Extractive Desulfurization Using Piperidinium Based Ionic Liquids with Lewis Acids

Assim A. Sabah[1*]

[1] Department of Science, College of Basic Education, University of Mosul, Mosul, Iraq

Abstract: This work includes the preparation of ionic liquid 1,4-dimethylpiperidinium iodide [MMPip]I and its salts with ferric chloride as Lewis acid in different molar proportions [MMPip]I/n$FeCl_3$ (n=1,2,3). The prepared compounds were diagnosed by spectroscopic and physical methods such as ^{1}H-NMR, FT-IR, elemental analysis (CHN) and other techniques. The thermal stability of these compounds was studied to use in the extractive desulfurization process (EDS). The efficiency of these compounds in removing sulfur compounds from the petroleum model was examined using dibenzothiophene (DBT) with a concentration of 1000 ppm dissolved in the solvent of normal hexane. The results showed that the compounds used had an acceptable efficiency of up to 30% despite using medium amounts of the extracted agent relative to the oil model; these compounds have a promising future in extractive sulfur removal processes.

Keywords: Piperidine ionic liquids, desulfurization, thermal study, lewis acid.

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***Corresponding author. E-mail:** assimsabah@uomosul.edu.iq.

INTRODUCTION

Desulfurization is one of the chemical processes used to remove sulfur from raw materials in industry or final products. These processes are critical because they provide a large portion of the sulfur used in other fields and other sulfur-free materials to reduce toxic and polluting emissions to the environment, such as SOx emissions that cause acid rain (1-3). The fuel refining process necessarily requires the removal of sulfur from the oil hardships. The Environmental Protection Agency has imposed global restrictions on the specifications of the fuels used in transportation (EPA)(4). The optimum allowable sulfur content in diesel and gasoline is 15-30 ppm, which was previously 500 ppm in most countries, and is now being reduced to 10 ppm (5). Thus, one of the critical processes in oil refineries is the removal of sulfur from oil. The price of oil production is determined by the sulfur content, which influences the price of crude oil and processing costs (1, 6-8).

Ionic liquids (ILs) with a high distribution coefficient for sulfur compounds, a low cross solubility for hydrocarbons, a low viscosity, and a fast separation phase after mixing and extraction are ideal. Unfortunately, natural ionic fluids perform less efficiently in liquid-liquid extraction for typical sulfur compounds such as dibenzothiophene (DBT). However, ionic liquids have a high distribution coefficient. In mixtures, the distribution coefficient is somewhat low; in other words, liquids are not ideal solvents for extraction desulfurization, especially with heavy oil, and the (EDS) process efficiency is lower. Because oxidizing sulfur compounds have a much higher distribution coefficient, the efficiency of the ionic liquid extraction process increases if organic sulfur compounds have previously been oxidized to sulfoxides and sulfonates (9-11).

Desulfurization by extracting fuel with ionic liquids instead of conventional organic solvents is an exciting alternative to extremely clean diesel oils. The use of different ionic liquids have been investigated within (EDS) (cations such as imidazolium, pyridinium, quinolinium, and pyrrolidinium, anions such as alkyl sulfate, alkyl phosphate, halogens, ethanoate, and thiocyanate), the treatment carried with (DBT) dissolved in dodecane as a model fuel. The results showed that the extraction efficiency of the cationic ions is in the following order: methylpyridinium ≥ pyridinium ≈ imidazolium ≈ pyrrolidinium. Methylpyridinium cation showed the highest sulfur removal, up to (80%) per batch (12-16).

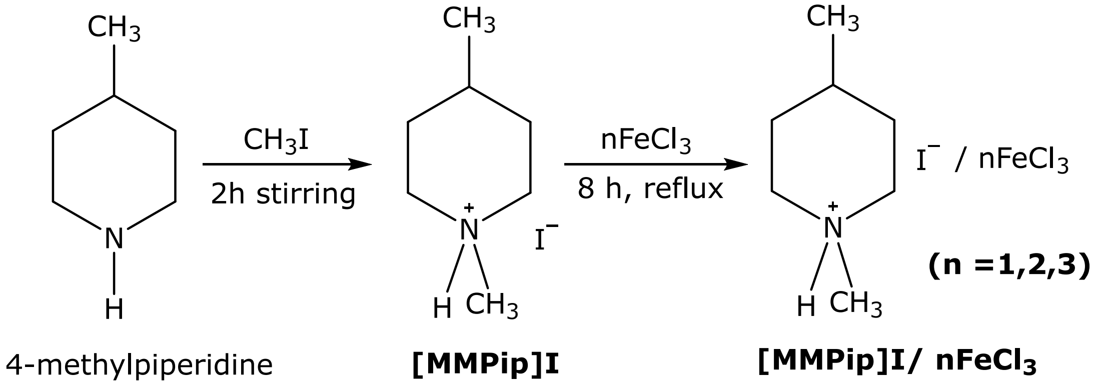
In practical experiments with the (EDS) process, it was found that ionic liquids containing Lewis acids such as $FeCl_3$, $AlCl_3$ and CuCl gave promising good results for the selective extraction process for aromatic sulfur compounds even when used in thermal conditions of up to 70 °C due to their solid presence (17, 18). In the (EDS) process, many ionic liquids mixed with Lewis acids were tested in different molar ratios, for example, the mixture between the ionic liquid (1-n-butyl-3-methyl imidazolium [BMIM]Cl) and with aluminium chloride $AlCl_3$ as Lewis acid in molar ratios [BMIM]Cl: $AlCl_3$ (0.35:0.65) where the bilayer system was formed with the petroleum model at room temperature. It was also tested in the (EDS) process of real diesel. In the extraction process, the ionic liquids containing Lewis acids showed higher efficiency than their counterparts, non-containing Lewis acids (18, 19). Also, ionic liquids containing $ZnCl_2$ were tested in the oxidative desulfurization process (ODS), [BMIM]Cl / n$ZnCl_2$ (n=1,2,3), using the fuel model with concentrations of 500 ppm and 1000 ppm of (DBT). The results showed that the desulfurization efficiency decreases with the increase in the percentage of $ZnCl_2$. These may be attributed to the strong binding of zinc chloride with the cation in ionic liquid; and its lack of participation in the desulfurization process (20). On the contrary, we notice the increase in extraction efficiency when using $FeCl_3$ when increasing the ratio of ferric chloride to ionic liquid n$FeCl_3$ /[BMIM]Cl (n=1,2,3), which is due to the increase in acidity and the closer association of aromatic sulfur compounds with ionic liquids of higher ferric chloride (15, 18). The use of ionic liquid alone or Lewis acid alone did not show high efficiency in the (EDS) process. However, when using the mixing technique between them, the efficiency was higher. Therefore, the process of mixing them is beneficial, as an ionic liquid containing $FeCl_3$ showed higher efficiency when compared with their counterparts containing $AlCl_3$ or CuCl under the same experimental conditions (15, 21).

MATERIALS AND METHODS

All chemicals are of high purity and from certified international companies and used without any additional treatment.

Preparation of ionic liquids systems

The ionic liquids (molten salts) were prepared as mentioned in the literature (22-26), the ionic liquid 1,4-dimethylpiperidinium iodide [MMPip]I was prepared through the reaction of 4-methylpiperidine dissolved in absolute ethanol with the gradual addition of methyl iodide with continuous stirring for two hours with cooling, the reaction is exothermic. At the end of the reaction, evaporation followed by a rotary evaporator at 80 °C concentrated the solution and removed the remaining solvent. After that, the ionic liquid [MMPip]I reacted with $FeCl_3$ in different molar proportions through mixing them with reflex for 4 hours and disposing of the used solvent (absolute ethanol) by rotary evaporator for 4 hours. Scheme 1 shows the preparation of the ionic liquids systems.



Scheme 1: Preparation of ILs systems.

Extractive desulfurization using ILs Systems

1000 ppm of sulfur content has been prepared by dissolving (DBT) in *n*-hexane (as model oil). In the process (EDS), the optimum conditions were determined by treating the prepared ionic liquid systems to several conditions of temperature, time and concentration of the extracted material. Conical flask 100 mL used in a shaker by adding 10 mL of the (DBT) model oil with a specified concentration of ionic liquid dissolved in 5 mL DMSO, 211DS Shaking Incubator used to control the operating conditions of the experiment. Analyzing the results of sulfur removal ratio was done by using absorption to create a standard calibration curve and determine the wavelength (λ_{max} = 285 nm) at the highest absorption intensity, as shown in Figure 5. The percentage of sulfur removed was calculated through the following relationship:

$$S_{removal}\ \% = \frac{Conc.i - Conc.t}{Conc.i} \times 100$$

Where $Conc._i$ = initial concentration of sulfur (1000 ppm) represented by concentration of organic sulfur compound (DBT), $Conc._t$ = sulfur concentration at certain time in a specific conditions (DBT) concentration.

Characterization and analysis data

Several physical and spectral methods were used; the ^{1}H-NMR was investigated by Bruker Avance DPX 400 MHz using DMSO-d_6 as solvent. Trio-1000 equipment was used for mass spectroscopy; the elemental analysis was investigated by Flash EA 1112 Series Thermo Electron Corporation. The FT\IR measured by JASCO Canvas 4200, Avanta 2.02 software for atomic absorption by SensAA GCB scientific equipment system. METTLER Toledo TGA\ DSC used for thermal analysis at 30-950 °C with a ramping heat rate of 10 °C/min under air, STARe evaluation software. The sulfur content was measured by Shimadzu UV-Vis 1800 spectrometer at (λ_{max} = 285 nm). Table (1) shows some physical properties of prepared compounds.

Table 1: Some physical properties of prepared compounds.

No.	Compound	Conductivity*	m.p. °C	Color
1	[MMPip]I	100	85	Off white
2	[MMPip]I/$FeCl_3$	90	70	Brown
3	[MMPip]I/2$FeCl_3$	90	68	Dark brown
4	[MMPip]I/3$FeCl_3$	90	68	Dark brown

* Conductivity (ohm^{-1}.mol^{-1}.cm^2) at (25 °C) and (10^{-3} M) by using water as solvent

RESULTS AND DISCUSSION

Characterization data

The characterization of the cation in the ionic liquids [MMPip]$^+$ by ^{1}H-NMR (DMSO-d_6, 400 MHz): δ0.9409 (3H-CH_3, d, *J* = 11.52 Hz), δ1.6512 (5H-CH,2CH_2, m), δ2.7547 (3H-CH_3, s), δ3.0718 (4H-2CH_2, m), δ8.2942 (1H-NH, br).

[MMPip]I **(1)** Anal. Calcd. for $C_7H_{16}IN$: C, 34.87; H, 6.69; N, 5.81. Found: C, 35.89; H, 6.84; N, 5.61.

[MMPip]I/$FeCl_3$ **(2)** Anal. Calcd. for $C_7H_{16}Cl_3FeIN$: C, 20.85; H, 4.00; Cl, 26.37; Fe, 13.85; N, 3.47. Found: C, 19.25; H, 3.76; Cl, 27.66; Fe, 14.65; N, 3.22.

[MMPip]I/2$FeCl_3$ **(3)** Anal. Calcd. for $C_7H_{16}Cl_6Fe_2IN$: C, 14.87; H, 2.85; Cl, 37.61; Fe, 19.75; N, 2.48. Found: C, 13.05; H, 2.66; Cl, 39.05; Fe, 21.55; N, 2.22.

[MMPip]I/3$FeCl_3$ **(4)** Anal. Calcd. for $C_7H_{16}Cl_9Fe_3IN$: C, 11.55; H, 2.22; Cl, 43.84; Fe, 23.02; N, 1.92. Found: C, 9.75; H, 1.98; Cl, 42.76; Fe, 24.25; N, 1.75. Figure 1 shows the ^{1}H-NMR of [MMPip]I **(1)**.

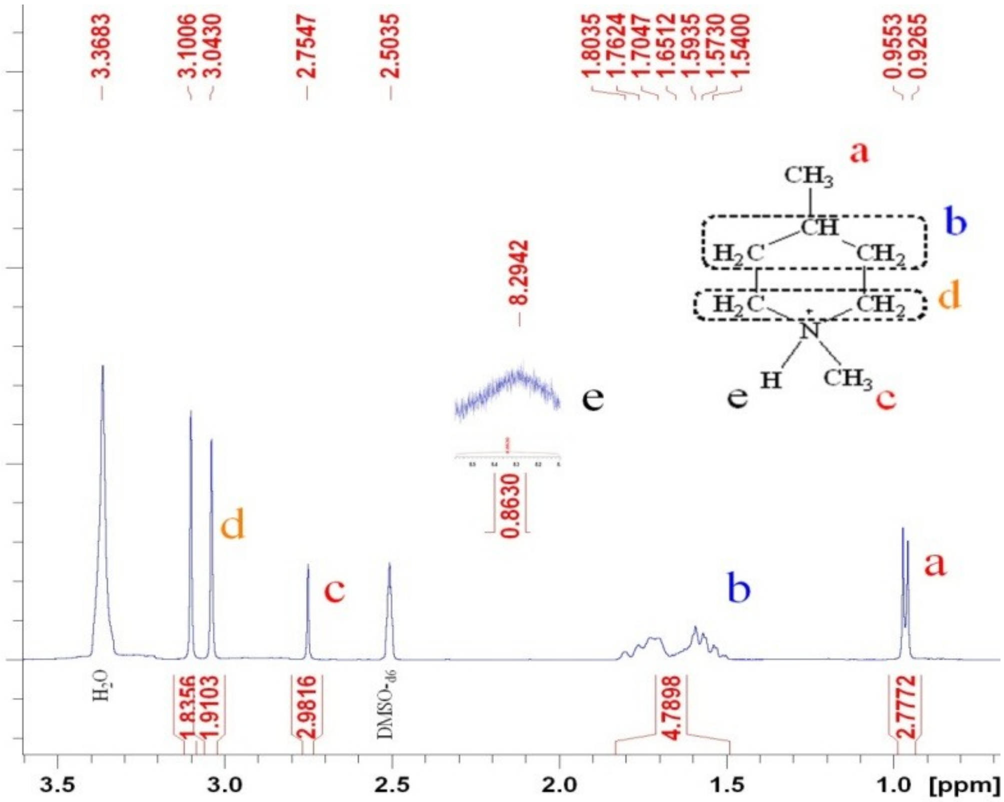


Figure 1: The ^{1}H-NMR of [MMPip]I (1) (400 MHz, DMSO-d$_6$).

