



Original Research Article

Investigation of Ionic Liquid with and Without Suspension of Nanomaterials as Catalysis for Sulfur Removal from Gas Oil at Room Temperature

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ABSTRACT

Keywords

Ionic liquids;
desulfurization;
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single-stage
extraction.

A new class of green catalytic solvents, known as ionic liquids (ILs), has recently been the subject of intensive research on the extractive desulfurization of liquid fuels because of the limitation of traditional hydrodesulfurization method. In present work, modified ionic liquids were synthesized and employed as promising extractants for deep desulfurization of the gas oil to test the desulfurization efficiency. [Bmim]Cl/Fe⁰ was the most promising ionic liquid and performed the best among studied ionic liquids under the same operating conditions. It can remove sulfur compounds from the gas oil in the single-stage extraction process with the maximum desulfurization efficiency of 83.6 %. It was also found that [Bmim]Cl Fe⁰ may be reused without regeneration with considerable extraction efficiency of 48.3 %. Huge saving on energy can be achieved if we make use of this ionic liquids behavior in process design, instead of regenerating ionic liquids after every time of extraction.

Introduction

The new requirements for sulfur content in liquid fuels demand the use of novel deep desulfurization processes. The compounds require higher hydrogen consumption in the hydrodesulfurization process and the use of additional infrastructure in the treatment facility. The common hydrogenation catalysts are not very effective for the hydrogenization of all sulfur compounds, and new innovation for catalysts is required (Rang et al., 2006).

Ionic liquids which immiscible with oil and containing halogen-free were used for oxidative desulfurization as both the catalyst and extractant. The Ionic liquids could be recycled 5 times without any apparent loss of the catalytic activity (Guia et al., 2010).

Ionic liquids as selective extraction agents of sulfur compounds are discussed separately, because of their novelty and

theoretical interest. The use of ionic liquids for selective extraction of sulfur compounds from gas oil was described for the first time by Bösman et al. (2001). Provisionally the best results were obtained with AlCl_3 -1-butyl-3-methylimidazolium chloride (BMIMCl/ AlCl_3) however, the desulfurization rate was not high (65%). The same authors have also obtained better results with this agent. Deep desulfurization using a chlorine-free ionic liquid (anion is octylsulfate and cation N-octyl-N-methylimidazolium) is also presented (Welton, 1999). Presently, ionic liquids are only of academic interest for desulfurization, much like as also biomethods for removing of sulfur (Olson, 2000).

Ionic liquids (IL) have been recognized as novel designable solvents, which are liquids over a wide temperature controlled by tailoring their cationic and anionic structures to optimize their physicochemical properties (Fukumoto et al., 2002; Visser and Rogers, 2003; Fadeev, and Meagher, 2001; Freemantle, 2001). As a kind of extraction solvent, IL does not remain in the organic phase, which can be greatly convenient for separation (Zhang et al., 2004), and therefore, the desulfurization using ionic liquids has received growing attention (Zhang, S.G., Zhang, 2002; Bösmann et al., 2001; Esser et al., 2004; Alonso et al., 2008). nZVI based ionic liquids are promising extractants in future industrial applications because of their low viscosities and wide liquid ranges (Wasserscheid and Bösmann, 2002; Hussey, 1979; Swatloski et al., 2002; Visser et al., 2001; Gu et al., 2002; Wasserscheid and Welton, 2003). Therefore, in the present article, we focused on the extraction of sulfur

compounds from gas oil using this type of ionic liquids. (Xuemei et al., 2008).

Materials and Methods

All chemicals used in this study were of reagent grade, Methylimidazolium chloride [Bmim]Cl FeCl_3 (99%), sodium borohydride and ethanol were purchased from Aldrich. Gas oil with fixed sulfur contents were provided by Cairo refining company.

Preparation of the NZVI and modified Ionic liquid

For the synthesis of Nanoscale Zero Valent Iron (NZVI); 0.5406 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in a 4/1 (v/v) ethanol/water mixture (24 ml ethanol + 6 ml deionized water) and stirred well. On the other hand, 0.1 M sodium borohydride solution was prepared i.e., 0.3783 g NaBH_4 was dissolved in 100 ml of deionized water; since for better growth of iron nanoparticles excess borohydride is needed. The borohydride solution is poured in a burette and added drop by drop (1 drop per 2 seconds) into iron chloride solution with vigorous hand stirring. After the first drop of sodium borohydride solution, black solid particles immediately appeared and then the remaining sodium borohydride is added completely to accelerate the reduction reaction. The mixture was left for another 10 minutes of stirring after adding the whole borohydride solution Figure 1. The vacuum filtration technique was used to separate the black iron nanoparticles from the liquid phase. The solid particles were washed three times with 25 ml portions of absolute ethanol to remove all of the water. This washing process is probably the key step of synthesis since it prevents the rapid oxidation of zero valent iron

