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Synthesis and Characterization of Some Transition Metals Complex Salts of Pyridinium Iodide Ionic Liquids: Application On Extractive Desulfurization

Assim A. SABAH*

Abstract: The ionic liquid of pyridine base [emPy]I was prepared. Then, a series of complex salts were designed from it with some transition metal chlorides Fe(III), Co(II), Ni(II) and Cu(II) as Lewis acids. The compounds were characterized by spectroscopic and physical methods such as nuclear magnetic resonance "^{1}H-NMR", infrared spectroscopy "FT-IR", electronic spectrum "UV", mass spectroscopy "MS", elemental analysis "CHN", magnetic susceptibility, molar conductivity, and other methods. The thermal stability of these compounds was also verified within the temperature range of (25-1000 °C). [emPy]I and its complex salts were tested in the extractive desulfurization process EDS. The procedure treats them with the model fuel of sulfur content of 2000 ppm, prepared from dissolving dibenzothiophene DBT in n-hexane. The ratio of sulfur removal was estimated using the GC-FID technique. The optimal conditions for EDS process were studied, and the possibility of reusing the extractant more than once without regeneration.

Keywords: Pyridine-based-ionic liquids, extractive desulfurization, complex salts, Lewis acids.

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

INTRODUCTION

The combustion process in vehicle engines generates emissions of sulfur gases, affecting pollution control equipment in vehicles and increasing pollution. To increase the efficiency of pollution control equipment, it is preferable to significantly reduce the sulfur content in the fuel (1-3).

The processes of hydrodesulfurization (HDS) has a good efficiency. Still, they have limited use, especially for aromatic sulfur compounds. Further, in aromatic sulfur compounds, the HDS process can cause a high cost. It requires particular temperature and pressure conditions, affecting the rest of the fuel components such as olefinic compounds and reducing the octane number. Also, the harsh conditions may affect catalysts used in the process (4, 5). Therefore, the choice of an appropriate approach for desulfurization depends mainly on the percentage and types of sulfur compounds in the fuel. It is possible to use alternative methods like oxidation desulfurization (ODS), adsorption desulfurization (ADS), and others (6-8). One of the essential alternative methods used is extraction desulfurization EDS, especially for aromatic sulfur compounds such as thiophene, benzothiophene, and their derivatives. The EDS process is carried out under appropriate laboratory conditions of temperature and pressure and does not require special equipment; thus, it does not change the fuel's chemical structure and physical properties, and the octane number value is not reduced (3, 9-12).

The most important solvents used in the EDS process are acetonitrile and pyrrolidine, DMF, and DMSO. It is noticed that the selectivity to extract the sulfur compounds is not accessible due to the proximity of polarity with some other aromatic compounds. The efficiency of the extraction process does not exceed 50% at most, which means that large quantities of solvent are used. Therefore, it is better to use other materials that help in increasing the selectivity of sulfur compounds, and among these materials are ionic liquids (ILs) (11, 13, 14). Ionic liquids are among the promising materials and solvents for having distinct properties such as viscosity, thermal stability, and solubility. It is possible to control and change the properties of ionic fluids by changing the anion or the cation. The solubility of (ILs) in the fuel is an essential factor in its use in the EDS process. On the other hand, the solubility of ionic liquids with a nitrogen base in fuel increases nitrogen gas emissions (NO_x), leading to increasing pollution and increasing the cost of reuse of ionic liquids. For these reasons, ionic liquids that do not dissolve in the fuel must be chosen for EDS of sulfur compounds (6, 15-17).