The infrared spectrum measured the ionic liquid (organic salt) and the ionic liquid mixture with $FeCl_3$. The results showed that the presence of Lewis acid makes slight displacements of some bands, and it may change the band's intensity (26-28). For example, a band appeared at 975 cm^{-1} due to the in-plane bending frequency of the (C-H) group and is shifted to a lower position when ferric chloride is present (20, 29). The bands observed at 1072 cm^{-1}, 1454 cm^{-1} belong to (C-N str. or C-C str.) and (C-H, scissoring bending) respectively (20, 30). The other bands investigated are 2472 cm^{-1} (N^+-CH_3 str.), 2734 cm^{-1} (N^+-H str.), 2954 cm^{-1} (C-H symmetric str.). Figure 2 shows the IR spectra of ILs systems (20).

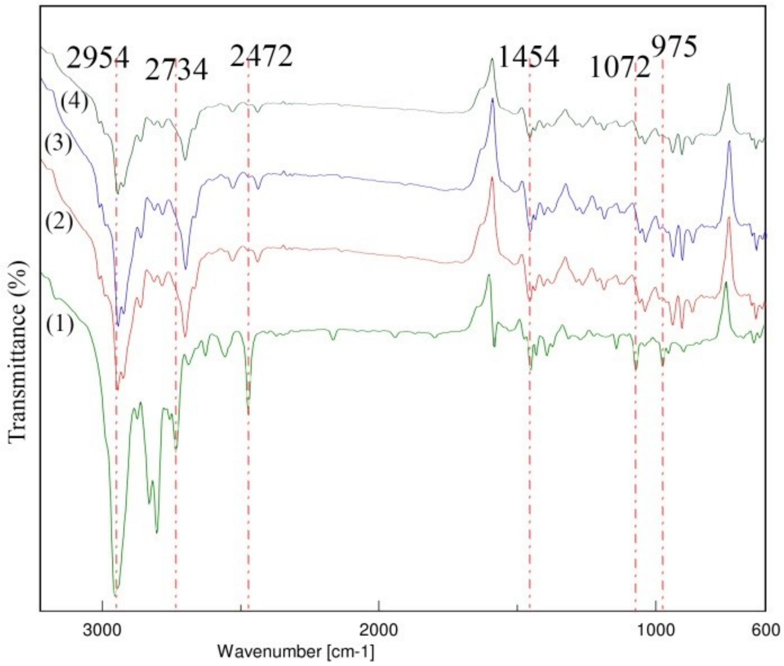


Figure 2: IR spectra of the IL systems: (1) [MMPip]I; (2) [MMPip]I/$FeCl_3$; (3) [MMPip]I/2$FeCl_3$; (4) [MMPip]I/3$FeCl_3$.

Thermal study data

The thermal stability of [MMPip]I and its mixtures with ferric chloride was studied. A noticeable decrease in the melting point of compounds containing ferric chloride was revealed. The study was under thermal conditions (30-950 °C) and a temperature rampage rate (15 °C/min). The results showed that the ionic liquid [MMPip]I is stable at temperatures up to 250 °C; as shown in Figure 3, the thermal degradation process occurs in one main stage (21, 31, 32). Although the presence of ferric chloride increases the presence of moisture water in the compound, as the results showed, the moisture water loses by cycling to 110 °C. Thus, the [MMPip]I/n$FeCl_3$ compounds have two main stages of thermal degradation. However, all mixes are relatively stable at the temperature of experimental conditions of the process (EDS). Figure 4 shows the thermal gravimetric analysis of the compounds.

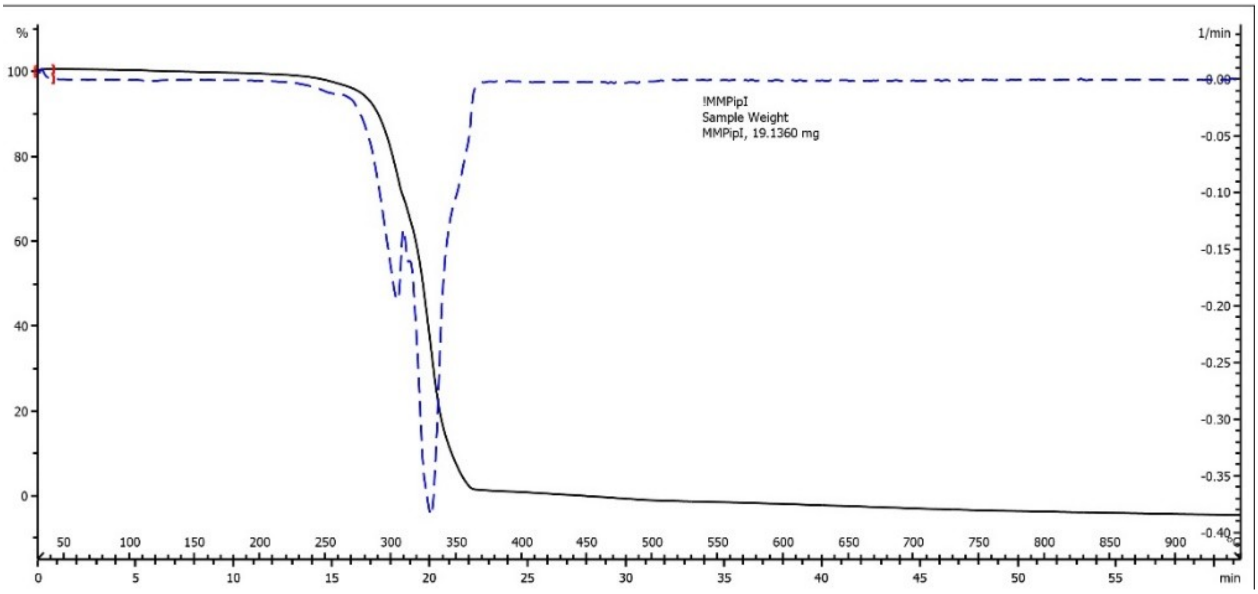


Figure 3: TGA and DTA of [MMPip]I.

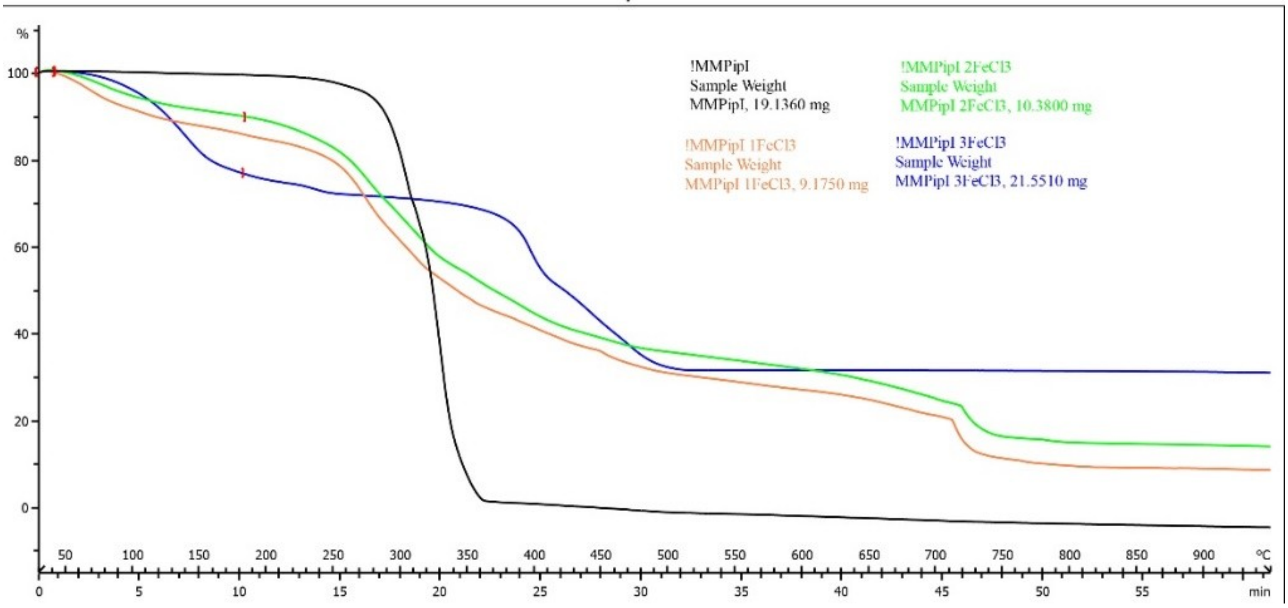


Figure 4: TGA analysis of [MMPip]I and its $FeCl_3$ mixtures.

Data for desulfurization analysis

Completing the standard curve by measuring the compound (DBT) absorbance for several standard concentrations (250, 500, 750, and 1000 ppm), as shown in Figure 5.

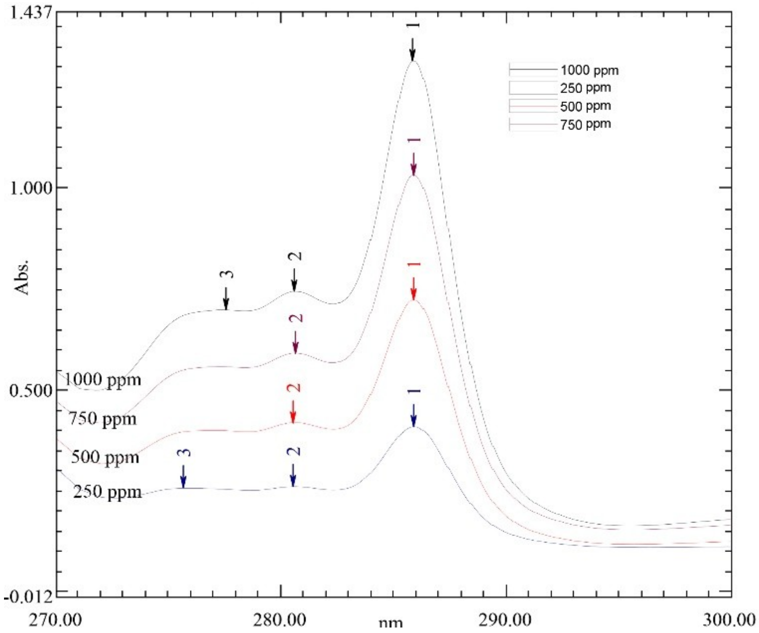


Figure 5: DBT absorbance with different concentrations.

The optimum conditions for the (EDS) process were determined by treating the model oil with prepared compounds for extraction at multiple temperatures (15, 30, 45 °C) using a fixed weight of the extracted materials (0.05 g) and 30 minutes. The results showed an increase in the removal efficiency with an increase in temperature. These results have good similarities to the literature (18, 20, 33), noting that there was no significant increase in efficiency when the temperature was increased from 30 °C to 45 °C, and it is preferable to use the laboratory temperature because it is more controllable, as shown in Figure 6. After stabilizing the temperature, the optimum time was verified under 30 °C and using the weight of the extracted substance (0.05 g). The results showed that the removal process increases with the increase of time, which have slightly different from the literature (20), and there is no significant difference between 60 minutes and 90 minutes, as the equilibrium is almost stable after 60 minutes and as illustrated in Figure 7. Finally, the efficiency was tested using many different weights, as the results showed that with the increase in the amount of extracted material, the extraction efficiency increases Figure 8.

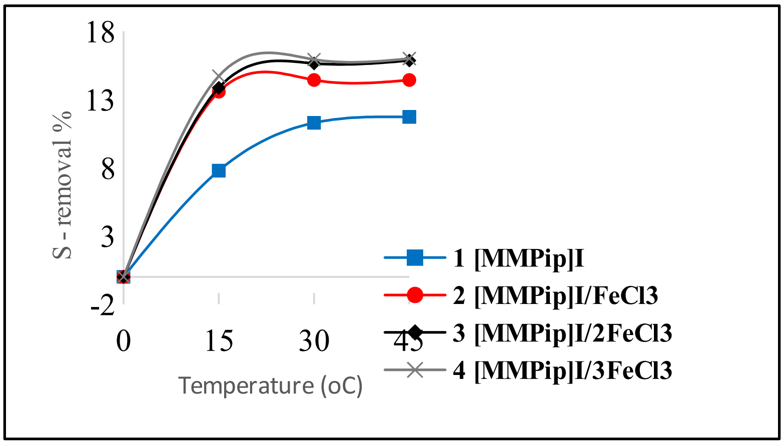


Figure 6: Effect of temperature: extractant used 0.05 g, 30 min.

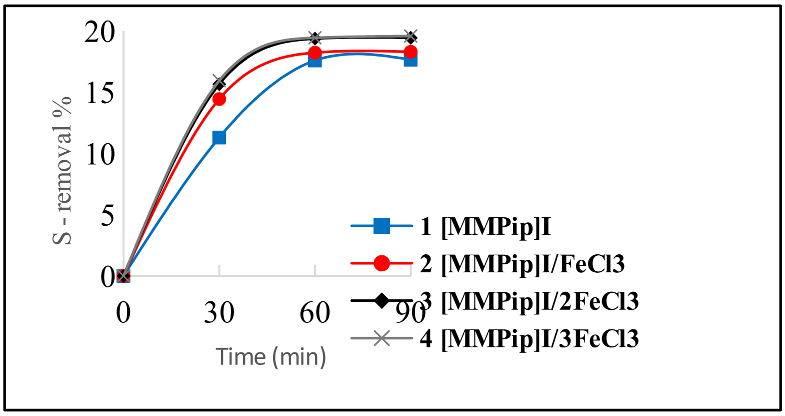


Figure 7: Effect of time: extractant used 0.05 g, 30 °C.

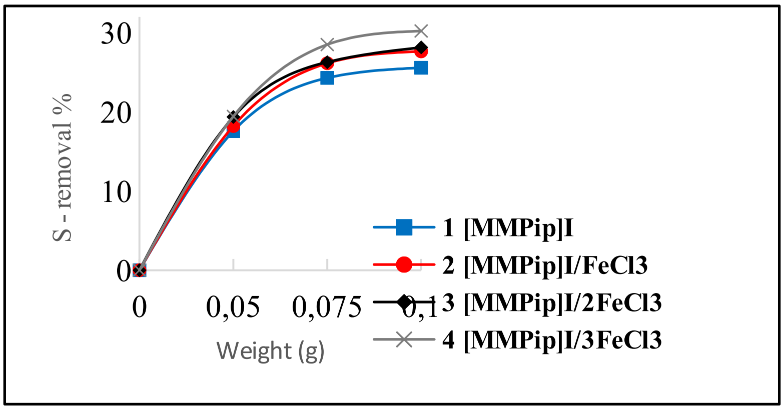


Figure 8: Effect of extractant weight: 60 min, 30 °C.

Through these results, it is noted that the increase in temperature from 30 °C to 45 °C and the increase in the time for the extraction process after 60 minutes does not significantly affect the efficiency of the extraction process, while the increase in the weight of the extracted material (ionic liquid or ionic liquid containing Lewis acid) is more considerable and more clearly. By comparing the results, we find that the highest percentage of sulfur removal is when using 0.1 g of compound (I), which is rather good when compared to efficiency results of up to 100%, but by using high amounts of the extracted substance to the oil model (18, 20). It also noted that the efficiency of the removal ratio increases with the increase in the ratio of ferric chloride to the ionic liquid, which is consistent with the published research (19, 34, 35).