Figure.1 Schematic diagram for synthesis of iron nanoparticles

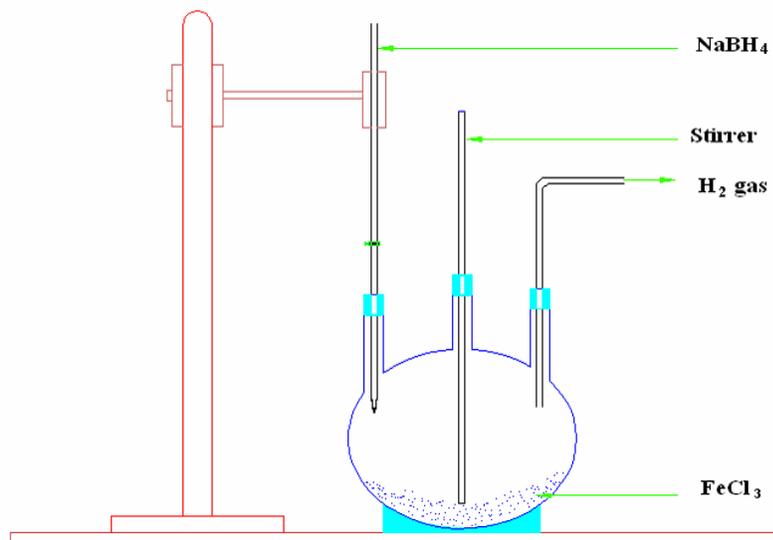
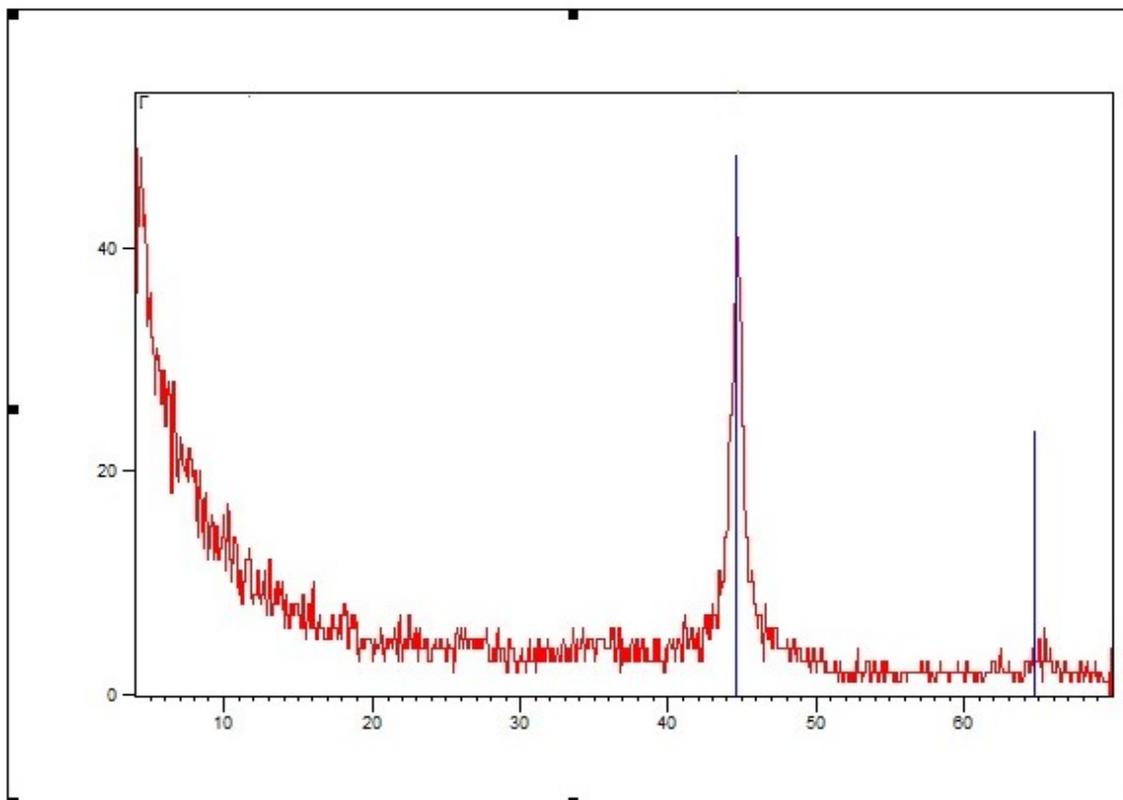
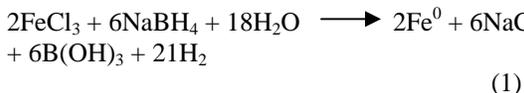


Figure.2 XRD pattern of zero-valent nanoparticles with weight content of $\approx 90\%$ and Fe_3O_4 as a by-product.



nanoparticles. The synthesized nanoparticles were finally dried in oven at 323 K overnight. For storage, a thin layer of ethanol was added to preserve the nano iron particles from oxidation equation (1).



The synthesis of the modified ionic liquid is as follows. Under the protection of nitrogen, the ionic liquid (modified ionic liquid) was prepared by simple addition of Nanoscale Zero Valent Iron to imidazolium cations (imidazolium chloride) (molar ratio 0.67:1) equation. (Zahran, 2013) Imidazolium cation was placed in the three-necked glass flask with a magnetic stirrer and Nanoscale Zero Valent Iron was then very slowly added under stirring. The reaction of Nanoscale Zero Valent Iron and imidazolium cations was highly exothermic and care had to be taken not to permit the temperature of the mixture to rise above 60°C; otherwise. The resulting melt was used for testing in the reactions.