Some pyridine-based ionic liquids have been tested in the EDS process after tested for their non-solubility in the fuel (diesel) by analyzing the treated fuel using (HPLC). The results showed that there was no package belonging to the ionic liquids. It was found that the efficiency of extraction increases with the increase of the aromatic character of the sulfur compounds (thiophene (T) < benzothiophene (BT) < dibenzothiophene DBT) under the same conditions (18, 19). In general, ionic liquids that do not contain a transition metal have low efficiency in the EDS process. The results confirmed that ionic liquids containing metals are more efficient than the ionic liquid alone and more efficient than the metal halide under the same conditions EDS. Many ionic liquids containing transition metal chlorides are used, such as non-hydrous $FeCl_3$ and CuCl with 3-butyl-1-methylimidazolium chloride [BMIM]Cl have been used in EDS. The amount of sulfur removed increases with metallic elements due to the increased acidity (20-22).

In this work, some pyridine-based ionic liquids were tested with some transition metal halides in the EDS process using a model of diesel oil containing DBT as an aromatic sulfur compound. The optimal conditions for extractive desulfurization were also determined.

EXPERIMENTAL PART

All chemical compounds used are of high purity and from trustworthy international companies without treatment. The chemical compounds were prepared and characterized according to the approved methods (6, 23-26).

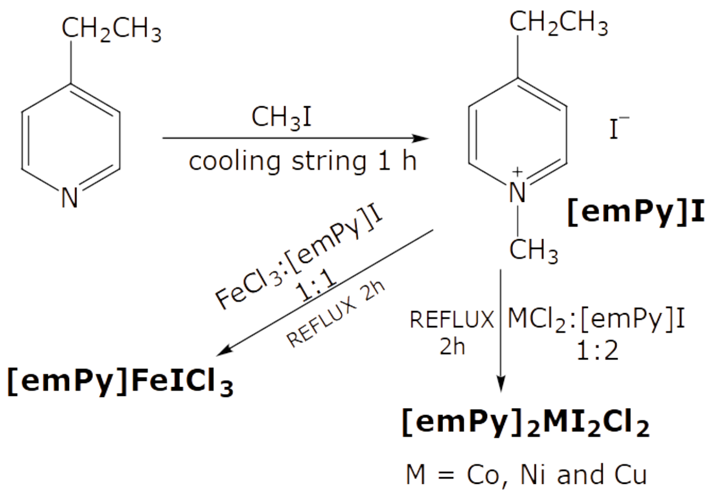
Preparation of the Compounds

Preparation of 4-ethyl-1-methylpyridinium iodide [emPy]I:

The ionic liquid [emPy]I was prepared by reacting 4-ethyl pyridine with methyl iodide in a molar ratio (1:1) by adding methyl iodide slowly and gradually with continuous stirring for one hour with cooling; the reaction is exothermic. An additional excess amount of methyl iodide is added to obtain a higher yield of the product. After completion, the brown-yellow precipitate was formed, unreacted methyl iodide was removed by washing the product formed with n-hexane for more than one time.

Preparation of complex salts of 4-ethylpyridinium iodide $[emPy]FeICl_3$, $[emPy]_2MI_2Cl_2$ (M= Co, Ni and Cu):

Some transition metal complex salts of the [emPy]I were prepared by reacting molar ratios (2:1) of the [emPy]I: metal chloride ($CoCl_2$, $NiCl_2$, and $CuCl_2$) and with a ratio (1:1) of the [emPy]I: iron(III) chloride ($FeCl_3$). The reaction is done by dissolving the ionic liquid with an appropriate amount of ethanol (10 mL) and adding the metal chloride dissolved in water (10 mL), and adding it gradually, refluxing the mixture for two hours with continuous stirring. After the end of the reaction, the solution is concentrated in half by evaporation, left for 24 hours, the complex salt precipitates, and then the solution is filtered and the precipitate washed with diethyl ether. Scheme 1 shows the preparation of compounds.



Scheme 1: Preparation of the compounds.

