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Amino Acid – based Deep Eutectic Solvents for Oxidative Extractive Desulphurization (OEDS) of Model Oil

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The removal of sulfur compounds from fuel oil is a key challenge in petroleum refining, as hydrodesulfurization (HDS) is ineffective for sterically hindered species such as dibenzothiophene, benzothiophene, and thiophene. This study explores oxidative extractive desulfurization (OEDS) using deep eutectic solvents (DESs) as sustainable alternatives. Three DESs were synthesized from glutaric acid, β-alanine, and polyethylene glycol (PEG). FTIR confirmed successful formation, while toxicity analysis suggested safe application. Experimental and COSMO-RS studies identified β-alanine–PEG as the most effective extractant, outperforming glutaric acid–PEG and glutaric acid–β-alanine–PEG. Response surface methodology (RSM) was employed to optimize thiophene extraction using β-alanine–PEG, considering temperature (25–100 °C), DES-to-oil ratio (0.2–1), and oxidant-to-sulfur ratio (1–15). DES dosage was the dominant factor, with optimal performance at 60 °C, DES-to-oil ratio of 1, and oxidant-to-sulfur ratio of 12, achieving 93.4% extraction efficiency. The solvent retained activity for at least five cycles. These findings demonstrate OEDS with DESs as a promising, energy-efficient, and environmentally friendly alternative to HDS.

Keywords: Oxidative-extractive desulfurization, deep eutectic solvent, glutaric acid, fuel purification

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The removal of sulfur compounds from fuel oil remains a major challenge in petroleum refining. During combustion, sulfur species in fuels such as gasoline and diesel oxidize to sulfur dioxide (SO_2), which contributes to smog, acid rain, and ocean acidification, leading to environmental and health concerns [1]. Key SO_2 sources include petroleum refineries, industrial boilers, smelting operations, vehicles, coal-fired plants, and volcanic activity. Sulfur occurs in fuels in several forms, including thiophenes, sulfides, sulfones, and disulfides [2].

Various desulfurization methods have been developed, including hydrodesulfurization (HDS), biodesulfurization (BDS), adsorptive desulfurization (ADS), extractive desulfurization (EDS), and oxidative desulfurization (ODS) [3]. While HDS, BDS, and ADS often require costly materials and harsh operating conditions, EDS and ODS offer advantages such as low temperature and pressure operation and improved selectivity [4]. However, ODS typically requires a catalyst, and EDS depends heavily on the choice of extractant.

Ionic liquids (ILs) have shown promise for sulfur removal due to their tunable properties [5], but limitations such as high cost, synthesis complexity, viscosity, and potential toxicity hinder their industrial use [6]. Deep eutectic solvents (DESs), formed by hydrogen bond donors (HBDs) and acceptors (HBAs), provide a sustainable alternative, combining IL-like properties with advantages such as simple synthesis, low cost, biodegradability, and reduced toxicity [7].

In oxidative extractive desulfurization (OEDS), DESs interact with sulfur compounds through hydrogen bonding and polarity-driven interactions, enhancing oxidation with H_2O_2 and facilitating sulfone extraction [8]. DES acidity also influences efficiency, with higher acidity promoting better sulfur removal. This study aims to synthesize and characterize DESs for OEDS, evaluate their toxicity, and test their extraction performance. Thiophene in heptane was used as model oil, with H_2O_2 as oxidant. Optimization considered DES-to-oil ratio (0.2–1), oxidant-to-sulfur ratio (1–5), and temperature (25–85 °C).

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EXPERIMENTAL

Materials

Glutaric acid, polyethylene glycol (PEG), and β-alanine are used for the synthesis of Deep Eutectic Solvents (DESs). Thiophene and heptane are used for the synthesis of model oil. Hydrogen peroxide is used as an oxidant in oxidative desulphurization.

Preparation and Characterization of Deep Eutectic Solvents (DESs)

DESs were prepared by mixing the hydrogen bond donor (HBD) and acceptor (HBA) at 80 °C for 2 h. Fourier transform infrared (FTIR) spectra were obtained using a Perkin Elmer spectrometer (450–4000 nm, four scans), applying the same parameters for all DES samples. Toxicity was evaluated using the In-House Method LAB-STP-4008 (disk diffusion). Bacteria were spread on agar plates, and disks impregnated with DES were placed on top. After incubation, inhibition zones were measured and compared with Clinical and Laboratory Standards Institute (CLSI) guidelines: resistant (≤11 mm), intermediate (12–14 mm), or susceptible (≥15 mm). This assessment indicated the relative toxicity of each DES formulation.

