

Extraction of Sulfur Compounds from Model Petroleum Products using Fe_3O_4 Nanoparticles and Acetic Acid-1-Butyl-3-Methylimidazolium Chloride based on Deep Eutectic Solvents

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Abstract—This research demonstrates that deep eutectic solvents (DESs) can eliminate sulfur compounds, which are corrosive and carcinogenic species, from model petroleum products through liquid-liquid extraction. Several monoprotic acids, including formic acid and acetic acid, are used to make DESs, along with 1-butyl-3-methylimidazolium chloride (BmimCl) as a hydrogen bond acceptor. These DESs are used for the first time to remove sulfur compounds (thiophene and dibenzothiophene) from an alkane as a model hydrocarbon (n-octane), which is used instead of crude oil as the latter contains a variety of species, including nitrogen compounds, hydrocarbons, and oxygen. The optimal parameters for the removal of sulfur are discussed, including the extraction temperature, reaction time, and mass ratio of DES to the model hydrocarbon, whilst the regeneration of DESs is also considered. H_2O_2 and iron oxide (Fe_3O_4) are also used as nanoparticle (NP) catalysts to enhance the sulfur removal process. Several characterization methods, including scanning electron microscopy, Fourier transform infrared, energy dispersive X-ray, and transmission electron microscopy, are used to determine the structural characteristics of the Fe_3O_4 NPs. The results show that acetic acid, as a monoprotic acid-based DES, is able to remove more than 86% of the sulfur molecules from model petroleum products

when the mass ratio of DES to model petroleum products is 2:1, at 30°C and within 60 min. This research provides an important opportunity to advance our understanding of the role of DESs in removing carcinogenic and corrosive particles in industrial processes.

Index Terms—Air pollution, Desulfurization, Deep eutectic solvents, Model petroleum, Solvent extraction

I. INTRODUCTION

With the rapid increase in the worldwide population, the consumption of fuels is very likely to show a commensurate increase itself. Therefore, it is vital to utilize a fuel with minimal health and environmental hazards. Consequently, we must employ a technique to obtain a fuel of superior quality, such as through enhancing the octane number of petrol (Qader, et al., 2021). With the present rate of progress in today's world, petroleum refineries should be able to produce more environmentally friendly fuels because of the unwanted and dangerous emissions currently related to their usage (Kiran, et al., 2019; Zhang, et al., 2017). Desulfurization of fuel plays a crucial role in the refining of crude oil. Hydrodesulfurization (HDS), which is commonly used in industry, is ineffective with regard to extracting complex-structured sulfur and aromatic compounds; thus, researchers have been using different methods as alternatives to desulfurization via this method (Gao, et al., 2018). Recently, Adsorption, oxidation, bioprocesses and ionic liquids (ILs) have been used as extractants and catalysts to reduce sulfur in diesel fuel as alternative manners to HDS. In addition,

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electrochemical photo-oxidation was used to minimize sulfur in diesel fuel, which represents an eco-friendly process. The authors converted sulfur compounds to more polar compounds like sulfones or sulfoxide using stainless steel and titanium to enhance desulfurization (Humadi, et al., 2024). Furthermore, the solid sorbent adsorption technique was applied to desulfurize diesel fuel via catalytic oxidization (Mohammed, et al., 2024).

ILs, which are compounds made up of anions and cations salts, have recently found use in various industrial applications (Abbott, et al., 2017a). They typically have melting points below 100°C and exhibit large potential ranges and significant levels of ionic conductivity that are effective in the desulfurization process. In the current study, a number of new deep eutectic solvents (DESs) (which behave in a similar manner to ionic ILs) are used to extract sulfur compounds. DESs are biodegradable solvents that include hydrogen bond donors like amides, carboxylic acids, and alcohols with quaternary ammonium moieties (Ismail, et al., 2022a). DESs are used in a variety of fields, such as conducting polymers (Alabdullah, et al., 2020), alloy and metal electrodeposition (Alesary, et al., 2023; Ismail, 2020), metal polishing (Abbott, et al., 2017b), natural product extraction (Qader, et al., 2023b), desulfurization (Qader, et al., 2021), medicines (Qu, Qader and Abbott, 2022; Qader, et al., 2024), and energy storage (Ismail, et al., 2022b). This is due to their affordability, ease of preparation, low volatility, biodegradability, insensitivity to water, and low toxicity, making them desirable for use in large-scale applications (Hillman, et al., 2017).

There are various methods that can be used in the extraction of the sulfur compounds present in kerosene, gasoline, diesel, or indeed any petroleum product, via ILs and/or DESs. These methods may involve varying temperatures and durations of extraction (Norouzi, et al., 2016). The existence of sulfur compounds is mainly responsible for affecting health, and in spite of that, the absorption of sulfur oxides in the effective place of catalysts during refining chemical processes can perform to deactivate it (Eßer, Wasserscheid and Jess, 2004). When sulfur compounds exceed the standard weight in crude oil, they must be treated in all areas during petroleum refinement because their presence as impurities can lead to major challenges during production, transportation, and refining, in addition to environmental pollution resulting from fuel combustion (Pauca, et al., 2021). Furthermore, nitrogen and sulfur compounds in fuels like NO_x and SO_x cause an imperfect change in air components, which can lead to the production of acid rain (Zolotareva, et al., 2019). Accordingly, the extraction of sulfur from fuel is one of the most studied and utilized technologies worldwide with regard to environmental considerations (Ahmad, et al., 2021).