Techniques

An X-ray measurement of various mixed solids was carried out using a BRUKER D8 advance diffractometer (Germany). The patterns were run with Cu K α radiation at 40 kV and 40 mA with scanning speed in 2 θ of 2 ° min⁻¹. TEM image and selected-area electron diffraction (SAED) was taken with a JEOL JEM-2000 EX model transmission electron microscope, using an accelerating voltage of 100 kv. The sample of TEM was prepared by two hours ultrasonic dispersion of 0.2 g of product in 50 ml ethanol. Then, a drop of the solution was placed on a copper micro grid, and dried in air before performance.

The surface characteristics of various solid catalysts, namely, The specific surface area (S_{BET}), total pore volume (V_p) and mean pore radius (r̄) were determined from nitrogen adsorption isotherms measured at -196 °C, using Nova 2000, Quanta Chrome (commercial BET unit). Before undertaking such measurements, each sample was degassed under a reduced pressure of 10⁻⁵ Torr for 2 h at 200°C.

Extractive Desulfurization of the gas oil

The desulfurization experiments were carried out in a 100mL two necked flask by mixing of gas oil and specific amount of ionic liquids with the fixed mass ratio between gas oil to ionic liquid as (1:1, 3:1 and 5:1) at room temperature for 40 minutes with vigorous stirring. On completion of the reaction, the upper phase (gas oil) was withdrawn and analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), to determine the concentration of sulfur in the gas oil. Then % removal of sulfur can be calculated by the following equation (Sun and Zhao,2006; Swapnil et al., 2013):

$$\% \text{ sulfur removal} = \frac{[\text{gas oil}]_{\text{initial}} - [\text{gas oil}]_{\text{final}}}{[\text{gas oil}]_{\text{initial}}} \times 100$$

Results and Discussion

Characterization of Zero Valent Irons (nZVI)

In the present work, nanoscaled (50-100 nm) zero valent irons (nZVI) have been synthesised in ethanol medium by the method of sulphate iron reduction using sodium borohydride as a reducing agent under atmospheric condition. The iron nanoparticles are mainly in zero valent oxidation state and remain without

significant oxidation for weeks. A systematic characterization of nZVI has been performed using XRD, TEM and BET studies.

Figure 2 shows the powder XRD pattern of nZVI samples under ambient conditions. The broad peak reveals the existence of an amorphous phase of iron. The characteristic broad peak at 2θ of 45° indicates that the zero valent iron is predominantly present in the sample.

Transmission Electron Microscopy image of iron nanoparticles is shown in Figure 3. It can be observed that the iron particles are in the form of nanorods, which exist in contact with each other and form chains having diameters of 5-20 nm. This linear orientation is nearly due to the magnetic properties of iron species (Feng and Lim, 2007). The rods having diameters of around 20 nm. With closer inspection, the metallic iron and iron oxide phases can be distinguished from the corresponding color contrast in TEM images. The lighter regions are mainly on the surface of the particle and the dark regions are concentrated in the center of the particle (Figure 3). One can know that a TEM instrument is designed so that the elements with higher atomic numbers seem darker than the ones with lower atomic numbers. One can conclude with the above point in mind that the average atomic number of central elements is higher than the average atomic number of the surface elements. The rod is formed of metallic iron and the surface (shell) is formed of iron oxides.

The BET surface area values were determined as $34.75 \text{ m}^2/\text{g}$ for nZVI as shown in Figure.4. Some of the BET surface area values reported in literature are $14.5 \text{ m}^2/\text{g}$ [26], $33.5 \text{ m}^2/\text{g}$ (Wang and Zhang, 1997) and $36.5 \text{ m}^2/\text{g}$ (Gu, Z.Y.,

Brennecke, 2002). In comparison, commercially available Fe powder ($<10 \mu\text{m}$) has a specific surface area of just $0.9 \text{ m}^2/\text{g}$ (Liu et al., 2005). The increase in specific surface area means an increase in the total amount of iron on the surfaces. The nitrogen physisorption data of nano iron is shown in Table 1. Therefore, it is evident that nanoscaled zero valent irons (nZVI) (50-100 nm) with good properties are synthesised in ethanol medium by sodium borohydride reduction method under atmospheric condition.

More detailed information on the porosity is available from the pore volume distribution curves shown in Fig. 3 constructed by plotting D_{Vp}/D_r against the pore radius (Li et al., 2007). It is seen from Figure 4 that the investigated solids exhibited models distribution in which most of the pores were located in the micro-pore range. However, the maxima of the pore volume distribution curves are located at range of 3.7 nm.

Characterization ionic liquid and modified

FT-IR results

IR spectrum of Bmim[Cl] reveals several absorption bands as follow: the absorption band at 3151 cm^{-1} corresponding to C-H stretching in aromatic, while the absorption band at $2870\text{-}2960 \text{ cm}^{-1}$ corresponding to C-H stretching in alkane. The absorption band at $1570, 1459$ and 1380 cm^{-1} are corresponding to C=N and CH₂& CH₃ respectively and that at 1160 cm^{-1} corresponding to C-N while the absorption band at 620 cm^{-1} is corresponding to chloride as shown in Figure 5.