Oxidative Extractive Desulfurization (OEDS)

Model oil (30 ppm thiophene in heptane) was oxidized with hydrogen peroxide for 15 min, followed by DES extraction under set conditions. The upper oil phase was analyzed for sulfur content. The best DES was optimized by varying DES-to-oil ratio (0.2–1), oxidant-to-sulfur ratio (1–5), and temperature (25–85 °C) using Box Behnken Design response surface methodology with aid of Design Expert 12 software. Sulfur concentration was measured by UV–vis (200–700 nm), and extraction efficiency (EE) was calculated using Equation (1).

$$Percentage\ Extraction\ Efficiency\ (EE\ \%) = \frac{S_i - S_f}{S_i} \times 100\% \qquad (1)$$

where and S_i are S_f the initial and final concentration of sulfur, accordingly.

Computational Study through Conductor-like Screening Model for Realistic Solvation (COSMO-RS)

Deep eutectic solvents (DESs) structures were optimized using Turbomole, and Conductor-like Screening Model for Realistic Solvation (COSMO-RS) calculations were performed with COSMOthermX (BP_TZVP parameterization) to predict thermodynamic properties. DFT with the resolution of identity approximation, Becke–Perdew functional, and TZVP basis set was applied for electronic energy evaluation. Solvent performance was assessed using capacity, defined as the amount of DES required to extract a solute, calculated using Equation (2) [9].

$$\left(C_{12}^{\infty} = \frac{1}{\gamma_1^{\infty}}\right)^{\text{DES phase}} \qquad (2)$$

where C_{12}^{∞} was the capacity, and γ_1^{∞} was the activity coefficient of molecular solute in their infinitely diluted solution with deep eutectic solvent.

RESULTS AND DISCUSSION

Characterization of Deep Eutectic Solvents (DESs)

Figure 1 presents the FTIR spectra of the individual components and their corresponding deep eutectic solvents (DESs): (a) β-alanine:PEG, (b) glutaric acid: β-alanine:PEG, and (c) glutaric acid:PEG. FTIR spectroscopy was employed to investigate inter-molecular interactions within these systems by comparing the characteristic vibrational bands of the pure components with those of the formed DESs.

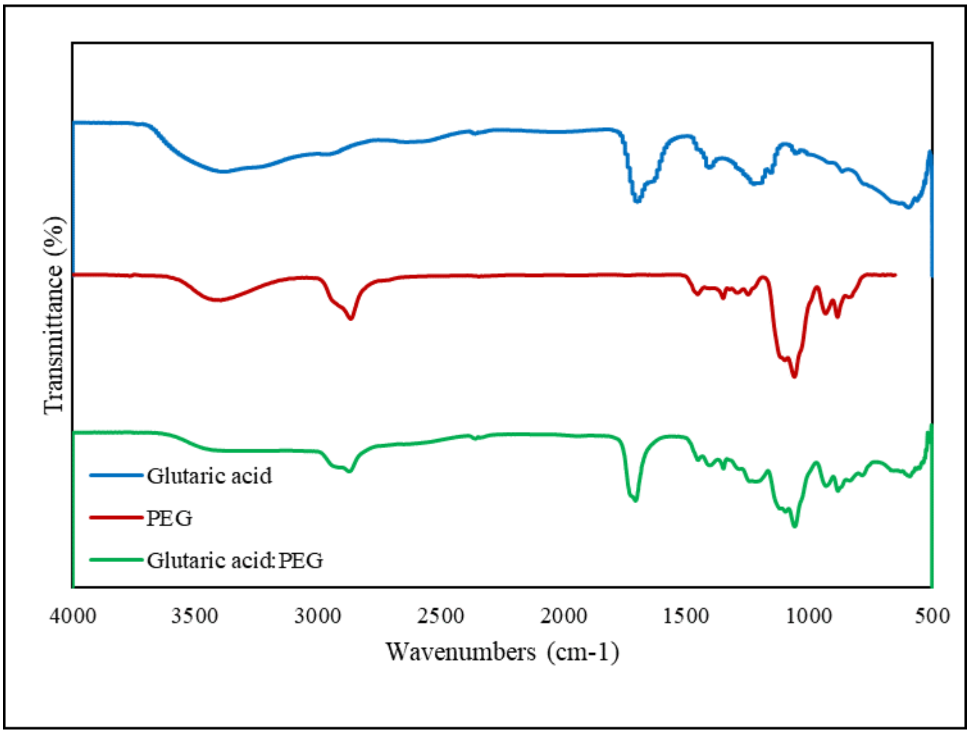
Across all systems, the most pronounced spectral changes are observed in the O–H/N–H stretching region (approximately 2500–3500 cm⁻¹), which is highly sensitive to hydrogen bonding interactions. The individual components—β-alanine, glutaric acid, and PEG-exhibit distinct but overlapping absorption bands in this region. β-Alanine shows broad O–H/N–H stretching due to its zwitterionic nature, PEG displays a broad O–H stretching band associated with terminal hydroxyl groups, while glutaric acid exhibits a very broad O–H band characteristic of carboxylic acid hydrogen bonding.

