ showing the prevailing role of dispersion interactions, being largely favorable for choline chloride:thiourea DES. Similarly, the possibility of designing DESs for the concurrent desulfurization and denitrogenation operations has been probed; Lima et al.¹⁴⁴ used tetrabutylphosphonium bromide:sulfolane DES with close to 99% elimination of sulfur and nitrogen compounds in less than four extraction cycles.

Fuel dearomatization operations have also been proposed using DESs.¹⁴⁵ Choline chloride-based DESs were considered for the dearomatization of gasolines by Larriba et al.,¹⁴⁶ showing excellent performance by using choline chloride:levulinic acid DESs. The reported results showed an extraction of 99.6% for benzene and 96.4% for toluene; thus, considering the restrictive regulations on benzene content for gasoline probes, these DESs are suitable extractant agents. Similarly, the results showed suitable recovery and solvent regeneration, thus leading to this DES as a suitable, inexpensive, and nontoxic solvent for aromatics recovery. Similarly, simultaneous dearomatization, denitrification, and desulfurization of fuels has been proposed; Kucan et al.¹⁴⁷ (betaine-based DES), Rogosic et al.¹⁴⁸ (choline chloride-based DES), and Warrag et al.¹⁴⁹ (phosphonium-based DESs) probed the efficient simultaneous removal of these compounds with a reasonable number of extraction steps and full recovery of the solvent. The removal of additional fuel contaminants was also considered using DESs. Mercury removal

from oil and gas was probed by Warrag et al.,¹⁵⁰ using choline chloride-based DESs leading up to 97% removal, which is being justified by the strong interaction of the Hg atoms with the Cl⁻ anion in the DESs.

The purification of biofuels with DESs has been successfully studied. Ammonium-based DESs were considered for the glycerol removal from crude biodiesel, choline chloride:glycerol DES reduces glycerol content up to 0.02 wt % with extraction yields of >50%.¹⁵¹ Ammonium and phosphonium DESs for glycerol removal from biodiesel were studied by Shahbaz et al.¹⁵² probing the largest extraction using phosphonium-based DES with glycerol as HBD. Therefore, it has been probed the use of DESs, mainly choline chloride-based ones for the reduction of glycerol content in biodiesel beyond the regulated limits.¹⁵³ Moreover, into a circular economy framework, glycerol waste byproduct from biodiesel synthesis has been proposed as a starting material for the fabrication of DESs, with the produced DES being applied for the subsequent biodiesel purification and upgrading (see Figure 10).¹⁵⁴

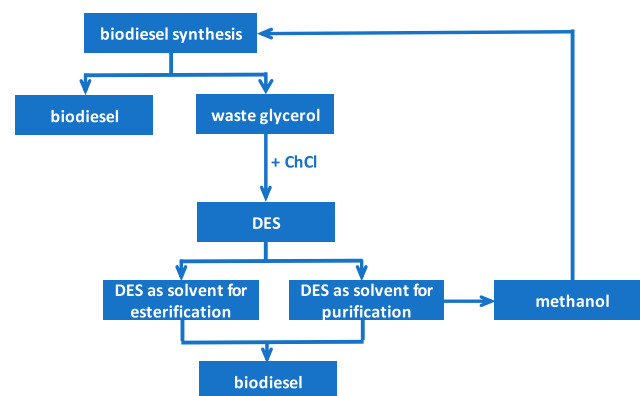


Figure 10. Scheme of DES use for biodiesel production and purification in the case of ChCl:glycerol (1:2).¹⁵⁴

Other relevant separation operations considering DESs involve their use as azeotrope breakers. Peng et al.¹⁵⁵ considered the ethanol + water binary mixture showing how the addition of 10 wt % ChCl:urea (1:2) led to the vanishing of azeotrope (see Figure 11a). Similarly, Jiang et al.¹⁵⁶ considered choline chloride:urea and choline chloride:glycerol (1:2 ratios) for the separation of allyl alcohol and water solutions, probing that the addition of the DES eliminates the azeotropic point with DES amounts in the range of 10–15 wt % (Figure 11b).

2.4. Water Treatment. One of the grand challenges of the 21st century is highlighted as water security and access to freshwater resources. Water scarcity motivated the scientific community to tackle this problem and develop novel technologies for water purification, treatment, and reuse. Besides process management issues, the most common and scientifically challenging issue with water treatment is removal of the hazardous materials, such as toxic metal ions and bacteria. The presence of metallic species in water has toxicological implications and can lead to chronic poisoning as they are absorbed by living organisms.^{157,158} Extreme exposure to toxic metal ions via bioaccumulation is known to cause health problems (such as mammalian cancer, nervous-system-related failures, and the collapse of organs such as the heart, kidney, and lungs, leading to respiratory disease, brain malfunctioning) and can cause fatality.^{159–162} Thus, it is critically important to provide fast, accurate, and reliable alternative solutions for the

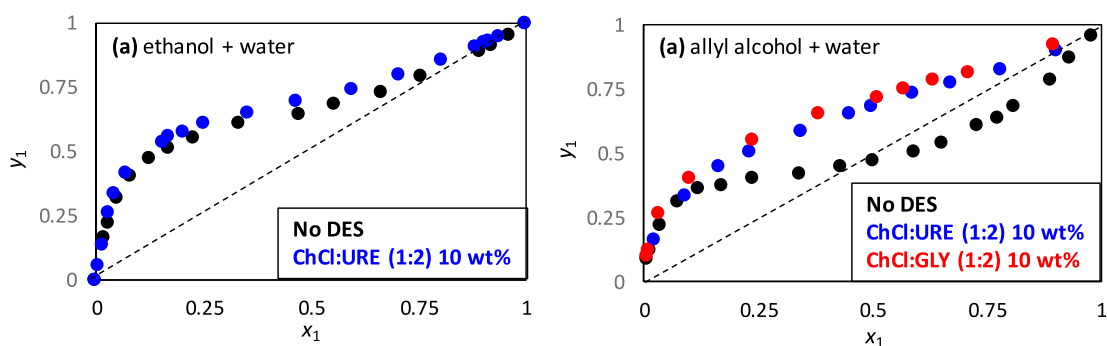


Figure 11. Isobaric (101.3 kPa) vapor–liquid equilibria for (a) ethanol + $(1 - x_1)$ water¹⁵⁵ and (b) x_1 allyl alcohol + $(1 - x_1)$ water¹⁵⁶ mixtures without any additive (no DES) and with the addition of the indicated DESs.

treatment of such compounds in water, and that has been one of the top priorities of both academia and industry over the last couple of decades. In recent years, DESs have been considered as one of the alternative water treatment chemicals for this purpose and in this section, advances in water treatment by using deep eutectic solvents has been reviewed and analyzed.

2.4.1. Metal Ion Removal. Classical adsorption method has been considered as one of the most common water treatment and metal-ion-removal techniques.¹⁶³ In recent years, because of their unique thermophysical and chemical properties, nanoparticles have been considered to be state-of-the-art adsorbents for many pollutants for water treatment, because of their unique features.¹⁶⁴ In this regard, because of their extraordinary physical, electrical, and chemical properties, carbon nanotubes (CNTs) are the most commonly used nanomaterial for water treatment,¹⁶⁴ including the capture of cadmium,¹⁶⁵ copper,¹⁶⁶ zinc,¹⁶⁷ lead,¹⁶⁸ 1,2-dichlorobenzene,¹⁶⁹ fluoride,¹⁷⁰ and trihalo-methanes.¹⁷¹ However, some disadvantages have been reported for CNTs, including poor solubility, aggregation, and difficulty of manipulation, which remains a major challenge and limitation on CNTs becoming an option for industrial use. Functionalization of CNTs is a key enhancement step, through which such drawbacks can be eliminated, if not minimized. For this purpose, functionalization of CNTs with DESs has been considered in recent years and applications on ion removal have been demonstrated for such compounds.

The presence of lead (or Pb(II)) in water causes a variety of health problems and has gained enormous concern worldwide, because of its specific effects on children.¹⁷² Most recent techniques on Pb(II) removal in water focuses on adsorptive methods utilizing rice husks, maize cobs, sawdust,¹⁷³ aquatic plants,¹⁷⁴ kaolinitic clay, giru clay,¹⁷⁵ and granulated blast-furnace slag.¹⁷⁶ Most recent efforts concentrated around utilization of CNTs for this purpose,^{177–182} such as nitric-acid-functionalized CNTs,¹⁸³ manganese oxide-CNT (CNT/MnO₂) nanocomposites,^{184,185} alumina-coated CNTs¹⁸⁶ and titanium dioxide/CNT (TiO₂/CNT) nanocomposites.¹⁸⁷ Despite reasonable progress via these functionalized combinations, there is still a need on more economically feasible and environmentally friendly functionalization agents; and thus, DESs have been considered for this purpose in recent years. In a study by AlOmar et al.,¹⁶³ choline chloride-based DESs were used as functionalization agents for KMnO₄-treated CNTs, HNO₃-treated CNTs, and H₂SO₄-treated CNTs, and their capacity to absorb Pb(II) from water was measured. They have reported that the Pb(II) adsorption behavior can be explained using a pseudo-second-order kinetics model and they have obtained a maximum adsorption capacity of as high as 288.4

mg/g for CNTs functionalized with KMnO₄ and TEG-based DES (KTEG-CNTs) through Langmuir isotherm analysis.

Similar to Pb(II), nickel is an essential element for living organisms in small quantities; however, it becomes toxic and hazardous at high concentrations through bioaccumulation.¹⁸⁸ Thus, nickel content at levels that are higher than the permissible levels in water resources must be eliminated, if not reduced to allowable limits.¹⁸⁹ To date, different methods have been used for the removal of Ni metal ions from water supplies, such as ion exchange, chemical deposition, membrane separators, microbial precipitation, biosorption, and adsorption.^{190–192} Similar to the case for Pb(II) removal, one of the most compelling methods is the use of CNTs and especially multiwall carbon nanotubes (MWCNTs) to remove Ni ions from a water source.¹⁹³ Ghani et al. reported a nickel adsorption capacity of 6.9 mg g⁻¹ (mg of nickel per g of MWCNTs). In order to enhance the adsorption performance, MWCNTs are functionalized because they have a high tendency to react with different materials negatively affecting their adsorption efficiency, capacity, and selectivity. These issues have been enhanced with proper functionalization groups on MWCNTs surface.^{164,194–196} Despite the improvement in physical properties and sorption performances achieved through the functionalization of MWCNTs via sulfuric acid and nitric acid, their hazardous chemical nature and toxic features does not make them favorable choices for proper functionalization.^{197,198}

Use of DES for functionalization of MWCNTs has been considered as a green technique by Rahmani et. al in a recent study. Tetra-*n*-butyl ammonium bromide (TBAB)- and glycerol (Gly)-based DESs have been considered as functionalization agents. MWCNTs functionalized by TBAB:Gly DES have shown the ability for nickel removal at maximum adsorption capacity and maximum removal percentage of 115.8 mg g⁻¹ and 93%, respectively, under reported optimum conditions with the reusability of 7 times.¹⁶³

Functionalization of MWCNTs with DESs were also used for the capture and removal of Hg²⁺, Cd²⁺, Pb²⁺, and Cr⁶⁺ as well.¹⁹⁹ The development of a biosensor based on glucose oxides immobilized on novel ultrathin poly(brilliant green) (PBG) films electrodeposited in ethaline DES on MWCNT-modified glassy carbon electrodes (GCE) for the trace amount of metal ion detection. The mechanism of reversible inhibition was found to be competitive for Hg²⁺ and Cd²⁺, uncompetitive for Pb²⁺, and mixed for Cr⁶⁺.