Recently, nanoparticles (NPs) such as ZnO, iron oxide (Fe_3O_4), NiO, Ti_2O_3 , SiO_2 , and MoO_2 have begun to see significant use in different fields, including biology, pharmacy, chemistry, etc. They exist in several forms, with sizes ranging from 1 to 100 nanometers. Furthermore, their nanoscale dimensions and extensive surface area contribute to their distinctive chemical and physical characteristics

(Khan, Saeed and Khan, 2019). In this study, a green synthesis method was employed to produce iron NPs using plant extracts from *Quercus infectoria*. *Q. infectoria* is known for having strong anticancer, antibacterial, and antioxidant properties. Because of this, it can be used as both a capping and reducing agent to synthesize these NPs without the need for costly, toxic, and abrasive substances.

In this study, the novel approach of a desulfurization-based DES and Fe_3O_4 NPs was applied for the first time to remove sulfur compounds (such as thiophen and dibenzothiophene) from model petroleum products, using X-ray fluorescence to determine the extent of their removal. The novel DES was formed from 1-butyl-3-methylimidazolium chloride (BmimCl) and acetic acid/formic acid. Optimal parameters for this removal were studied, including extraction temperature, reaction time, NP used, and mass ratio of DES to alkane (n-octane), as well as the regeneration of the DES used in the desulfurization process. Fe_3O_4 was utilized as a catalyst in this work to enhance the sulfur removal in a mixture of dibenzothiophene and thiophene prepared in n-octane. We will specifically evaluate the removal of sulfur compounds (thiophene and dibenzothiophene) from petroleum products in the presence and absence of the Fe_3O_4 catalyst. In addition, The Fe_3O_4 NPs were characterized using scanning electron microscopy (SEM), energy dispersive X-ray (EDX), Fourier-transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM) techniques.

II. EXPERIMENTAL AND METHODS

A. Materials and Instrumentation

All the chemicals reported in Table I were used in this study without further purification. In addition, a water bath with a single chamber controlled by a thermostatic system and a laboratory reactor system were utilized. SEM and EDX analyses were conducted using a Philips XL20SEM instrument with an accelerator voltage of 20 keV. TEM images were obtained using a ZEISS EM900 microscope operating at 80 kV. The Fe_3O_4 sample was examined via FTIR using a Bruker Equinox55 spectrophotometer, covering a wavenumber range of 400–4000 cm^{-1} .

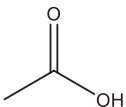
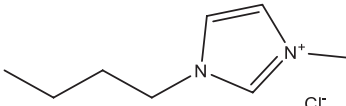
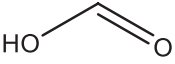
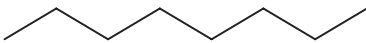

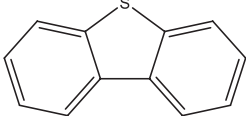
B. Preparation of DESs

The preparation of DESs follows a previously reported method (Qader, et al., 2021). Typically, acetic acid and formic acid, as hydrogen bond donors, were separately mixed with 1-butyl-3-methylimidazolium chloride, as a quaternary ammonium salt, in molar ratios of 2:1, respectively. This is in agreement with the study conducted previously by Qader in terms of the formation of DESs from hydrogen bond donors and acceptors (Qader, 2021). We then placed the prepared mixtures on a hotplate, stirring them at 50°C until they formed clear, homogenous liquids, and then stored them in an oven at 40°C for later use.

C. Synthesis of Fe_3O_4 NPs

The *Q. infectoria* solution was made by dissolving 5.0 g of *Q. infectoria* powder in 200 mL of distilled water and heating

TABLE I
THE STRUCTURE, PURITY, AND SOURCES OF THE CHEMICALS EMPLOYED IN THIS WORK

Chemicals	Structure	Source	Purity %
Acetic acid		Thomas Baker	99
1-Butyl-3-methylimidazolium chloride		Sigma-Aldrich	≥99
Hydrogen peroxide	H ₂ O ₂	Scharlau	50
Ferric chloride	FeCl ₃	Sigma-Aldrich	97
Formic acid		Sigma-Aldrich	98
n-octane		Carlo Erba	99
Thiophene		Merck	≥99
Dibenzothiophene		Merck	≥99

the solution to a temperature of 70°C for 2 h. Subsequently, the solution was filtered using a Whatman No. 1 filter paper to isolate the individual components. Further, a 0.10 M FeCl₂ solution was prepared by dissolving 1.99 g of solid FeCl₂·4H₂O in 100 mL of deionized water. Thereafter, the FeCl₂ solution was combined with the *Q. infectoria* solution. 1.0 M NaOH solution was subsequently added to the above mixture and agitated using a magnetic stirrer until the pH was 6.0. This led to the formation of Fe₃O₄ NPs, which appeared as a black precipitate within the solution. After reducing the volume of the solution by half through evaporation using a hot plate at a temperature of 70°C, the Fe₃O₄ NPs were then isolated using a magnetic field. The solid Fe₃O₄ obtained was thoroughly washed with deionized water and then dried for 12 h in a fume hood. It was further dried for an additional 12 h in a vacuum oven at a temperature of 100°C (Qader, et al., 2023a).

D. Preparation of Petroleum Model

A model petroleum product (sulfur compounds) was prepared by dissolving 0.25 g of thiophene and 0.25 g of dibenzothiophene in 500 mL of n-octane. A number of groups have reported that DESs and ILs can effectively remove sulfur compounds such as thiophene and dibenzothiophene from model petroleum products (Kareem, 2017). In our case, we used two new DESs: acetic acid + BmimCl and formic acid + BmimCl. It is known that real diesel contains impurities in the form of a number of organic compounds, including oxygen and nitrogen species. In addition, real diesel contains aromatic compounds, which are problematic to the desulfurization processes (Zhu, et al., 2015); therefore, we used a model petroleum product to avoid this effect on sulfur extraction.