The proposed mechanism for the extraction of organic sulfur compounds is through the interactions between the п electrons of organic sulfur compounds (DBT) with п electrons of the ionic liquid and their interaction with the metallic element in Lewis acid (36, 37). The results showed that ionic liquid mixed with Lewis acid has a higher extraction efficiency than the ionic liquid alone and higher than the use of Lewis acid alone, and the extraction process is more selective for aromatic sulfur compounds (17, 20, 21).

CONCLUSION

The pyridinium base's ionic liquid and salt were prepared with ferric chloride as Lewis acid, and their efficiency was tested in extracting the organic sulfur compounds from the petroleum model. It was found that the best extraction factor among the compounds used is [MMPip]I/3$FeCl_3$, where the percentage of sulfur removal from the oil model was (30%) under the optimal conditions (10 mL of model oil of 1000 ppm DBT, 0.1 g of extractant, 60 min at 30 °C). Compared with the previous work, these results are considered promising due to the use of acceptable quantities of the extracted agent relative to the quantity of the oil model used. It also noticed that the extraction efficiency increased with the increase in Lewis acid (ferric chloride) ratio to the ionic liquid under the same experimental conditions for the extraction process.

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Assim A. Sabah[1]*

Supporting Information

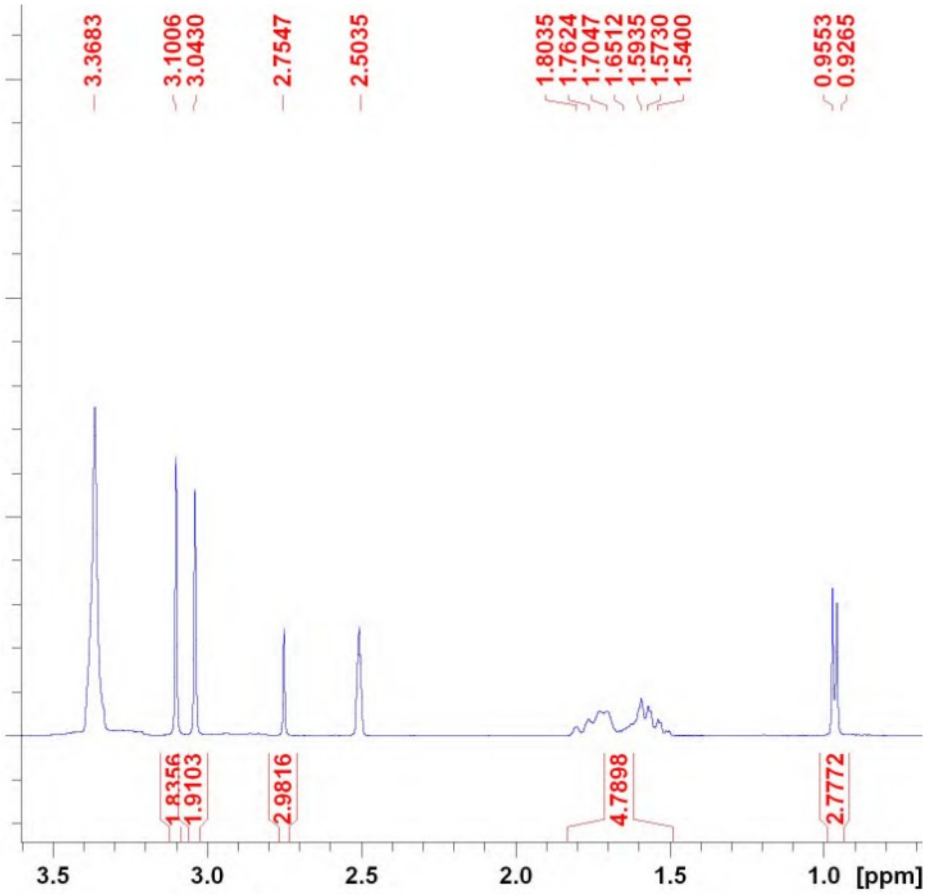


Figure S1: 1H-NMR of [MMPip]I ionic liquids.

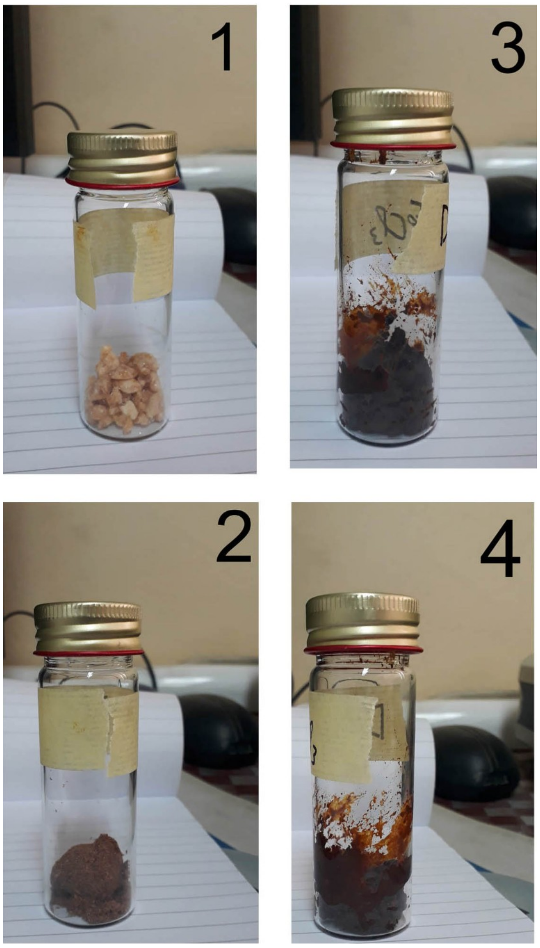


Figure S2: Pictures of the prepared compounds.

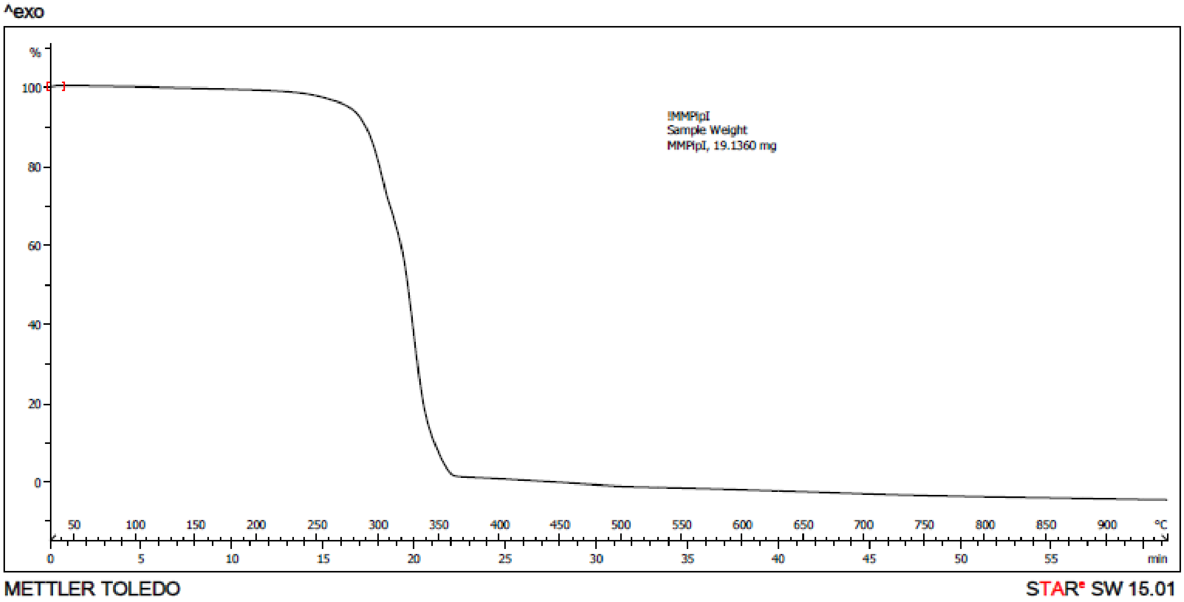


Figure S3: TGA analyses of [MMPip]I ionic liquids.

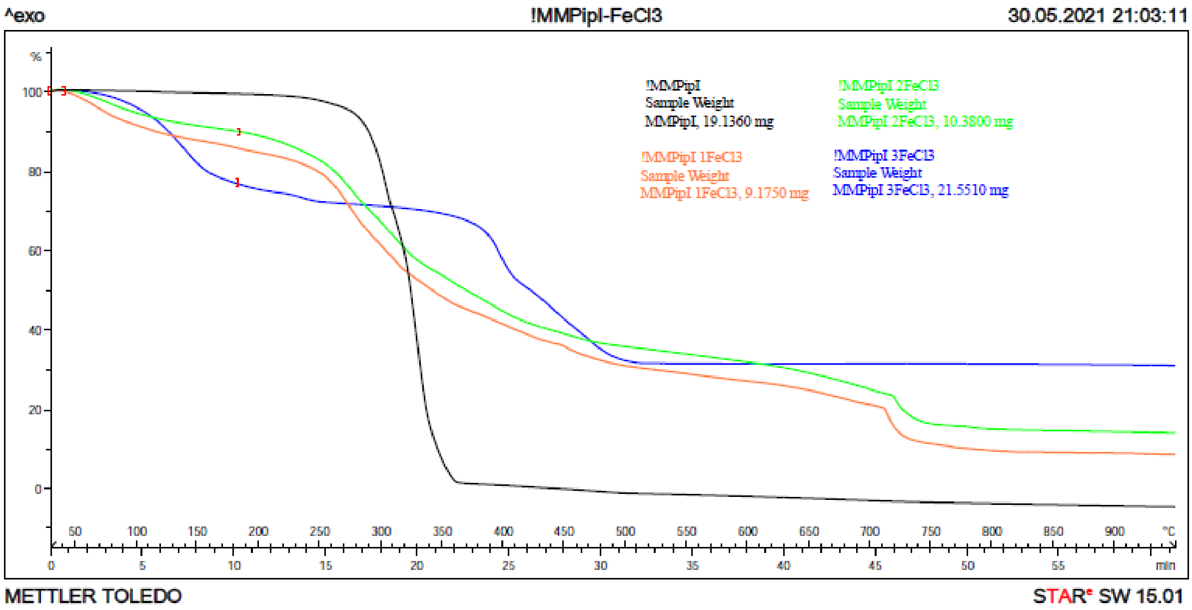


Figure S4: TGA analysis of prepared compounds.

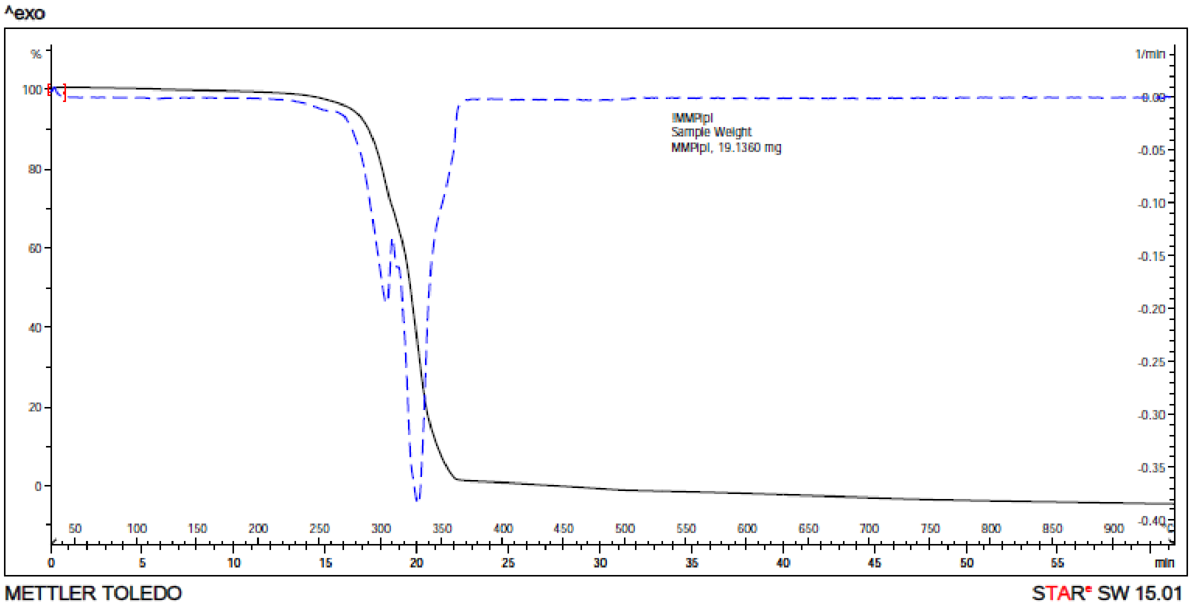


Figure S5: TGA and DTA analyses of [MMPip]I ionic liquids.

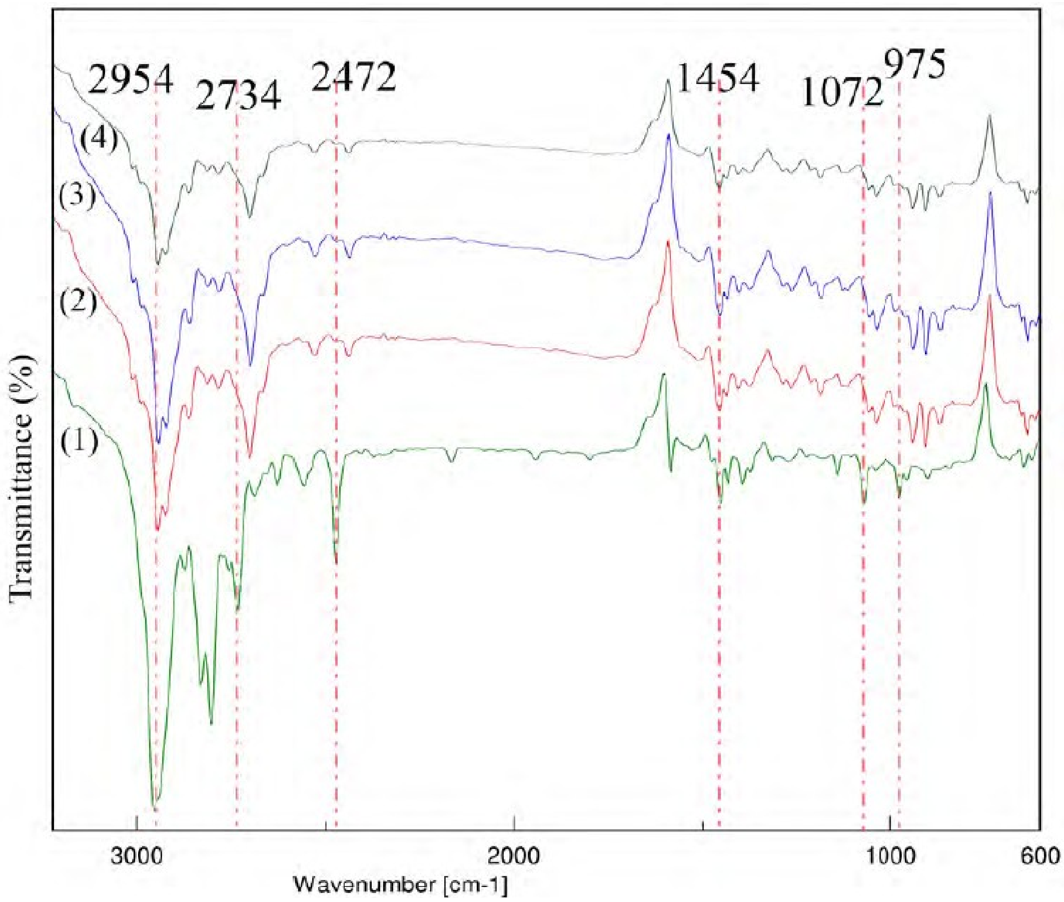


Figure S6: FT-IR spectrum of prepared compounds.