Furthermore, DESs functionalized MWCNTs were also considered for the removal of mercury and arsenic in several other studies.^{200,201} AlOmar et al. used methyl triphenylphosphonium (MTPB) and benzyl triphenylphosphonium chloride

(BTPC) salts combined with Gly to form DESs to functionalize MWCNTs for the removal of As metal ions from water. This study resulted in the superior performance of MTPB:Gly functionalized MWCNT and provided maximum adsorption capacity and removal percentages of 23.4 mg g⁻¹ and 95.5%, respectively.²⁰² In another study, TBAB-based DES-functionalized MWCNTs showed good performance on mercury removal from water with an adsorption capacity of 177.76 mg g⁻¹ and a removal percentage of 96.3%.¹⁹ Utilization of DESs made these studies possible and demonstrated the potential of DES and their promising applications for water treatment purposes.

2.4.2. Water Purification. In addition to metal ion removal, DESs have been considered to remove various other contaminants, such as fluorine, iodine, and bisphenol from water.

Fluorine is the world's 13th most abundant element, has the highest electronegativity, and is one of the most reactive elements.²⁰³ It has various industrial uses such as nuclear fuel processing, high-temperature plastics (e.g., Teflon), and synthesis material to produce sodium fluoride and hydrofluoric acid. One of the most widely known fluorine uses was discovered in the early 1900s, and it was suggested to be used as an additive in toothpaste to prevent dental cavities, for which the benefits and harms still have been debated since its introduction in the USA in the 1950s. There have been concerns raised on fluorine use because it is considered to cause cognitive impairment, hypothyroidism, enzyme and electrolyte derangement, and uterine cancer, because of its toxic nature. Therefore, there has been a trend in the reduction, if not the elimination, of fluorine for children's dental treatments. More improvements in water treatment to reduce the fluoride level have been discussed for occupational health and safety practices purposes; thus, DESs have been considered from this perspective. Alternative methods that use DESs on the removal of fluorine in contaminated groundwater were proposed by Sharma et al.²⁰⁴ Graphene nanosheets were functionalized to contain metal oxides, and for this purpose, ChCl were combined with metal salts (as HBD), and several DESs such as ChCl–FeCl₃ (1:2), ChCl–ZnCl₂ (1:2), and ChCl–SnCl₂ (1:2) DESs were used in this work. DES-modified graphene nanosheets could remove fluoride from the water with 75%–87% removal efficiency. The concern regarding the presence of metal salts in DESs and their potential transfer to the water was also studied and ruled out, since no trace amount of metal ions were observed after the treatment process. Thus, the final DES-modified graphene structure has been reported to be very stable for repeated trials for the intended purpose. The biocompatibility of the studied compounds was also studied through cytotoxicity measurements, and it was proved that these compounds do not impose any toxic effect against humans. This study paves the way to the utilization of DESs for water treatment, and there is a great potential to test several HBA and HBD among their more environmentally benign alternatives.

In another study by Florindo et al., the utilization of hydrophobic DESs for micropollutant removal in water reservoirs has been studied. Despite their small concentration in water streams, Bisphenol-A (BPA) have been hazardous to both humans and animals due to their carcinogenic and endocrine-disrupting effects. The need behind moving toward DES-based BPA removal is simply because of the high cost of the current state-of-the-art solvents and their issues with reusability. Thus, more environmentally friendly and highly recyclable DES

have been considered for this purpose. Extraction of BPA from water sources were evaluated by utilizing DESs, which were obtained through natural compounds. D,L-Menthol was used as an HBA and different quaternary ammonium salts with long alkyl chains were used as HBD in the study by Florindo et al. In particular, [N7777]Br, [N8888]Br, and [N8881]Br were used as HBD. Various DESs (e.g., alternate molar mixing ratio of HBA/HBD) and BPA removal process variables such as stripping speed, contact time, and DES/water ratio were considered in this study and marginal optimizations has shown almost 100% BPA removal with high reusability and recyclability when [N8888]Br:C₁₀ was used. Utilization of DESs for removal of BPA at such high efficiency is very attractive from economical point of view. In addition to high removal efficiency, it has been shown that multiple cyclic extractions are possible with DES-based BPA removal without losing the extraction capacity of the DESs.

Another application of DESs in water treatment has recently been studied for iodine removal in water disposal streams of nuclear power plants. Isotopes of iodine are produced as a result of power generation in nuclear power stations, and they impose severe threat to humans and habitat in general, since there is a risk that radioactive isotopes of iodine can be released to the atmosphere from the discharged water in these plants. Several materials have been considered for the capture and removal of iodine in water discharge streams and among those, activated carbon,²⁰⁵ zeolites,^{206–209} and metal-organic frameworks^{210–213} are the prominent ones, as per the literature. However, because of their poor iodine capture performance and high cost, alternative materials such as DESs have been considered for this purpose. Li et al.²¹⁴ have considered the synthesis of DESs based on ChCl as HBAs, which were coupled with conventional HBD (e.g., urea, glycerol, and other common organic acids) for iodine capture. Fu et al.²¹⁵ followed “greener” methods to produce DESs and used urea and guanidine hydrochloride for the same purpose. Both studies showed not only remarkable iodine capture performances (~100%) but also resulted in considerable storage efficiency. Although these studied DESs showed a slow iodine capture process, they did not exhibit any issues with reusability and recyclability. Li et al. also studied the specific effect of HBA and HBD effect on the iodine capture and they have shown that more-efficient iodine removal occurs as larger volume cations in HBA are used. This phenomenon was explained as follows: the larger volume of the cation weakens the electrostatic force between Cl⁻ and ammonium ions, thus leading to a stronger attraction between Cl⁻ and I⁻ ions. These studies suggest that DESs can be considered as an efficient agent for radioactive iodine removal from effluent water streams. However, there is still room for detailed investigation on the effect of HBA and HBD mixing ratios, optimization of iodine capture time with improved removal kinetics.

2.5. Biodiesel Production. In the past couple of decades, in order to respond to ever-increasing energy consumption rates and securing energy supply, but more importantly to combat human-caused climate change, various different energy sources have been explored and considered as an alternative to classical fossil-based fuels (e.g., oil and gas). Biodiesel is made from renewable resources such as vegetable oils, recycled (or wasted) cooking oils, algae, and animal fats.²¹⁶ Biodiesel has a great potential to create its local economy, especially in remote and rural communities, because its production steps do not require complex processing at small-scale applications. However, in order to ramp up its production capacity and consider it as an

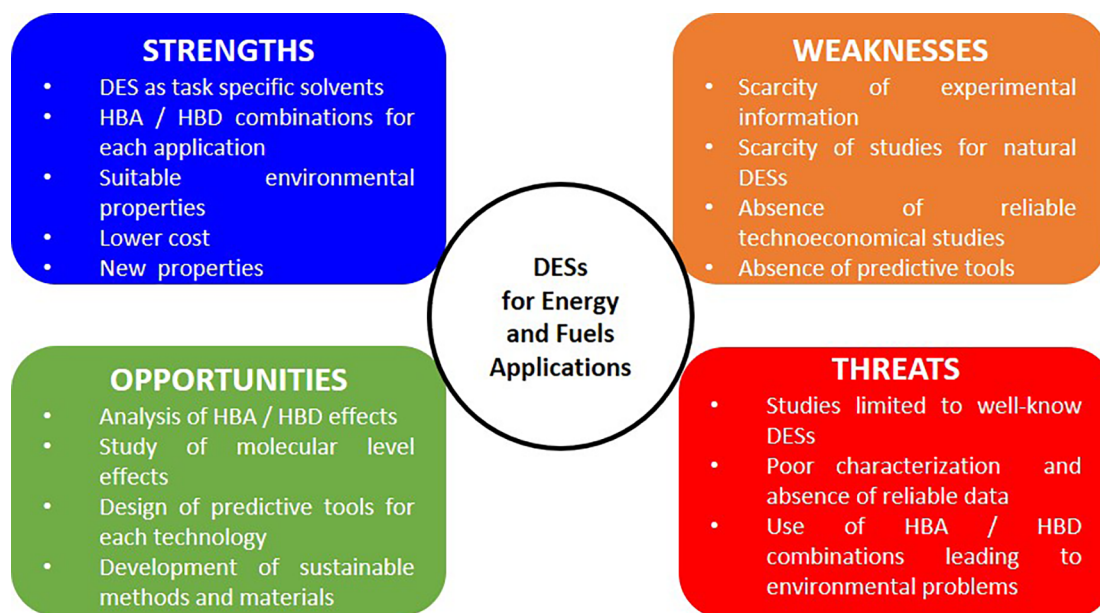


Figure 12. SWOT analysis of the application of DESs for energy and fuels technologies.

alternative fuel recourse for mass-scale applications, the process must be revamped on a more economical scale. In addition to economic concerns, increasing concerns on the environmental issues that are related with the current processing of biodiesel production lead to several reconsiderations, especially with regard to the catalyst selection and design of novel solvents for the extraction of lipids from the main resources. ILs have been studied as an alternative solvent to be employed in biodiesel production.²¹⁷ However, despite their promising performance, because of their toxic nature, high cost, and requirement of complex process steps, the search for alternative solvents has been an ongoing task in both academia and industry.^{218,219} As DESs provide several major advantages over the ILs, including simpler synthesis and preparation, low cost, biocompatibility, and low toxicity.²²⁰ Thus, in the past few years, the number of publications that focus on the utilization of DESs in biodiesel production has been on the rise.

In a recent study by Lu et al., biomass lipid extraction via three different DESs has been studied.²²⁰ In this work, aqueous compounds of choline chloride:oxalic acid, choline chloride:ethylene glycol, and urea:acetamide were studied for their effect on the lipid recovery rate. This study showed that when biomass is treated with DES, there was a significant lipid recovery rate with superior performance by relatively conventional choline chloride:oxalic acid DES. In a different study by Kim et al., integration of renewable DESs with biomass genetic engineering has been studied with the aim of moving toward achieving closed-loop biorefineries. Authors proposed the utilization of renewable biomass-based DESs for extraction of cellulose and sugars from specific biomass.²²¹ In this work, authors used various molar mixing ratios of ChCl + vanillin and ChCl + 4-hydroxybenzaldehyde as DESs. It has been claimed that DESs synthesized from phenolic aldehydes showed superior efficiency at biomass pretreatment. Furthermore, ChCl + 4-hydroxybenzaldehyde was more effective than ChCl + vanillin for lignin removal during pretreatment and sugar release upon saccharification, which is likely attributed to the strong intermolecular interaction in ChCl + 4-hydroxybenzaldehyde, compared to ChCl + vanillin.

Another study that uses DESs in biodiesel production focused on the utilization of DESs as a reaction medium rather than extraction solvent for enzymatic biodiesel production from waste soybean oils. A study by Merza et al. compared the ChCl-based DESs against their predecessors, ILs, for the biodiesel production yield.²²² In this study, ChCl is coupled with glycerol as HBD at various molar mixing ratios. Furthermore, water was also considered as a part of ternary DES system in order to reduce the highly viscous nature of the DES. It was shown that the 34% biodiesel production yield could be achieved by using the ChCl + glycerol DES system at a 1:2 molar mixing ratio, which was reported to be only 23% when [bmim][PF₆] IL was used. Moreover, in the case of 3% water addition to the DES, biodiesel yield has reported to reach to 44% at 45 °C. The main issue with the proposed production method was reported on the reusability of the DES for the intended purpose. It was observed that reusability of the DES decreased sharply after the first cycle of 60 min, because of the accumulation of undissolved glycerol in *n*-hexane, which was used as an extraction solvent. In order to improve this condition, authors proposed a two-solvent extraction system, which, in turn, have significantly improved the reusability of the DES with the additional cost involved with the extra solvent requirement. A similar attempt to utilize DESs as reaction medium on biodiesel production by using sesame oil.²²³ In this study, authors not only focused on the biodiesel yield rate, but also studied other processing parameters, such as the molar ratio of alcohol to oil and agitation speed at fixed temperature and contact time. A yield of 97.8% at 60 °C and 1200 rpm in reaction vessel was reported for the DES case with a 2:1 molar mixing ratio of ChCl and ethylene glycol.