E. Extraction of Sulfur Compounds

In this study, sulfur was extracted using DESs mixed with the model petroleum products in different molar ratios (wt/wt%), see appropriate figure caption. After that, the mixture was stirred for specific reaction times at 30 ± 2°C. Furthermore, the quantity (*X*) of sulfur compounds removed at 1 atm pressure was determined using equation (1):

$$X = \frac{Ci - Cr}{Ci} * 100\% \quad (1)$$

whereas *C_i* is the original sulfur amount in model diesel fuel, and *C_r* is the remaining amount of sulfur in the model diesel phase after the reaction had continued for a definite period of time. The same procedure was conducted after adding 1.0 mol H₂O₂ and 0.01 g Fe₃O₄ NPs as a catalyst into the DESs phase. The amount of sulfur in the treated model petroleum products phase before and after removal was measured via X-ray fluorescence spectroscopy.

C_i represents the initial sulfur content in the model diesel fuel, whereas *C_r* represents the sulfur content that remains in the model diesel phase after a specific period has passed in the course of the reaction.

III. RESULTS AND DISCUSSION

A. Effect of Different Hydrogen Bond Donors

The extraction processes are principally controlled by functional groups and intermolecular forces. For this investigation, three extraction agents, which are commonly associated with DESs, were utilized. The DESs used in this study consist of formic acid, acetic acid, and a combination of formic acid and acetic acid, with each individually combined

with 1-butyl-3-methylimidazolium chloride. It is important to note that the eutectic point varies for each solvent. Fig. 1 shows that the DES containing BmimCl: acetic acid had the highest sulfur removal percentage, approximately 36%, compared to the other DES mixtures. It is well known that formic acid is stronger than acetic acid in terms of acidity. This means that the species in the DES formed by formic acid and 1-butyl-3-methylimidazolium chloride physically interact more strongly than the species in the DES formed by acetic acid. As a result, the latter mixture interacted and removed sulfur more effectively than the former from the model petroleum products, as shown in Fig. 1. Therefore, we selected BmimCl: acetic acid for further research.

B. Influence of Temperature

Temperature is a key factor that has a considerable impact on sulfur removal. Caero, et al. studied the elimination of aromatic sulfur-containing species from a petroleum phase, as accomplished at a reaction temperature of around 70°C (Caero, et al., 2005). Correspondingly, Shiraishi et al. noted that the removal of sulfur species from the petroleum into the extractants part increases with increasing reaction temperature (Shiraishi, et al., 2002). To investigate the optimal temperature for desulfurization processes, the sulfur extraction from the model petroleum products was performed over a range of temperatures. Fig. 2 illustrates the influence of temperature (20–70°C) on the desulfurization of the selected DES (2 acetic acid: 1 BmimCl) from model petroleum products. The model petroleum product and DES phases were mixed in a mass ratio of 2:1 for 30 min under constant stirring at 500 rpm.

According to Fig. 2, the removal effectiveness of sulfur species increases from 38% to 58.2% as the temperature rises from 20 to 30°C. However, the ability to extract sulfur from petroleum product into a DES containing acetic acid did not significantly change as the temperature increased from 30 to 70°C, with only a slight increase in the extraction percentage from 58.2% to 59.9%. A decline in extraction efficiency as extraction temperature increased could potentially indicate that elevated temperatures are detrimental to extraction-desulfurization employing DESs. The exothermic process related to acid-base complexation is believed to have impeded the reaction more at elevated temperatures (Chandran, et al., 2019). Concerning the exothermic phenomena, elevated temperatures accelerate electrophilic substitution onto the thiophene and dibenzothiophene aromatic rings (Tang, et al., 2015). This suggests that the process can be conducted at ambient temperature, in contrast to the conventional HDS approach which necessitates temperatures of up to 623 K. The viscosity of DESs varies linearly with temperature, as seen in Equation 2. Increased temperatures result in a decrease in the sulfur partitioning coefficient (K_N). This further substantiates the hypothesis that reduced temperatures are adequate for this process (Wang, et al., 2016). Comparable results were also found in several other research efforts (Gano, et al., 2015; Jiang, et al., 2016; Li, et al., 2016).

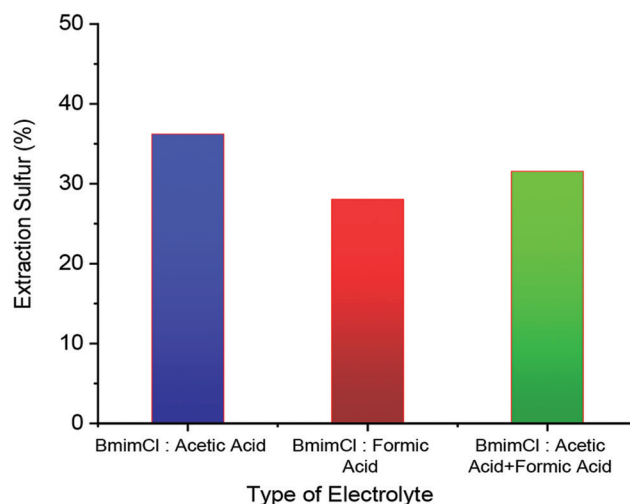


Fig. 1. Sulfur removal as a function of deep eutectic solvent (DES) at 20°C. The mass ratio was two parts model petroleum product (thiophene + dibenzothiophene in n-octane) to one part DES for 30 min while stirring at 500 rpm.