Characterization of the prepared compounds

All the prepared compounds were well characterized using various physical and spectroscopic methods. ^1H-NMR was carried out by using DMSO-d_6 as a solvent (Bruker Avance DPX 400 MHz). Elemental analysis was measured by Flash EA 1112 Series Thermo electron corporation. The GC-Mass is obtained using a Trio-1000 mass spectrometer; an infrared spectrum is carried out by JASCO Canvas FT/IR 4200 (KBr and CsI disks). At the same time, atomic absorption spectrophotometry was measured by SensAA GCB scientific equipment system (Avanta 2.02 software). A Shimadzu 1800 spectrometer UV-Vis was used for collecting electronic spectra, and magnetic susceptibility was tested by using Sherwood MK1, an electrothermal melting point 9100 was used to determine the melting points. The thermal study was tested using Mettler Toledo TGA\DSC with STARe evaluation software virgin (15.01) at 25-1000 ˚C with a ramping heat rate of 10 ˚C/min under air. Conductivity was recorded via the HANNA EC214 conductivity meter. Gas chromatography was carried out by using (STRUMENTAZIONE 4200 CARLO ERBA) FID-detector, the programmed temperature: Intake injector temperature: 280 ˚C, detector temperature: 275 ˚C, oven temperature: 125 ˚C for 3 min then ramping till 185 ˚C for 10 min. Gases' flow rate details:hydrogen gas: 1 kg / cm^2, make up gas (air): 1 kg/cm^2, air: 1.5 kg / cm^2, helium gas: 2 kg/cm^2. Column properties: Name: SE-30, length: 28 m, diameter: 0.50 mm, film thickness: 1.2 µm. Table 1 shows the quantitative analysis and physical data of the prepared compounds.

Extraction desulfurization analysis

The model fuel oil contained 2000 ppm dibenzothiophene DBT, and it was prepared by dissolving DBT in n-hexane in weight percentage. All prepared compounds were used for EDS using 100 mL quick-fit conical flask 10 mL of model fuel mixing with salts at 25 ºC with a specific time, SK-L180. Pro linear array laboratory shaker used for shaking (350 rpm) to optimize the best conditions and make systematic testing with a different time and concentration. The concentration of DBT before and after the treatment was measured by GC-FID equipment; hexadecane C_{16} was used as the reference.

Table 1: Quantitative analysis and physical data of the prepared compounds.

No.	Compounds	CHN calcd./(found)			M%	Cl%	Color	m.p˚C
		C%	H%	N%				
1	[emPy]I $C_8H_{12}IN$	38.57 (38.23)	4.86 (4.62)	5.62 (5.44)	---	---	Brown yellow	45
2	[emPy]FeICl$_3$ $C_8H_{12}Cl_3INFe$	23.36 (22.43)	2.94 (2.61)	3.41 (3.24)	13.58 (14.32)	25.86 (26.43)	Black red	80
3	[emPy]$_2$CoICl$_3$ $C_{16}H_{24}Cl_3IN_2Co$	35.82 (35.03)	4.51 (4.22)	5.22 (4.85)	10.98 (11.32)	19.82 (20.42)	Dark olive	140
4	[emPy]$_2$NiICl$_3$ $C_{16}H_{24}Cl_3IN_2Ni$	35.83 (34.67)	4.51 (4.42)	5.22 (5.02)	10.94 (11.14)	19.83 (20.78)	Olive	90
5	[emPy]$_2$CuICl$_3$ $C_{16}H_{24}Cl_3IN_2Cu$	35.51 (35.03)	4.47 (4.32)	5.18 (4.84)	11.74 (12.22)	19.65 (20.76)	Brown	160

RESULTS AND DISCUSSION

Characterization of ionic liquid and its complex salts

The structure of IL as [emPy]I was confirmed with spectroscopy (^{1}H-NMR, FTIR, and UV-Vis), elemental analysis, and high resolution mass spectrometry. ^{1}H-NMR (DMSO-d$_6$, 400 MHz): δ1.255 (3H-CH$_3$, t, *J* = 7.56 Hz), δ2.904 (2H-CH$_2$, q, *J* = 7.56 Hz), δ4.288 (3H-CH$_3$, s), δ8.006 (2H-Ar, d, *J* = 6.40 Hz), δ8.860 (2H-Ar, d, *J* = 6.52 Hz). MS *m/z* (relative intensity): 122 (0.02%), 119 (1.30%), 118 (14.50%), 117 (3.37%), 92 (2.03%), 91 (51.80%), 90 (2.12%), 75 (3.62%), 74 (100.00%), 73 (5.75%), 72 (0.39%). Figures 1 and 2 show the ^{1}H-NMR of [emPy]I and the cation mass spectra, respectively.