3. CHALLENGES AND PERSPECTIVES

The successful application of DES for energy and fuels related technologies has been probed in this Review. The large number of HBA/HBD combinations constitutes a huge opportunity for developing new materials with suitable properties, as well with proper environmental behavior, in terms of toxicity, biodegradability, and sustainability. The main challenge associated with DESs-based technologies stands on the development of task-

specific DESs for each technology. Most of the available studies consider common DESs with well-known properties and behavior, which is a clear limitation on the applicability of DESs. The extension of DESs technologies to new types of fluids would require the development of predictive methods and tools, thus allowing the screening of suitable molecular combinations leading to *ex novo* and *in silico* design of DESs, improving the available methods. For this purpose, the development of systematic multiscale computational studies is required in order to get a deeper understanding of the DESs microscopic behavior, as well as its relationship with macroscopic properties. Similarly, another relevant challenge stands on the extension of DESs to sustainable and natural materials as well as the technoeconomical and life cycle analysis of DES-based technologies, which are almost absent in the literature. The analysis of the whole product cycle for DESs-based technologies is required to show their sustainability and to ensure avoiding the errors of previous technologies.

The use of DESs for energy and fuels technologies may be considered as a solution to current pivotal environmental and technological problems. The possibility of developing DESs based on low cost and natural origin sources allows one to establish technologies within a sustainable approach as well as into a circular economy viewpoint. Similarly, the number of HBA/HBD combinations leading to DES would lead to studies considering new groups of molecules, which are fitted to solve the current environmental problems into the energy area as well as for the treatment and use of nonrenewable fuel sources.

A strengths, weaknesses, opportunities, and threats (SWOT) analysis is included in Figure 12 to summarize the state-of-the-art for the application of DESs in energy and fuels technologies.

4. CONCLUSIONS

Because of the search for alternative green solvents in both academia and industry, there has been a noticeable boom in the recent studies that uses DESs and NADESs as emerging novel materials. Most recent literature on the utilization of DESs and NADESs has involved gas capture/separation, fuel desulfurization, biodiesel production, and water treatment processes. The available literature shows that DESs are a suitable alternative solvent for CO₂ capture. However, there is still a gap that must be filled on the performance of gas separation and selectivity via DESs when gas mixtures or flue gas are considered. However, literature findings showed that the possibility of tailoring the DES properties through the wise selection of HBA and HBD with different molar mixing ratios would yield the development a high throughput production of sorbents at lower cost and better physicochemical properties, in comparison to current state-of-the-art solvents.

Regarding to biodiesel synthesis and production process, DESs are used as catalyst media, cosolvents, and extracting solvents. Although there is still a lot to establish in this niche field, DESs being environmentally friendly makes the separation of biodiesel from the reaction mixture effortless and can be successfully reused. Additionally, the catalytic activity performance of DESs in biodiesel synthesis showed promising results in comparison to well-established conventional methods, which gives DESs leverage in future applications in this field. Similarly, for water treatment and fuel desulfurization, hydrophobic DESs have attracted considerable attention in extraction micro-pollutants, metal ions, and sulfur removal from oil (up to 99%). Thus, DESs has a bright future in industrial applications as

designer solvents for all these processes, and it is expected to attract more research works in the coming years.

AUTHOR INFORMATION

Corresponding Authors

Mert Atilhan – Department of Chemical and Paper Engineering, Western Michigan University, Kalamazoo, Michigan 49008-5462, United States; orcid.org/0000-0001-8270-7904; Email: mert.atilhan@wmich.edu

Santiago Aparicio – Department of Chemistry, University of Burgos, 09001 Burgos, Spain; orcid.org/0000-0001-9996-2426; Email: sapar@ubu.es

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.energyfuels.1c00303>

Notes

The authors declare no competing financial interest.

Biographies

Mert Atilhan graduated from Ege University and obtained his Ph.D. degree in chemical engineering from Texas A&M University. Dr. Atilhan is an Associate Professor at Western Michigan University in the Department of Chemical and Paper Engineering. He is active in applied and computational thermodynamics, as well as multiscale materials modelling with an emphasis on the development of novel materials for energy and environmental related fields.

Santiago Aparicio graduated from University of Burgos and obtained his Ph.D. degree in physical chemistry. He is a Professor of Physical and Theoretical Chemistry. He is director of the Consolidated Research Unit on New Materials for Energy and Environment. His research interests stand on the design and development of novel materials for energy, environmental, and biological applications using experimental and multiscale computational methods.

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REFERENCES

- (1) García, G.; Aparicio, S.; Ullah, R.; Atilhan, M. Deep Eutectic Solvents: Physicochemical Properties and Gas Separation Applications. *Energy Fuels* **2015**, *29*, 2616–2644.
- (2) Khajeh, A.; Shakourian-Fard, M.; Parvaneh, K. Quantitative Structure-Property Relationship for Melting And Freezing Points of Deep Eutectic Solvents. *J. Mol. Liq.* **2021**, *321*, 114744.
- (3) Dutta, S.; Nath, K. Prospect of Ionic Liquids and Deep Eutectic Solvents As New Generation Draw Solution in Forward Osmosis Process. *J. Water Process Eng.* **2018**, *21*, 163–176.
- (4) Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060–11082.
- (5) Abranches, D. O.; Martins, M. A. R.; Silva, L. P.; Schaeffer, N.; Pinho, S. P.; Coutinho, J. A. P. Phenolic Hydrogen Bond Donors in The Formation of Non-Ionic Deep Eutectic Solvents: The Quest For Type V DES. *Chem. Commun.* **2019**, *55*, 10253–10256.
- (6) Hansen, B. B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J. M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B. W.; Gurkan, B.; Maginn, E. J.; Ragauskas, A.; Dadmun, M.; Zawodzinski, T. A.; Baker, G. A.; Tuckerman, M. E.; Savinell, R. F.; Sangoro, J. R. Deep Eutectic Solvents: A Review of Fundamentals and Applications. *Chem. Rev.* **2021**, *121*, 1232–1285.