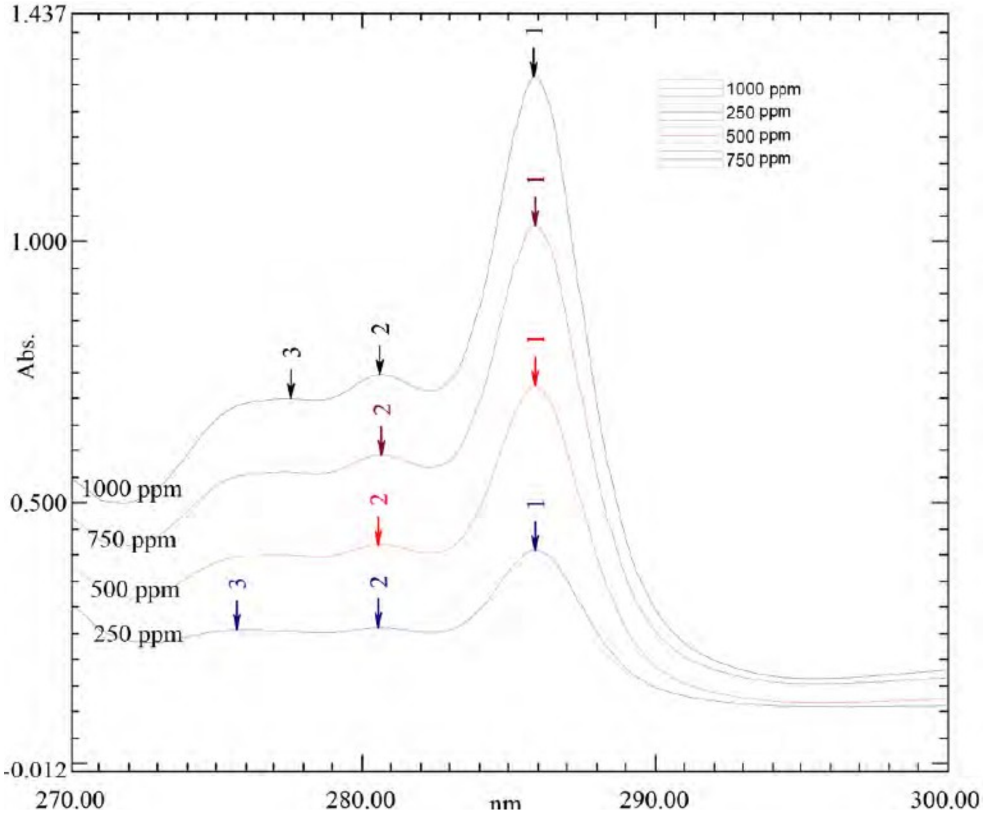


Figure S7: Calibration curve stander solutions spectrum.

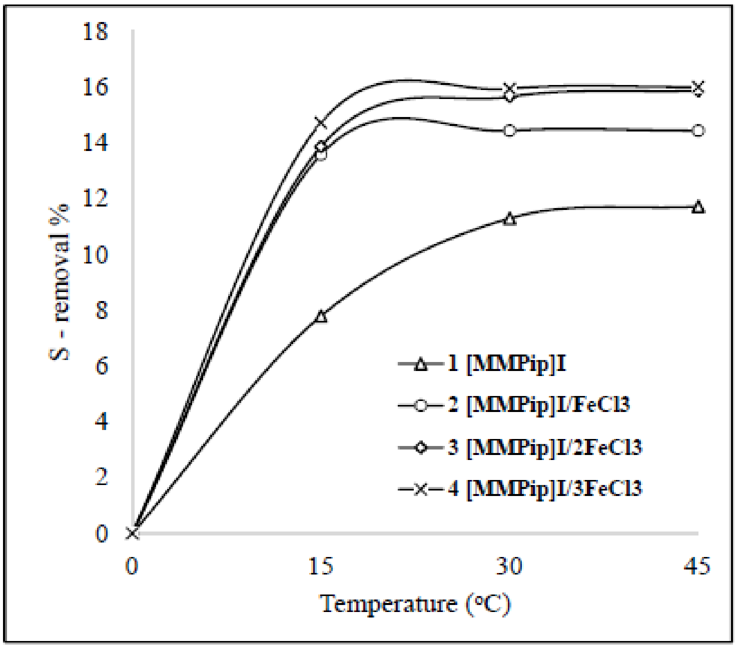


Figure S8: Effect of temperature: extractant used 0.05 g, 30 min.

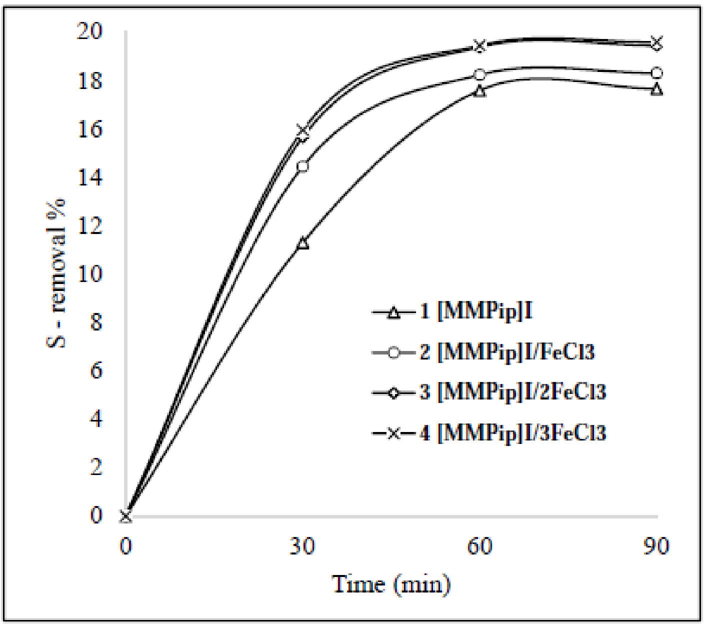


Figure S9: Effect of time: extractant used 0.05g, 30 °C.

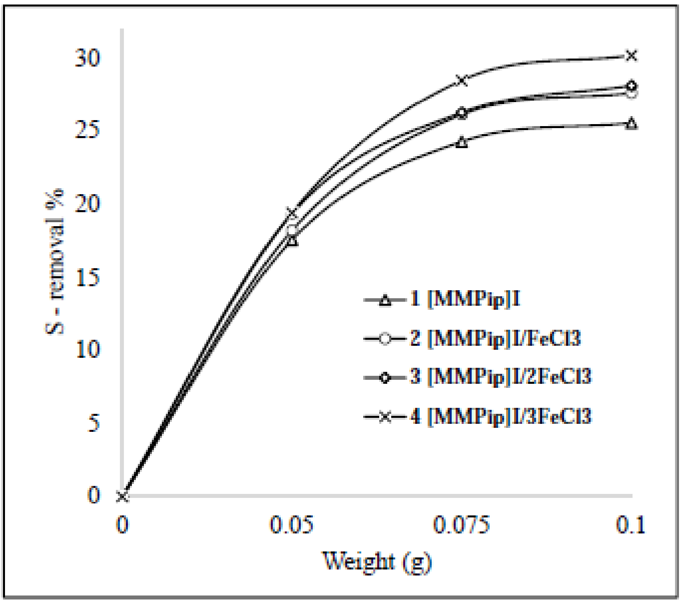
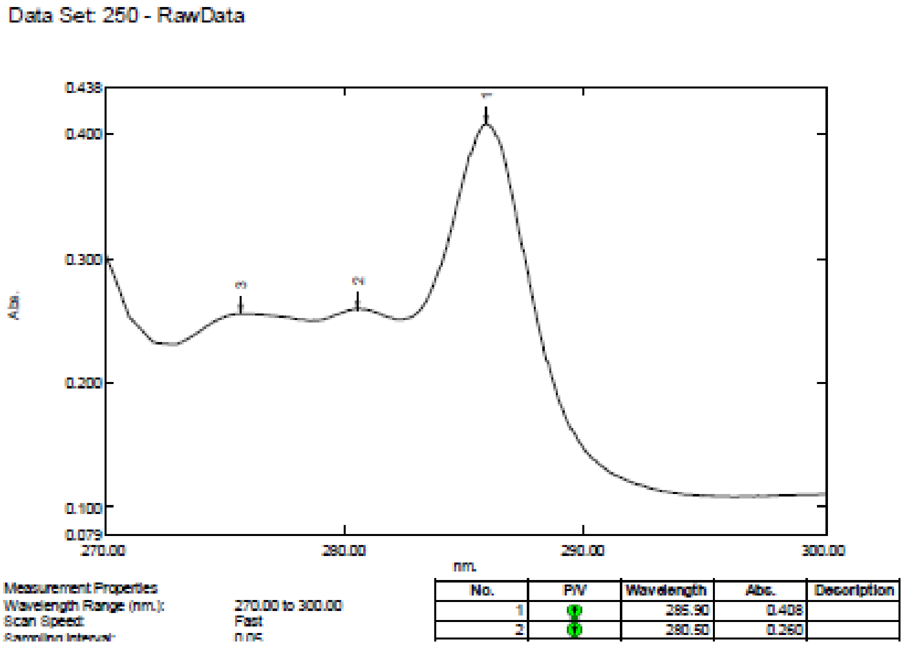


Figure S10: Effect of extractant weight: 60 min, 30 °C.

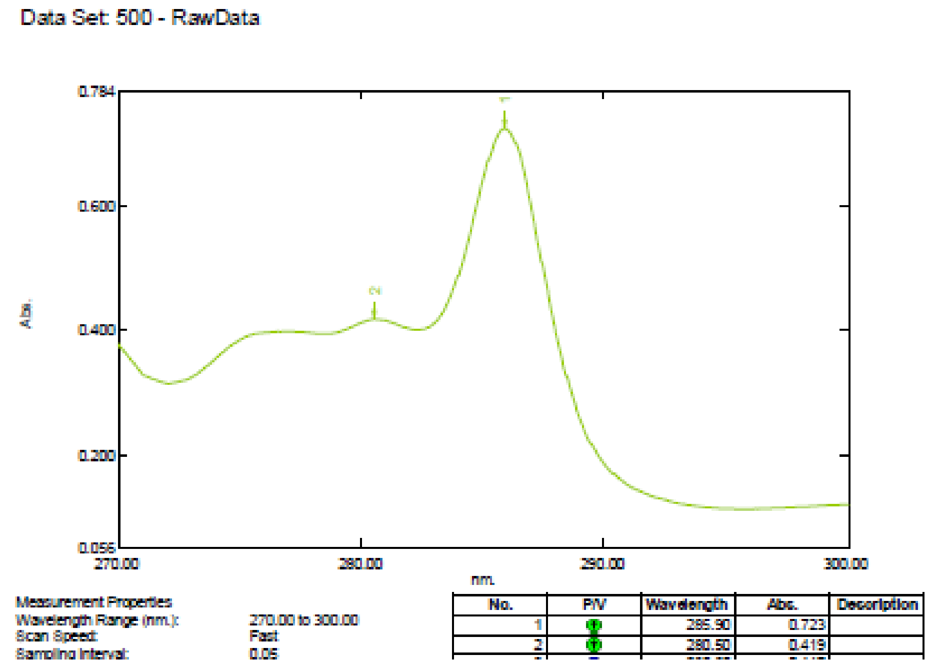


Data Set: 250 - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Description
1	●	285.90	0.408	
2	●	280.50	0.260	

Figure S11: UV- Spectrum peak pick report of 250 ppm of DBT stranded solution.

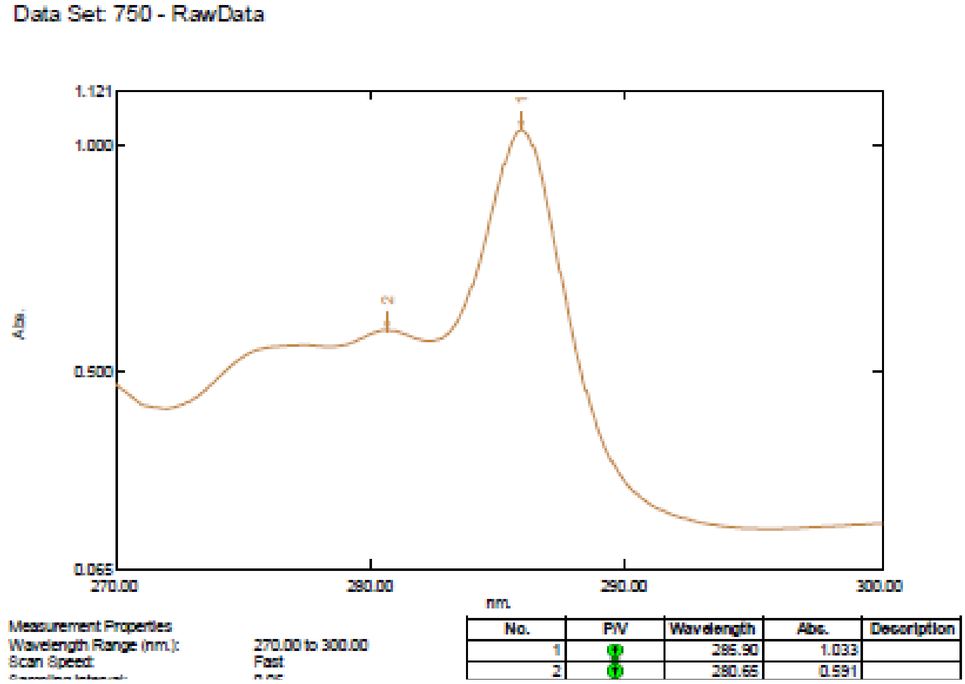


Data Set: 500 - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Description
1	●	285.90	0.723	
2	●	280.50	0.419	

Figure S12: UV- Spectrum peak pick report of 500 ppm of DBT stranded solution.