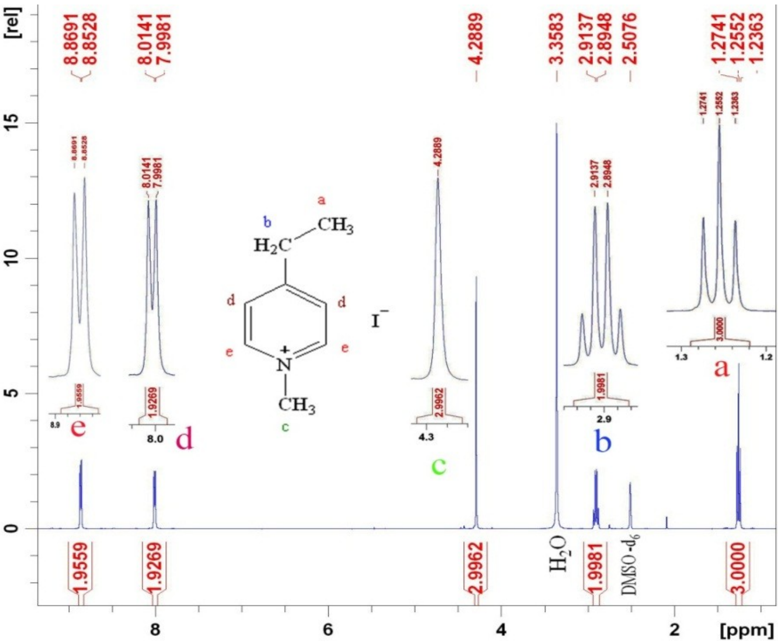


Figure 1: ^{1}H-NMR analysis of [emPy]I.

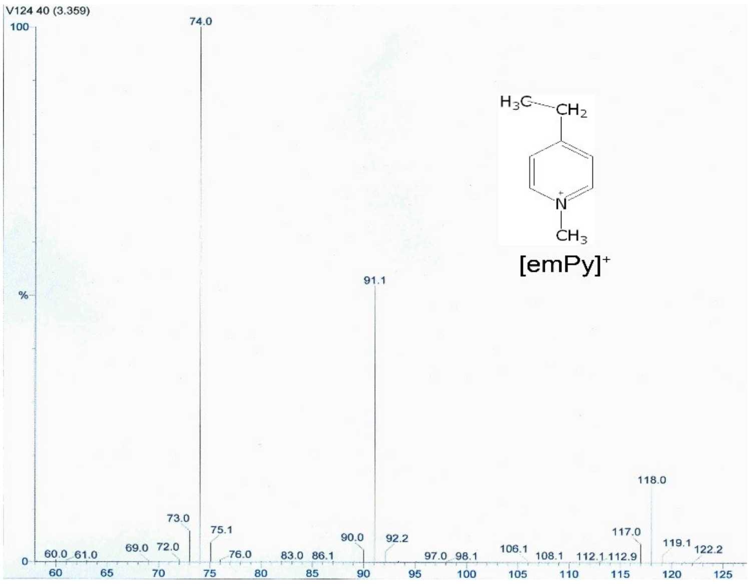


Figure 2: Positive ion mass spectrum of [emPy]$^+$.