- (7) Beyersdorff, T.; Schubert, T. J. S.; Welz-Biermann, U.; Pitner, W.; Abbott, A. P.; McKenzie, K. J.; Ryder, K. S. In *Electrodeposition From Ionic Liquids*; MacFarlane, D. R., Abbott, A. P., Eds.; Wiley-VCH: Weinheim, Germany, 2008.
- (8) Zhang, N.; Huang, Z.; Zhang, H.; Ma, J.; Jiang, B.; Zhang, L. Highly Efficient and Reversible CO₂ Capture by Task-Specific Deep Eutectic Solvents. *Ind. Eng. Chem. Res.* **2019**, *58*, 13321–13329.
- (9) Perna, F. M.; Vitale, P.; Capriati, V. Deep Eutectic Solvents and Their Applications as Green Solvents. *Curr. Opin. Green Sus. Chem.* **2020**, *21*, 27–33.
- (10) Van Osch, D. J. G. P.; Dietz, C. H. J. T.; Warrag, S. E. E.; Kroon, M. C. The Curious Case of Hydrophobic Deep Eutectic Solvents: A Story on the Discovery, Design, and Applications. *ACS Sustainable Chem. Eng.* **2020**, *8*, 10591–10612.
- (11) Vanda, H.; Dai, Y.; Wilson, W. G.; Verpoorte, R.; Choi, Y. H. Green solvents from ionic liquids and deep eutectic solvents to natural deep eutectic solvents. *C. R. Chim.* **2018**, *21*, 628–638.
- (12) Vanda, H.; Dai, Y.; Wilson, E. G.; Verpoorte, R.; Choi, Y. H. Green solvents from ionic liquids and deep eutectic solvents to natural deep eutectic solvents. *C. R. Chim.* **2018**, *21*, 628–638.
- (13) Liu, Y.; Friesen, J. B.; McAlpine, J. B.; Lankin, D. C.; Chen, S. N.; Pauli, G. F. Natural Deep Eutectic Solvents: Properties, Applications, and Perspectives. *J. Nat. Prod.* **2018**, *81*, 679–690.
- (14) Marcus, Y. Applications of Deep Eutectic Solvents. In *Deep Eutectic Solvents*; Springer: Cham, Switzerland, 2019; DOI: 10.1007/978-3-030-00608-2_4.
- (15) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. Novel Solvent Properties of Choline Chloride/Urea Mixtures. *Chem. Commun.* **2003**, 70–71.
- (16) Ge, X.; Gu, C.; Wang, X.; Tu, J. Deep Eutectic Solvents (DESS)-Derived Advanced Functional Materials for Energy and Environmental Applications: Challenges, Opportunities, and Future Vision. *J. Mater. Chem. A* **2017**, *5*, 8209–8229.
- (17) Florindo, C.; Lima, F.; Dias-Ribeiro, B.; Marrucho, I. M. Deep Eutectic Solvents: Overcoming 21st Century Challenges. The Perspectives of Natural Deep Eutectic Solvents in Agri-food Sector. *Curr. Opin. Green Sustain. Chem.* **2019**, *18*, 31–36.
- (18) Misan, A.; Nadpal, J.; Stupar, A.; Pojic, M.; Mandic, A.; Verpoorte, R.; Choi, Y. H. *Crit. Rev. Food Sci. Nutr.* **2020**, *60*, 2564–2592.
- (19) Emami, S. E.; Shayanfar, A. Deep Eutectic Solvents for Pharmaceutical Formulation and Drug Delivery Applications. *Pharm. Dev. Technol.* **2020**, *25*, 779–796.
- (20) Liu, P.; Hao, J. W.; Mo, L. P.; Zhang, Z. H. Recent Advances in the Application of Deep Eutectic Solvents as Sustainable Media as Well as Catalysts in Organic Reactions. *RSC Adv.* **2015**, *5*, 48675–48704.
- (21) Roda, A.; Matias, A. A. A.; Paiva, A.; Duarte, A. R. C. Polymer Science and Engineering Using Deep Eutectic Solvents. *Polymers* **2019**, *11*, 912.
- (22) Zante, G.; Boltoeva, M. Review on Hydrometallurgical Recovery of Metals with Deep Eutectic Solvents. *Sustain. Chem.* **2020**, *1*, 238–255.
- (23) Warrag, S. E. E.; Peters, C. J.; Kroon, M. C. Deep Eutectic Solvents For Highly Efficient Separations In Oil And Gas Industries. *Curr. Opin. Green Sustain. Chem.* **2017**, *5*, 55–60.
- (24) Sander, A.; Petracic, A.; Parlov Vukovic, J.; Husinec, L. From Coffee to Biodiesel—Deep Eutectic Solvents for Feedstock and Biodiesel Purification. *Separations* **2020**, *7*, 22.
- (25) Nguyen, C. H.; Augis, L.; Fourmentin, S.; Barratt, G.; Legrand, F. X. Deep Eutectic Solvents for Innovative Pharmaceutical Formulations. In *Deep Eutectic Solvents for Medicine, Gas Solubilization and Extraction of Natural Substances*; Fourmentin, S., Costa Gomes, M., Lichtfouse, E., Eds.; Environmental Chemistry for a Sustainable World, Vol. 56; Springer: Cham, Switzerland, 2021; DOI: 10.1007/978-3-030-53069-3_2.
- (26) Chakrabarti, M. H.; Mjalli, F. S.; AlNashef, I. M.; Hashim, M. A.; Hussain, M. A.; Bahadori, L.; Low, C. T. J. Prospects of Applying Ionic Liquids and Deep Eutectic Solvents for Renewable Energy Storage by Means of Redox Flow Batteries. *Renewable Sustainable Energy Rev.* **2014**, *30*, 254–270.
- (27) Chen, Y.; Mu, T. Application of deep eutectic solvents in biomass pretreatment and conversion. *Green Energy Environ.* **2019**, *4*, 95–115.
- (28) Tome, L. I. N.; Baiao, V.; da Silva, W.; Brett, C. M. A. Deep Eutectic Solvents for the Production And Application of New Materials. *Appl. Mater. Today* **2018**, *10*, 30–50.
- (29) Florindo, C.; Monteiro, N. V.; Ribeiro, B. D.; Branco, L. C.; Marrucho, I. M. Hydrophobic Deep Eutectic Solvents for Purification of Water Contaminated with Bisphenol-A. *J. Mol. Liq.* **2020**, *297*, 111841.
- (30) Chen, Y.; Han, X.; Liu, Z.; Yu, D.; Guo, W.; Mu, T. Capture of Toxic Gases by Deep Eutectic Solvents. *ACS Sustainable Chem. Eng.* **2020**, *8*, 5410–5430.
- (31) Koytsoompa, E. I.; Bergins, C.; Kakaras, E. The CO₂ Economy: Review of CO₂ Capture And Reuse Technologies. *J. Supercrit. Fluids* **2018**, *132*, 3–16.
- (32) Borhani, T. N.; Wang, M. Role of Solvents In CO₂ Capture Processes: The Review Of Selection And Design Methods. *Renewable Sustainable Energy Rev.* **2019**, *114*, 109299.
- (33) Liang, Z.; Fu, K.; Idem, R.; Tontiwachwuthikul, P. Review on Current Advances, Future Challenges And Consideration Issues For Post-Combustion CO₂ Capture Using Amine-Based Absorbents. *Chin. J. Chem. Eng.* **2016**, *24*, 278–288.
- (34) Gouedard, C.; Picq, D.; Launay, F.; Carrette, P. L. Amine Degradation in CO₂ Capture. I. A Review. *Int. J. Greenhouse Gas Control* **2012**, *10*, 244–270.
- (35) Aghaie, M.; Rezaei, N.; Zendehboudi, S. A Systematic Review on CO₂ Capture with Ionic Liquids: Current Status And Future Prospects. *Renewable Sustainable Energy Rev.* **2018**, *96*, 502–525.
- (36) Ma, T.; Wang, J.; Du, Z.; Abdeltawab, A. A.; Al-Enizi, A. M.; Chen, X.; Yu, G. A Process Simulation Study of CO₂ Capture By Ionic Liquids. *Int. J. Greenhouse Gas Control* **2017**, *58*, 223–231.
- (37) Cevasco, G.; Chiappe, C. Are Ionic Liquids A Proper Solution to Current Environmental Challenges? *Green Chem.* **2014**, *16*, 2375–2385.
- (38) Ma, C.; Sarmad, S.; Mikkola, J. P.; Ji, X. Development of Low-Cost Deep Eutectic Solvents for CO₂ Capture. *Energy Procedia* **2017**, *142*, 3320–3325.
- (39) Liu, Y.; Yu, H.; Sun, Y.; Zeng, S.; Zhang, X.; Nie, Y.; Zhang, S.; Ji, X. Development of Low-Cost Deep Eutectic Solvents for CO₂ Capture. *Front. Chem.* **2020**; DOI: 10.3389/fchem.2020.00082.
- (40) Slupek, E.; Makos, P.; Gebicki, J. Theoretical and Economic Evaluation of Low-Cost Deep Eutectic Solvents for Effective Biogas Upgrading to Bio-Methane. *Energies* **2020**, *13*, 3379.
- (41) Halder, A. K.; Cordeiro, M. N. D. S. Probing the Environmental Toxicity of Deep Eutectic Solvents and Their Components: An In Silico Modeling Approach. *ACS Sustainable Chem. Eng.* **2019**, *7*, 10649–10660.
- (42) Zhang, Y.; Ji, X.; Lu, X. Choline-Based Deep Eutectic Solvents For CO₂ Separation: Review And Thermodynamic Analysis. *Renewable Sustainable Energy Rev.* **2018**, *97*, 436–455.
- (43) Wang, Y.; Liu, Y.; Liu, X.; Li, G.; Qi, J.; Yang, J.; Zhu, Z.; Ma, Y.; Gao, J.; Meng, F. Novel Postcombustion Capture Process for CO₂ from the Flue Gas of Coal-Fired Power Plants Using a Green Deep Eutectic Solvent. *ACS Sustainable Chem. Eng.* **2020**, *8*, 2236–2245.
- (44) Xie, Y.; Dong, H.; Zhang, S.; Lu, X.; Ji, X. Effect of Water on the Density, Viscosity, and CO₂ Solubility in Choline Chloride/Urea. *J. Chem. Eng. Data* **2014**, *59*, 3344–3352.
- (45) Li, X.; Hou, M.; Han, B.; Wang, X.; Zou, L. Solubility of CO₂ in a choline chloride + urea eutectic mixture. *J. Chem. Eng. Data* **2008**, *53*, 548–550.
- (46) Leron, R. B.; Caparanga, A.; Li, M. H. Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T = 303.15–343.15 K and moderate pressures. *J. Taiwan Inst. Chem. Eng.* **2013**, *44*, 879–885.
- (47) Mirza, N. R.; Nicholas, N. J.; Wu, Y.; Mumford, K. A. A.; Kentish, S. E.; Stevens, G. W. Experiments and Thermodynamic Modeling of the

Solubility of Carbon Dioxide in Three Different Deep Eutectic Solvents (DESS). *J. Chem. Eng. Data* **2015**, *60*, 3246–3252.

(48) Liu, F.; Chen, W.; Mi, J.; Zhang, J.-Y.; Kan, X.; Zhong, F.-Y.; Huang, K.; Zheng, A.-M.; Jiang, L. Thermodynamic and molecular insights into the absorption of H₂S, CO₂, and CH₄ in choline chloride plus urea mixtures. *AIChE J.* **2019**, *65*, e16574.

(49) Xie, Y.; Dong, H.; Zhang, S.; Lu, X.; Ji, X. Solubilities of CO₂, CH₄, H₂, CO and N₂ in choline chloride/urea. *Green Energy Environ.* **2016**, *1*, 195–200.

(50) Chen, Y.; Ai, N.; Li, G.; Shan, H.; Cui, Y.; Deng, D. Solubilities of Carbon Dioxide in Eutectic Mixtures of Choline Chloride and Dihydric Alcohols. *J. Chem. Eng. Data* **2014**, *59*, 1247–1253.

(51) Li, G.; Deng, D.; Chen, Y.; Shan, H.; Ai, N. Solubilities of Carbon Dioxide in Eutectic Mixtures of Choline Chloride and Dihydric Alcohols. *J. Chem. Thermodyn.* **2014**, *75*, 58–62.

(52) Chen, Y.; Ai, N.; Li, G.; Shan, H.; Cui, Y.; Deng, D. Solubilities of Carbon Dioxide in Eutectic Mixtures of Choline Chloride and Dihydric Alcohols. *J. Chem. Eng. Data* **2014**, *59*, 1247–1253.

(53) Lu, M.; Han, G.; Jiang, Y.; Zhang, X.; Deng, D.; Ai, N. Solubilities of carbon dioxide in the eutectic mixture of levulinic acid (or furfuryl alcohol) and choline chloride. *J. Chem. Thermodyn.* **2015**, *88*, 72–77.

(54) Su, W. C.; Wong, D. S. H.; Li, M. H. Effect of Water on Solubility of Carbon Dioxide in (Aminomethanamide + 2-Hydroxy-N,N,N-trimethylethanaminium Chloride). *J. Chem. Eng. Data* **2009**, *54*, 1951–1955.

(55) Xie, Y.; Dong, H.; Zhang, S.; Lu, X.; Ji, X. Effect of Water on Solubility of Carbon Dioxide in (Aminomethanamide + 2-Hydroxy-N,N,N-trimethylethanaminium Chloride). *J. Chem. Eng. Data* **2014**, *59*, 3344–3352.

(56) Bhawna; Pandey, A.; Pandey, S. Superbase-Added Choline Chloride – Based Deep Eutectic Solvents for CO₂ Capture and Sequestration. *ChemistrySelect* **2017**, *2*, 11422–11430.

(57) Jiang, B.; Ma, J.; Yang, N.; Huang, Z.; Zhang, N.; Tantai, X.; Sun, Y.; Zhang, L. Superbase/Acylamido-Based Deep Eutectic Solvents for Multiple Site Efficient CO₂ Absorption. *Energy Fuels* **2019**, *33*, 7569–7577.

(58) Zhang, N.; Huang, Z.; Zhang, H.; Ma, J.; Jiang, B.; Zhang, L. Highly Efficient and Reversible CO₂ Capture by Task-Specific Deep Eutectic Solvents. *Ind. Eng. Chem. Res.* **2019**, *58*, 13321–13329.

(59) Yan, H.; Zhao, L.; Bai, Y.; Li, F.; Dong, H.; Wang, H.; Zhang, X.; Zeng, S. Superbase Ionic Liquid-Based Deep Eutectic Solvents for Improving CO₂ Absorption. *ACS Sustainable Chem. Eng.* **2020**, *8*, 2523–2530.

(60) Liu, Y.; Dai, Z.; Dai, F.; Ji, X. Ionic Liquids/Deep Eutectic Solvents-Based Hybrid Solvents for CO₂ Capture. *Crystals* **2020**, *10*, 978.

(61) García-Arguelles, S.; Ferrer, M. L.; Iglesias, M.; Del Monte, F.; Gutiérrez, M. C. Study of Superbase – Based Deep Eutectic Solvents as the Catalyst in the Chemical Fixation of CO₂ into Cyclic Carbonates under Mild Conditions. *Materials* **2017**, *10*, 759.

(62) Chen, L.; Zhao, J.; Yin, S. F.; Au, C. T. A Mini-Review on Solid Superbase Catalysts Developed In The Past Two Decades. *RSC Adv.* **2013**, *3*, 3799–3814.

(63) Hsu, Y. H.; Leron, R. B.; Li, M. H. Solubility of carbon dioxide in aqueous mixtures of (reline + monoethanolamine) at T = (313.2 to 353.2) K. *J. Chem. Thermodyn.* **2014**, *72*, 94–99.

(64) Mahi, M. R.; Mokbel, I.; Negadi, L.; Dergal, F.; Jose, J. Experimental Solubility Of Carbon Dioxide In Monoethanolamine, Ordiethanolamine Or N-Methyldiethanolamine (30 Wt%) Dissolved In Deep eutectic Solvent (Choline Chloride And Ethylene Glycol Solution). *J. Mol. Liq.* **2019**, *289*, 111062.

(65) Adeyemi, I.; Abu-Zahra, M. R. M.; Alnashef, I. Experimental Study of the Solubility of CO₂ in Novel Amine Based Deep Eutectic Solvents. *Energy Procedia* **2017**, *105*, 1394–1400.