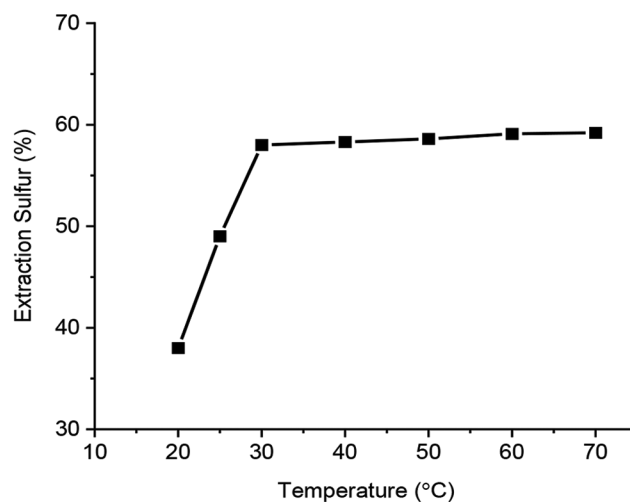


Fig. 2. Effect of temperature on the extraction efficiency of sulfur. The mass ratio was 2:1 for the model petroleum product (thiophene + dibenzothiophene in n-octane) to the deep eutectic solvent (1 BmimCl: 2 acetic acid). The stirring rate was 500 rpm at 30°C for 30 min.

For the current investigation, 30°C was chosen as the ideal temperature for the constructed system to avoid the consumption of large amounts of energy, as mentioned above.

$$\ln(\eta) = \ln \eta_0 + \frac{E_\eta}{RT} \quad (2)$$

C. Influence of Reaction Time

This study investigated the impact of extraction time on sulfur species. The experiment was run using a mass ratio of 1:2 between the fuel and BmimCl + acetic acid at 30°C and a 500-rpm stirring speed. Fig. 3 illustrates the impact of reaction time on the sulfur compounds present in the modeled oil sample (n-octane). The elimination of

sulfur compounds improves significantly from 31% to 65% as the response time is extended from 5 min to 60 min; however, it plateaus after 60 min and then gradually drops from 65% to 58% as the reaction time is extended further. There are a number of possible reasons for this beyond the effect of reaction time itself in the extraction of sulfur molecules, as follows: first, according to Abbott et al., the extraction reaction most likely approaches equilibrium after about an hour, at which point the desulfurization process' effectiveness decreases (Abbott, et al., 2017b). Sulfur uptake was rapid during the early contact period, specifically between 10 and 60 min of extraction. This observation can be ascribed to the disparity in the concentration of polar sulfur between the model petroleum and the extracting agent, the DES, leading to the swift movement of sulfur compounds from the model petroleum to the DES, to which they can easily attach. With an increase in contact duration, a greater quantity of sulfur compounds adhered to the DES (extracting agent), resulting in a reduction of accessible sites. At this juncture, electrostatic repulsion transpired between sulfur compounds adhered to the DES (extracting agent) and those retained in the model petroleum. Similar behavior has also been documented in previous research (De Luna, et al., 2018; Almashjary, et al., 2018; Tahir, et al., 2021). Moreover, the extraction rate may exhibit a natural drop due to thermodynamic or kinetic constraints, contingent upon factors such as temperature, solvent, and the characteristics of the sulfur compounds. Subsequently, the reaction may attain an equilibrium state, resulting in a substantial reduction in the rate of sulfur extraction (Chandran, et al., 2019). In summary, the reduction in sulfur extraction after 60 min may be attributed to DES saturation, depletion of sulfur compounds, thermodynamic or kinetic constraints, or the generation of inhibitory by-products. In general, we observed the most positive results within a 60-min period after treatment. Therefore, we conclude that

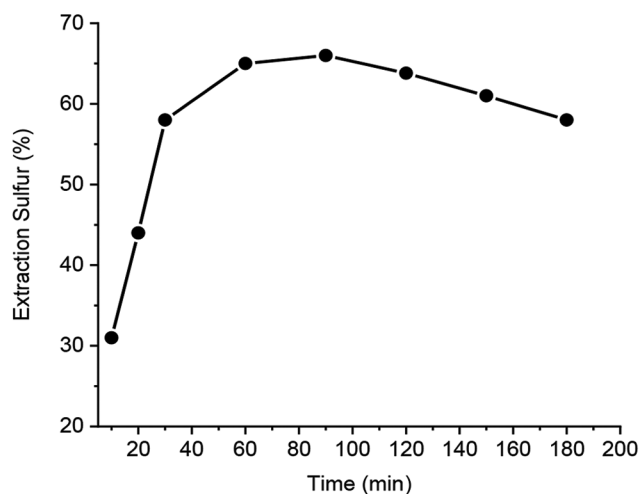


Fig. 3. Effect of reaction time on the extraction efficiency of sulfur. The stirring speed was 500 rpm at a constant temperature of 30°C. The mass ratio of model petroleum product (thiophene + dibenzothiophene in n-octane) to the deep eutectic solvent (1 BmimCl: 2 acetic acid) was 2:1

60 min is a suitable period for the oxidation system in this specific investigation.