The infrared measurements were made using the KBr disk of the region (600-4000 cm^{-1}), while the CsI disk within the (200-500 cm^{-1}) region was used. The stretching frequencies of the pyridine aromatic ring of [emPy]I and it is complex salts were investigated, and υ(C=C) group appeared in the region of (1608-1646 cm^{-1}). While υ(C=N) and υ(C-N) bands appeared in the region (1430-1473 cm^{-1}) and (1110-1245 cm^{-1}) respectively, while the υ(C-H) bands appeared in the (3019-3370 cm^{-1}) region (27, 28). The new active group υ(N$^+$-CH$_3$) was noticed at (2356-2854 cm^{-1}), while the metal-halide bond υ(M-X) (X= Cl, I) appeared at (239-331 cm^{-1}) all these values matching with literature (27-29). Table 2 shows the stretching frequencies of the main active groups in the prepared compounds.

Table 2: Stretching frequencies (cm^{-1}) of FT/IR spectral data of prepared compounds.

No.	Compounds	υ(C=C)	υ(C=N)	υ(C-N)	υ(C-H)	υ(N^+-CH_3)	υ(M-X)
1	[emPy]I	1643s	1473m	1187m	3019s	---	---
2	[emPy]$FeICl_3$	1608m	1454m	1214s	3370s	2356w	239s,331s
3	$[emPy]_2CoICl_3$	1643s	1446w	1118m	3320s	2854w	254m,316s
4	$[emPy]_2NiICl_3$	1646s	1454w	1110m	3336s	2368w	242s,327s
5	$[emPy]_2CuICl_3$	1612m	1430m	1245w	3359s	2846w	246s,331s

DMF was used in the electronic spectra as a solvent. Also, the magnetic susceptibility was measured at a temperature of 25 °C to investigate the geometrical shape of complex salts. The results proved the tetrahedral shape of complex salts and using conductivity to verify the ionic state of the prepared salts at the same temperature by using DMF as a solvent with concentration 10^{-3} M. The percentage of metal in the complex salt was measured by the atomic absorption technique, which showed a good match with theoretical values, as well as similar the other works (30-35). Table 3 clarifies the spectral, magnetic susceptibility, and conductivity data of prepared compounds.

Table 3: Spectral, magnetic susceptibility, and conductivity data

No.	Compounds	Bands cm^{-1}	Suggested transitions	μ_{eff}(BM)	Conductivity ($ohm^{-1}.cm^2.mol^{-1}$)
1	[emPy]I	28248	$n \rightarrow \pi^*$	---	74
		34602	$\pi \rightarrow \pi^*$		
2	[emPy]$FeICl_3$	11961 12562	$^5E \rightarrow {}^5T_2$	5.72	79
3	$[emPy]_2CoICl_3$	14836	$^4A_2$ (F)→ $^4T_2$ (F)	4.20	145
		16477	$^4A_2$ (F)→ $^4T_1$ (F)		
		17761	$^4A_2$ (F)→ $^4T_1$ (P)		
4	$[emPy]_2NiICl_3$	12610	$^3T_1$ (F)→ $^3T_2$ (F)	3.61	140
		14164	$^3T_1$ (F)→$^3A_2$ (F)		
		14310	$^3T_1$ (F)→$^3T_1$ (P)		
5	$[emPy]_2CuICl_3$	14310	$^2T_2 \rightarrow {}^2E$	2.42	144

The thermal stability of the prepared compounds was tested. As shown in Figure 3, the ionic liquid shows good stability up to 250 °C, as it decomposes in two primary stages (the first loses 70% by weight, and the second loses 20% by weight). The isothermal stability was studied for [emPy]I at 100 °C up to 120 min; it is proved that the compounds stable at this temperature as well as same in previous studies literature (36-38). The thermal stability of the complex salts was also measured under the same thermal conditions. All the prepared compounds showed good stability below 100 °C, within the operational conditions for the desulfurization extractive process EDS. The Ni(II) complex salt loses the moisture water (10% mass loss) below 100 °C. Figure 4 shows the thermogravimetric analysis curve of all prepared compounds.