IR spectrum of [Bmim]ClFe⁰ reveals

several absorption bands as follow: the absorption band at 3151 cm⁻¹ corresponding to C-H stretching in aromatic, while the absorption band at 2870-2961 cm⁻¹ corresponding to C-H stretching in alkane. The absorption band at 1568, 1459 and 1381 cm⁻¹ are corresponding to C=N and CH₂& CH₃ respectively and that at 1164 cm⁻¹ corresponding to C-N while the absorption band at 651 cm⁻¹ is corresponding to chloride as show in Figure 6.

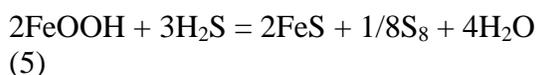
Sorption and surface mineralization – sequestration of H₂S

Hydrogen sulfide (H₂S) is a major sulfur-containing compound contributing to nuisance odors in gas oil and municipal solid wastes. (Wieckowska, 1995) H₂S sequestration with nZVI is studied here to exploit the strong iron-sulfur interactions. For dose of nZVI studied effectively 60 % of hydrogen sulfide was removed within 30 min Figure 7. Doping nZVI into the solutions resulted in rapid uptake of hydrogen sulfide.

FeS may be produced when hydrogen sulfide reacts directly with the zerovalent iron (Cantrell et al., 2003):

$$\text{Fe}^0 + \text{H}_2\text{S} = \text{FeS} + \text{H}_2(\text{g}) \quad (4)$$

H₂S can also react with the oxyhydroxide shell of the nanoparticles (FeOOH) via Eq. (5) (Sun et al., 2006):

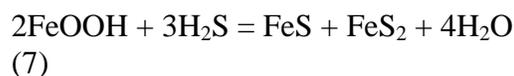


Under this condition, H₂S exists primarily in the deprotonated form (HS⁻). The isoelectric point of nZVI in aqueous solution is reported to be similar to iron oxide (Sun et al., 2006):. Hence, in the

reaction medium it is electrostatically favorable for HS⁻ to attach to the iron particles, where it undergoes further reactions. The FeS formed is metastable and it is readily oxidized by the elemental sulfur to form iron disulfide (FeS₂) (Mullet et al., 2002) Figure 8:



The net reaction of Eqs. (5) and (6) is therefore:



It has been suggested that FeS₂ may also be produced from reaction between FeS and H₂S, where H₂S in its protonated form acts as an electrophile (Rickard, and Luther, 2007).

This particular pathway was unlikely to play a significant role in the present case due to the prevalent existence of hydrogen sulfide as HS⁻ and the rapid depletion of H₂S upon the addition of nZVI. (Yan et al., 2010).

Desulfurization of gas oil Various Ionic Liquids with and without Suspension of Nanomaterials

The experiments were carried out to test the feasibility of ionic liquids for desulfurization of gas oil. The sulfur removal efficiency of [Bmim]Cl, nZVI, [Bmim]Cl Fe⁰ for liquid fuel is shown in Table 1. The ionic liquid based on nZVI showed the best sulfur removal efficiency among nZVI and based ionic liquid slowly. It was also found that the extraction process went on quickly, and it could reach extraction equilibrium in little time (Say 30 minutes).

Figure.3 TEM image of nanoscaled zero valent irons (nZVI)

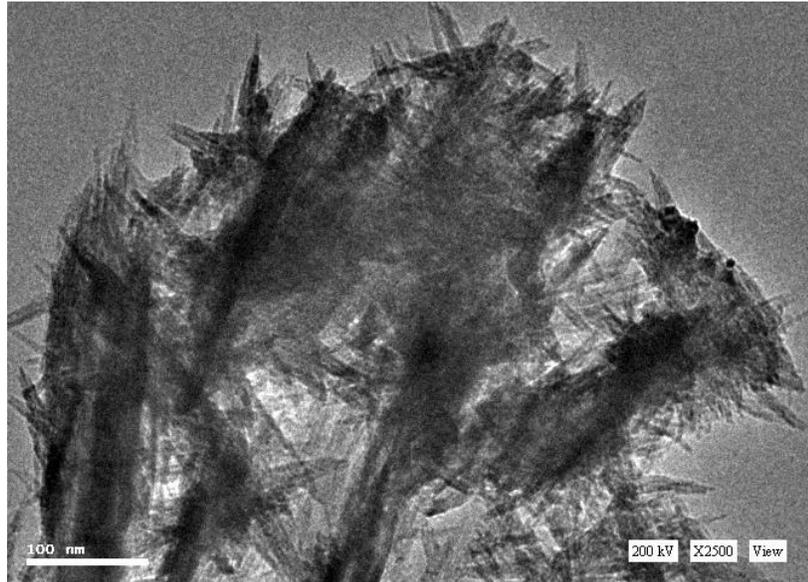


Figure.4 BET adsorption-desorption isotherms of Fe(0) nanoparticles with surface area of $\approx 35 \text{ m}^2/\text{g}$.

