ABSTRACT: Four deep eutectic solvents (DESs) were synthesized, and 5–30% polyethylenimine (PEI) was added to make functional DESs (FDESs) for dynamic absorption experiments of hydrogen sulfide. The synthesized FDESs were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, and nuclear magnetic resonance. The results demonstrated the successful synthesis of FDESs. The interaction between H$_2$S and the FDESs was discussed at a molecular level via the quantum chemical calculations. It was noticed that FDESs prefer chemisorption on H$_2$S. In this work, the 25% PEI/FDES@EG showed the highest desulfurization performance. The effects of H$_2$S concentration and temperature on the desulfurization performance were investigated. It was found that a relatively low temperature (30 °C) was favorable for the absorption of H$_2$S. The 25% PEI/FDES@EG could remove H$_2$S efficiently over a low H$_2$S concentration. Moisture played an important role in the FDES desulfurization system. The absorption/desorption cycle experiment indicated that the FDESs retain their good regeneration performance for at least five times.

1. INTRODUCTION

As an extremely toxic and corrosive gas, hydrogen sulfide (H$_2$S) usually exists in the industrial production, such as biogas, coal gasification gas, oil, and natural gas. The toxicity and corrosiveness of H$_2$S can cause serious health problems and industrial pipeline damage, especially causing poisoning of noble metal catalysts. Therefore, the development of an efficient and low-cost method for removal of H$_2$S has caused great concern of many researchers in the oil, natural gas, and catalytic fields. At present, the common methods for removing H$_2$S can be divided into wet desulfurization and dry desulfurization depending on the type of desulfurizing agent. The absorption using alcohol amine solution, which is one of most common wet methods, has been widely used to remove hydrogen sulfide gas in the industry. However, the traditional amine absorption method has several disadvantages such as high volatility, high flammability, high energy consumption, high regeneration cost, and the evaporation of water during long-term operation that will also accelerate the corrosion of equipment and pipelines. Moreover, the process cannot operate at high temperatures. These deficiencies limit the exploitation of an aqueous solution in the field of gas separation applications. On the other hand, for dry desulfurization, activated carbon, molecular sieves, and membrane reactors have been widely used, but the relatively low desulfurization efficiency and cost problem still exist.

Hence, it is vital to find an alternative absorbent for capturing H$_2$S, which is more environmental friendly and stable.

Ionic liquids (ILs) are the organic salts in liquid form that are composed of various organic cations and inorganic or organic anions with a melting point below 100 °C. ILs have drawn the attention of researchers around the world because of their advantages such as high dissolving capability, thermal and chemical stability, negligible vapor pressure, and so on. In recent years, studies have found that ILs have high absorption capacity for acid gases such as CO$_2$, SOx, and NOx. ILs have been introduced into the desulfurization process. In the present study, the functionalized ILs have been investigated for removing H$_2$S. Zheng et al. designed three kinds of aqueous multiple Lewis base-functionalized protic IL solutions for highly efficient absorption of H$_2$S. In our previous work, oxidized substances and amines were introduced into the ILs, where the result showed that the mixtures could reach high H$_2$S removal efficiency. However, the high synthesis cost, poor biodegradability, and complex preparative technol-
ogy restrict the practical utilization of ILs in gas cleaning applications.30

Therefore, to overcome the limitations of ILs, deep eutectic solvents (DESs) are used as a new kind of solvents.29 They were usually prepared by a two-component or three-component combination with a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD).30−32 DESs have the same advantages as ILs, even some extra advantages, for instance, low toxicity, low cost, biodegradability, and simple synthesis process.33−37 More importantly, DESs have been used in many fields as an alternative of ILs. For example, Fattahi et al.38−41 introduced a new extraction method based on dispersive liquid−liquid microextraction and the solidification of DES. They found that DESs showed excellent extraction efficiency of different organic and inorganic compounds from the environment, food, and biological samples. The excellent characteristics of DESs also make it a new material for absorption of gases, such as CO2.42,43 SO2,19,44 and NOx.45−47 Li et al.45 found that the solubility of CO2 in a DES composed of ChCl and urea with a mole ratio of 1:2 increased with the increasing pressure and decreasing temperature. Dou et al.46 synthesized a DES from ethylene glycol and tetrabutylammonium bromide (EG−TBAB) for NO absorption. They found that the DES had excellent absorption and regeneration performance for removing NO. However, reports on the removal of H2S using DES are still rare. Wu et al.47 introduced iron salts into the conventional DES of propionic acid and tetrabutylammonium bromide ([Bmim]Br−TBAB) for the absorption of CO2 in a DES composed of ChCl and urea with a mole ratio of 1:2. Their results indicated that PEI was successfully introduced into the DES system, which proved that the structural characteristics of ChCl were essentially maintained in the DES.48,50