Upon DES formation, all three systems exhibit significant band broadening and a shift of the O–H/N–H stretching bands towards lower wavenumbers. This red shift indicates the formation of stronger and more extensive hydrogen bonding networks compared to the individual components. Notably, the extent of band broadening increases with system complexity, with the ternary glutaric acid:β-alanine:PEG DES (Figure 1b) showing the most pronounced broadening, suggesting the coexistence of multiple hydrogen bond donor–acceptor interactions.

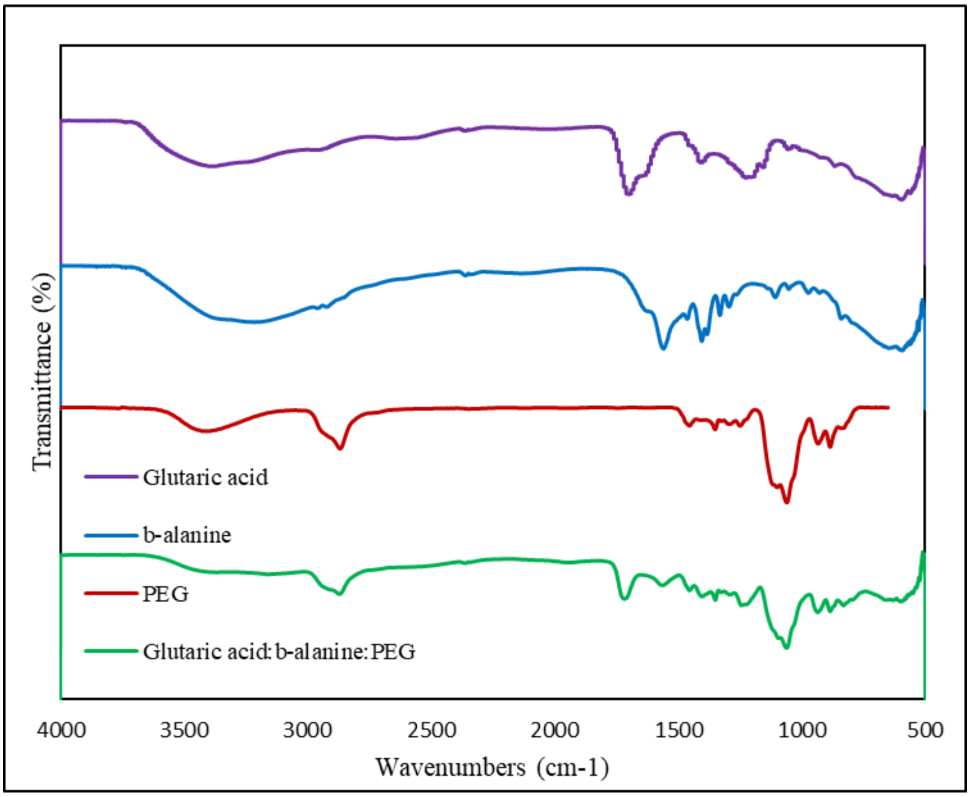
In the β-alanine:PEG system (Figure 1a), the observed broadening and red shift of the O–H/N–H stretching band indicate hydrogen bonding between the amino and hydroxyl groups of β-alanine and the ether oxygen atoms of PEG. Subtle shifts in the carboxylate stretching vibrations of β-alanine further suggest changes in the local electronic environment due to intermolecular interactions within the DES matrix.