D. Effect of DES/Model Petroleum Product Mass Ratio

In terms of environmental safety, the removal of sulfur compounds from petroleum products is vital. Hence, five different mass ratios for the DES (acetic acid + BmimCl)/petroleum products were used to investigate the efficiency of the removal of sulfur compounds from petroleum products, keeping other parameters constant (Fig. 4). Fig. 4 shows that changing the mass ratio of DES to petroleum products affects sulfur removal from petroleum products. The proportion of sulfur compounds extracted from the petroleum products into the DES (2 acetic acid: 1BmimCl) was 28.1% when the ratio of the mass of the petroleum products to the DES was 3:1, which may be due to a less active interaction between the DES and petroleum products, leading to lesser desulfurization efficiency. The results obtained are presented in Fig. 4, showing that a maximum removal of sulfur compounds of up to 75% could be achieved at a molar ratio of 2:1 for the DES (1 BmimCl: 2 acetic acid) to the model petroleum product. However, for other ratios, the percentage of desulfurization decreases. The study suggests that mass ratio affects extraction efficiency.

E. Influence of Stirring Speed

In this section, we studied the effect of the stirring speed on the extraction of sulfur by varying the stirrer speed from 100 to 2000 rpm, as shown in Fig. 5. It was observed that the percentage removal of sulfur compounds increased from 35% (100 rpm) to 74.8% with increasing the stirrer speed up to 500 rpm, beyond which there was a slight decrease with increasing stirring speed. Exceeding the optimal speed might hinder effective interaction between species in the system, resulting in reduced desulfurization efficiency due to the dispersion of species in the system. Therefore, all subsequent experiments were carried out at 500 rpm. This was in

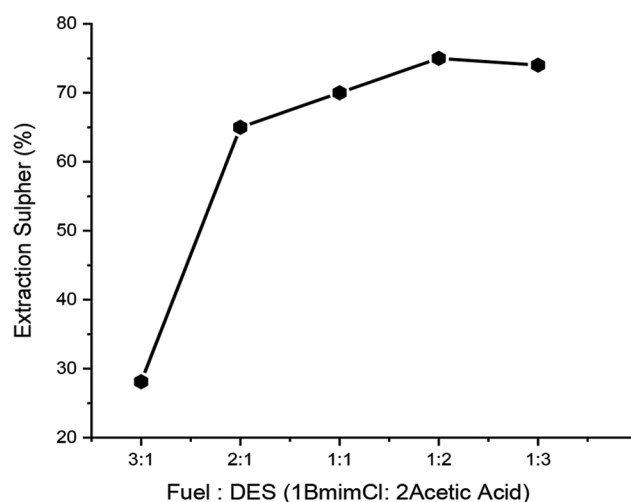


Fig. 4. Effect of mass ratio of deep eutectic solvent (1 BmimCl: 2 acetic acid) to model petroleum product on sulfur removal at 30°C for 60 min and a stirring rate of 500 rpm.

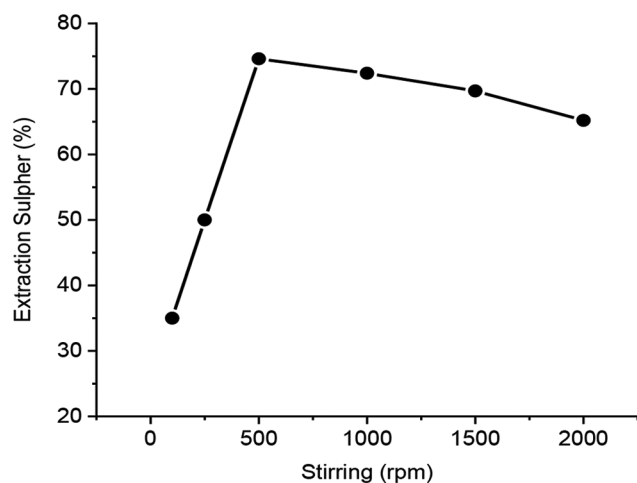


Fig. 5. Effect of stirring rate on the efficiency of sulfur removal from the petroleum model. The extraction time was 60 min with a 1:2 mass ratio of model petroleum product (thiophene + dibenzothiophene in n-octane) to deep eutectic solvent (1 BmimCl: 2 acetic acid) at a fixed temperature of 30°C.

agreement with the study conducted by Qader et al. (2021) in which they used phenol and ChCl as a DES to remove sulfur from diesel.

F. Effect of H_2O_2 and Fe NPs as Catalysts on the Sulfur Extraction Process

According to Yang, et al.'s investigation, the production of catalytic present species increases the desulfurization rate when H_2O_2 is used as a catalyst in certain concentrations (Yang, et al., 2019). In a similar vein, Al-Shahrani et al. demonstrated that hydrogen peroxide (H_2O_2) can effectively serve as a catalyst in the elimination of sulfur from fuel (Al-Shahrani, et al., 2007). In order to examine the impact of H_2O_2 as an oxidizing agent on the desulfurization process of actual diesel fuel, experiments were conducted at a temperature of 30°C, keeping other parameters constant, as described in the caption to Fig. 6. The molar ratio between the petroleum model and the oxidant was 8:1, according to our previous study (Qader, et al., 2021). Depending on the particular monoprotic acid (DES) employed, the effectiveness of the sulfur removal from model petroleum products was improved by adding hydrogen peroxide (H_2O_2). The findings show that when the H_2O_2 catalyst was introduced, a maximum removal of 78% of the sulfur compounds could be achieved.