In this paper, we present an industrial attraction and unprecedented method to realize the H2S removal performance of PEI while utilizing the desirable properties of DESs. Four common choline-based DESs were synthesized.9,16,19,49,50 EG, urea, glycerol, and propylene glycol (PG) were used as HBD and chlorinated choline as HBA. PEI was added to form four FDESs, and the desulfurization and regeneration performance were measured by H2S dynamic absorption experiments. The effects of different types of DESs, PEI ratio, temperature, and moisture content were investigated. The applicability of an FDES to H2S concentration is also verified. The prepared FDESs have the same advantages as ILs, even have some extra advantages, for instance, low toxicity, low cost, biodegradability, and simple synthesis process.33−37 More importantly, DESs have been used in many fields as an alternative of ILs. For example, Fattahi et al.38−41 introduced a new extraction method based on dispersive liquid−liquid microextraction and the solidification of DES. They found that DESs showed excellent extraction efficiency of different organic and inorganic compounds from the environment, food, and biological samples. The excellent characteristics of DESs also make it a new material for absorption of gases, such as CO2.42,43 SO2,19,44 and NOx.45−47 Li et al.45 found that the solubility of CO2 in a DES composed of ChCl and urea with a mole ratio of 1:2 increased with the increasing pressure and decreasing temperature. Dou et al.46 synthesized a DES from ethylene glycol and tetrabutylammonium bromide (EG−TBAB) for NO absorption. They found that the DES had excellent absorption and regeneration performance for removing NO. However, reports on the removal of H2S using DES are still rare. Wu et al.47 introduced iron salts into the conventional DES of propionic acid and tetrabutylammonium bromide ([Bmim]Br−TBAB) for the absorption of CO2 in a DES composed of ChCl and urea with a mole ratio of 1:2. Their results indicated that PEI was successfully introduced into the DES system, which proved that the structural characteristics of ChCl were essentially maintained in the DES.48,50

In this paper, we present an industrial attraction and unprecedented method to realize the H2S removal performance of PEI while utilizing the desirable properties of DESs. Four common choline-based DESs were synthesized.9,16,19,49,50 EG, urea, glycerol, and propylene glycol (PG) were used as HBD and chlorinated choline as HBA. PEI was added to form four FDESs, and the desulfurization and regeneration performance were measured by H2S dynamic absorption experiments. The effects of different types of DESs, PEI ratio, temperature, and moisture content were investigated. The applicability of an FDES to H2S concentration is also verified. The prepared FDESs were characterized by Fourier transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), and thermogravimetric analysis (TGA). Quantum chemical calculations have been used to investigate the interaction between H2S and FDESs at a molecular level. The results show that the absorption between FDESs and H2S is chemical absorption. All this confirms that the FDESs are excellent desulfurizers.

2. RESULTS AND DISCUSSION

2.1. Characterization of FDESs and DESs. The FT-IR spectra of DESs with different compositions of HBDS are shown in Figure 1. The spectrum of ChCl indicates the presence of a strong O−H bond stretching vibration at 3253 cm−1 along with a −CH3 bending vibration peak at 1482 cm−1. The C−H bond stretching vibration peaks at 3017 and 2906 cm−1 and the C−N bond symmetric stretching vibration at 628 cm−1 were observed.51 Comparing the spectra of ChCl with the spectra of DES, the peaks at 3393 cm−1 (broad) and 1654 cm−1 should be assigned to the interaction of hydrogen bonds between HBD and ChCl and the introduction of water content.52 The C−O bond stretching vibration at 955 cm−1 indicated that the structure of Ch+ is not destroyed in the FDES system, which proved that the structural characteristics of ChCl were essentially maintained in the FDES.53,54

The FT-IR spectra of 25% PEI and FDESs are shown in Figure 2. The peak at 1584 cm−1 could be attributed to the bending vibration of the amine −NH2.54 The broad and strong adsorption peak at 3357 cm−1 was ascribed to the overlapping of the N−H and O−H stretching vibrations.55 The broad band between 2700 and 3800 cm−1 was attributed to the tensile vibration of −NH2 and O−H. Furthermore, the bands at 1584, 2936, and 3357 cm−1 for PEI all appeared in FDESs. These results indicated that PEI was successfully introduced into the FDES.48,56 The amine N−H stretching vibration of PEI at 3357 cm−1 widened in FDES. The possible reason was that it might be overlapped by the broad band of hydrogen bonding formed by EG and ChCl.57−60