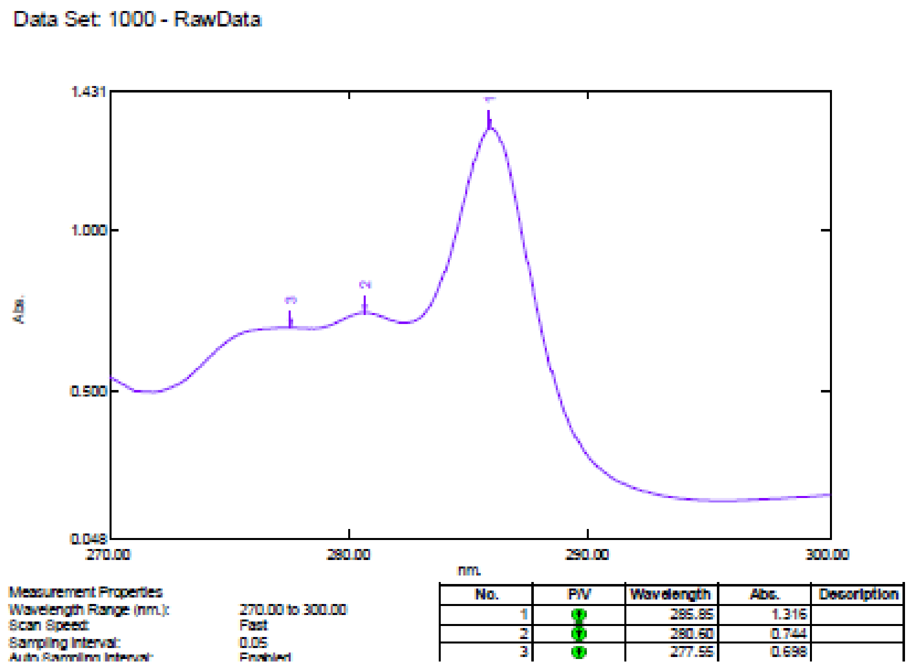


Data Set: 750 - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast

No.	P/V	Wavelength	Abs.	Description
1	●	285.90	1.033	
2	●	280.65	0.591	

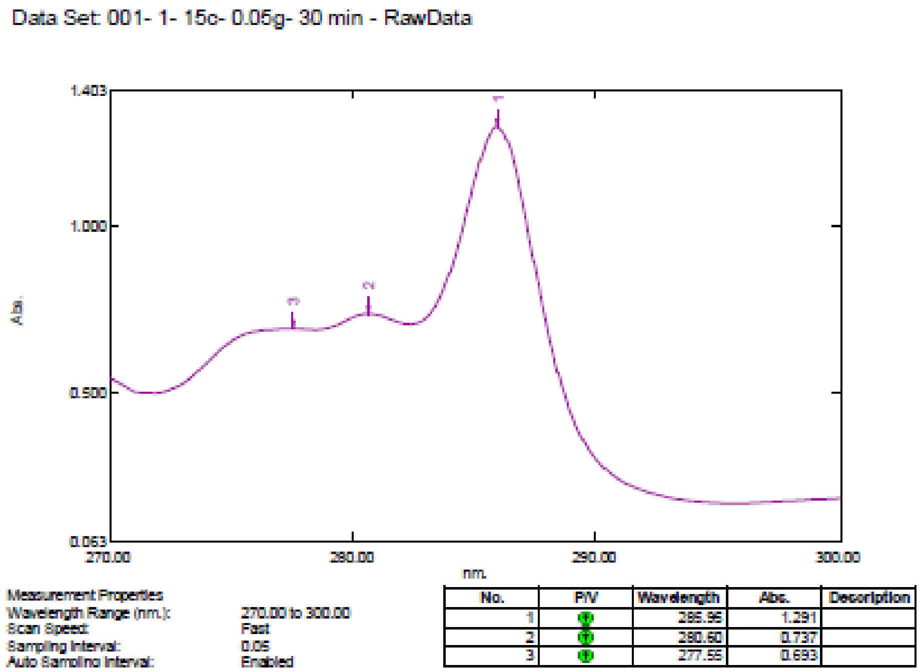
Figure S13: UV- Spectrum peak pick report of 750 ppm of DBT stranded solution.


Data Set: 1000 - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Description
1	●	285.85	1.316	
2	●	280.60	0.744	
3	●	277.55	0.698	

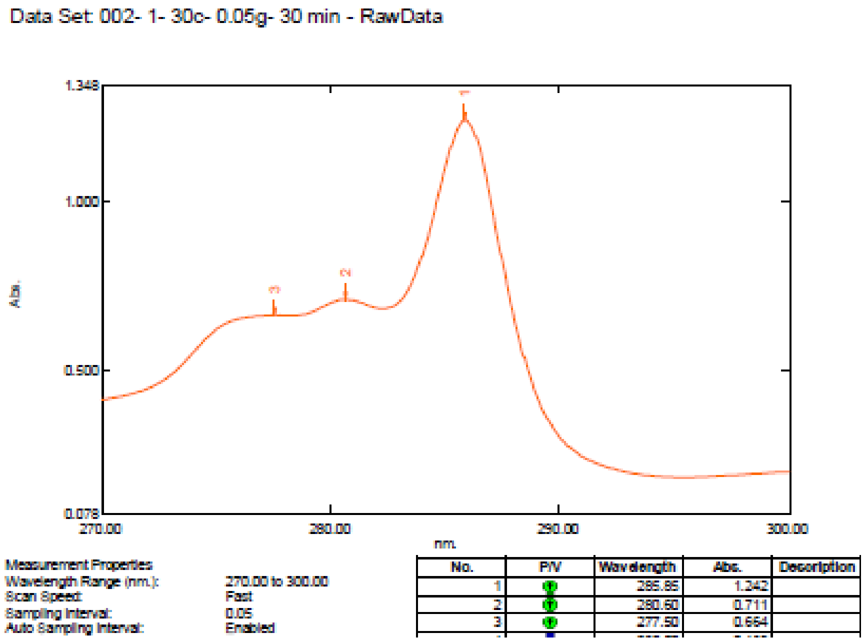
Figure S14: UV- Spectrum peak pick report of 1000 ppm of DBT stranded solution.


Data Set: 001- 1- 15c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Description
1	●	285.95	1.291	
2	●	280.60	0.737	
3	●	277.55	0.693	

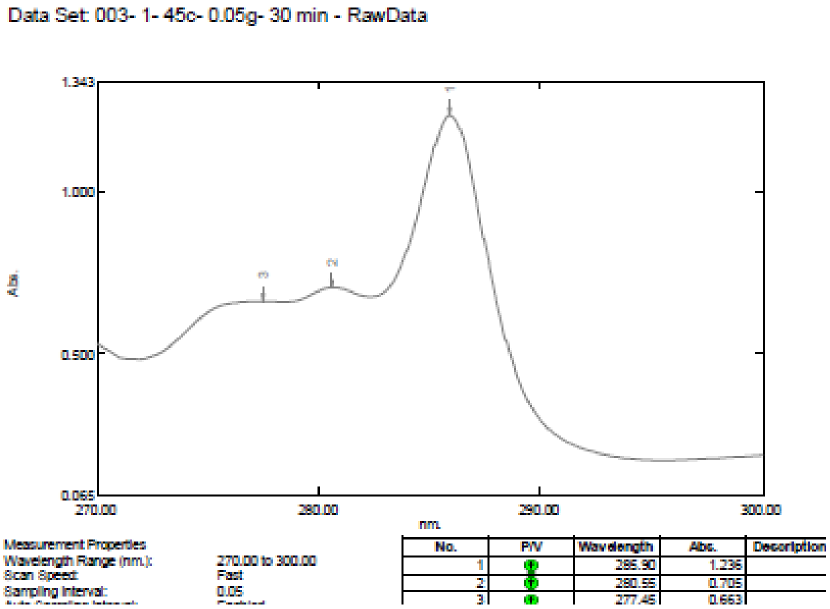
Figure S15: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (1), at 15 °C, weight of extractant 0.05 g, time = 30 min.


Data Set: 002- 1- 30c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Description
1	●	285.85	1.242	
2	●	280.60	0.711	
3	●	277.50	0.664	

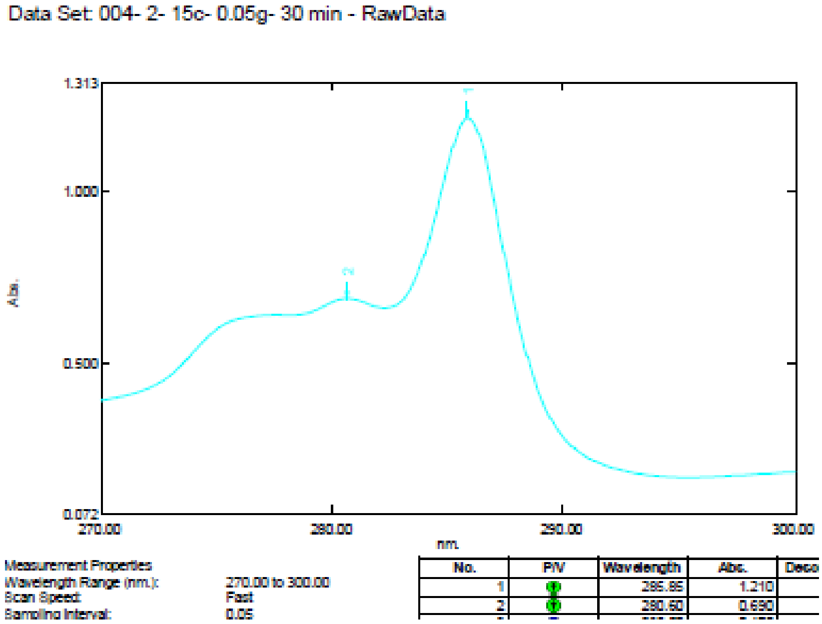
Figure S16: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (1), at 30 °C, weight of extractant 0.05 g, time = 30 min.


Data Set: 003- 1- 45c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Description
1	●	285.90	1.236	
2	●	280.55	0.705	
3	●	277.45	0.663	

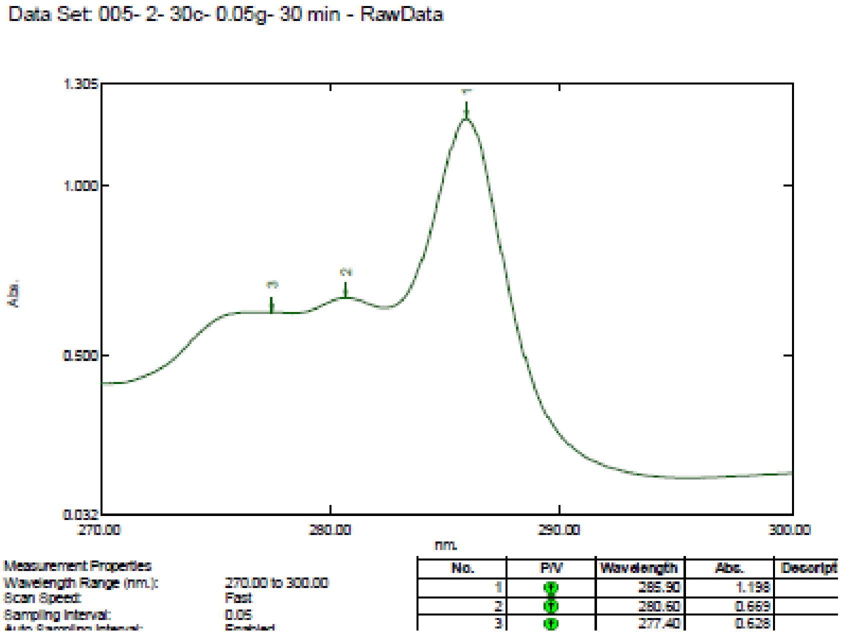
Figure S17: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (1), at 45 °C, weight of extractant 0.05 g, time = 30 min.


Data Set: 004- 2- 15c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Deco
1	●	285.85	1.210	
2	●	280.60	0.690	

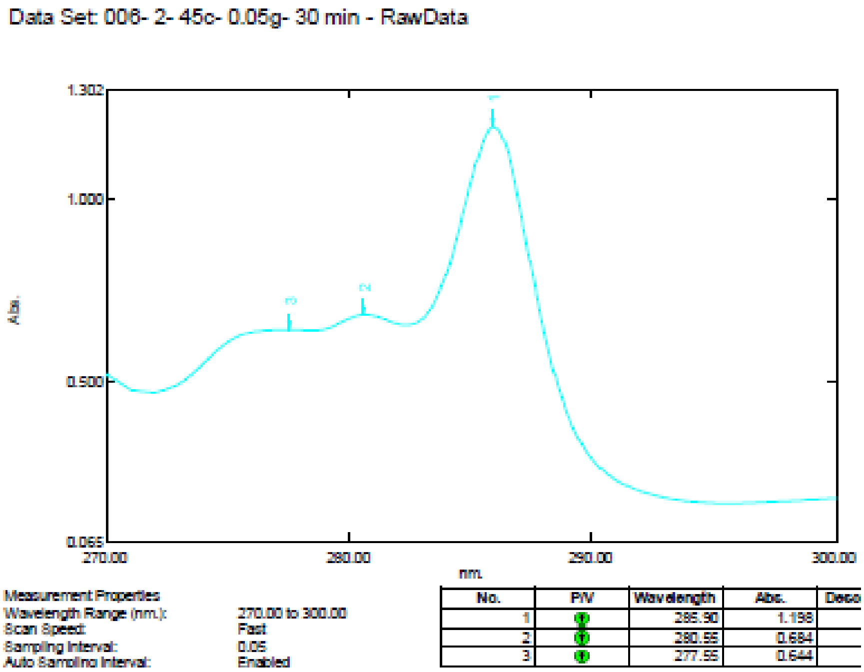
Figure S18: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (2), at 15 °C, weight of extractant 0.05 g, time = 30 min.


Data Set: 005- 2- 30c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Descript
1	●	285.90	1.198	
2	●	280.60	0.669	
3	●	277.40	0.628	

Figure S19: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (2), at 30 °C, weight of extractant 0.05 g, time = 30 min.