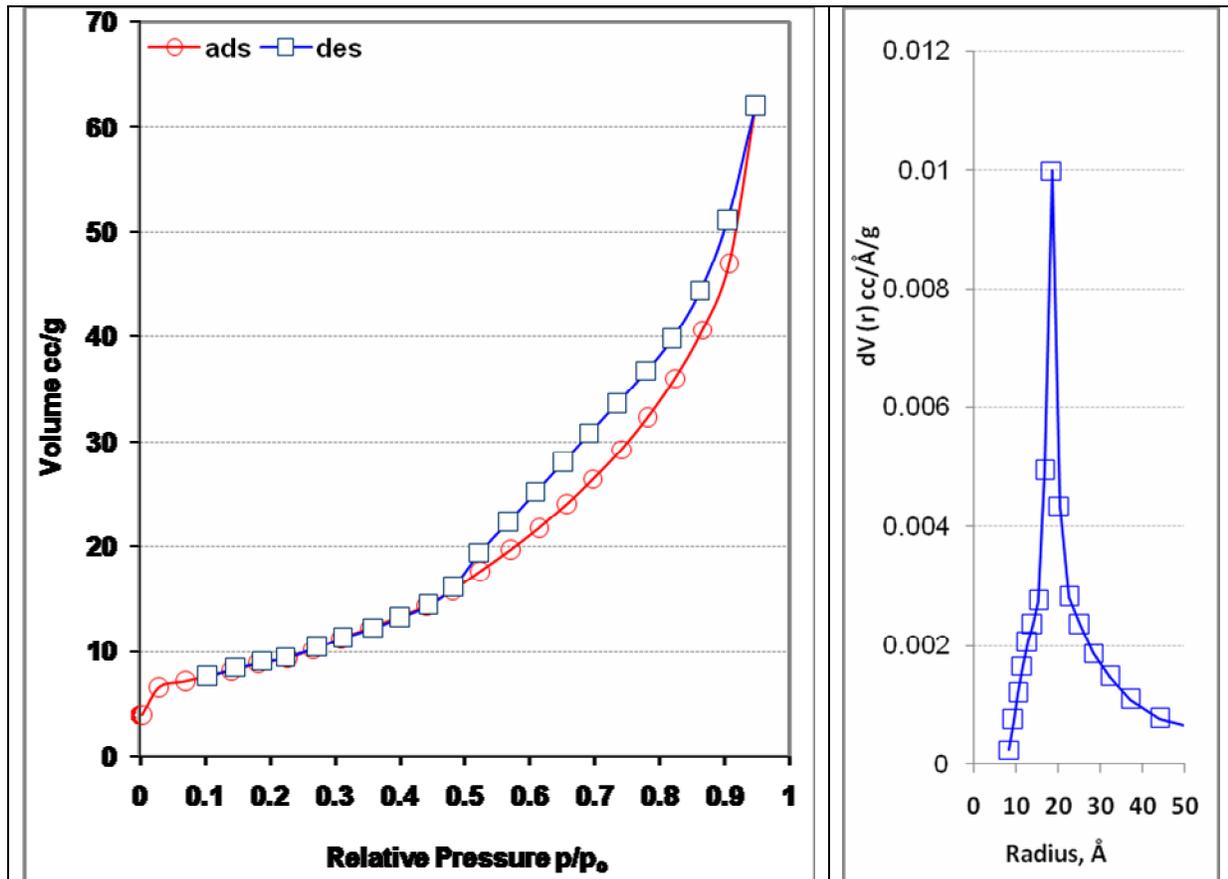


Figure.5 IR spectroscopy for Bmim[Cl] based ILs.