Further evidence of the interaction between FDES and PEI was provided by the 1H NMR spectra of FDESs of 25% PEI and DESs, from the results shown in Figure 3: δ 2.57 (a, 2H, NH2CH2CH2NH2), 3.07 (b, 3H, s, HOCH2CH2N(CH3)), 3.39 (c, 2H, HOCH2CH2N(CH3)), 3.53 (d, 2H, HOCH2CH2N(CH3), HOCH2CH2OH), 3.93 (e, 2H, HOCH2CH2N(CH3), and 4.70 (f, 1H, s, HOCH2CH2OH,
HOCH₂CH₂N(CH₃)₃, HDO). It can be found that a new amine peak appears at 2.57 ppm (a) after the addition of 25% PEI. From the FT-IR spectra (Figure 2), it is indicated that PEI was successfully introduced into FDES.

The TGA−differential thermal analysis (DTA) curves of EG, ChCl, 2EG/ChCl, and FDES are shown in Figure 4. The decomposition temperatures of ChCl, EG, 2EG/ChCl, and FDES were around 570, 460, 544, and 586 K, respectively, which are higher than the absorption and regeneration temperatures in this experiment. A slight inclination of the TGA curves at temperatures lower than 100 °C could be assigned to the loss of a small amount of water. The exothermic peak generated by the FDES at 478 K in the DTA curve is due to the decomposition of PEI in FDES. The decrease in decomposition temperature could be attributed to the uniform dispersion of PEI in FDES.

2.2. Quantum Chemical Calculations. To obtain an understanding of the interactions between H₂S and the FDES at a molecular level, quantum chemical calculations have been performed. Several kinds of complexes (ChCl, EG, and PEI) could be hypothesized in the FDES. Therefore, the molecular systems taken into account were the 1:1 complexes between H₂S and ChCl, EG, and PEI, defined here as H₂S−A.

Subsequently, calculations on the complexes between H₂S and ChCl, EG, and PEI have been performed. Minimum structures were fully optimized, and the final structures of the absorption conformations of H₂S in the FDES are shown in Figure 5. The calculation results prove that DES (ChCl and EG) will not react with H₂S. PEI will form a hydrogen bond with H₂S, and the binding energy $E_{\text{int}}(\text{H}_2\text{S}−\text{PEI}) = -30.5676 \text{ kJ/mol}$ was calculated by quantum chemical calculations. The H₂S molecule interacts with a nitrogen atom in the amine group of PEI through the H atoms in H₂S, and the H₂S molecule prefers to adhere to the 16 N atom. DES is preferred as an excellent solvent. This calculation result basically confirms that the absorption between FDES and H₂S is chemical absorption.

2.3. Desulfurization Performance of DESs and FDESs. The desulfurization performances of DESs with different HBDs and ChCl are shown in Figure 6. The absorption temperature was controlled at 30 °C. It can be seen that the removal rate dropped sharply at the beginning of the absorption experiment. The dissolve effect of DESs on H₂S is not ideal. In order to strengthen the absorption capacity of DESs for H₂S, four kinds of FDESes were prepared by adding PEI with a mass ratio of 5% to the four DESs. The desulfurization performances of the four 5% PEI/FDESes at 30 °C are shown in Figure 7. The desulfurization performances of the four 5% PEI/FDESes decline in the following order: 5% PEI/FDES@EG > 5% PEI/FDES@Gly ≈ 5% PEI/FDES@Urea > 5% PEI/FDES@PG. The results prove that 2EG/ChCl was used as an optimum FDES desulfurizer, which could maintain the H₂S removal efficiency above 95% for at least 30 min. After the addition of PEI, the H₂S absorption capabilities of FDESes improved significantly. The improvement can be attributed to the contribution of the amine groups in PEI. Therefore, FDES@EG was chosen for further study.

2.4. Desulfurization Performances of FDES@EG with Different PEI Contents. The desulfurization performances of FDES@EG with different PEI contents at 30 °C are shown in Figure 8. It can be seen that FDESes have a relatively high desulfurization performance, and the H₂S removal efficiency could remain above 80% for at least 1 h. When the PEI content in FDES@EG increased to 25%, the desulfurization efficiency
reached the maximum level. Even if the PEI content increased, no increase of FDES@EG desulfurization performance was observed, which may be due to the fact that the amount of PEI that can be reacted is saturated in a limited medium. Therefore, 25% PEI/FDES@EG was selected as a desulfurizing agent for the subsequent experiments.