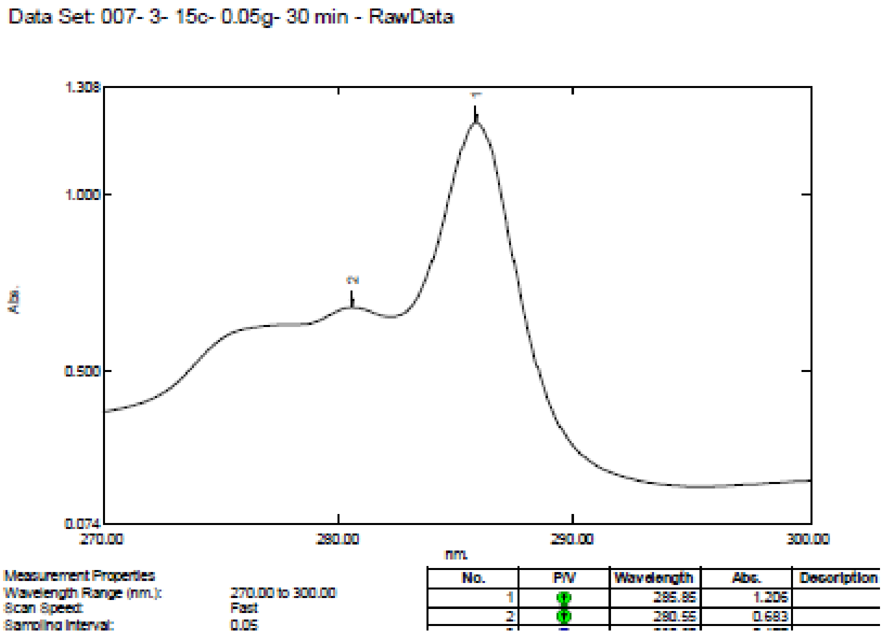


Data Set: 006- 2- 45c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Deco
1	●	285.90	1.198	
2	●	280.55	0.684	
3	●	277.55	0.644	

Figure S20: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (2), at 45 °C, weight of extractant 0.05 g, time = 30 min.

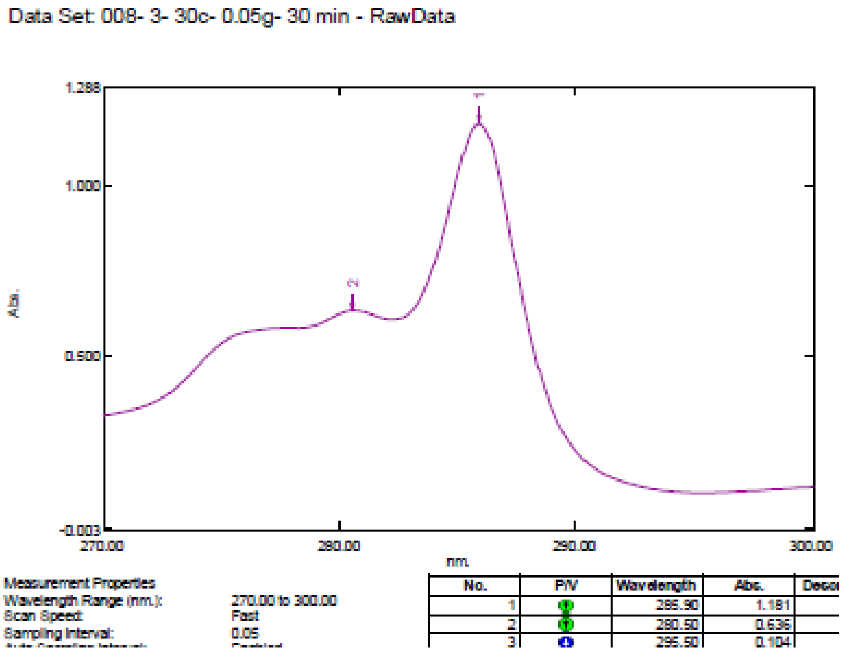


Data Set: 007- 3- 15c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Description
1	●	285.85	1.206	
2	●	280.55	0.683	

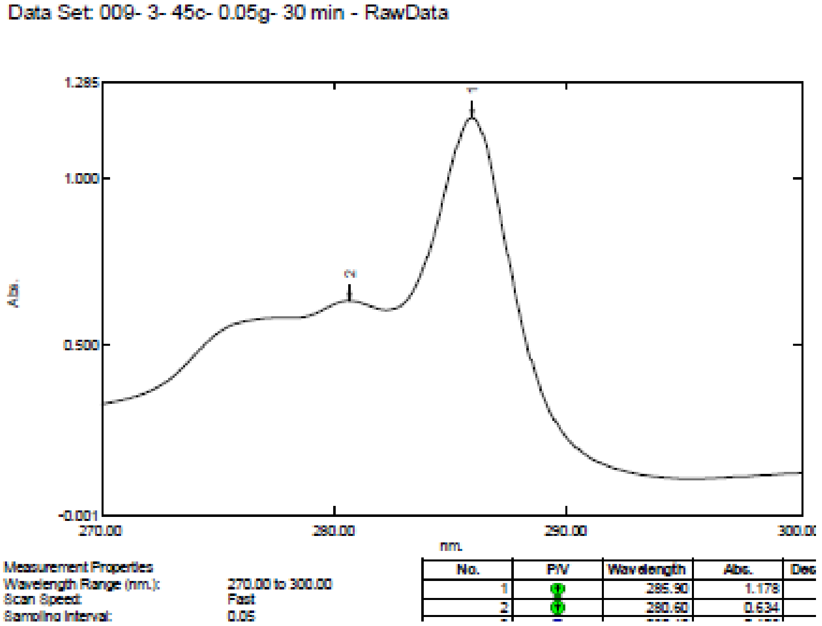
Figure S21: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (3), at 15 °C, weight of extractant 0.05 g, time = 30 min.


Data Set: 008- 3- 30c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Deco
1	🟢	285.90	1.181	
2	🟢	280.50	0.636	
3	🔵	295.50	0.104	

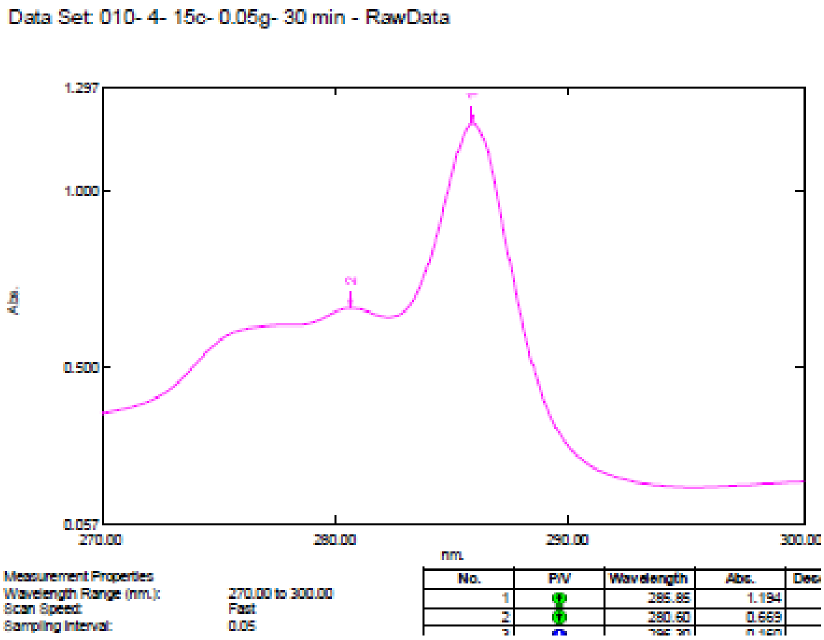
Figure S22: UV- Spectrum peak pick report of extractive desulfurization condition: Extractant (3), at 30 °C, weight of extractant 0.05 g, time = 30 min.


Data Set: 009- 3- 45c- 0.05g- 30 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Dec
1	🟢	285.90	1.178	
2	🟢	280.60	0.634	

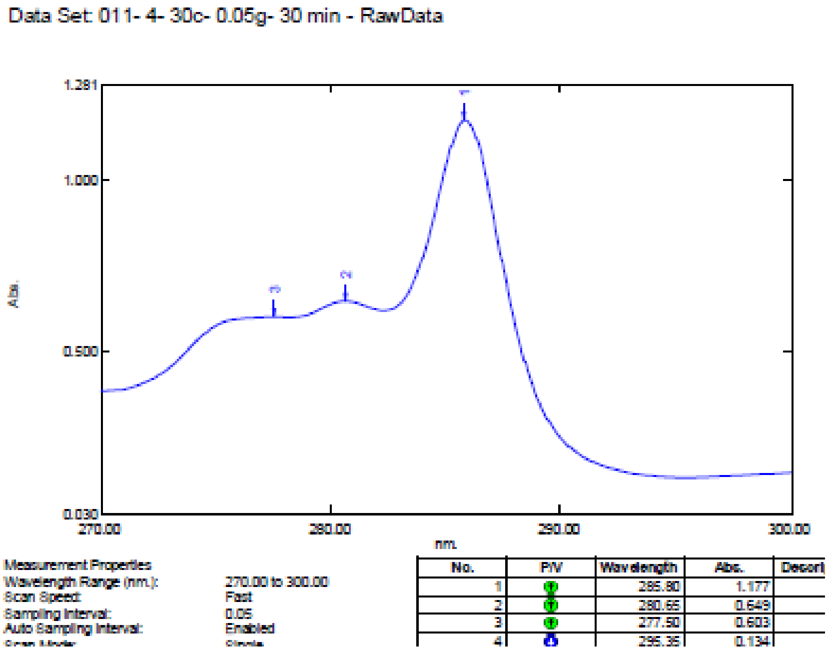
Figure S23: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (3), at 45 °C, weight of extractant 0.05 g, time = 30 min.



Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Des
1	●	285.85	1.194	
2	●	280.60	0.669	

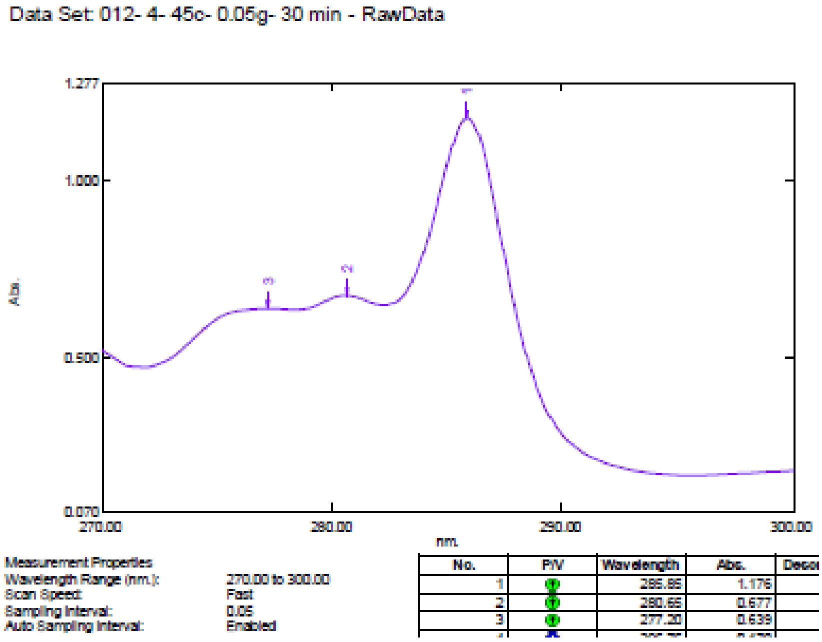
Figure S24: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (4), at 15 °C, weight of extractant 0.05 g, time = 30 min.



Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Descri
1	●	285.80	1.177	
2	●	280.65	0.649	
3	●	277.50	0.603	
4	○	295.35	0.134	

Figure S25: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (4), at 30 °C, weight of extractant 0.05 g, time = 30 min.

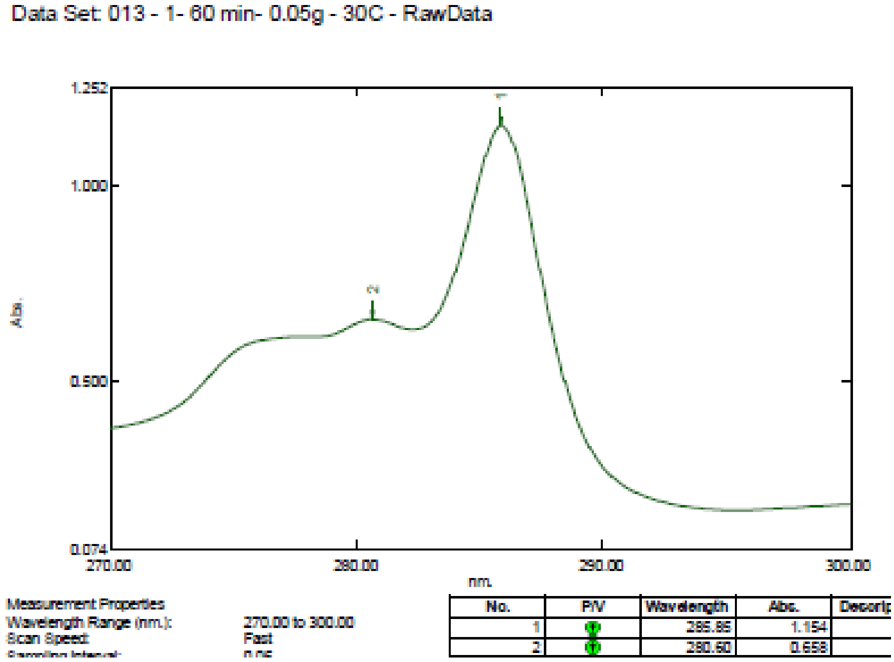


Data Set: 012- 4- 45c- 0.05g- 30 min - RawData

Measurement Properties	
Wavelength Range (nm.):	270.00 to 300.00
Scan Speed:	Fast
Sampling Interval:	0.05
Auto Sampling Interval:	Enabled

No.	P/V	Wavelength	Abs.	Desc
1	●	285.85	1.176	
2	●	280.65	0.677	
3	●	277.20	0.639	

Figure S26: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (4), at 45 °C, weight of extractant 0.05 g, time = 30 min.