(66) Li, Z.; Wang, L.; Li, C.; Cui, Y.; Li, S.; Yang, G.; Shen, Y. Absorption of Carbon Dioxide Using Ethanolamine-Based Deep Eutectic Solvents. *ACS Sustainable Chem. Eng.* **2019**, *7*, 10403–10414.

(67) Sarmad, S.; Nikjoo, D.; Mikkola, J. P. Amine Functionalized Deep Eutectic Solvent For CO₂ Capture: Measurements and Modeling. *J. Mol. Liq.* **2020**, *309*, 113159.

(68) Haider, M. B.; Kumar, R. Solubility of CO₂ and CH₄ in Sterically Hindered Amine-Based Deep Eutectic Solvents. *Sep. Purif. Technol.* **2020**, *248*, 117055.

(69) Trivedi, T. J.; Lee, J. H.; Lee, H. J.; Jeong, Y. K.; Choi, J. W. Deep Eutectic Solvents As Attractive Media For CO₂ Capture. *Green Chem.* **2016**, *18*, 2834–2842.

(70) Cui, G.; Lv, M.; Yang, D. Efficient CO₂ absorption by azolide-based deep eutectic solvents. *Chem. Commun.* **2019**, *55*, 1426–1429.

(71) Chemat, F.; Gnanasundaram, N.; Shariff, A. M.; Murugesan, T. Effect of L-arginine on Solubility of CO₂ in Choline Chloride + Glycerol Based Deep Eutectic Solvents. *Procedia Eng.* **2016**, *148*, 236–242.

(72) Gu, Y.; Hou, Y.; Ren, S.; Sun, Y.; Wu, W. Hydrophobic Functional Deep Eutectic Solvents Used for Efficient and Reversible Capture of CO₂. *ACS Omega* **2020**, *5*, 6809–6816.

(73) Zubeir, L. F.; van Osch, D. J. G. P.; Rocha, M. A. A.; Banat, F.; Kroon, M. C. Carbon Dioxide Solubilities in Decanoic Acid-Based Hydrophobic Deep Eutectic Solvents. *J. Chem. Eng. Data* **2018**, *63*, 913–919.

(74) Dietz, C. H. J. T.; van Osch, D. J. G. P.; Kroon, M. C.; Sadowski, G.; van Sint Annaland, M.; Gallucci, F.; Zubeir, L. F.; Held, C. PC-SAFT Modeling Of CO₂ Solubilities In Hydrophobic Deep Eutectic Solvents. *Fluid Phase Equilib.* **2017**, *448*, 94–98.

(75) Lin, H.; Gong, K.; Ying, W.; Chen, D.; Zhang, J.; Yan, Y.; Peng, X. CO₂-Phylic Separation Membrane: Deep Eutectic Solvent Filled Graphene Oxide Nanoslits. *Small* **2019**, *15*, 1904145.

(76) Mubashir, M.; Jusoh, N.; Majeed, Z.; Rambabu, K.; Banat, F.; Tao, Y. Sustainable Liquid Membrane Separation Using Interfacial Engineering Of Deep Eutectic Solvent And Cellulose Acetate. *J. Hazard. Mater.* **2020**, 124345.

(77) Shen, Y.; Hung, F. R. A Molecular Simulation Study of Carbon Dioxide Uptake by a Deep Eutectic Solvent Confined in Slit Nanopores. *J. Phys. Chem. C* **2017**, *121*, 24562–24575.

(78) Ghazali, Z.; Yarmo, M. A.; Othaman, R. Confinement and Characterization Of Deep Eutectic Solvent Based On Choline Chloride:Alcohol Into Nanoporous Silica For CO₂ Capture. *AIP Conf. Proc.* **2018**, *2111*, 050014.

(79) Ghazali, Z.; Suhaili, N.; Tahari, M. N. A.; Yarmo, M. A. A.; Hassan, N. H.; Othaman, R. Impregnating Deep Eutectic Solvent Choline Chloride:Urea:Polyethyleneimine Onto Mesoporous Silica Gel For Carbon Dioxide Capture. *J. Mater. Res. Technol.* **2020**, *9*, 3249–3260.

(80) Lin, H.; Gong, K.; Hykys, P.; Chen, D.; Ying, W.; Sofer, Z.; Yan, Y.; Li, Z.; Peng, X. Nanoconfined Deep Eutectic Solvent In Laminated Mxene For Efficient CO₂ Separation. *Chem. Eng. J.* **2021**, *405*, 126961.

(81) Li, Z.; Sun, W.; Chen, C.; Guo, Q.; Li, X.; Gu, M.; Feng, N.; Ding, J.; Wan, H.; Guan, G. Deep eutectic solvents appended to UiO-66 type metal organic frameworks: Preserved open metal sites and extra adsorption sites for CO₂ capture. *Appl. Surf. Sci.* **2019**, *480*, 770–778.

(82) Saeed, U.; Khan, A. L.; Gilani, a.; Aslam, M.; Khan, A. U. CO₂ Separation By Supported Liquid Membranes Synthesized With Natural Deep Eutectic Solvents. *Environ. Sci. Pollut. Res.* **2020**, DOI: 10.1007/s11356-020-10260-x.

(83) Sun, S.; Niu, Y.; Xu, Q.; Sun, Z.; Wei, X. Efficient SO₂ Absorptions by Four Kinds of Deep Eutectic Solvents Based on Choline Chloride. *Ind. Eng. Chem. Res.* **2015**, *54*, 8019–8024.

(84) Yang, D.; Zhang, S.; Jiang, D.-E.; Dai, S. SO₂ absorption in EmimCl-TEG deep eutectic solvents. *Phys. Chem. Chem. Phys.* **2018**, *20*, 15168–15173.

(85) Chen, Y.; Jiang, B.; Dou, H.; Zhang, L.; Tantai, X.; Sun, Y.; Zhang, H. Highly Efficient and Reversible Capture of Low Partial Pressure SO₂ by Functional Deep Eutectic Solvents. *Energy Fuels* **2018**, *32*, 10737–10744.

(86) Atilhan, M.; Altamash, T.; Aparicio, S. Quantum Chemistry Insight into the Interactions Between Deep Eutectic Solvents and SO₂. *Molecules* **2019**, *24*, 2963.