2.5. Effect of Absorption Temperature and Moisture.

The desulfurization performances of 25% PEI/FDES@EG at different absorption temperatures are shown in Figure 9. The H$_2$S removal efficiency could remain above 95% within 80 min at 30 and 40 $^\circ$C. When the absorption temperature increased to 70 $^\circ$C, the desulfurization rate reduced to about 20%. It is clear that the removal efficiency of H$_2$S significantly reduced with the increase of temperature because the absorption of H$_2$S is an exothermic process, and the increase of the reaction temperature hinders the absorption reaction process. Besides, considering that high temperature may accelerate the loss of a small amount of water content existed in the FDES, the effect of water should be taken into account.

To verify the effect of water content, 25% PEI/FDES@EG was treated under reduced pressure at 100 $^\circ$C to eliminate most of the water content. The treated 25% PEI/FDES@EG was used to remove H$_2$S at 30 $^\circ$C. The absorption results are shown in Figure 10. It could be seen that the removal efficiency of H$_2$S was significantly lower than that of the untreated adsorbent. To further analyze the possible absorption mechanism, the $^1$H NMR spectroscopy of 25% PEI/FDES@EG before and after absorption was analyzed. The results are shown in Figure 11. For the $^1$H NMR spectrum of the sample after H$_2$S absorption, the peak became smaller at 4.70 ppm (f, 1H, s, CH$_2$OH, CH$_2$N(CH$_3$)$_2$, and HDO), which could be attributed to the loss of water in the absorption process. Therefore, from Figure 10, it can be seen that the water content should be an important factor which affected the desulfurization performance. The presence of proper water content is beneficial to the absorption reaction of H$_2$S in 25% PEI/FDES@EG. It has been reported that the amine group

Figure 5. Energy-minimized structures of H$_2$S$^-$A complexes. Color code: green, chloride; yellow, carbon; light gray, sulfur; light blue, hydrogen; pink, nitrogen; and orange, oxygen.

Figure 6. Desulfurization performances of different HBDs of DESs at 30 $^\circ$C.

Figure 7. Desulfurization performances of different HBDs of FDESs at 30 $^\circ$C.

Figure 8. Desulfurization performances of FDES@EG for different PEI contents at 30 $^\circ$C.

Figure 9. Desulfurization performances of 25% PEI/FDES@EG at different absorption temperatures.
will react directly with H$_2$S in the presence of water.$^{15,63}$ In our previous work,$^{12}$ it was also found that the proper water content has a positive effect on the absorption of H$_2$S. In conclusion, the increase of temperature will hinder the exothermic reaction and accelerate the evaporation of water. Low temperature and proper water content are beneficial to the absorption of H$_2$S in FDESs.

2.6. Desulfurization Performances of FDES under Different H$_2$S Concentrations. The desulfurization performances of 25% PEI/FDES@EG at different H$_2$S concentrations are shown in Figure 12. The desulfurization rates of 25% PEI/FDES@EG at different H$_2$S concentrations are not lower than 90% within 60 min. The results showed that 25% PEI/FDES@EG has a high desulfurization efficiency over a H$_2$S concentration range from 750 to 1250 mg/m$^3$. When the concentration of H$_2$S continued to increase, the absorption performance of FDES decreased. Therefore, the 25% PEI/FDES@EG could remove H$_2$S efficiently over a low H$_2$S concentration.

2.7. Regeneration Performance. 2.7.1. Effect of Regeneration Temperature. The regeneration of exhausted FDESs was conducted by air bubbling for 1 h at different regeneration temperatures. The results are shown in Figure 13.

When the regeneration temperature is 70 °C, the desulfurization rate of 25% PEI/FDES@EG after regeneration is restored to 85%. The desulfurization rates at the regeneration temperature 30 and 50 °C can only reach 70%. The absorption of H$_2$S is exothermic, and high temperature is conducive to the desorption of H$_2$S. The decline of the desulfurization performances of FDES may be caused by the evaporation of water during regeneration. Therefore, 70 °C was selected as the regeneration temperature for the subsequent experiments.

2.7.2. Effect of Regeneration Time. After selecting the regeneration temperature, the effect of the regeneration time was evaluated, and the results are shown in Figure 14. The different regeneration time leads to the various regeneration effects. When the regeneration time was longer than 5 h, the desulfurization rate of 25% PEI/FDES@EG after regeneration reduced to 40%. The desulfurization rates of 25% PEI/FDES@EG after the regeneration times of 1 and 3 h could remain above 80%. It could be seen that bubbling for 3 h has been conducted during the regeneration process. Thus, a regener-
ation time of 3 h was selected. The decline of regeneration performance after long-time regeneration may be attributed to the loss of moisture in FDESs.