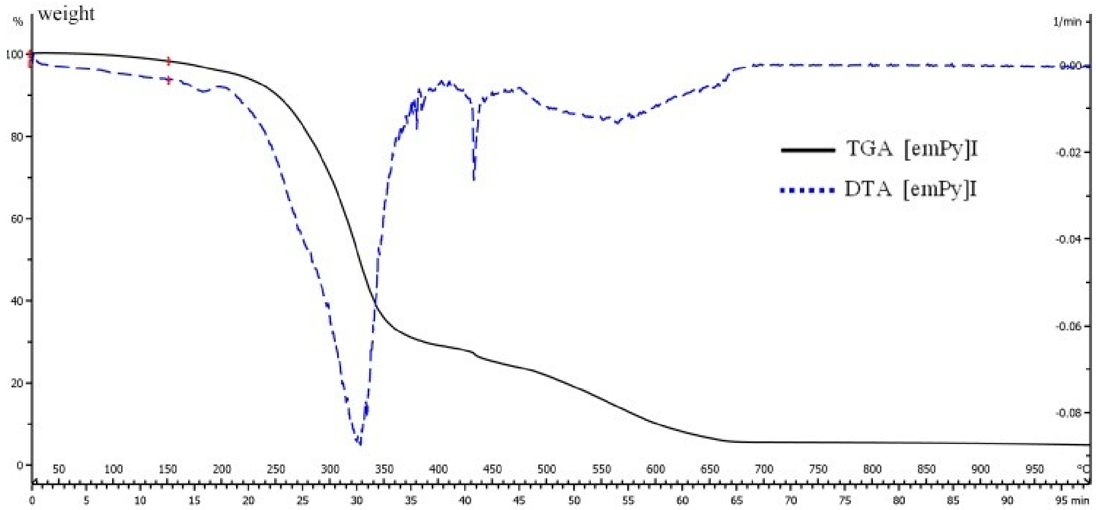


Figure 3: TGA and DTA analyses of [emPy]I.

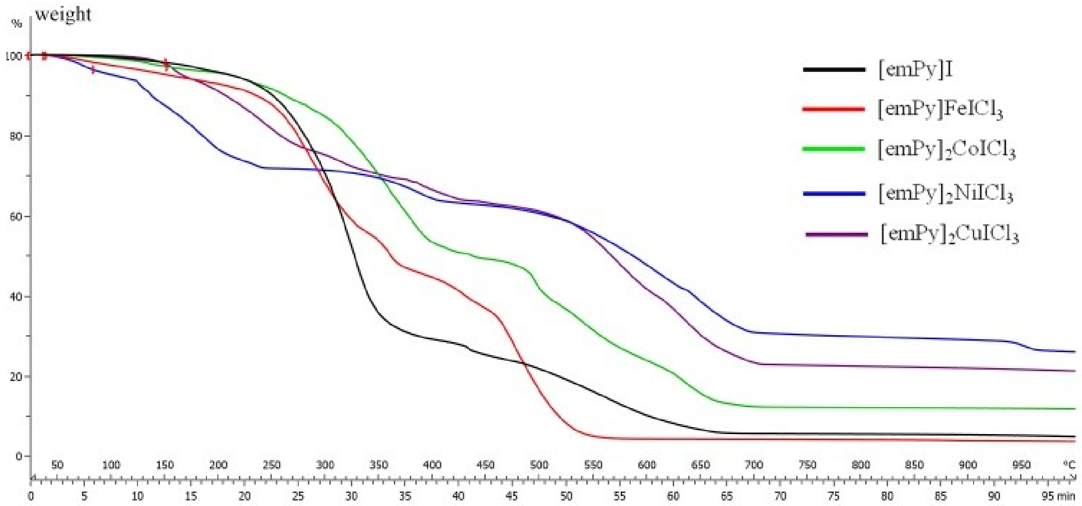


Figure 4: TGA analyses of prepared compounds.