Previous research has demonstrated that the utilization of Fe NPs as a catalyst is significant in desulfurization when using H_2O_2 . For example, the presence of Fe NPs in the organic phase resulted in a considerable reduction of sulfur compounds in diesel fuel, as shown when the concentration of Fe^{3+} was increased (Zhu, et al., 2012; Zhang, Zhang and Zhang, 2004). Consequently, this point was further examined in the current research. The catalytic role of Fe_3O_4 in combination with H_2O_2 enhances the extraction of sulfur by facilitating the oxidation of sulfur-containing compounds to more extractable forms. The generation of hydroxyl

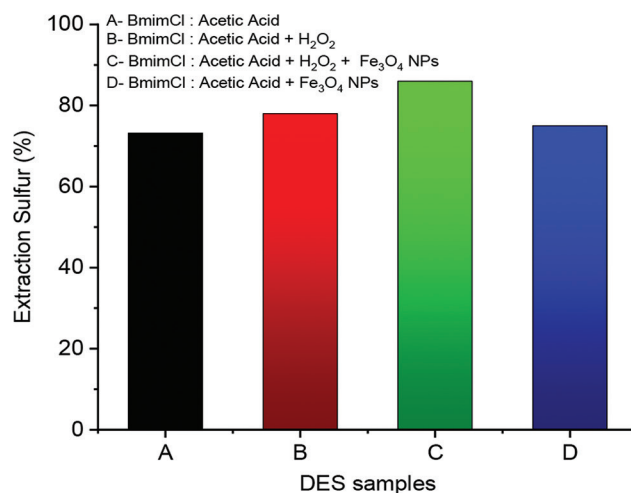


Fig. 6. Effect of H_2O_2 and Fe_3O_4 nanoparticles on sulfur removal. The extraction time was 60 min at 30°C whilst stirring at 500 rpm. The mass ratio of the model petroleum product (thiophene + dibenzothiophene in n-octane) to the deep eutectic solvent (1 BmimCl: 2 acetic acid) was 1:2.

radicals and other ROS accelerates the breakdown of the sulfur species, leading to improved extraction efficiency. This approach holds promise for more sustainable and efficient sulfur recovery processes (Liochev, 1996).

Fig. 6 illustrates the impact of adding Fe_3O_4 on the effectiveness of sulfur removal. The addition of Fe_3O_4 was found to significantly enhance the effectiveness of sulfur removal by up to 86%. This improvement could be attributed to the presence of Fe=O catalytic sites, which play a crucial role in activating iron superoxide for the oxidation reaction. Thus, the BmimCl: Acetic acid: H_2O_2 : Fe_3O_4 NP model yielded the most efficient desulfurization.

G. Regeneration of BmimCl: Acetic Acid

The recycling of the spent DES following extractive desulfurization is undeniably important (Jeong, et al., 2015). Fig. 7 shows the extractive desulfurization ability of sulfur species in model petroleum products into DES. The current experiment was conducted at 30°C and a stirring speed of 500 rpm for 60 min with a mass ratio for the DES (2 acetic acid + 1BmimCl) to the model petroleum product of 2:1.

After completing the extraction process for the sample, the DES (BmimCl: acetic acid) was regenerated and thereafter utilized for a maximum of three cycles. This shows that all such cycles allowed for the regeneration of the prepared DESs without any reduction in their sulfur-removal capability. We regenerated the BmimCl: acetic acid solvent employed through extraction using diethyl ether in a rotary evaporator. Each instance showed no alteration in the synthesized DES composition subsequent to recycling. Fig. 7 shows that using BmimCl: acetic acid as a DES for a minimum of three cycles does not reduce the extraction effectiveness. In addition, the synthesis of DESs is straightforward and does not require organic solvents, thereby mitigating the environmental repercussions associated with toxic organic solvents. These DESs are degradable and environmentally benign due to their

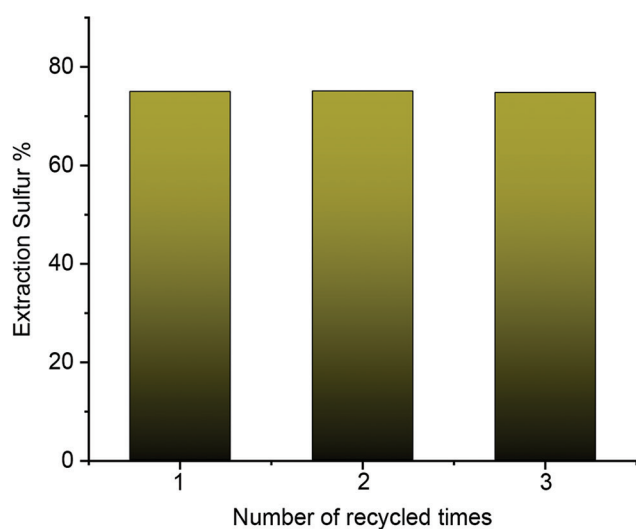


Fig. 7. Extraction performance with recycled BmimCl: Acetic acid. Reactions conditions: 2:1 mole ratio of deep eutectic solvent to model petroleum product (thiophene + dibenzothiophene in n-octane), 60 min reaction time. Stirring at 500 rpm, at a fixed temperature of 30°C.

components being interconnected through hydrogen bonding. The interacting components consist of environmentally friendly, readily accessible, and inexpensive raw materials. DESs benefit from this, as they can allow for extraction-desulfurization at ambient temperature and pressure, unlike the traditional HDS procedure, which requires elevated temperatures and pressures.