- (87) Zhang, C.; Zhu, L.; Wang, J.; Wang, J.; Zhou, T.; Xu, Y.; Cheng, C. The Acute Toxic Effects Of Imidazolium-Based Ionic Liquids With Different Alkyl-Chain Lengths and Anions On Zebrafish (Danio Rerio). *Ecotoxicol. Environ. Saf.* **2017**, *140*, 235–240.
- (88) Yang, D.; Han, Y.; Qi, H.; Wang, Y.; Dai, S. Efficient Absorption of SO₂ by EmimCl-EG Deep Eutectic Solvents. *ACS Sustainable Chem. Eng.* **2017**, *5*, 6382–6386.
- (89) Yang, D.; Zhang, S.; Jiang, D. Efficient Absorption of SO₂ by Deep Eutectic Solvents Formed by Biobased Aprotic Organic Compound Succinonitrile and 1-Ethyl-3-methylimidazolium Chloride. *ACS Sustainable Chem. Eng.* **2019**, *7*, 9086–9091.
- (90) Liu, B.; Zhao, J.; Wei, F. Characterization of Caprolactam Based Eutectic Ionic Liquids and Their Application in SO₂ Absorption. *J. Mol. Liq.* **2013**, *180*, 19–25.
- (91) Zhao, T.; Liang, J.; Zhang, Y.; Wu, Y.; Hu, X. Unexpectedly Efficient SO₂ Capture and Conversion to Sulfur in Novel Imidazole-Based Deep Eutectic Solvents. *Chem. Commun.* **2018**, *54*, 8964–8967.
- (92) Jiang, B.; Zhang, H.; Zhang, L.; Zhang, N.; Huang, Z.; Chen, Y.; Sun, Y.; Tantai, X. Novel Deep Eutectic Solvents for Highly Efficient and Reversible Absorption of SO₂ by Preorganization Strategy. *ACS Sustainable Chem. Eng.* **2019**, *7*, 8347–8357.
- (93) Liu, B.; Wei, F.; Zhao, J.; Wang, Y. Characterization of Amidethiocyanates Eutectic Ionic Liquids and their Application in SO₂ Absorption. *RSC Adv.* **2013**, *3*, 2470–2476.
- (94) Sheng, K.; Kang, Y.; Li, J.; Xu, H.; Li, D. High-Efficiency Absorption of SO₂ by a New Type of Deep Eutectic Solvents. *Energy Fuels* **2020**, *34*, 3440–3448.
- (95) Long, G.; Yang, C.; Yang, X.; Zhao, T.; Liu, F.; Cao, J. BisazoleBased Deep Eutectic Solvents for Efficient SO₂ Absorption and Conversion without Any Additives. *ACS Sustainable Chem. Eng.* **2020**, *8*, 2608–2613.
- (96) Wu, H.; Shen, M.; Chen, X.; Yu, G.; Abdeltawab, A. A.; Yakout, S. M. New Absorbents For Hydrogen Sulfide: Deep Eutectic Solvents Of Tetrabutylammonium Bromide/Carboxylic Acids And Choline Chloride/ Carboxylic Acids. *Sep. Purif. Technol.* **2019**, *224*, 281–289.
- (97) Waite, S. L.; Li, H.; Page, A. J. NO₂ Solvation Structure in Choline Chloride Deep Eutectic Solvents-The Role of the Hydrogen Bond Donor. *J. Phys. Chem. B* **2018**, *122*, 4336–4344.
- (98) Chen, C. C.; Wang, C. Y.; Huang, Y. H. Reversible Absorption of Nitrogen Dioxide By Choline Chloride-Based Deep Eutectic Solvents And Their Aqueous Mixtures. *Chem. Eng. J.* **2021**, *405*, 126760.
- (99) Duan, E.; Guo, B.; Zhang, D.; Shi, L.; Sun, H.; Wang, Y. Absorption of NO and NO₂ in Caprolactam Tetrabutyl Ammonium Halide Ionic Liquids. *J. Air Waste Manage. Assoc.* **2011**, *61*, 1393–1397.
- (100) Sun, Y.; Wei, G.; Tantai, X.; Huang, Z.; Yang, H.; Zhang, L. Highly Efficient Nitric Oxide Absorption by Environmentally Friendly Deep Eutectic Solvents Based on 1,3-Dimethylthiourea. *Energy Fuels* **2017**, *31*, 12439–12445.
- (101) Zhang, L.; Ma, H.; Wei, G.; Jiang, B.; Sun, Y.; Tantai, X.; Huang, Z.; Chen, Y. Efficient and Reversible Nitric Oxide Absorption by LowViscosity, Azole-Derived Deep Eutectic Solvents. *J. Chem. Eng. Data* **2019**, *64*, 3068–3077.
- (102) Sun, Y.; Gao, M.; Ren, S.; Zhang, Q.; Hou, Y.; Wu, W. Highly Efficient Absorption of NO by Amine-Based Functional Deep Eutectic Solvents. *Energy Fuels* **2020**, *34*, 690–697.
- (103) Atilhan, M.; Aparicio, S. A Nanoscopic Explanation of Nitric Oxide Solubility In Natural Deep Eutectic Solvents. *J. Mol. Liq.* **2021**, *324*, 114673.
- (104) Li, Y.; Ali, M. C.; Yang, Q.; Zhang, Z.; Bao, Z.; Su, B.; Xing, H.; Ren, Q. Hybrid Deep Eutectic Solvents with Flexible HydrogenBonded Supramolecular Networks for Highly Efficient Uptake of NH₃. *ChemSusChem* **2017**, *10*, 3368–3377.
- (105) Duan, X.; Gao, B.; Zhang, C.; Deng, D. Solubility and Thermodynamic Properties Of NH₃ In Choline Chloride-Based Deep Eutectic Solvents. *J. Chem. Thermodyn.* **2019**, *133*, 79–84.
- (106) Jiang, W.; Zhong, F.; Liu, Y.; Huang, K. Effective and Reversible Capture of NH₃ by Ethylamine Hydrochloride Plus Glycerol Deep Eutectic Solvents. *ACS Sustainable Chem. Eng.* **2019**, *7*, 10552–10560.
- (107) Deng, D.; Duan, X.; Gao, B.; Zhang, C.; Deng, X.; Gong, L. Efficient and Reversible Absorption Of NH₃ By Functional Azole-Glycerol Deep Eutectic Solvents. *New J. Chem.* **2019**, *43*, 11636–11642.
- (108) Zhong, F.-Y.; Zhou, L.; Shen, J.; Liu, Y.; Fan, J.-P.; Huang, K. Rational Design of Azole-Based Deep Eutectic Solvents for Highly Efficient and Reversible Capture of Ammonia. *ACS Sustainable Chem. Eng.* **2019**, *7*, 14170–14179.
- (109) Deng, D.; Gao, B.; Zhang, C.; Duan, X.; Cui, Y.; Ning, J. Investigation of Protic NH₄SCN-based Deep Eutectic Solvents as Highly Efficient and Reversible NH₃ Absorbents. *Chem. Eng. J.* **2019**, *358*, 936–943.
- (110) Zhong, F.-Y.; Peng, H.-L.; Tao, D.-J.; Wu, P.-K.; Fan, J.-P.; Huang, K. Phenol-Based Ternary Deep Eutectic Solvents for Highly Efficient and Reversible Absorption of NH₃. *ACS Sustainable Chem. Eng.* **2019**, *7*, 3258–3266.
- (111) Jiang, W.-J.; Zhong, F.-Y.; Zhou, L.-S.; Peng, H.-L.; Fan, J.-P.; Huang, K. Chemical Dual-Site Capture of NH₃ by Unprecedentedly Low Viscosity Deep Eutectic Solvents. *Chem. Commun.* **2020**, *56*, 2399–2402.
- (112) Smith, S. J.; van Aardenne, J.; Klimont, Z.; Andres, R. J.; Volke, A.; Delgado Arias, S. Anthropogenic Sulfur Dioxide Emissions: 1850–2005. *Atmos. Chem. Phys.* **2011**, *11*, 1101–1116.
- (113) Spengler, J. D.; Ferris, B. G., Jr.; Dockery, D. W.; Speizer, F. E. Sulfur Dioxide And Nitrogen Dioxide Levels Inside And Outside Homes And The Implications On Health Effects Research. *Environ. Sci. Technol.* **1979**, *13*, 1276–1280.
- (114) Hammershoi, P. S.; Jensen, A. D.; Janssens, T. V. W. Impact of SO₂-poisoning over the lifetime of a Cu-CHA catalyst for NH₃-SCR. *Appl. Catal., B* **2018**, *238*, 104–110.
- (115) Javadli, R.; de Klerk, A. Desulfurization of Heavy Oil. *Appl. Petrochem. Res.* **2012**, *1*, 3–19.
- (116) Brunet, S.; Mey, D.; Perot, G.; Bouchy, C.; Diehl, F. On the Hydrodesulfurization of FCC Gasoline: A Review. *Appl. Catal., A* **2005**, *278*, 143–172.
- (117) Shafiq, I.; Shafique, S.; Akhter, P.; Yang, W.; Hussain, M. Recent Developments In Alumina Supported Hydrodesulfurization Catalysts For The Production Of Sulfur-Free Refinery Products: A Technical Review. *Catal. Rev.: Sci. Eng.* **2020**, *1*.
- (118) Srivastava, V. C. An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Adv.* **2012**, *2*, 759–783.
- (119) Tanimu, A.; Alhooshani, K. Advanced Hydrodesulfurization Catalysts: A Review of Design and Synthesis. *Energy Fuels* **2019**, *33*, 2810–2838.
- (120) Saleh, T. A.; Al-Hammadi, S. A.; Tanimu, A.; Alhooshani, K. Ultra-Deep Adsorptive Desulfurization Of Fuels On Cobalt And Molybdenum Nanoparticles Loaded On Activated Carbon Derived From Waste Rubber. *J. Colloid Interface Sci.* **2018**, *513*, 779–787.
- (121) Gao, J.; Zhu, S.; Dai, Y.; Xiong, C.; Li, C.; Yang, W.; Jiang, X. Performance and Mechanism For Extractive Desulfurization Of Fuel Oil Using Modified Polyethylene Glycol. *Fuel* **2018**, *233*, 704–713.
- (122) Abro, R.; Abdeltawab, A. A.; Al-Deyab, S. S.; Yu, G.; Qazi, A. B.; Gao, S.; Chen, X. A Review Of Extractive Desulfurization Of Fuel Oils Using Ionic Liquids. *RSC Adv.* **2014**, *4*, 35302–35317.
- (123) Zhao, H.; Baker, G. A.; Wagle, D. V.; Ravula, S.; Zhang, Q. Tuning Task-Specific Ionic Liquids for the Extractive Desulfurization of Liquid Fuel. *ACS Sustainable Chem. Eng.* **2016**, *4*, 4771–4780.
- (124) Song, Z.; Zhang, C.; Qi, Z.; Zhou, T.; Sundmacher, K. Computer-Aided Design Of Ionic Liquids As Solvents For Extractive Desulfurization. *AIChE J.* **2018**, *64*, 1013–1025.
- (125) Li, J. J.; Xiao, H.; Tang, X. D.; Zhou, M. Green Carboxylic Acid-Based Deep Eutectic Solvents as Solvents for Extractive Desulfurization. *Energy Fuels* **2016**, *30*, 5411–5418.
- (126) Chandran, D.; Khalid, M.; Walvekar, R.; Mubarak, N. M.; Dharaskar, S.; Wong, W. Y.; Gupta, T. C. S. M. Deep Eutectic Solvents For Extraction-Desulphurization: A Review. *J. Mol. Liq.* **2019**, *275*, 312–322.
- (127) Majid, M. F.; Mohd Zaid, H. F.; Kait, C. F.; Jumbri, K.; Yuan, L. C.; Rajasuriyan, S. Futuristic Advance And Perspective Of Deep

Eutectic Solvent For Extractive Desulfurization Of Fuel Oil: A Review. *J. Mol. Liq.* **2020**, *306*, 112870.

(128) Cevalco, G.; Chiappe, C. Are Ionic Liquids A Proper Solution To Current Environmental Challenges? *Green Chem.* **2014**, *16*, 2375–2385.

(129) Oskarsson, A.; Wright, M. C. Ionic Liquids: New Emerging Pollutants, Similarities with Perfluorinated Alkyl Substances (PFASs). *Environ. Sci. Technol.* **2019**, *53*, 10539–10541.

(130) Cheng, H.; Liu, C.; Zhang, J.; Chen, L.; Zhang, B.; Qi, Z. Screening Deep Eutectic Solvents For Extractive Desulfurization of Fuel Based on COSMO-RS model. *Chem. Eng. Process.* **2018**, *125*, 246–252.

(131) Makos, P.; Boczkaj, G. Deep Eutectic Solvents Based Highly Efficient Extractive Desulfurization Of Fuels – Eco-Friendly Approach. *J. Mol. Liq.* **2019**, *296*, 111916.

(132) Mohd Zaid, H. F.; Chong, F. K.; Abdul Mutalib, M. I. Extractive Deep Desulfurization Of Diesel Using Choline Chloride-Glycerol Eutectic-Based Ionic Liquid As A Green Solvent. *Fuel* **2017**, *192*, 10–17.

(133) Almashjary, K. H.; Khalid, M.; Dharaskar, S.; Jagadish, P.; Walvekar, R.; Gupta, T. C. S. M. Optimisation of Extractive Desulfurization Using Choline Chloride-Based Deep Eutectic Solvents. *Fuel* **2018**, *234*, 1388–1400.

(134) Jiang, W.; Dong, L.; Liu, W.; Guo, T.; Li, H.; Yin, S.; Zhu, W.; Li, H. Biodegradable Choline-Like Deep Eutectic Solvents For Extractive Desulfurization Of Fuel. *Chem. Eng. Process.* **2017**, *115*, 34–38.

(135) El-Hoshoudy, A. N.; Soliman, F. S.; Abd El-Aty, D. M. Extractive Desulfurization Using Choline Chloride-Based DES/Molybdate Nanofluids; Experimental and Theoretical Investigation. *J. Mol. Liq.* **2020**, *318*, 114307.

(136) Lima, F.; Gouvenaux, J.; Branco, L. C.; Silvestre, A. J. D.; Marrucho, I. M. Towards a Sulfur Clean Fuel: Deep Extraction Of Thiophene And Dibenzothiophene Using Polyethylene Glycol-Based Deep Eutectic Solvents. *Fuel* **2018**, *234*, 414–421.

(137) Li, J. J.; Xiao, H.; Tang, X. D.; Zhou, M. Green Carboxylic Acid-Based Deep Eutectic Solvents as Solvents for Extractive Desulfurization. *Energy Fuels* **2016**, *30*, 5411–5418.

(138) Yang, D.; Zhang, S.; Jiang, D. Efficient Absorption of SO₂ by Deep Eutectic Solvents Formed by Biobased Aprotic Organic Compound Succinonitrile and 1-Ethyl-3-methylimidazolium Chloride. *ACS Sustainable Chem. Eng.* **2019**, *7*, 9086–9091.

(139) Jiang, W.; Dong, L.; Liu, W.; Guo, T.; Li, H.; Yin, S.; Zhu, W.; Li, H. *Chem. Eng. Process.* **2017**, *115*, 34–38.

(140) Wagle, D. V.; Zhao, H.; Deakye, C. A.; Baker, G. A. Quantum Chemical Evaluation of Deep Eutectic Solvents for the Extractive Desulfurization of Fuel. *ACS Sustainable Chem. Eng.* **2018**, *6*, 7525–7531.

(141) Shah, D.; Gapeyenko, D.; Urakpayev, A.; Torkmahalleh, M. Molecular Dynamics Simulations On Extractive Desulfurization Of Fuels By Tetrabutylammonium Chloride Based Deep Eutectic Solvents. *J. Mol. Liq.* **2019**, *274*, 254–260.

(142) Hizaddin, H. F.; Ramalingam, A.; Hashim, M. A.; Hadj-Kali, M. K. O. Evaluating the Performance of Deep Eutectic Solvents for Use in Extractive Denitrification of Liquid Fuels by the Conductor-like Screening Model for Real Solvents. *J. Chem. Eng. Data* **2014**, *59*, 3470–3487.

(143) Rogosic, M.; Zagajski Kucan, K. Deep Eutectic Solvent Based On Choline Chloride And Propylene Glycol As A Potential Medium For Extraction Denitrification Of Hydrocarbon Fuels. *Chem. Eng. Res. Des.* **2020**, *161*, 45–57.

(144) Lima, F.; Dave, M.; Silvestre, A. J. D.; Branco, L. C.; Marrucho, I. M. Concurrent Desulfurization and Denitrogenation of Fuels Using Deep Eutectic Solvents. *ACS Sustainable Chem. Eng.* **2019**, *7*, 11341–11349.