For the glutaric acid:PEG system (Figure 1c), changes in the characteristic C=O stretching band of glutaric acid (approximately 1700–1725 cm⁻¹) are observed upon DES formation, including slight shifts and intensity reductions. These changes imply the involvement of carboxylic acid groups in hydrogen bonding with PEG, particularly through interactions between the acidic hydroxyl protons and ether oxygen atoms. Minor shifts in the C–O–C stretching vibrations of PEG further support the role of PEG as a hydrogen bond acceptor in this binary DES.

(a)



(b)



(c)

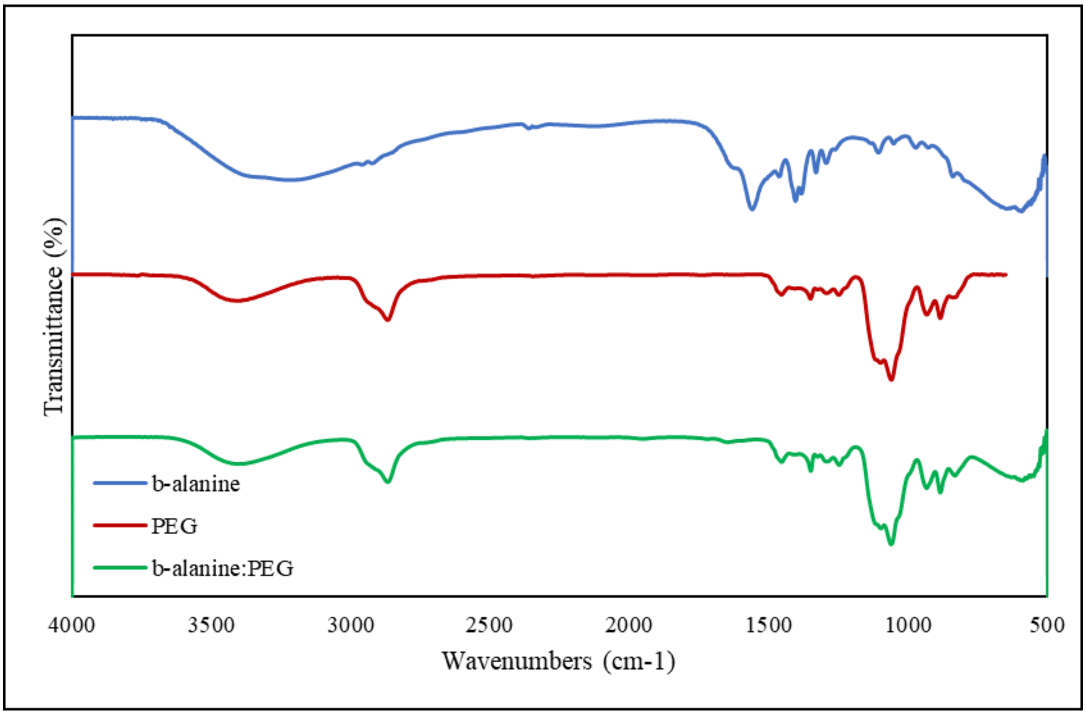


Figure 1. FTIR Spectra of (a) Glutaric Acid + Polyethylene Glycol, (b) Glutaric Acid + β-Alanine + Polyethylene Glycol, and (c) β-Alanine + Polyethylene Glycol.

The ternary glutaric acid:β-alanine:PEG DES (Figure 1b) exhibits combined spectral features of both binary systems, with more pronounced changes in both the O–H/N–H stretching region and the carbonyl/carboxylate stretching regions. The C=O stretching band of glutaric acid and the carboxylate bands of β-alanine display noticeable shifts, indicating strong interactions involving carboxylic acid–amine, carboxylic acid–ether, and hydroxyl–ether hydrogen bonding. These cumulative effects reflect a more complex hydrogen-bonded supramolecular network within the ternary DES.

Additionally, changes in the C–O–C stretching region (approximately 1100–1150 cm^{-1}) across all DES spectra suggest the participation of PEG ether oxygen atoms as key hydrogen bond acceptors. The altered vibrational environments of these functional groups indicate that the interactions in the DES systems extend beyond simple physical mixing.

Overall, the consistent peak shifts, band broadening, and intensity variations observed across the three DES systems demonstrate the formation of extensive hydrogen bonding interactions between the constituent components. While FTIR spectroscopy alone does not directly confirm eutectic behavior, the observed spectral modifications strongly support the successful formation of hydrogen-bond-dominated deep eutectic solvent structures in all three systems.