H. Characterization of Fe_3O_4 NPs

The synthesized Fe_3O_4 NPs were characterized via the SEM, EDX, TEM, and FTIR techniques. In order to examine the various bonds and functional groups present in the Fe_3O_4 NPs, an FTIR analysis was conducted, as depicted in Fig. 8. The features in the FTIR spectrum observed at about 3440 and 625 cm^{-1} were indicative of the presence of Fe_3O_4 , as illustrated in Fig. 8a. These peaks can be attributed to the bending vibrations of the O–H groups (due to solvent that has been adsorbed) and the stretching vibration of the Fe–O bonds, respectively. In addition, peaks were observed at about 1606 and 1388 cm^{-1} , which could be attributed to out-of-plane and in-plane O–H vibrations (Babakir, et al., 2022; Qader, et al., 2023a).

When compared to Fig. 8b (after desulfurization), all the peaks associated with Fe_3O_4 (described above) are observed at lower wavenumbers (3350, 1559, 1365, and 597 cm^{-1}) and exhibit reduced band intensities. In addition, numerous additional peaks were seen in the FTIR spectrum of Fe_3O_4 during the process of desulfurization. The absorption peak located around 1511 cm^{-1} corresponds to the vibration of a C=C bond in the thiophene and dibenzothiophene. The bands detected around 1175, 1042, and 783 cm^{-1} represent a C–C vibration in an organic ring, an in-plane =C–H stretch, and an out-of-plane C–H bend, respectively, for thiophene and/or dibenzothiophene. The peaks observed at 1313 and 1365 cm^{-1} correspond to the presence of an S=O bond in

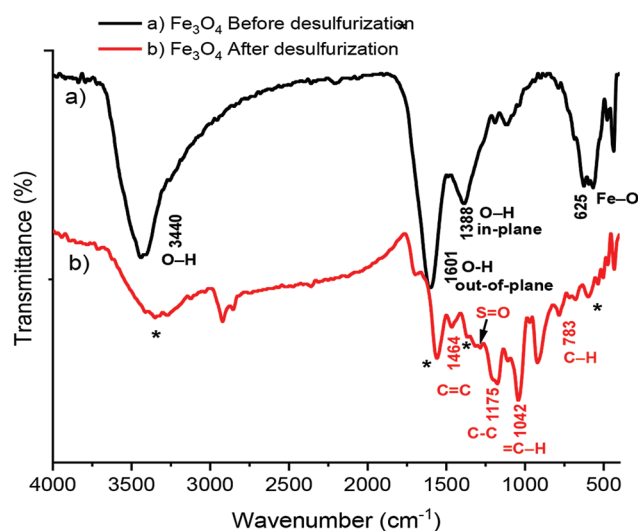


Fig. 8. Fourier-transform infrared spectroscopy spectra of Fe_3O_4 , (a) before and (b) after the desulfurization process.

a sulfone and an organic sulfate compound, respectively, in thiophene and/or dibenzothiophene. Accordingly, the FTIR data confirmed that sulfur compounds (such as thiophene and dibenzothiophene) had been adsorbed onto the Fe_3O_4 composite.

The surface morphologies and particle size of the Fe_3O_4 composite were analyzed via SEM and TEM, as shown in Fig. 9, both before and after the desulfurization process. The surface of Fe_3O_4 before desulfurization, shown in Fig. 9a has a uniform and porous structure made up of almost separate spherical formations. These spherical formations range in size from 5 nm to 50 nm, contributing to the nanostructure of the particles created. However, on desulfurization (Fig. 9b), the morphology of the Fe_3O_4 surface changes (as compared to Fig. 9a) to show more irregular structures and smaller pores, indicating the presence of sulfur compounds on the surface of the Fe_3O_4 nanocomposites.

Furthermore, the TEM image in Fig. 9c provides further proof of the porous nanostructure shape of Fe_3O_4 particles smaller than 50 nm. The image reveals a semi-spherical, nearly hexagonal shape for Fe_3O_4 . On the other hand, Fig. 9d shows a structure that is less porous, a result of the desulfurization process that occurred on the surface of Fe_3O_4 and which is consistent with the SEM data.

In order to verify the successful formation of Fe_3O_4 NPs and validate the adsorption of sulfur compounds onto the Fe_3O_4 adsorbent surface, an EDX study was conducted, as shown in Fig. 9e and f. This research effectively demonstrates the presence of iron (Fe) and oxygen (O) atoms in the composition of the Fe_3O_4 composite catalyst (Fig. 9e). The EDX spectra display the distinctive peaks of iron at 0.85 keV ($\text{L}\alpha_1$) and 6.45 keV ($\text{K}\alpha_1$), which is consistent with earlier findings (Kargar, et al., 2021; Luis, Behera and Sorokhaibam, 2023). The EDX spectrum (Fig. 9f) showed that after desulfurization, there was an extra peak associated with sulfur (S) at around 2.85 keV ($\text{K}\alpha_1$), along with Fe, O, and N. This confirms the adsorption of sulfur compounds