(145) Hadj-Kali, M. K.; Salleh, Z.; Ali, E.; Khan, R.; Hashim, M. A. Separation of Aromatic And Aliphatic Hydrocarbons Using Deep Eutectic Solvents: A Critical Review. *Fluid Phase Equilib.* **2017**, *448*, 152–167.

(146) Larriba, M.; Ayuso, M.; Navarro, P.; Delgado-Mellado, N.; Gonzalez-Miquel, M.; García, J.; Rodríguez, F. Choline Chloride-Based Deep Eutectic Solvents in the Dearomatization of Gasolines. *ACS Sustainable Chem. Eng.* **2018**, *6*, 1039–1047.

(147) Kucan, K. Z.; Perkovic, M.; Cmrk, K.; Nacinovic, D.; Rogosic, M. Betaine + (Glycerol or Ethylene Glycol or Propylene Glycol) Deep Eutectic Solvents for Extractive Purification of Gasoline. *ChemistrySelect* **2018**, *3*, 12582–12590.

(148) Rogosic, M.; Kucan, K. Z. Deep Eutectic Solvents Based On Choline Chloride And Ethylene Glycol As Media For Extractive Denitrification/Desulfurization/Dearomatization of Motor Fuels. *J. Ind. Eng. Chem.* **2019**, *72*, 87–99.

(149) Warrag, S. E. E.; Darwish, A. S.; Abuhatab, F. O. S.; Adeyemi, I. A.; Kroon, M. C.; AlNashef, I. M. Combined Extractive Dearomatization, Desulfurization, and Denitrogenation of Oil Fuels Using Deep Eutectic Solvents: A Parametric Study. *Ind. Eng. Chem. Res.* **2020**, *59*, 11723–11733.

(150) Warrag, S. E. E.; Fetisov, E. O.; van Osch, D. J. G. P.; Harwood, D. B.; Kroon, M. C.; Siepmann, I.; Peters, C. J. Mercury Capture from Petroleum Using Deep Eutectic Solvents. *Ind. Eng. Chem. Res.* **2018**, *57*, 9222–9230.

(151) Troter, D. Z.; Todorovic, Z. B.; Dokic-Stojanovic, D. R.; Stamenkovic, O. S.; Veljkovic, V. B. Application Of Ionic Liquids And Deep Eutectic Solvents In Biodiesel Production: A Review. *Renewable Sustainable Energy Rev.* **2016**, *61*, 473–500.

(152) Shahbaz, K.; Baroutian, S.; Mjalli, F. S.; Hashim, M. A.; Alnashef, I. M. Application of Ionic Liquids And Deep Eutectic Solvents In Biodiesel Production: A Review. *Chemom. Intell. Lab. Syst.* **2012**, *118*, 193–199.

(153) Sander, A.; Petravic, A.; Vukovic, J. P.; Husinec, L. From Coffee to Biodiesel—Deep Eutectic Solvents for Feedstock and Biodiesel Purification. *Separations* **2020**, *7*, 22.

(154) Bewley, B. R.; Berkaliyev, A.; Henriksen, H.; Ball, D. B.; Ott, D. B. Waste Glycerol From Biodiesel Synthesis As A Component In Deep Eutectic Solvents. *Fuel Process. Technol.* **2015**, *138*, 419–423.

(155) Peng, Y.; Lu, X.; Liu, B.; Zhu, J. Separation of Azeotropic Mixtures (Ethanol and Water) Enhanced by Deep Eutectic Solvents. *Fluid Phase Equilib.* **2017**, *448*, 128–134.

(156) Jiang, H.; Diaio, B.; Xu, D.; Zhang, L.; Ma, Y.; Gao, J.; Wang, Y. Deep Eutectic Solvents Effect On Vapor-Liquid Phase Equilibrium For Separation Of Allyl Alcohol From Its Aqueous Solution. *J. Mol. Liq.* **2019**, *279*, 524–529.

(157) Anastácio, M.; dosSantos, A. P. M.; Aschner, M.; Mateus, L. Determination of Trace Metals In Fruit Juices In The Portuguese Market. *Toxicol.Rep.* **2018**, *5*, 434–439.

(158) Millour, S.; Noël, L.; Kadar, A.; Chekri, R.; Vastel, C.; Sirot, V.; Leblanc, J. C.; Guérin, T. *Food Chem.* **2011**, *126*, 1787–1799.

(159) Tan, D.; He, Y.; Xing, X.; Zhao, Y.; Tang, H.; Pang, D. Aptamer Functionalized Gold Nanoparticles Based Fluorescent Probe For the Detection of Mercury(II) Ion In Aqueous Solution. *Talanta* **2013**, *113*, 26–30.

(160) Ge, S.; Wu, K.; Zhang, Y.; Yan, M.; Yu, J. Paper-based biosensor relying on flower-like reduced graphene guided enzymatically deposition of polyaniline for Pb²⁺ detection. *Biosens. Bioelectron.* **2016**, *80*, 215–221.

(161) Huang, K. W.; Yu, C. J.; Tseng, W. L. Sensitivity Enhancement in the Colorimetric Detection of Lead(II) Ion Using Gallic Acid-Capped Gold Nanoparticles: Improving Size Distribution and Minimizing Interparticle Repulsion. *Biosens. Bioelectron.* **2010**, *25*, 984–989.

(162) Qian, Z. S.; Shan, X. Y.; Chai, L. J.; Chen, J. R.; Feng, H. A Fluorescent Nanosensor Based on Graphene Quantum Dots-Aptamer Probe And Graphene Oxide Platform for Detection of Lead(II) Ion. *Biosens. Bioelectron.* **2015**, *68*, 225–231.

(163) AlOmar, M. K.; Alsaadi, M. A.; Hayyan, M.; Akib, S.; Ibrahim, R. K.; Hashim, M. A. Lead Removal From Water by Choline Chloride Based Deep Eutectic Solvents Functionalized Carbon Nanotubes. *J. Mol. Liq.* **2016**, *222*, 883–894.

- (164) Ali, I. New Generation Adsorbents for Water Treatment. *Chem. Rev.* **2012**, *112*, 5073–5091.
- (165) Ruthiraan, M.; Mubarak, N. M.; Thines, R. K.; Abdullah, E. C.; Sahu, J. N.; Jayakumar, N. S.; Ganesan, P. Comparative Kinetic Study Of Functionalized Carbon Nanotubes And Magnetic Biochar For Removal of Cd²⁺ Ions From Wastewater. *Korean J. Chem. Eng.* **2015**, *32*, 446–457.
- (166) Mubarak, N. M.; Sahu, J. N.; Abdullah, E. C.; Jayakumar, N. S.; Ganesan, P. Novel Microwave-Assisted Multiwall Carbon Nanotubes Enhancing Cu (II) Adsorption Capacity In Water. *J. Taiwan Inst. Chem. Eng.* **2015**, *53*, 140–152.
- (167) Mubarak, N. M.; Alicia, R. F.; Abdullah, E. C.; Sahu, J. N.; Haslija, A. B. A.; Tan, J. Statistical Optimization And Kinetic Studies on Removal of Zn²⁺ Using Functionalized Carbon Nanotubes And Magnetic Biochar. *J. Environ. Chem. Eng.* **2013**, *1*, 486–495.
- (168) Mubarak, N. M.; Sahu, J. N.; Abdullah, E. C.; Jayakumar, N. S. Rapid Adsorption Of Toxic Pb(II) Ions From Aqueous Solution Using Multiwall Carbon Nanotubes Synthesized By Microwave Chemical Vapor Deposition Technique. *J. Environ. Sci.* **2016**, *45*, 143–155.
- (169) Peng, X.; Li, Y.; Luan, Z.; Di, Z.; Wang, H.; Tian, B.; Jia, Z. Adsorption of 1,2-Dichlorobenzene From Water to Carbon Nanotubes. *Chem. Phys. Lett.* **2003**, *376*, 154–158.
- (170) Li, Y. H.; Wang, S.; Zhang, X.; Wei, J.; Xu, C.; Luan, Z.; Wu, D. Adsorption of Fluoride From Water By Aligned Carbon Nanotubes. *Mater. Res. Bull.* **2003**, *38*, 469–476.
- (171) Lu, C.; Chung, Y. L.; Chang, K. F. Adsorption of Trihalo-methanes From Water With Carbon Nanotubes. *Water Res.* **2005**, *39*, 1183–1189.
- (172) Ngueta, G.; Prévost, M.; Deshombres, E.; Abdous, B.; Gauvin, D.; Levallois, P. Exposure of Young Children To Household Water Lead in the Montreal Area (Canada): The Potential Influence of Winter-summer Changes in Water Lead Levels on Children's Blood Lead Concentration. *Environ. Int.* **2014**, *73*, 57–65.
- (173) Abdel-Ghani, N. T.; Hefny, M.; El-Chaghaby, G. A. F. Removal of Lead from Aqueous Solution Using Low Cost Abundantly Available Adsorbents. *Int. J. Environ. Sci. Technol.* **2007**, *4*, 67–73.
- (174) Axtell, N. R.; Sternberg, S. P. K.; Claussen, K. Lead And Nickel Removal Using Microspora and Lemna Minor. *Bioresour. Technol.* **2003**, *89*, 41–48.
- (175) Orumwense, F. F. O. Removal of Lead from Water by Adsorption on A Kaolinitic Clay. *J. Chem. Technol. Biotechnol.* **1996**, *65*, 363–369.
- (176) Dimitrova, S. V.; Mehandgiev, D. R. Lead Removal from Aqueous Solutions By Granulated Blast-Furnace Slag. *Water Res.* **1998**, *32*, 3289–3292.
- (177) Wang, H. J.; Zhou, A. L.; Peng, F.; Yu, H.; Chen, L. F. Adsorption Characteristic Of Acidified Carbon Nanotubes for Heavy Metal Pb(II) In Aqueous Solution. *Mater. Sci. Eng., A* **2007**, *466*, 201–206.
- (178) Goel, J.; Kadirvelu, K.; Rajagopal, C.; Kumar Garg, V. Removal of Lead(II) By Adsorption Using Treated Granular Activated Carbon: Batch and Column Studies. *J. Hazard. Mater.* **2005**, *125*, 211–220.
- (179) Netzer, A.; Hughes, D. E. Adsorption of copper, lead and cobalt by activated carbon. *Water Res.* **1984**, *18*, 927–933.
- (180) Imamoglu, M.; Tekir, O. Removal of Copper (II) And Lead (II) Ions from Aqueous Solutions by Adsorption On Activated Carbon From A New Precursor Hazelnut Husks. *Desalination* **2008**, *228*, 108–113.
- (181) Sekar, M.; Sakthi, V.; Rengaraj, S. Kinetics and Equilibrium Adsorption Study of Lead(II) Onto Activated Carbon Prepared From Coconut Shell. *J. Colloid Interface Sci.* **2004**, *279*, 307–313.
- (182) Tao, H. C.; Zhang, H. R.; Li, J. B.; Ding, W. Y. Biomass Based Activated Carbon Obtained from Sludge and Sugarcane Bagasse for Removing Lead Ion from Waste Water. *Bioresour. Technol.* **2015**, *192*, 611–617.
- (183) Wang, H. J.; Zhou, A. L.; Peng, F.; Yu, H.; Chen, L. F. Adsorption Characteristic of Acidified Carbon Nanotubes for Heavy Metal Pb(II) In Aqueous Solution. *Mater. Sci. Eng., A* **2007**, *466*, 201–206.
- (184) Wang, S. G.; Gong, W. X.; Liu, X. W.; Yao, Y. W.; Gao, B. Y.; Yue, Q. Y. Removal of Lead(II) From Aqueous Solution by Adsorption onto Manganese Oxide-Coated Carbon Nanotubes. *Sep. Purif. Technol.* **2007**, *58*, 17–23.
- (185) Salam, M. A. Coating Carbon Nanotubes with Crystalline Manganese Dioxide Nanoparticles and Their Application for Lead Ions Removal from Model and Real Water. *Colloids Surf., A* **2013**, *419*, 69–79.
- (186) Gupta, V. K.; Agarwal, S.; Saleh, T. A. Synthesis and Characterization of Alumina-Coated Carbon Nanotubes and Their Application for Lead Removal. *J. Hazard. Mater.* **2011**, *185*, 17–23.
- (187) Zhao, X.; Jia, Q.; Song, N.; Zhou, W.; Li, Y. Adsorption of Pb(II) from an Aqueous Solution by Titanium Dioxide/Carbon Nanotube Nanocomposites: Kinetics, Thermodynamics, and Isotherms. *J. Chem. Eng. Data* **2010**, *55*, 4428–4433.
- (188) Rahmati, N.; Rahimnejad, M.; Pourali, M.; Muallah, S. K. Effective Removal of Nickel Ions from Aqueous Solution Using Multi-Wall Carbon Nanotube Functionalized by Glycerol-Based Deep Eutectic Solvent. *Colloid Surf. Sci. Commun.* **2021**, *40*, 100347.
- (189) Ngueta, G.; Prévost, M.; Deshombres, E.; Abdous, B.; Gauvin, D.; Levallois, P. Exposure of Young Children to Household Water Lead in the Montreal Area (Canada): The Potential Influence of Winter-To-Summer Changes in Water Lead Levels On Children's Blood Lead Concentration. *Environ. Int.* **2014**, *73*, 57–65.
- (190) Gad, S. C.; Pham, T. Lead. In *Encyclopedia of Toxicology*, Third Edition; Wexler, P., Ed.; Academic Press: Oxford, U.K., 2014; pp 61–65.
- (191) Tong, Y. E.; Schirnding, V.; Prapamontol, T. Environmental Lead Exposure: A Public Health Problem of Global Dimensions. *Bull. World Health Organ.* **2000**, *78*, 1068–1077.
- (192) Wang, H. J.; Zhou, A. L.; Peng, F.; Yu, H.; Chen, L. F. Adsorption Characteristic of Acidified Carbon Nanotubes for Heavy Metal Pb(II) in Aqueous Solution. *Mater. Sci. Eng., A* **2007**, *466*, 201–206.
- (193) Sekar, M.; Sakthi, V.; Rengaraj, S. Kinetics and Equilibrium Adsorption Study of Lead(II) Onto Activated Carbon Prepared from Coconut Shell. *J. Colloid Interface Sci.* **2004**, *279*, 307–313.
- (194) Tao, H. C.; Zhang, H. R.; Li, J. B.; Ding, W. Y. Biomass Based Activated Carbon Obtained from Sludge and Sugarcane Bagasse for Removing Lead Ion from Wastewater. *Bioresour. Technol.* **2015**, *192*, 611–617.
- (195) Ibrahim, R. K.; Hayyan, M.; AlSaadi, M. A.; Hayyan, A.; Ibrahim, S. Environmental Application of Nanotechnology: Air, Soil, and Water. *Environ. Sci. Pollut. Res.* **2016**, *23*, 13754–13788.
- (196) Long, R. Q.; Yang, R. T. Carbon Nanotubes as Superior Sorbent for Dioxin Removal. *J. Am. Chem. Soc.* **2001**, *123*, 2058–2059.
- (197) Bienfait, M.; Zeppenfeld, P.; Dupont-Pavlovsky, N.; Muris, M.; Johnson, M. R.; Wilson, T.; DePies, M.; Vilches, O. E. Thermodynamics and Structure of Hydrogen, Methane, Argon, Oxygen, and Carbon Dioxide Adsorbed on Single-Wall Carbon Nanotube Bundles. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *70*, 035410.
- (198) Bauschlicher, C. W.; Ricca, A. Binding of NH₃ to Graphite and to a (9,0) Carbon Nanotube. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *70*, 115409.
- (199) da Silva, W.; Ghica, M. E.; Brett, C. M. A. Biotoxic Trace Metal Ion Detection by Enzymatic Inhibition of a Glucose Biosensor Based on a Poly(Brilliant Green)–Deep Eutectic Solvent/Carbon Nanotube Modified Electrode. *Talanta* **2020**, *208*, 120427.
- (200) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. Storage of Hydrogen in Single-Walled Carbon Nanotubes. *Nature* **1997**, *386*, 377–379.
- (201) Peng, X.; Li, Y.; Luan, Z.; Di, H.; Wang, T.; Tian, B.; Jia, Z. Adsorption of 1,2-Dichlorobenzene from Water to Carbon Nanotubes. *Chem. Phys. Lett.* **2003**, *376*, 154–158.
- (202) Li, Y. H.; Wang, S.; Zhang, X.; Wei, J.; Xu, C.; Luan, Z.; Wu, D. Adsorption of Fluoride from Water by Aligned Carbon Nanotubes. *Mater. Res. Bull.* **2003**, *38*, 469–476.