EDS optimization conditions analysis

For optimizing the best conditions in EDS process, the model oil was treated with several reaction conditions (concentration, time, and temperature) through systematic experiments. All tests carried at 25 °C, to choose the best compound, 10 mL of 2000 ppm DBT was tested with 0.05 g of extractant dissolved in 5 mL of DMSO with 30 min of shaking. Figure 5 clarifies the result of EDS with mentioned conditions.

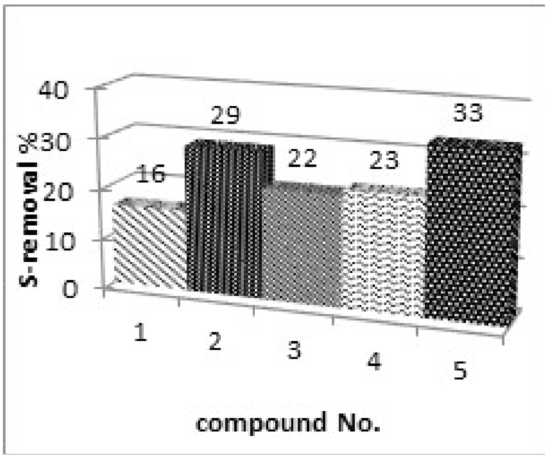


Figure 5: S-removal in condition: 2000 ppm of DBT, 30 min and 0.05 g of extractant at 25 ˚C.

Ionic liquids of pyridine have one of the essential extracting factors used in desulfurization processes (39, 40), and from the results in Figure 5, the [emPy]I (IL) gave 16% of sulfur removal, as the proposed removal mechanism depends on the interference of aromatic electrons in the sulfur compounds with their counterparts in a pyridine ring (π-π interactions), which depends on electron density (6, 41). The extractant factor efficiency depends on the type of the cation and type of the anion, as all the compounds under study have the same cation. Therefore, the difference in the efficiency of desulfurization is attributed to the anion. From a comparison of the results, it becomes clear that the complex salts have a higher efficiency than the ionic liquid alone. Lewis acids (metal chlorides) act as extraction agents in addition to the ionic liquid. The proposed mechanism is the interference of sulfur and aromatic electrons in sulfur compounds with the metal (M= Fe(II), Ni(II), Co(II) and Cu(II)) and the halide bound with the metal (6, 26, 42). In general, Lewis acids show less ability in desulfurization processes than complex salts, which confirms the important role of ionic liquids, while the previous work have better efficiency as they use a large amounts of extractants (3, 15, 43). The copper complex salt $[emPy]_2CuICl_3$ has been chosen for study the best condition as shown in the Figures 6-8.

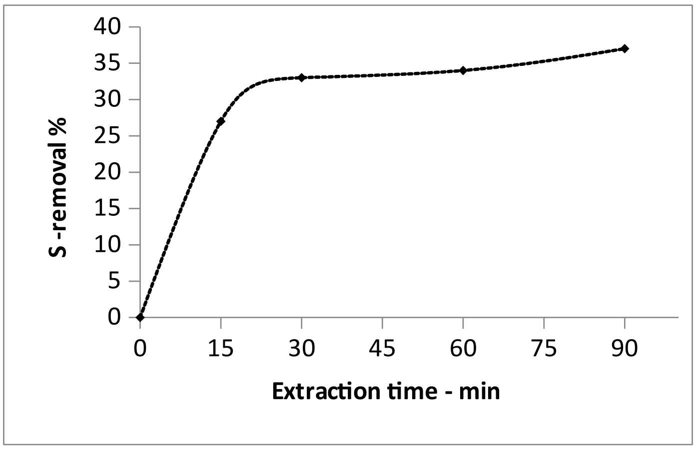


Figure 6: Effect the time of extraction, treatment conditions: 2000 ppm DBT and 0.05 g of $[emPy]_2CuICl_3$ at 25 °C.