2.7.3. Effect of Moisture on the Regeneration Performance. In the previous discussion, the loss of water content was considered as the main reason for the decline of regeneration performances. The effect of moisture on the regeneration performance was investigated. The regeneration condition was chosen as bulling at 70 °C for 3 h. It was found that the desulfurization rate within 3 h after four regenerations was reduced to 20%, and the results are shown in Figure 15(1). In another experiment, a small amount of deionized water was added before every regeneration process to simulate the water lost during the regeneration, and the results are shown in Figures 15(2) and 16. It was found that the regeneration rate returned to the original 98%. From Figures 10 and 11, it has been proved that the presence of moisture plays an important role in H₂S removal. Lower temperature and H₂S concentrations favored the absorption of H₂S. The structures of the absorption conformations of H₂S in FDES have been found at a molecular level via the quantum chemical calculations. It was noticed that FDESs prefer chemisorption on H₂S. The results of regeneration experiments showed that 25% PEI/FDES@EG can remove H₂S well at least five times only by gas stripping regeneration. It is also found that the presence of moisture plays an important role in H₂S removal. The FDES adsorbent has been proved as an industrially attractive desulfurizer for H₂S removal.

3. CONCLUSIONS

In the present work, the DES of four different HBDs was synthesized. An FDES was prepared by adding PEI and used for H₂S removal. EG/ChCl was chosen as the best reaction solvent. Efforts were taken to combine the desirable properties of DESs for excellent stability with the reactivity of PEI. The absorption experiments showed that 25% PEI/FDES@EG is the best absorbent. Lower temperature and H₂S concentrations favored the absorption of H₂S. The structures of the absorption conformations of H₂S in FDES have been found at a molecular level via the quantum chemical calculations. It was noticed that FDESs prefer chemisorption on H₂S. The results of regeneration experiments showed that 25% PEI/FDES@EG can remove H₂S well at least five times only by gas stripping regeneration. It is also found that the presence of moisture plays an important role in H₂S removal. The FDES adsorbent has been proved as an industrially attractive desulfurizer for H₂S removal.

4. EXPERIMENTAL DETAILS

4.1. Materials. Choline chloride (C₅H₁₄ClNO, ChCl) was purchased from Sinopharm Chemical Reagent Co., Ltd., China; PEI ((CH₂CH₂NH)ₙ) was purchased from Shanghai Macklin Biochemical Co., Ltd., China; and glycerol (C₃H₈O₃, ACS Omega http://pubs.acs.org/journal/acsofb Article

https://dx.doi.org/10.1021/acsomega.0c01467
ACS Omega 2020, 5, 15353−15361
Gly)), EG ((CH2OH)2), PG (C3H6O2), and urea (CH4N2O, Urea) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd., China; the reagents are all analytically pure (98–99%). All the above chemicals were used as received.

### 4.2. Computational Details

All quantum chemical calculations in this study were performed by ORCA. Geometry optimizations have been performed using the dispersion including density functional theory with the M06-2X functional using 6-311G** basis set. The DFT-D3 dispersion correction is used to improve the accuracy of weak interaction description. The binding energy (E_{\text{inter}}) was defined and estimated on the basis of the following equation

\[ E_{\text{inter}} = E_{\text{comp}} - (E_{\text{mol}A} + E_{\text{mol}B}) \]

where \( E_{\text{comp}} \), \( E_{\text{mol}A} \), and \( E_{\text{mol}B} \) are the total energies of the adsorption complex, \( \text{H}_2\text{S} \), and the other component, respectively.\(^\text{15,64}\)

#### 4.3. Preparation of FDESs

The four choline-based DESs were synthesized according to the literature studies.\(^\text{49–51,66}\) The DES of 2Gly/ChCl was prepared by mixing ChCl (0.05 mol, 6.981 g) and Gly (0.1 mol, 9.209 g) complexes with a molar ratio of 1:2 [limit of detection (LOD): 0.1 mg; relative standard deviation (RSD): ±0.1 mg]. The mixture was heated at 80 °C with continuous stirring for 2 h until a clear uniform liquid is formed. In the same way, the other three DESs were produced. The DESs obtained were collected and identified as 2Gly/ChCl, 2EG/ChCl, 2PG/ChCl, and 2Urea/ChCl. The prepared DESs were in the form of liquid at room temperature. PEI was added to the DESs with a mass ratio of 5–30%.