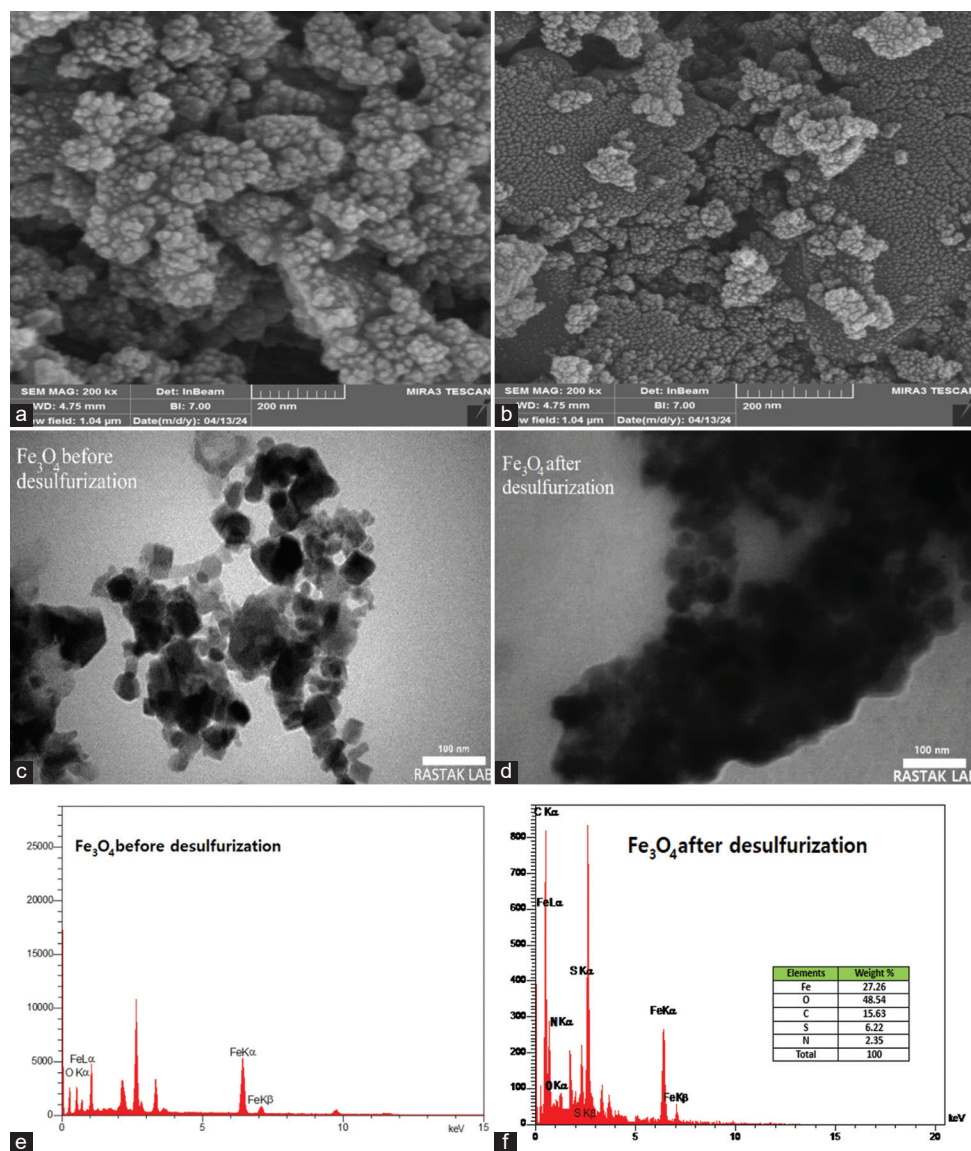


Fig. 9. (a and b) Scanning electron microscopy images of Fe_3O_4 before and after the desulfurization process; (c and d) transmission electron microscopy images of Fe_3O_4 before and after the desulfurization process; and (e and f) energy dispersive X-ray data of Fe_3O_4 before and after the desulfurization process, respectively.

onto the adsorbent's surface, a process associated with the presence of thiophene and dibenzothiophene compounds in the petroleum model.

Following the desulfurization process, we can conclude that the FTIR, SEM, EDX, and TEM approaches provided clear evidence of the adsorption of sulfur compounds onto the Fe_3O_4 's spherical surface, thereby enhancing the removal of sulfur compounds from the petroleum models.

IV. CONCLUSION

This study involved the extraction of sulfur compounds from model petroleum products (thiophene and dibenzothiophene in n-octane) using liquid-liquid extraction in new types of DES. Two hydrogen bond donors, acetic acid and formic acid, were utilized to create DESs in various molar ratios with 1-butyl-3-methylimidazolium chloride (BmimCl), which served as

a quaternary ammonium salt. The hydrocarbon-based fuels (HBDs) used in this study play a crucial role in extraction procedures across various practical domains. Experiments were conducted to investigate the impact of monoprotic acids in HBDs, as well as the presence of oxidants (H_2O_2) and Fe_3O_4 in the petroleum model, on the process of desulfurization. Within the optimization parameters, we also examined the impact of temperature, reaction duration, and the mass ratio of DES to the petroleum model. The study's results indicate that increasing the temperature from 20°C to 30°C enhanced the removal of sulfur from the petroleum model into an acetic acid-containing DES. However, above 30°C , the removal of sulfur declined slightly.

Furthermore, the results show that the BmimCl:acetic acid: H_2O_2 : Fe_3O_4 NP model successfully eliminated the largest proportion of sulfur, up to 86%, in 60 min at 30°C using 2:1 mass ratio of DES (1BmimCl: 2acetic) to model

petroleum product, owing to the synergistic impact of the materials and the absence of intramolecular hydrogen bonding in this composite. The synthesized Fe_3O_4 was characterized using various techniques, including FTIR, SEM, EDX, and TEM. Following the desulfurization process, these approaches provided evidence of the presence of sulfur compounds on Fe_3O_4 's spherical surface, enhancing the removal of sulfur compounds from the petroleum models. Finally, the ability to regenerate the DES was tested over a series of repeated recovery cycles, which demonstrated that DESs may be regenerated without any decline in the sulfur removal potential after three desulfurization cycles. The results of this study have significant implications for potential future applications; specifically, they could be valuable in addressing environmental concerns by eliminating cancer-causing and corrosive substances in industrial operations.

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