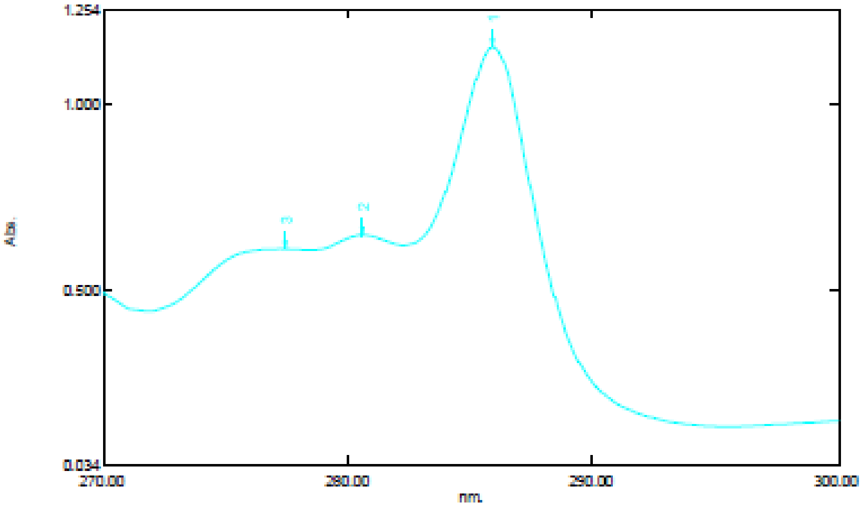
Data Set: 013 - 1- 60 min- 0.05g - 30C - RawData

Measurement Properties	
Wavelength Range (nm.):	270.00 to 300.00
Scan Speed:	Fast

No.	P/V	Wavelength	Abs.	Descrip
1	●	285.85	1.154	
2	●	280.60	0.658	

Figure S27: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (1), at 30 °C, weight of extractant 0.05 g, time = 60 min.

Data Set: 014 - 1- 90 min- 0.05g - 30C - RawData

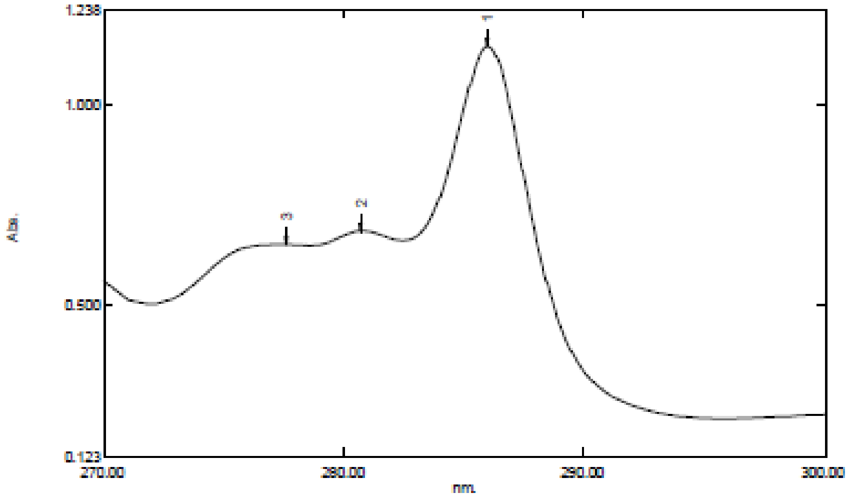


Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Desc
1	●	285.90	1.153	
2	●	280.55	0.649	

Figure S28: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (1), at 30 °C, weight of extractant 0.05 g, time = 90 min.

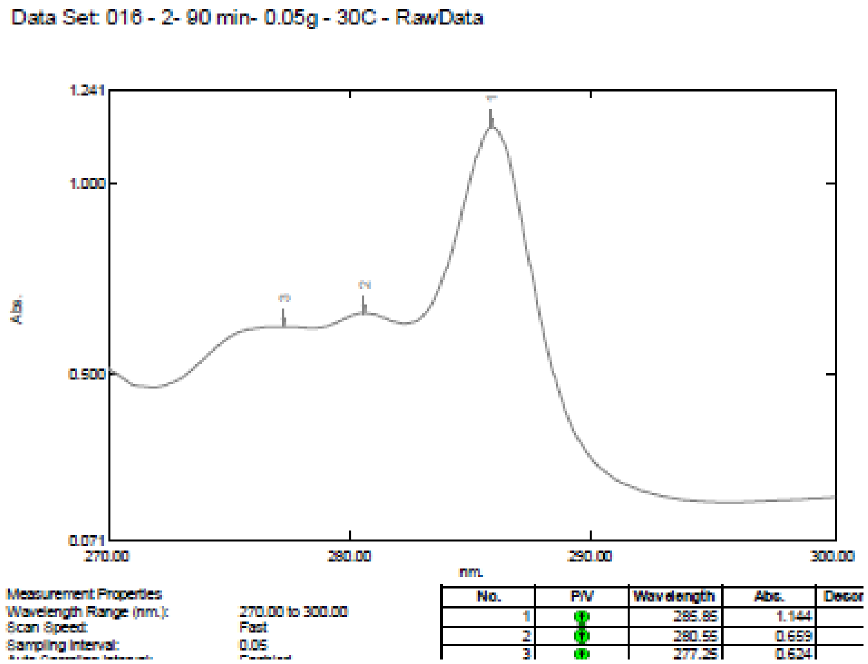
Data Set: 015 - 2- 60 min- 0.05g - 30C - RawData



Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Desc
1	●	285.95	1.145	
2	●	280.70	0.685	
3	●	277.60	0.651	
4	○	295.95	0.216	

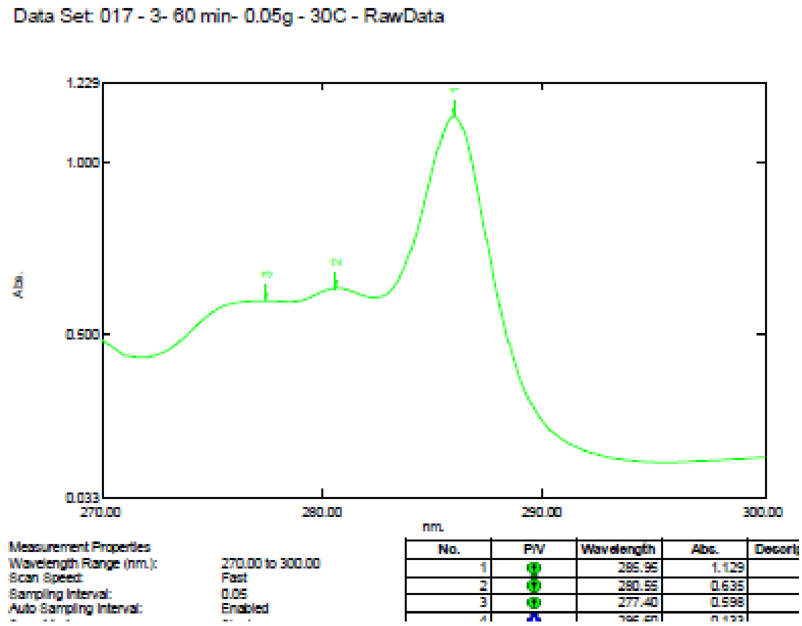
Figure S29: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (2), at 30 °C, weight of extractant 0.05 g, time = 60 min.



Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Decor
1	●	285.85	1.144	
2	●	280.55	0.659	
3	●	277.25	0.624	

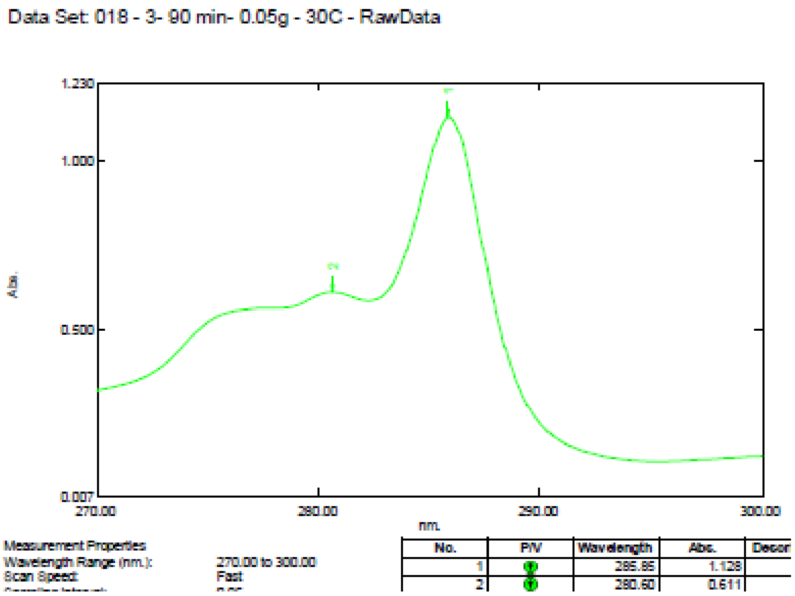
Figure S30: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (2), at 30 °C, weight of extractant 0.05 g, time = 90 min.



Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Decori
1	●	285.95	1.129	
2	●	280.55	0.635	
3	●	277.40	0.598	

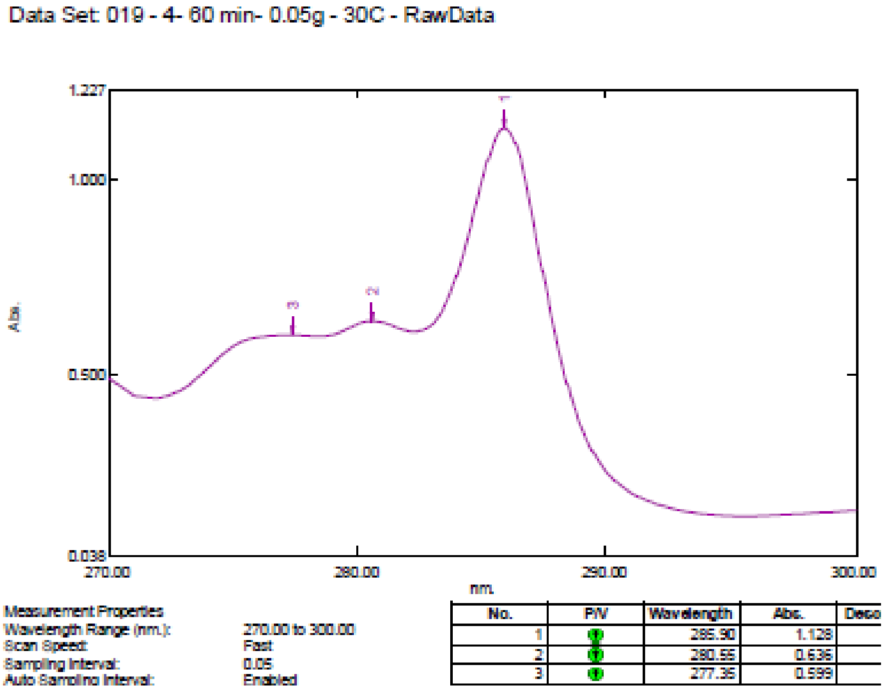
Figure S31: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (3), at 30 °C, weight of extractant 0.05 g, time = 60 min.



Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast

No.	P/V	Wavelength	Abs.	Decor
1	●	285.85	1.128	
2	●	280.60	0.611	

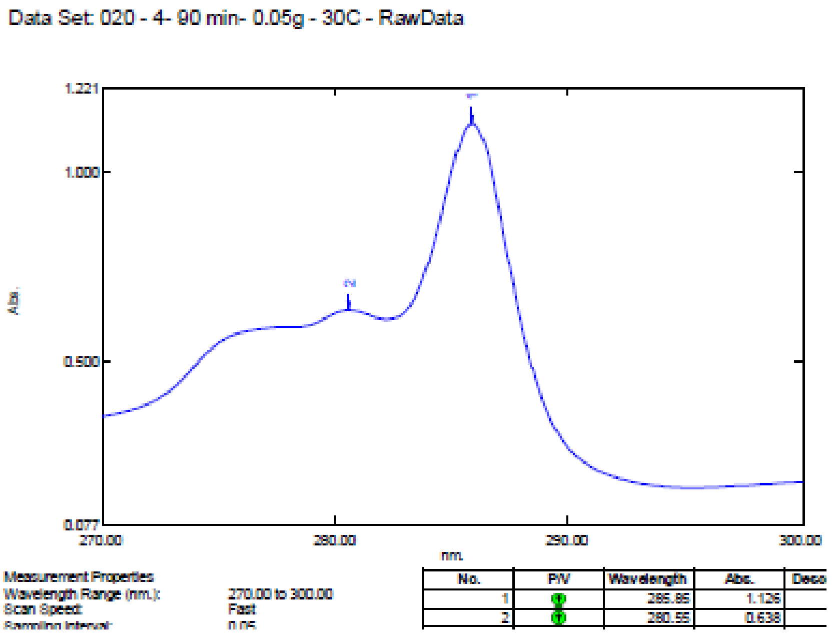
Figure S32: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (3), at 30 °C, weight of extractant 0.05 g, time = 90 min.



Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Deco
1	●	285.90	1.128	
2	●	280.55	0.636	
3	●	277.35	0.599	

Figure S33: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (4), at 30 °C, weight of extractant 0.05 g, time = 60 min.

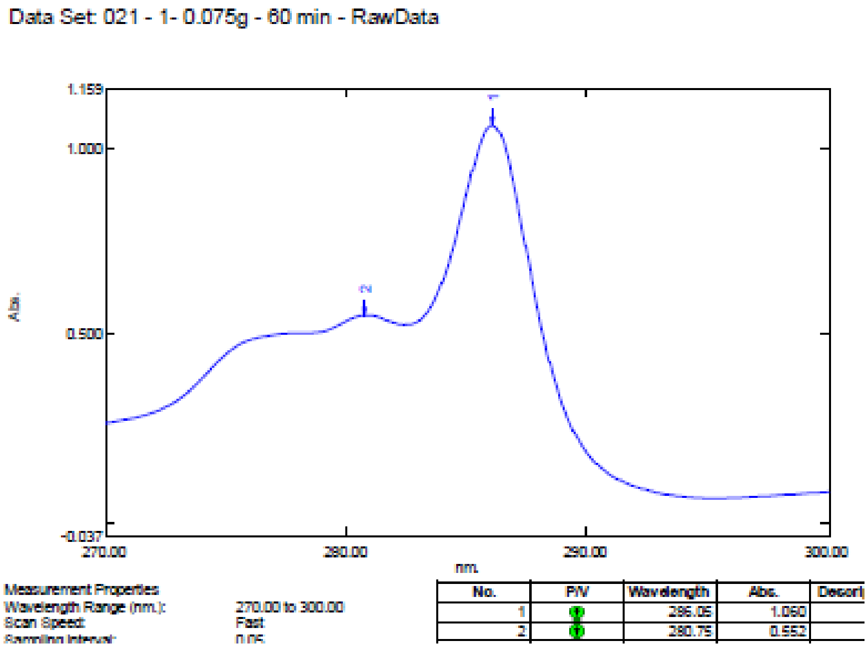


Data Set: 020 - 4- 90 min- 0.05g - 30C - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Deco
1	●	285.85	1.126	
2	●	280.55	0.638	

Figure S34: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (4), at 30 °C, weight of extractant 0.05 g, time = 90 min.