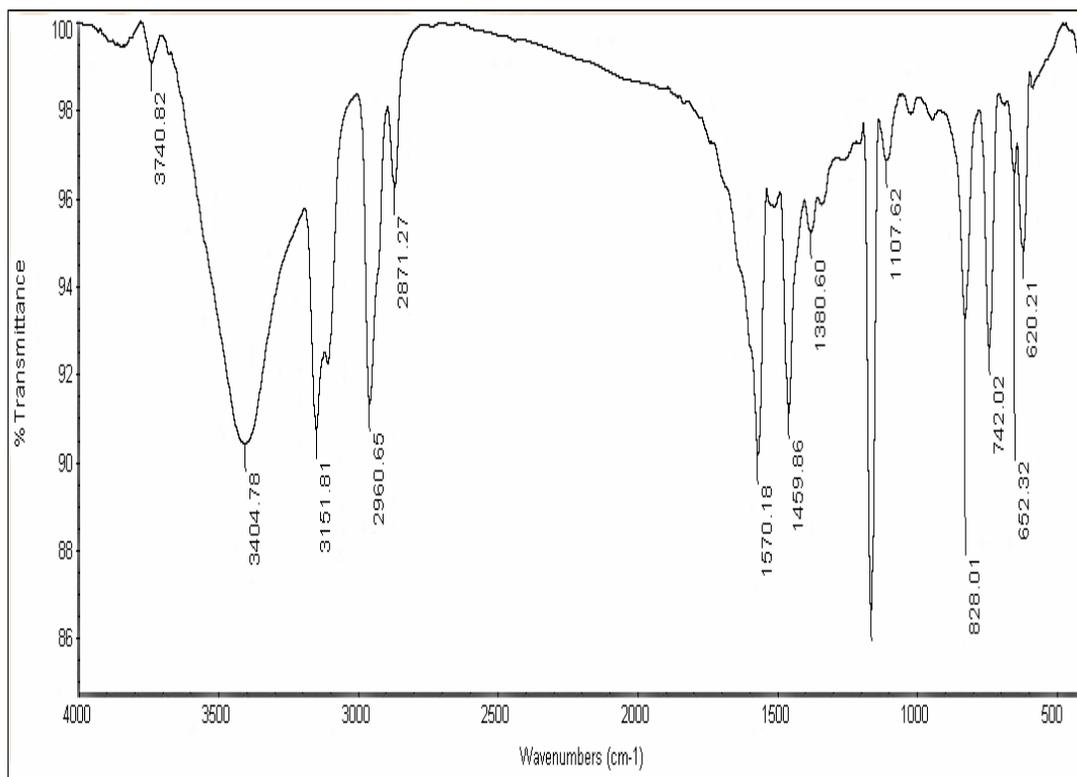


Figure.6 IR spectroscopy for [Bmim]ClFeO based ILs

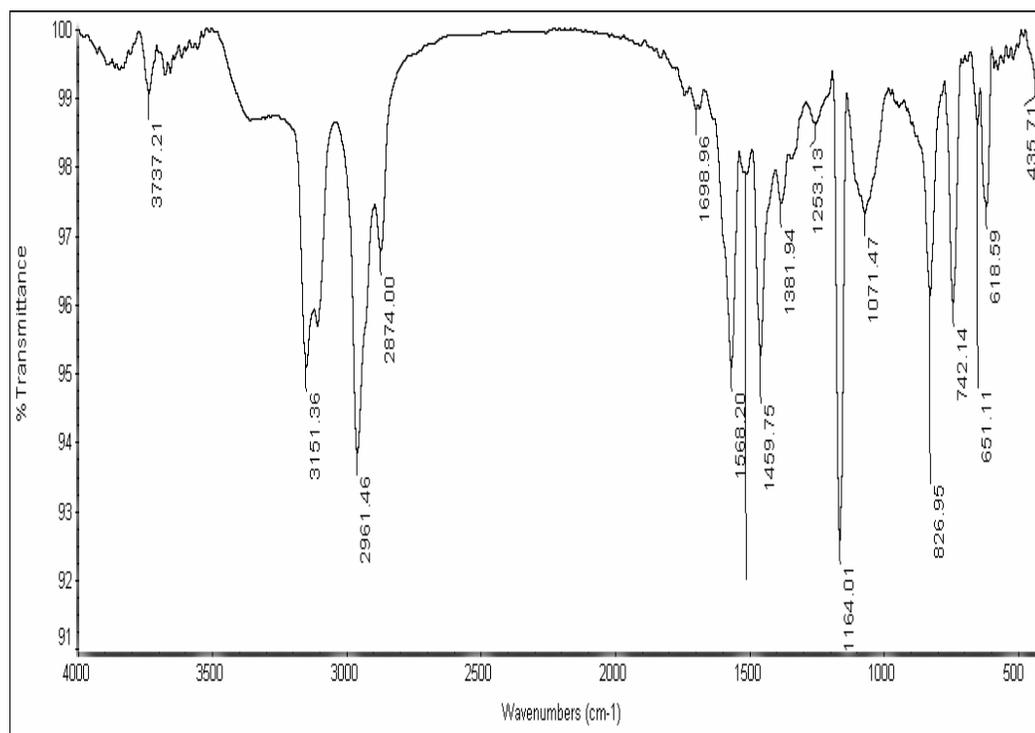


Figure.7 Concentrations variation of sulfur with time in presence of nZVI

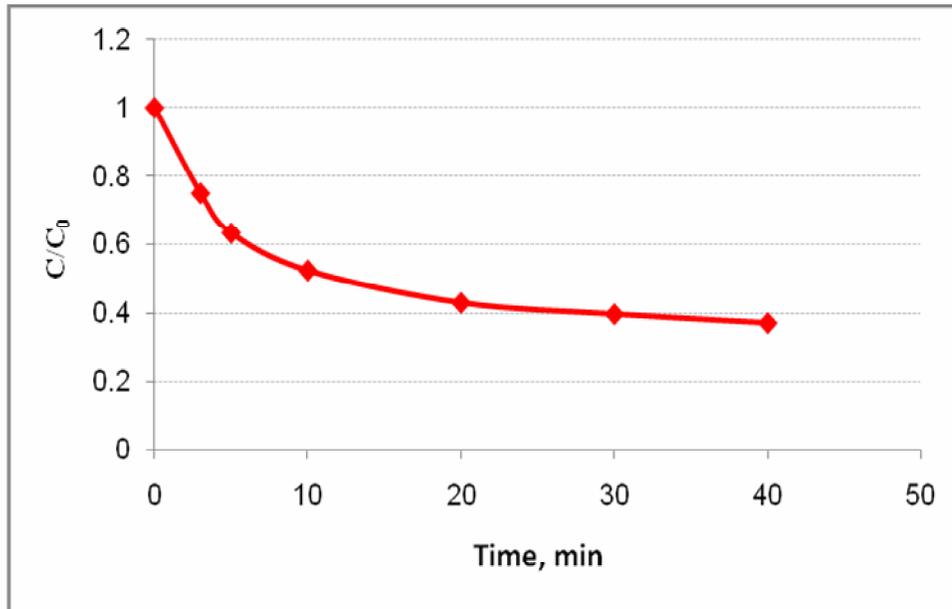


Figure.8 The core-shell model of nZVI and schematic representations of the reaction mechanisms for the removal of H₂S investigated in this study