#### 4.4. Characterization Instruments

The FT-IR spectra of the samples were collected by a Nicolet 5700 Fourier transform infrared spectrometer (Thermo Nicolet Corp., America). The NMR spectra of the samples were collected by an AVANCE III HD 400 MHz NMR spectrometer (Bruker Corp., Switzerland) (ppm, D2O, 400 MHz, 300 K). The TGA and the corresponding DTA curves of the samples were collected by a STA 449 C Integrated thermal analyzer (Netzsch Corp., Germany); the data were collected with a heating rate of 10 °C/min under flowing nitrogen.

#### 4.5. \( \text{H}_2\text{S} \) Sorption Measurement

The dynamic \( \text{H}_2\text{S} \) absorption experiment equipment is shown in Figure 18: a model gas (a \( \text{H}_2\text{S} \) concentration of 750–1750 mg/m\(^3\) and nitrogen as a diluent gas) was introduced into the reactor consisting 4 g of FDES with a flow rate (LOD: 1 × 10\(^{-8}\) Pa·m\(^3\)/s; RSD: ≤0.2%) of 250 mL/min. The temperature was controlled at 30–100 °C by a constant temperature water bath. The \( \text{H}_2\text{S} \) concentration in the outlet gas was measured by an AP-B \( \text{H}_2\text{S} \) gas online analyzer (LOD: 0.1 ppm; RSD: ≤1%). Finally, the tail gas was passed through a NaOH solution to remove the residual \( \text{H}_2\text{S} \). During the desorption step, the depletion of FDES was performed by bubbling air with a flow rate of 500 mL/min at 30–70 °C for 1–5 h. The \( \text{H}_2\text{S} \) removal efficiency can be calculated by the following equations

\[ \eta = \frac{(C_0 - C_t)}{C_0} \]

where \( \eta \) is the desulfurization rate, \( C_0 \) is the \( \text{H}_2\text{S} \) concentration in the model gas, and \( C_t \) is determined as the \( \text{H}_2\text{S} \) concentration at the exit. The experimental data obtained were repeatedly measured three times or more.

#### ACKNOWLEDGMENTS

This work was supported by funding from the National Natural Science Foundation of China (nos. 21908134 and 41771348) and Natural Science Foundation of Shandong Province (no. ZR2019BB045).

#### REFERENCES

1. Santiago, R.; Lemus, J.; Outomuro, A. X.; Bedia, J.; Palomar, J. Assessment of ionic liquids as \( \text{H}_2\text{S} \) physical absorbents by...
thermodynamic and kinetic analysis based on process simulation. Sep. Purif. Technol. 2020, 233, 116050.

(2) Salehin, F. N. M.; Jumbril, K.; Ramli, A.; Daud, S.; Abdul Rahman, M. B. In silico solvation free energy and thermodynamics properties of H$_2$S in cholinium-based amino acid ionic liquids. J. Mol. Liq. 2019, 294, 111641.

(3) Shokouhi, M.; Sakheinia, H.; Jalili, A. H.; Zoghi, A. T.; Mehdizadeh, A. Experimental diffusion coefficients of CO$_2$ and H$_2$S in some ionic liquids using semi-infinite volume method. J. Chem. Thermodyn. 2019, 133, 300–311.

(4) Liu, X.; Li, J.; Wang, R. Desulfurization and regeneration performance of heteropoly compound/ionic liquid solutions at high temperature. Chem. Eng. J. 2017, 316, 171–178.

(5) Liu, X.; Wang, R. Effective removal of hydrogen sulfide using 4A molecular sieve zeolite synthesized from attapulgite. J. Hazard. Mater. 2017, 326, 157–164.

(6) Ma, Y.; Liu, X.; Wang, R. Efficient removal of H$_2$S at high temperature using the ionic liquid solutions of [C$_4$mim]$_3$PMo$_{12}$O$_{40}$ and methylimidazolium tetrafluoroborate. J. Hazard. Mater. 2017, 331, 109–116.

(7) Han, X.; Chen, H.; Liu, Y.; Pan, J. Study on removal of gaseous hydrogen sulfide based on macroligand biosorbs. J. Nat. Gas Sci. Eng. 2020, 73, 103068.

(8) Ali, F. I. M.; Awwad, F.; Greish, Y. E.; Abu-Hani, A. F. S.; Mahmoud, S. T. Fabrication of low temperature and fast response H$_2$S gas sensor based on organic-metal oxide hybrid nanocomposite membrane. Org. Electron. 2020, 76, 105486.