Screening of Deep Eutectic Solvent

The toxicity and desulfurization performance of three DES systems were evaluated experimentally and through COSMO-RS predictions (Figure 2). Glutaric acid–PEG showed moderate toxicity, mainly due to the irritant nature of glutaric acid, raising concerns for large-scale use. Incorporating β-alanine reduced toxicity, with the glutaric acid–β-alanine–PEG ternary system exhibiting improved safety. The β-alanine–PEG binary system was the least toxic, reflecting the biocompatibility of β-alanine and offering an eco-friendly alternative. Experimental screening and COSMO-RS analysis consistently identified β-alanine–PEG as the most effective extractant, followed by glutaric acid–PEG and glutaric acid–β-alanine–PEG. COSMO-RS predictions aligned closely with experimental data by accounting for functional groups such as hydroxyl, carboxyl, and amine moieties that form hydrogen bonds and polarity-driven interactions with thiophene. This agreement highlights the utility of COSMO-RS in guiding DES design while confirming the need for experimental validation. Given its high capacity and low toxicity, β-alanine–PEG was selected for further optimization.

Optimization of Oxidative-extractive Desulfurization (OEDS)

Analysis of Variance (ANOVA) and Fit Statistics

The analysis of variance (ANOVA) results for the model indicate that it is statistically significant, with an F-value of 184.45 and a p-value of <0.0001, meaning the factors significantly affect extraction efficiency (EE). Significant model terms include Temperature (A), DES to model oil volume ratio (B), Oxidant to sulfur volume ratio (C), as well as the interactions AB (Temperature * DES to model oil volume ratio) and the quadratic term A^2 (Temperature^2), all with p-values less than 0.05. Among these, C (Oxidant to sulfur volume ratio) has the highest F-value of 331.06, indicating its dominant effect. The lack of fit F-value of 4.03 and a p-value of 0.1058 suggest that the model fits the data well and that the observed lack of fit is not significant, confirming the reliability of the model for predicting extraction efficiency (EE). The high coefficient of determination (R^2) value of 0.9958 was also proven with the good alignment of predicted and actual value as shown in Figure 3(a). Overall, the ANOVA analysis demonstrates that the model is robust, with key parameters influencing EE and a good fit to the data. Hence, the extraction efficiency (EE) can be represented using the following second-order polynomial equation:

$$\frac{1}{\text{Extraction Efficiency}-0.50} = 0.037368 - 0.000551\text{A} + 0.005398\text{B} - 0.001007\text{C} + 0.000058\text{AB} + (3.17\times10^{-6})\text{AC} + 0.000059\text{BC} + (3.58\times10^{-6})A^2 - 0.010374B^2 + 0.000028C^2 \tag{3}$$

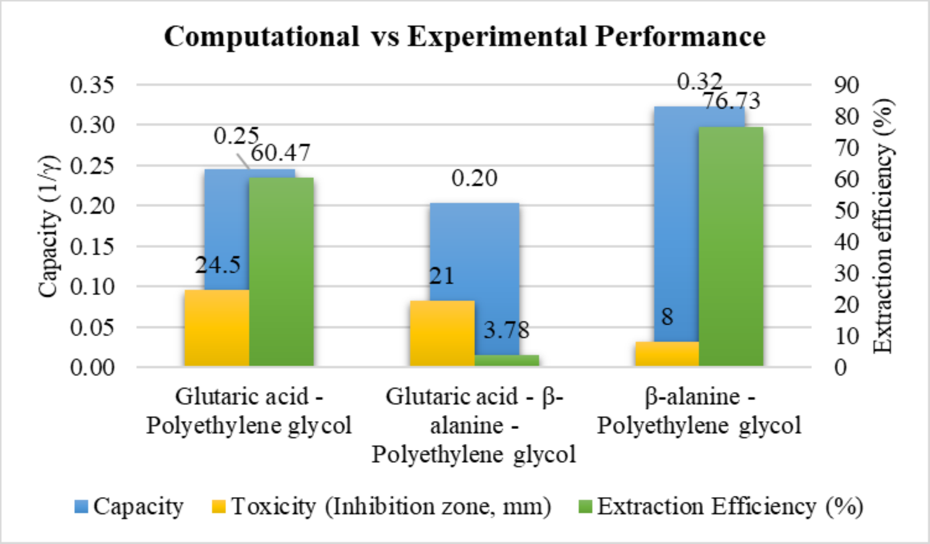


Figure 2. Toxicity and sulfur extractive efficiency using different type of DESs

Table 1. ANOVA for quadratic modelling of Extraction Efficiency (EE).