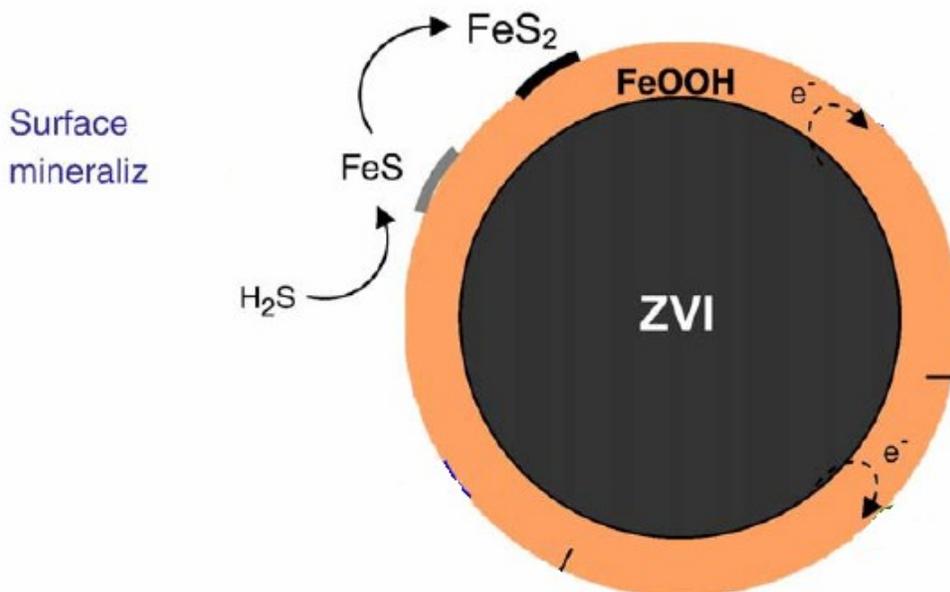


Table.1 Effects of the time on sulfur removal of gas oil using ionic liquid and Nzvi based ionic liquid.

Time,min	Sulfur removal (volume %)		
	[Bmim]Cl	nZVI	[Bmim]ClFe ⁰
3	17.2	26.6	47.5
5	23.2	35.2	56.4
10	37.2	46.6	67.2
20	48.3	56.9	77.7
30	54.4	60.2	84.3
40	56.5	61.4	85.1

Figure.9 Effects of the time on sulfur removal of gas oil using ionic liquid and Nzvi based ionic liquid

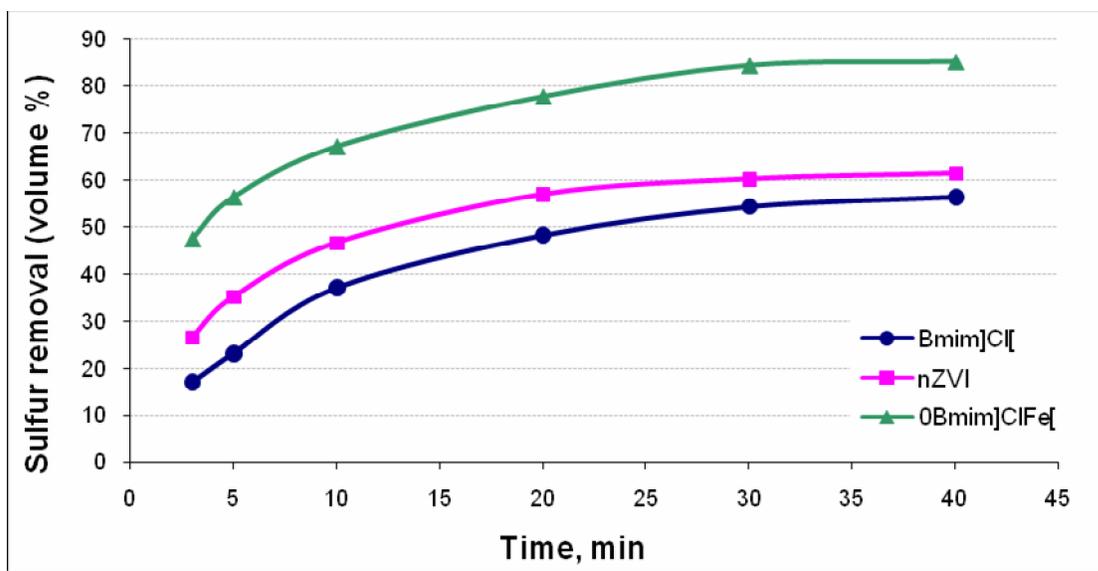


Table.2 Effects of the ionic liquids mass ratios on sulfur removal from gas oil (time, 30 min)