(9) Wang, Y.; Wang, Z.; Pan, J.; Liu, Y. Removal of gaseous hydrogen sulfide using Fenton reagent in a spraying reactor. Fuel 2019, 239, 70–75.

(10) Wihee, A. D.; Shamsudin, I. K.; Ahmad, M. A.; Murat, M. N.; Vorotyntsev, A. V.; Nyuchev, A. V.; Vorotyntsev, I. V. Solubility of H$_2$S and CO$_2$ in imidazolium-based ionic liquids with bis(2-ethylhexyl) sulfo succinate anion. J. Chem. Thermodyn. 2019, 130, 173–182.

(11) Zhao, T.; Li, P.; Feng, X.; Hu, X.; Wu, Y. Study on absorption and spectral properties of H$_2$S in carbamate protonic liquids with low viscosity. J. Mol. Liq. 2018, 266, 806–813.

(12) Huang, K.; Zhang, X.-M.; Hu, X.-B.; Wu, Y.-T. Hydrophobic protonic liquidic tethers combined with tertiary amine group for highly efficient and selective absorption of H$_2$S from CO$_2$. AIChE J. 2016, 62, 4480–4490.

(13) Jalili, A. H.; Mehrabi, M.; Zoghi, A. T.; Shokouhi, M.; Taheri, S. A. Solubility of carbon dioxide and hydrogen sulfide in the ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate. Fluid Phase Equilib. 2017, 453, 1–12.

(14) Jalili, A. H.; Shokouhi, M.; Maurer, G.; Zoghi, A. T.; Sadeghzah Ahari, J.; Forsat, K. Measuring and modelling the absorption and volumetric properties of CO$_2$ and H$_2$S in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate. J. Chem. Thermodyn. 2019, 131, 544–556.

(15) Zheng, W.; Wu, D.; Feng, X.; Hu, J.; Zhang, F.; Wu, Y.-T.; Hu, X.-B. Low viscous Protonic ionic liquids functionalized with multiple Lewis Base for highly efficient capture of H$_2$S. J. Mol. Liq. 2018, 263, 209–217.

(16) Liu, X.; Wang, R. H$_2$S removal by peryxo heteropoly compound/ionic liquid solution. Fuel Process. Technol. 2017, 160, 78–85.

(17) Liu, X.; Li, J.; Wang, R. Study on the desulfurization performance of hydramine/ionic liquid solutions at room temperature and atmospheric pressure. Fuel Process. Technol. 2017, 167, 382–387.

(18) Abbott, A. P.; Capper, G.; Davies, D. I.; Rasheed, R. K.; Tambrayahaj, V. Novel solvent properties of choline chloride/urea mixtures. Chem. Commun. 2003, 70–71.

(19) Xu, H.; Peng, J.; Kong, Y.; Liu, Y.; Su; Z.; Li, B.; Song; X.; Liu, S.; Tian, W. Key process parameters for deep eutectic solvents pretreatment of lignocellulosic biomass materials: A review. Bioresource Technol. 2020, 310, 123416.

(20) Li, W.; Wang, N.; Liu, Z.; Fei, Z.; Zheng, M.; Zhao, J.; Zhao, H. Solubility modeling and thermodynamic properties of allopurinol in aqueous solutions of four deep eutectic solvents. J. Chem. Thermodyn. 2019, 132, 363–372.

(21) Xie, Y.; Dong, H.; Zhang, S.; Lu, X.; Ji, X. Solubilities of CO$_2$, CH$_4$, H$_2$, CO and N$_2$ in choline chloride/urea. Green Energy Environ. 2016, 1, 195–200.

(22) Oh, Y.; Park, S.; Yoo, E.; Jo, S.; Hong, J.; Kim, H. J.; Kim, K. J.; Oh, K. K.; Lee, S. H. Dihydrogen-bonding deep eutectic solvents as reaction media for lipase-catalyzed transesterification. Biochem. Eng. J. 2019, 142, 34–40.

(23) Milker, S.; Pitzold, M.; Bloh, J. Z.; Holtmann, D. Comparison of deep eutectic solvents and solvent-free reaction conditions for aldol production. Mol. Catal. 2019, 466, 70–74.

(24) Lu, Y.; Geng, S.; Wang, S.; Rao, S.; Huang, Y.; Zou, X.; Zhang, Y.; Xu, Q.; Lu, X. Electrodeposition of Ni Mo Cu coatings from roasted nickel matte in deep eutectic solvent for hydrogen evolution reaction. Int. J. Hydrogen Energy 2019, 44, 5704–5716.