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0002	9	0	184.45	< 0.0001	significant
A-Temperature	0	1	0	166.95	< 0.0001	
B-DES to model oil volume ratio	0	1	0	91.86	< 0.0001	
C-Oxidant to sulfur volume ratio	0	1	0	331.06	< 0.0001	
AB	3.01E-06	1	3.01E-06	24.47	0.0017	
AC	2.77E-06	1	2.77E-06	22.55	0.0021	
BC	1.08E-07	1	1.08E-07	0.8773	0.3801	
A^2	0.0001	1	0.0001	870.56	< 0.0001	
B^2	0	1	0	94.41	< 0.0001	
C^2	8.04E-06	1	8.04E-06	65.42	< 0.0001	
Residual	8.60E-07	7	1.23E-07			
Lack of Fit	6.46E-07	3	2.15E-07	4.03	0.1058	not significant
Pure Error	2.14E-07	4	5.35E-08			
Cor Total	0.0002	16				

Effect of Process Condition

The 3D response surface plots (Figure 3b-d) highlight the interactive effects of temperature, DES-to-model oil ratio, and oxidant-to-sulfur ratio on extraction efficiency. In Figure 3 (b), extraction efficiency increases with temperature up to an optimum point, after which it declines. This trend is attributed to the direct influence of temperature on the kinetic rate constant, which accelerates sulfur removal until DES saturation limits further efficiency [10]. Similar trends were reported by Hanan and Shofiur, where higher desulfurization efficiency was achieved at elevated temperatures, with maximum efficiencies of 76.0, 71.5, and 68.9% at IL-to-model fuel ratios of 1:1, 1:2, and 1:3, respectively [10]. Figure 3 (c) shows that increasing the DES-to-model oil ratio (0.2–1) and oxidant-to-sulfur ratio (1–15) enhances extraction efficiency, as more DES provides additional active sites for sulfur interaction. This finding is consistent with earlier studies, which noted gradual increases in desulfurization efficiency with higher DES dosage within 15 min [11]. However, hydrogen bonding alone is insufficient for complete removal in this short period, supporting the use of multi-stage extraction or extraction-oxidation strategies [11]. In Figure 3 (d), desulfurization efficiency improves with both oxidant-to-sulfur ratio and temperature. A higher oxidant ratio increases availability of the oxidizing agent, boosting sulfur compound conversion, while elevated temperatures further accelerate kinetics [12]. This observation aligns with reports that increasing H_2O_2 volume from 5 mL to 10 mL enhanced desulfurization from 58 to 88% using α-ketoglutaric acid as catalyst [13].