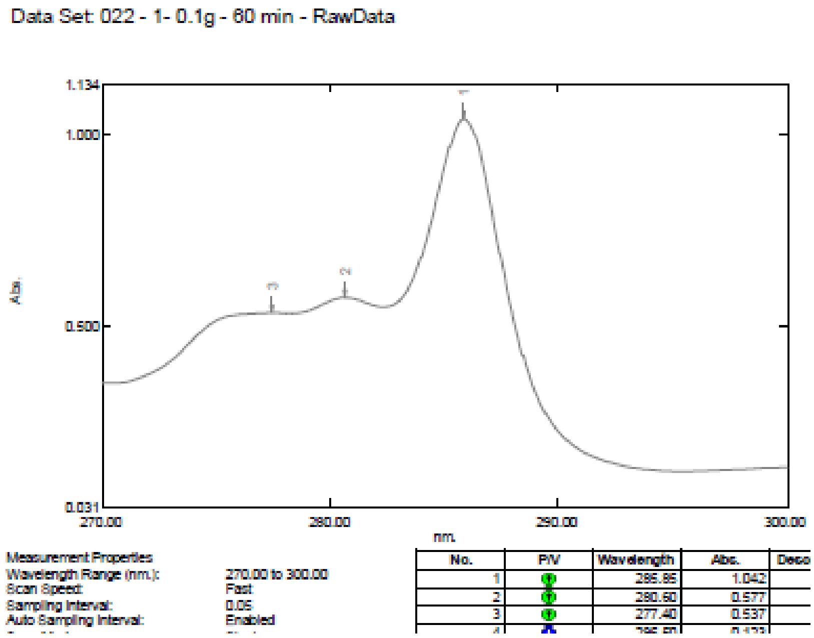


Data Set: 021 - 1- 0.075g - 60 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Decri
1	●	286.05	1.060	
2	●	280.75	0.552	

Figure S35: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (1), at 30 °C, weight of extractant 0.075 g, time = 60 min.

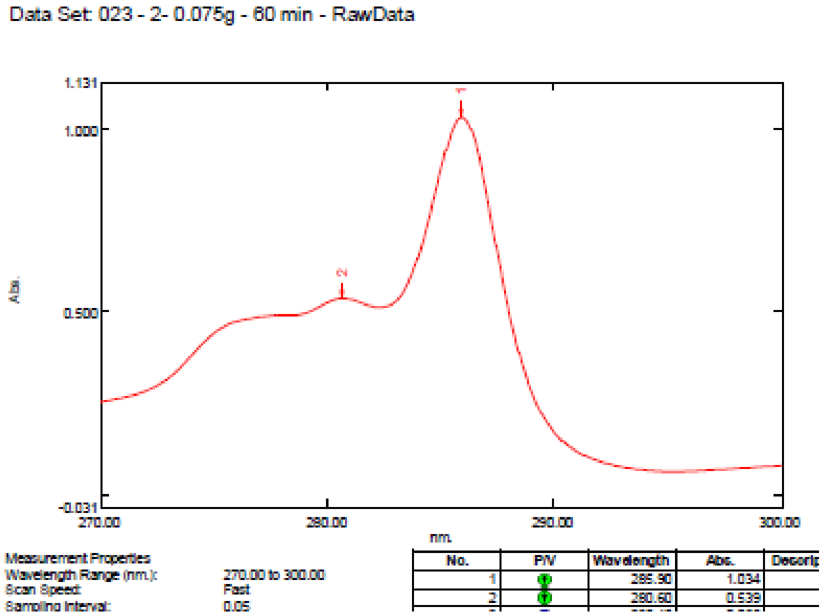


Data Set: 022 - 1- 0.1g - 60 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05
Auto Sampling Interval: Enabled

No.	P/V	Wavelength	Abs.	Deco
1	●	285.85	1.042	
2	●	280.60	0.577	
3	●	277.40	0.537	

Figure S36: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (1), at 30 °C, weight of extractant 0.1 g, time = 60 min.

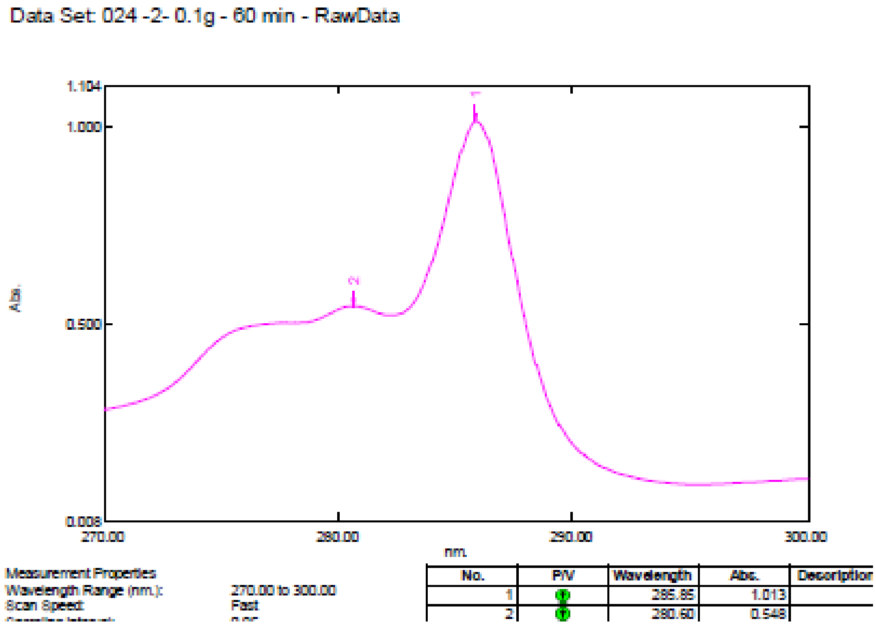


Data Set: 023 - 2- 0.075g - 60 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Descrip
1	●	285.90	1.034	
2	●	280.60	0.539	

Figure S37: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (2), at 30 °C, weight of extractant 0.075 g, time = 60 min.

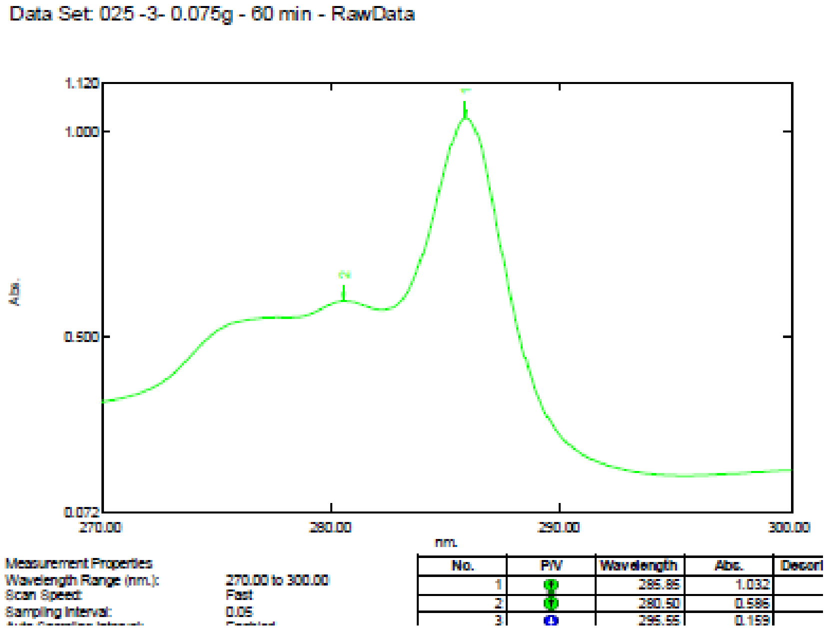


Data Set: 024 -2- 0.1g - 60 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast

No.	P/V	Wavelength	Abs.	Description
1	↑	285.85	1.013	
2	↑	280.60	0.548	

Figure S38: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (2), at 30 °C, weight of extractant 0.1 g, time = 60 min.

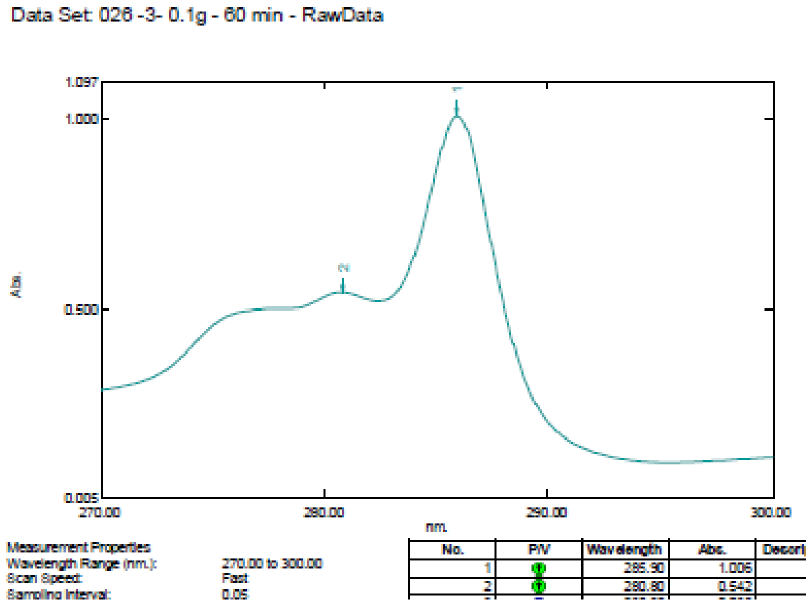


Data Set: 025 -3- 0.075g - 60 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Descri
1	↑	285.85	1.032	
2	↑	280.50	0.586	
3	↓	295.55	0.159	

Figure S39: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (3), at 30 °C, weight of extractant 0.075 g, time = 60 min.

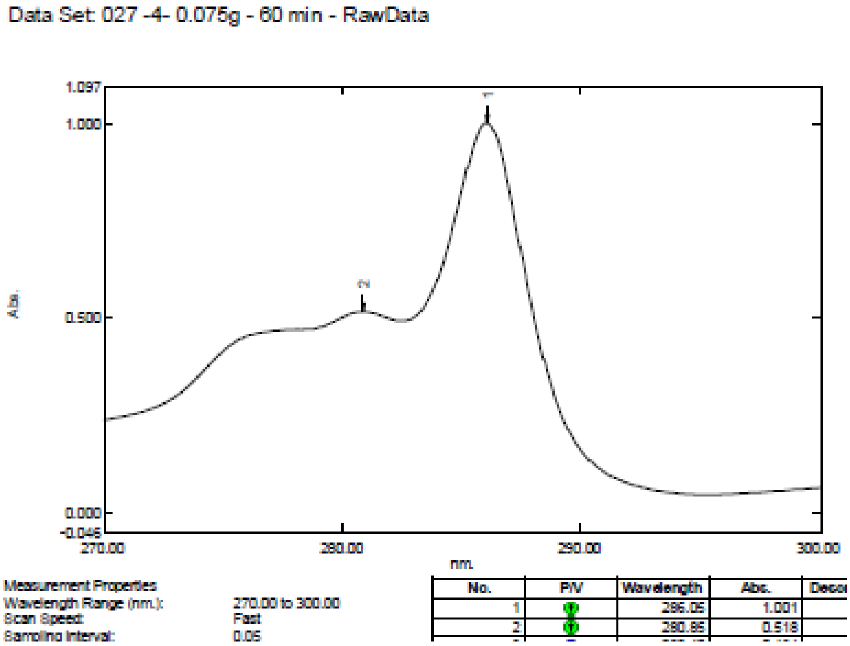


Data Set: 026 -3- 0.1g - 60 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Descri
1	●	285.90	1.006	
2	●	280.80	0.542	

Figure S40: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (3), at 30 °C, weight of extractant 0.1 g, time = 60 min.

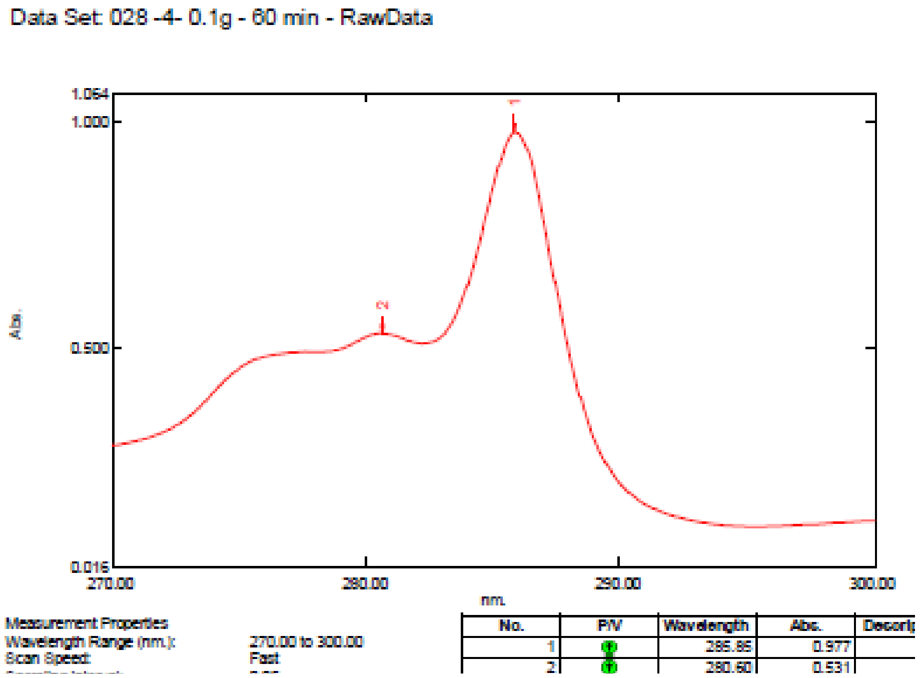


Data Set: 027 -4- 0.075g - 60 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast
Sampling Interval: 0.05

No.	P/V	Wavelength	Abs.	Deco
1	●	286.05	1.001	
2	●	280.85	0.518	

Figure S41: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (4), at 30 °C, weight of extractant 0.075 g, time = 60 min.



Data Set: 028 -4- 0.1g - 60 min - RawData

Measurement Properties
Wavelength Range (nm.): 270.00 to 300.00
Scan Speed: Fast

No.	P/V	Wavelength	Abs.	Descri
1	●	285.85	0.977	
2	●	280.60	0.531	

Figure S42: UV- Spectrum peak pick report of extractive desulfurization condition: extractant (4), at 30 °C, weight of extractant 0.1 g, time = 60 min.