(25) Duan, X.; Gao, B.; Zhang, C.; Deng, D. Solubility and thermodynamic properties of NH$_3$ in choline chloride-based deep eutectic solvents. J. Chem. Thermodyn. 2019, 133, 79–84.

(26) Kamgar, A.; Mohsenpour, S.; Esmaeilzadeh, F. Solubility prediction of CO$_2$, CH$_4$, H$_2$, CO and N$_2$ in Choline Chloride/Urea as a eutectic solvent using NRTL and COSMO-RS models. J. Mol. Liq. 2017, 247, 70–74.

(27) Akramipour, R.; Golpayegani, M. R.; Gheini, S.; Fattahi, N. Specification of organic/inorganic mercury and total mercury in blood samples using vortex assisted dispersive liquid-liquid microextraction based on the freezing of deep eutectic solvent followed by GFAAS. Talanta 2018, 186, 17–23.

(28) Pirsahab, M.; Fattahi, N. Development of a liquid-phase microextraction based on the freezing of a deep eutectic solvent followed by HPLC-UV for sensitive determination of common
(40) Akramipour, R.; Golpayegani, M. R.; Ghasemi, M.; Noori, N.; Fattahi, N. Development of an efficient sample preparation method for the speciation of Se(iv)/Se(vi) and total inorganic selenium in blood of children with acute leukemia. New J. Chem. 2019, 43, 6951−6958.

(41) Habibollahi, M. H.; Karimyan, K.; Afraeenia, H.; Mirzaei, N.; Safari, Y.; Akramipour, R.; Sharafi, H.; Fattahi, N. Extraction and determination of heavy metals in soil and vegetables irrigated with treated municipal wastewater using new mode of dispersive liquid-liquid microextraction based on the solidified deep eutectic solvent followed by GFAAS. J. Sci. Food Agric. 2019, 99, 656−665.

(42) Haider, M. B.; Jha, D.; Marriyappan Sivagnanam, B.; Kumar, R. Modelling and simulation of CO2 removal from shale gas using deep eutectic solvents. J. Environ. Eng. 2019, 7, 102747.

(43) Isik, M.; Zulficar, S.; Edhaim, F.; Ruiperez, F.; Rothenberger, A.; Mecerreyes, D. Sustainable Poly(ionic Liquids) for CO2 Capture Based on Deep Eutectic Monomers. ACS Sustainable Chem. Eng. 2016, 4, 7200−7208.

(44) Wagle, D. V.; Zhao, H.; Deakyne, 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.

(45) Lerom, R. B.; Caparanga, A.; Li, M.-H. Carbon dioxide solubility in a deep eutectic solvent based on choline chloride and urea at T=303.15−343.15K and moderate pressures. J. Taiwan Inst. Chem. Eng. 2013, 44, 879−885.

(46) Wu, H.; Shen, M.; Chen, X.; Yu, G.; Abdeltwab, A. A.; Yakout, S. M. New absorbents for hydrogen sulfide: Deep eutectic solvents of tetrahydroammonium bromide/carboxylic acids and choline chloride/carboxylic acids. Sep. Purif. Technol. 2019, 224, 281−289.

(47) Sui, L.; Yang, F.; Luo, G. X.; Han, C. Hydrogen Sulfide Removal by Fe-Based Deep Eutectic Solvents. Pet. Process. Petrochem. 2015, 46, 22−26.

(48) Wang, X.; Ma, X.; Sun, L.; Song, C. A nanoporous polymeric sorbent for deep removal of H2S from gas mixtures for hydrogen purification. Green Chem. 2007, 9, 695.

(49) 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.

(50) 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.

(51) Uma Maheswari, A.; Palanivelu, K. Carbon Dioxide Capture and Utilization by Alkanolamines in Deep Eutectic Solvent Medium. Ind. Eng. Chem. Res. 2015, 54, 11383−11392.

(52) Keuleers, R.; Janssens, J.; Deseyn, H. O. Thermal analysis and vibrational spectroscopy of Mn (II)−urea−halide complexes: comparative study of the metal−ligand bond strength. Thermochim. Acta 2000, 354, 125−133.

(53) Wang, X.; Lin, K. S. K.; Chan, J. C. C.; Cheng, S. Direct synthesis and catalytic applications of ordered large pore amino- propyl-functionalized SBA-15 mesoporous materials. J. Phys. Chem. B 2005, 109, 1763−1769.

(54) Liu, F.; Zhou, L.; Wang, W.; Yu, G.; Deng, S. Adsorptive recovery of Au(III) from aqueous solution using crosslinked polyethyleneimine resins. Chemosphere 2020, 241, 125122.