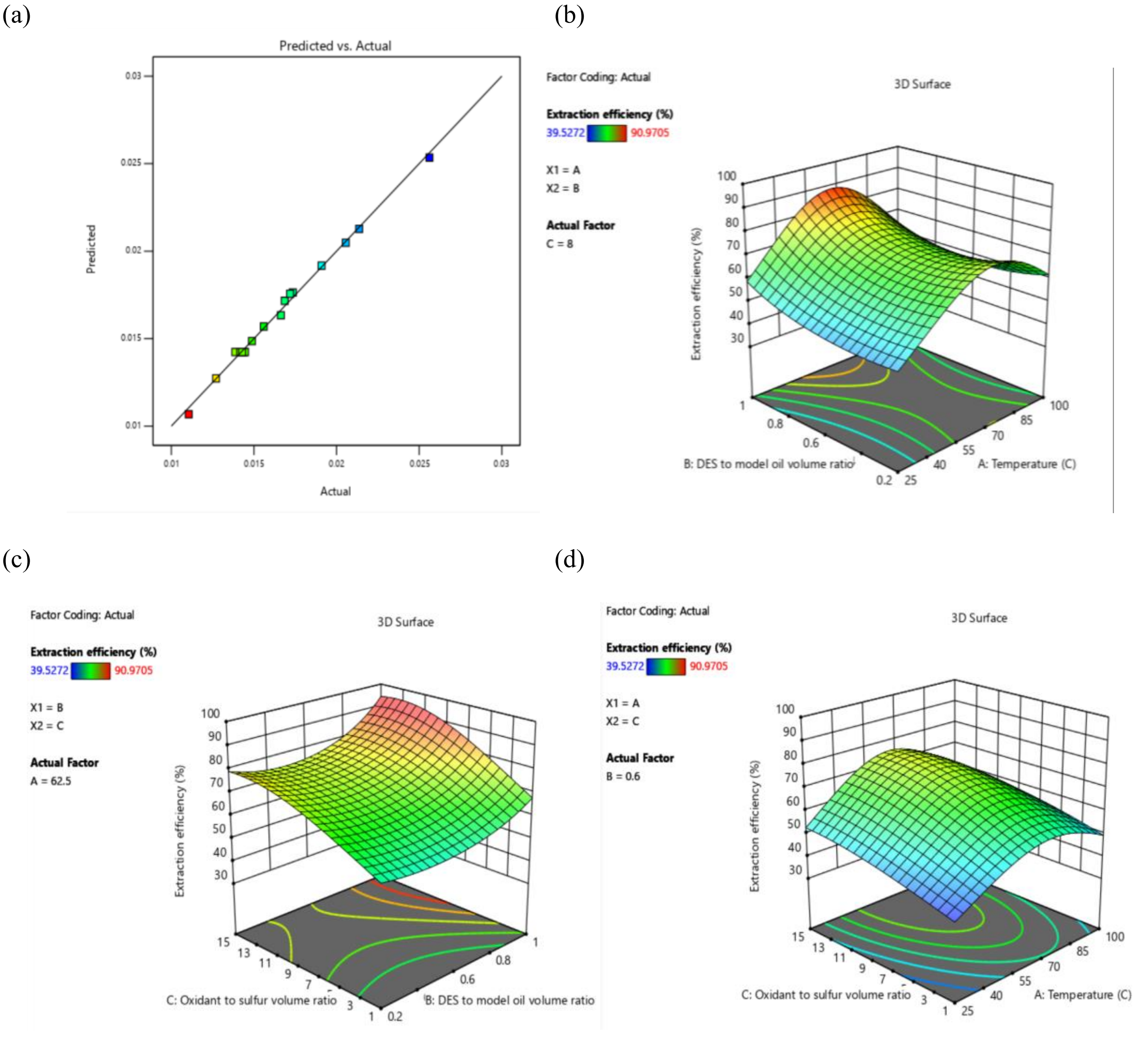


Figure 3. (a) Predicted values versus actual response of Extraction Efficiency and 3D response surface plot of effect of (b) temperature and DES to model oil volume ratio, (c) DES to model oil volume ratio and oxidant to sulfur volume ratio and (d) temperature and oxidant to sulfur volume ratio towards Extraction Efficiency.

Optimization of Oxidative-extractive Desulfurization Process and Reusability of DES

The desirability function was applied to optimize extraction efficiency, yielding 84 proposed solutions. The best conditions were 60 °C, a DES-to-model oil ratio of 1, and an oxidant-to-sulfur ratio of 12, giving a desirability of 1 and a predicted efficiency of 93.87%. Experimental results confirmed the model with only 0.19% error, achieving 93.4% efficiency. This outperformed literature reports, where cyclodextrin-based DESs achieved up to 73% [14], sulfosalicylic acid-based DESs 26% [15], and choline chloride-based systems only 14.9% [16]. The superior performance of β-alanine–polyethylene glycol is attributed to its aliphatic structure and strong hydrogen-bonding ability. Reusability tests under optimized conditions showed gradual efficiency loss over five cycles. Extraction dropped from 78% in the first cycle to 68%, 57%, 51%, and finally 45%. Declines were linked to H_2O_2 depletion, DES saturation with oxidized sulfur, viscosity increase, and mass transfer limitations. Despite the reductions, the DES maintained functionality for multiple cycles, demonstrating better stability compared to many single-use solvents.

CONCLUSION

This work demonstrated the potential of glutaric acid–based deep eutectic solvents (DESs) for oxidative extractive desulfurization (OEDS) of model oil. Among the tested systems, β-alanine–polyethylene glycol showed the highest efficiency and reusability, confirming its suitability as a green extractant. The study also established the influence of key process variables and verified the predictive accuracy of the optimization model. Overall, the results highlight DESs as cost-effective, low-toxicity, and environmentally sustainable alternatives to conventional desulfurization techniques, offering practical promise for future applications in cleaner fuel production.

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