- (203) Peckham, S.; Awofeso, N. Water Fluoridation: A Critical Review of the Physiological Effects of Ingested Fluoride as a Public Health Intervention. *Sci. World J.* **2014**, *2014*, 293019.
- (204) Sharma, M.; Mondal, D.; Singh, N.; Upadhyay, K.; Rawat, A.; Devkar, R. V.; Sequeira, R. A.; Prasad, K. Seaweed-Derived Nontoxic Functionalized Graphene Sheets as Sustainable Materials for the Efficient Removal of Fluoride from High Fluoride Containing Drinking Water. *ACS Sustainable Chem. Eng.* **2017**, *5*, 3488–3498.
- (205) Kubota, T.; Fukutani, S.; Ohta, T.; Mahara, Y. Removal of Radioactive Cesium, Strontium, and Iodine from Natural Waters Using Bentonite, Zeolite, And Activated Carbon. *J. Radioanal. Nucl. Chem.* **2013**, *296*, 981–984.
- (206) Chapman, K. W.; Chupas, P. J.; Nenoff, T. M. *J. Am. Chem. Soc.* **2010**, *132*, 8897–8899.
- (207) Sava, D. F.; Rodriguez, M. A.; Chapman, K. W.; Chupas, P. J.; Greathouse, J. A.; Crozier, P. S.; Nenoff, T. M. Capture of Volatile Iodine, a Gaseous Fission Product, by Zeolitic Imidazolate Framework-8. *J. Am. Chem. Soc.* **2011**, *133*, 12398–12401.
- (208) Bennett, T. D.; Saines, P. J.; Keen, D. A.; Tan, J. C.; Cheetham, A. K. Ball-Milling-Induced Amorphization of Zeolitic Imidazolate Frameworks (ZIFs) for the Irreversible Trapping of Iodine. *Chem. - Eur. J.* **2013**, *19*, 7049–7055.
- (209) Huang, P. S.; Kuo, C. H.; Hsieh, C. C.; Horng, Y. C. Selective Capture of Volatile Iodine Using Amorphous Molecular Organic Solids. *Chem. Commun.* **2012**, *48*, 3227–3229.
- (210) Choi, H. J.; Suh, M. P. Dynamic and Redox Active Pillared Bilayer Open Framework: Single-Crystal-to-Single-Crystal Transformations upon Guest Removal, Guest Exchange, and Framework Oxidation. *J. Am. Chem. Soc.* **2004**, *126*, 15844–15851.
- (211) Abrahams, B. F.; Moylan, M.; Orchard, S. D.; Robson, R. Zinc Saccharate: A Robust, 3D Coordination Network with Two Types of Isolated, Parallel Channels, One Hydrophilic and the Other Hydrophobic. *Angew. Chem., Int. Ed.* **2003**, *42*, 1848–1851.
- (212) Zhang, Z. J.; Shi, W.; Niu, Z.; Li, H. H.; Zhao, B.; Cheng, P.; Liao, D. Z.; Yan, S. P. A New Type of Polyhedron-Based Metal–Organic Frameworks with Interpenetrating Cationic And Anionic Nets Demonstrating Ion Exchange, Adsorption and Luminescent Properties. *Chem. Commun.* **2011**, *47*, 6425–6427.
- (213) Falaise, C.; Volkringer, C.; Facqueur, J.; Bousquet, T.; Gasnot, L.; Loiseau, T. Capture of Iodine in Highly Stable Metal–Organic Frameworks: A Systematic Study. *Chem. Commun.* **2013**, *49*, 10320–10322.
- (214) Li, G.; Yan, C.; Cao, B.; Jiang, J.; Zhao, W.; Wang, J.; Mu, T. Highly Efficient I₂ Capture by Simple and Low-Cost Deep Eutectic Solvents. *Green Chem.* **2016**, *18*, 2522.
- (215) Fu, L.; Hu, X.; Yu, S.; Guo, Y.; Liu, H.; Zhang, W.; Lou, Y.; Li, D.; Yu, Q. Sustainable Wastewater Treatment By Deep Eutectic Solvents And Natural Silk For Radioactive Iodine Capture. *Water Sci. Technol.* **2019**, *80*, 1683–1691.
- (216) Merza, F.; Fawzy, A.; AlNashef, I.; Al-Zuhair, S.; Taher, H. Effectiveness of Using Deep Eutectic Solvents as An Alternative to Conventional Solvents in Enzymatic Biodiesel Production From Waste Oils. *Energy Reports* **2018**, *4*, 77–83.
- (217) Lee, H.; Shin, W. S.; Jung, J. Y.; Kim, C. W.; Lee, J. W.; Kwon, J. H.; Yang, J. W. Optimization of Variables Affecting the Direct Transesterification of Wet Biomass From *Nannochloropsis oceanica* Using Ionic Liquid as a Co-Solvent. *Bioprocess Biosyst. Eng.* **2015**, *38*, 981–987.
- (218) Thuy Pham, T. P.; Cho, C. W.; Yun, Y. S. Environmental Fate and Toxicity of Ionic Liquids: a Review. *Water Res.* **2010**, *44*, 352–372.
- (219) Dominguez de María, P.; Maugeri, Z. Ionic Liquids in Biotransformations: from Proof-of-Concept to Emerging Deep-Eutectic-Solvents. *Curr. Opin. Chem. Biol.* **2011**, *15*, 220–225.
- (220) Torregrosa-Crespo, J.; Marsset, X.; Guillena, G.; Ramón, D. J.; Martínez-Espinosa, R. M. New Guidelines for Testing “Deep Eutectic Solvents” Toxicity And Their Effects On The Environment And Living Beings. *Sci. Total Environ.* **2020**, *704*, 135382.
- (221) Kim, K. H.; Eudes, A.; Jeong, K.; Yoo, C. G.; Kim, C. S.; Ragauskas, A. Integration of Renewable Deep Eutectic Solvents with Engineered Biomass to Achieve a Closed-Loop Biorefinery. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 13816–13824.
- (222) Merza, F.; Fawzy, A.; AlNashef, I.; Al-Zuhair, S.; Taher, H. Effectiveness of Using Deep Eutectic Solvents as an Alternative to Conventional Solvents in Enzymatic Biodiesel Production from Waste Oils. *Energy Reports* **2018**, *4*, 77–83.
- (223) Kadapure, S. A.; Kadapure, P.; Savadatti, A.; Bhojvani, N.; Joshi, O. Experimental investigation on biodiesel production incorporating deep eutectic solvents. *Proc. Inst. Civ. Eng.: Energy* **2020**, *173*, 150–156.