Mass ratio gas oil to IL	[Bmim]Cl	nZVI	[Bmim]ClFe ⁰
1 : 1	18.8	20.5	36.3
3 : 1	48.2	52.6	61.2
5 : 1	54.4	60.2	84.3

Table.3 Sulfur removal of [Bmim]Cl and [Bmim]ClFe⁰ which was reused for three times in gas oil

Ionic liquid spent	No. of cycle	Sulfur removal (%)
[Bmim]Cl	I	54.4
[Bmim]Cl	II	45.4
[Bmim]Cl	III	28.6
[Bmim]ClFe ⁰	I	83.6
[Bmim]ClFe ⁰	II	62.1
[Bmim]ClFe ⁰	III	48.3

The desulfurization process went quite quickly and sulfur concentration in gas oil decreased with an increase in extraction time and was reduced from 1187 to 541.5 ppmw (S-removal 54.4 %), 472.2 ppmw (S-removal 61.4 %), and 186.5 ppmw (S-removal 84.3 %) with [Bmim]Cl, nZVI, [Bmim]Cl Fe⁰ respectively (mass ratios of 5:1 in 30 min).

At the initial stage of the reaction, sulfur content in the gas oil was very high hence the extraction rate became high with high S-removal rate. As the reaction proceeds extraction rate becomes low with S-removal rate no longer distinctly increases. (Swapnil et al., 2013).

The results, in Figure 9, show that contact time of 30 min between the gas oil and IL phase is more than enough to achieve the equilibrium. So the optimum time required for the desulfurization of gas oil was 30 min. The result indicated that the reaction is fast enough to reach equilibrium. (Swapnil et al., 2013).

Imidazolium ILs are more capable of efficiently extracting S-containing compounds (Asumana et al., 2010; Yu et al., 2011a,b). The extraction process for

imidazolium based ILs which was attributed for higher polarizable ρ - electron density of S-containing compounds (as example DBT) which tends to insert the molecular structure of ILs (Nie et al., 2006). DBT extraction with imidazolium based [BMIM]Cl is recognized to the $\rho - \rho$ interaction between the aromatic ring of imidazolium and the thiophenic ring of DBT. (Olson, 2000). The removal of sulfur with [Bmim]Cl, nZVI, [Bmim]Cl Fe⁰ were carried out for 30 min at room temperature with mass ratios of 5:1, 3:1, and 1:1 (Mass ratio gas oil to IL) as shown in Table 2.

The amount of sulfur extracted can be increased with an increased molar ratios of [Bmim]Cl and [Bmim]Cl Fe⁰ which can be recognized to the increased Lewis acidity of the resulting IL at higher molar ratios of [Bmim]Cl (Ko et al., 2008,2010). In general [Bmim]Cl alone exhibited lower extraction ability than the Fe⁰-containing IL (Ko et al., 2010). It was also found that [Bmim]Cl/Fe⁰ is less viscous than other ionic liquid. However, [Bmim]ClFe⁰ is considered as a promising extractive agent in extractive deep desulfurization for the removal of sulfur (Li et al., 2009; Swapnil et al., 2013).

Ionic Liquid Reusability without Regeneration

In order to examine the reusability of the ionic liquid, the spent [Bmim]Cl and [Bmim]ClFe⁰ studied. Table 3 shows the desulfurization efficiency of [Bmim]Cl and [Bmim]ClFe⁰ which were reused for three times without regeneration. It was observed that the spent ionic liquids was able to extract sulfur from gas oil even without regeneration, however, at a lower efficiency of 28.6 and 48.3 % from 54.4 and 83.6 % with fresh ionic liquid. (Welton, 1999).

Nanoscaled zero valent iron (nZVI) (50-100 nm) was synthesized in ethanol medium by borohydride reduction method under atmospheric conditions. It was observed that iron nanoparticles are mainly in zero valent oxidation state and that no significant oxidation took place for weeks of storage under atmospheric conditions. The characterization of the nZVI was performed using XRD TEM and BET studies and indicated partial dispersion of the chainlike structure of iron nanoparticles. From the results of TEM, it was observed that iron nanoparticles consist of a zero valent core and surrounding an oxide shell. The iron nanoparticles tend to form chain like structures with a particle size in the range 5-20 nm. BET surface area of pure nZVI was determined as 34.75 m²/g.

A series of ionic liquids based on FeCl₃, nZVI, Fe⁰ were synthesized and employed in extractive desulfurization systems, the IL containing nZVI showed the highest extractive efficiency. The sulfur removal of gas oil could reach 54.4, 60.2 and 84.3 % with [Bmim] FeCl₃, nZVI and [Bmim]ClFe⁰, respectively, as extractant at room temperature, even when the gas

oil/IL ratio got to 5:1. For S-removals were also achieved in 30 min.

Moreover, this IL [Bmim] FeCl₃ and [Bmim]ClFe⁰ could be recycled three times without a significant decrease in activity. With the efficient production of ionic liquids in the chemical industry, this method of extractive desulfurization may be a simple, promising and environmentally friendly process.

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