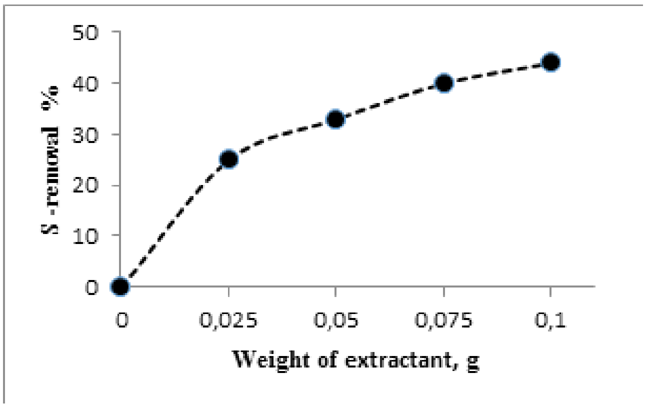


Figure 7: Effect the concentration of extractant $[emPy]_2CuICl_3$, treatment conditions: 2000 ppm DBT and 30 min at 25 ˚C.

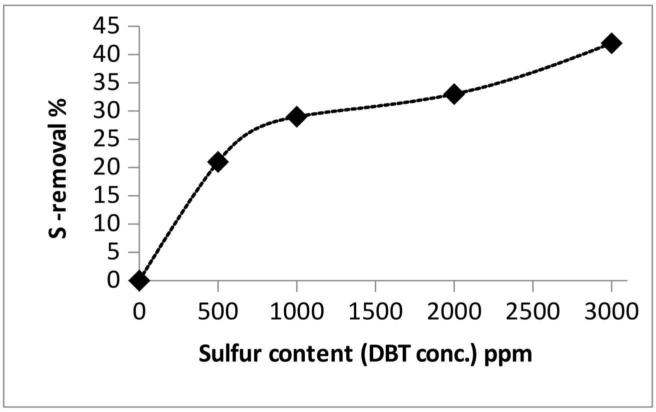


Figure 8: Effect the concentration of DBT, treatment conditions: 30 min, 0.05 g of $[emPy]_2CuICl_3$ at 25 °C.

Through the above diagrams (Figures 6-8), we notice that increasing the time has a positive effect on the efficiency of the extraction process, but it is limited. The increase in the concentration of complex salt reflects positively on the efficiency of the sulfur removal process, which matches the literature (6, 41), but with very few differences, and is not economically feasible. Furthermore, increasing the sulfur content leads to an increase in the efficiency of the extraction process in a limited way. The use of high concentrations of sulfur content may negatively affect the reusability of complex salt or ionic liquid more than once without regeneration. It is possible to suggest that the optimal conditions for the extraction process are (time = 30 minutes, complex salt concentration, 0.05 g, and the sulfur content DBT is 1000 ppm).

Extractants reusability tests

The ionic liquid [emPy]I and its complex salts were tested for the reusability experiment without regeneration, where the prepared compounds were used three times, and the reuse results showed less efficiency than the use of extractant for the first time as fresh extractant, as shown in Table 4.

Table 4: EDS efficiency after three times of usage of extractant (reaction conditions: time = 30 min, extractant weight = 0.05 g and DBT concentration = 2000 ppm) at 25 °C.

No.	Compounds	Sulfur removal %		
		1st	2nd	3rd
1	[emPy]I	16%	13%	10%
2	$[emPy]FeICl_3$	29%	20%	16%
3	$[emPy]_2CoICl_3$	22%	10%	10%
4	$[emPy]_2NiICl_3$	23%	13%	10%
5	$[emPy]_2CuICl_3$	33%	22%	13%

CONCLUSION

The new ionic liquids prepared from pyridine-base compensators showed promising efficacy in the EDS process, especially those containing Lewis acids (transition metal chlorides). The results showed that the efficiency of the extraction process increased when the concentration of the extracted material increased, as well as when the extraction time increased, furthermore, the increase in the sulfur concentration in the oil model. The study also showed the possibility of reusing the ionic liquid and its complex salts without regeneration but with less EDS efficiency. The prepared compounds also showed good thermal stability under the experimental conditions used in the extraction sulfur removal processes.

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