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## Sodium phenyldithiocarbamate and sodium cyclohexyldithiocarbamate ligands' extractive abilities of heavy metals from aqueous media at metal-ligand ratio of 1:1

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### Abstract

Dithiocarbamate ligands are known to readily form chelates with all transition metal ions through its two donor sulphur atoms. In this research, two derivatives of dithiocarbamate ligands (sodium phenyldithiocarbamate and sodium cyclohexyldithiocarbamate) were used to extract metal (Fe, Cu, Zn and Pb) ions with initial concentration of the metals kept at 5.0 ppm. The analyses were performed in five different pH to observe its effect on heavy metal extraction. Metals and ligands were dissolved in the same solvent (ethanol for Fe, Cu and Zn; and dimethylsulphoxide for Pb) and ligand-metal ratio of 1:1 used in the experiment. The ligands showed metal extractive abilities. It was observed that highest percentage metal extractive abilities were at the same pH value (11.0) for all the metals except for Cu which was at pH 3.0 for sodium phenyldithiocarbamate ligand. Even though both ligands were effective in metal extraction, sodium phenyldithiocarbamate ligand showed better percentage extractive abilities. Statistical analysis carried out on the data generated showed significant difference in the extraction of copper and iron by both ligands.

**Keywords:** Dithiocarbamate, ligands, metal extractive ability, aqueous media

### Introduction

Interaction of metal complexes with various ligating Lewis bases (adduct formation) brings about an increase in coordination number of metal ions in a complex, without change in the oxidation state <sup>[1]</sup>. Most a times, physical properties of the resulting interaction are different from their parent metal complexes, and this influences their biological activities <sup>[1]</sup>. The tendencies of metal complexes to form adducts are significantly different and are closely related to the structure of the coordinated ligand, the ability of the Lewis base to accept  $\pi$ -electrons and on the size of the central metal ion <sup>[2]</sup>. The movement of the of electron density to the sulphur atoms of dithiocarbamate bases, due to mesomeric effect of  $-NR_2$  group, impacts on the adduct formation of dithiocarbamate complexes <sup>[3]</sup>. Comparing to other dithiolates, the  $-NR_2$  group gives larger electrons towards the sulphur atoms resulting in the donation of electrons from the sulphur atoms to the non-bonding molecular orbital of the metal <sup>[4]</sup>. This reduces its availability for axial interaction with Lewis bases <sup>[5]</sup>. The properties of the R-group in the  $-NR_2$  moiety has effects on the stability and other physicochemical properties of a metal complex. Depending on the inductive effect which can be either positive or negative, the group(s) on the nitrogen atom, the flow of electrons towards the ligating  $CS_2$  group could either be reduced or increased <sup>[6]</sup>.

Dithiocarbamates have been employed in the environment in the separation of metal ions via solvent extraction, due to the strong chelating ability towards inorganic species <sup>[7]</sup>. Solvent extraction, involving chelation, has been reported as one of the most widely used techniques in the pre-concentration and separation of metal ions from aqueous samples for analytical purposes because of its ease, speed, and wide scope <sup>[8]</sup>. The technique has become more useful in recent times due to the development of selective chelating agents for trace metal determination <sup>[9]</sup>. In solvent extraction, the right choice of extracting agents can achieve group separation or selective separation of trace elements with high efficiencies <sup>[10]</sup>. For instance, sodium diethyldithiocarbamate can extract over 40 metal species from aqueous solutions into organic solvents <sup>[11]</sup>. The ability of these compounds to form complexes is the reason for their

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extensive use as analytical reagents of environmental importance [9]. The high tendencies of forming chelates with metal ions at very low concentrations ( $\mu\text{g/mL}$ ) make them versatile in removal, pre-concentration, and as extractive agents in the determination of toxic heavy metal ions at trace and ultra-trace levels [10]. Dialkyl dithiocarbamates have been reported to have poor extractive ability in acidic environment (low pH) and are highly unstable [9]. The half-life of 0.3 seconds of diethyldithiocarbamate at pH 2 describes the extreme instability of dialkyldithiocarbamate, and this hinders measurement in acidic environments. Monoalkyldithiocarbamates are more stable than dialkyldithiocarbamates in acidic solutions [9]. Hence, there is need to develop dithiocarbamate bases that will function as good pre-concentration and extractive agents in different environment (acidic and basic) media. Considering the wide spread interest in dithiocarbamate compounds [12] and the interesting properties which occurs due to the change in the coordination number by the addition of Lewis bases to already existing square planer/tetrahedral metal complexes, it was considered of interest to also study their ability in the extraction of selected heavy metals.

## Materials and Methods

### Chemicals

Chemicals used in carrying out this study were of high purity. Diethyl ether (99.5%) was obtained from Riedel-deHaen, carbon disulfide (99.5%) was supplied by Riedel-deHaen, cyclohexylamine (99.0%) by Fluka, sodium hydroxide (98%) by May and Baker, dimethyl sulphoxide by Sigma-Aldrich and aniline (99.5%) by Fluka.

### Instrumentation

Metal concentrations were determined using a UNICAM 929 model flame atomic absorption spectrometer (AAS) with an ATI UNICAM hollow cathode lamp. A mixture of acetylene as a fuel, air as an oxidizing agent and a laminar flow burner was used. The pH determination was carried out using a Metrohm pH meter.

### Statistical Analysis

Statistical package for the social sciences (SPSS) version 23 was the statistical software used to analyze the experimental results. Analysis of variance (ANOVA) was used to analyze the overall significance of the data obtained from the study.

## Syntheses of Ligands

Syntheses of sodium cyclohexyldithiocarbamate and sodium phenyldithiocarbamate salts have already been reported in our earlier publication [13].

## Preparation of stock solutions

Each of the reference solution was prepared by weighing appropriate amount of the metal chloride salt and dissolving in 1 liter of ethanol. The reference solution of lead was prepared by weighing 1.342 g of lead chloride salt and dissolving in 1 liter of dimethylsulphoxide (DMSO) with 30 minutes stirring using a magnetic stirrer at 40 °C. Solutions (5 ppm) of the metals (lead, iron, copper and zinc) used in the analysis were prepared by diluting 0.5 ml of reference solution (1000 ppm) with 99.5 ml of solvent.

## Extraction of heavy metals from aqueous solution

The pH of metal solutions was varied and adjusted using drops of 1M perchloric acid ( $\text{HClO}_4$ ) and 1M NaOH [14]. To 10 ml of 5 ppm of each metal solution in a glass vial was added 10 ml of 5 ppm ligand solution to give a ratio of 1:1 (ligand-metal). Deionised water (10 ml) was also added to precipitate the complex. The complex was then filtered using a filter paper and the filtrate analysed to determine the amount of metal remaining after the complexation. Each of the samples was repeated in triplicate, and arithmetic mean taken as the value.

A blank metal solution (absence of ligand) for each metal was also prepared and analysed to confirm the initial concentration. Samples were properly agitated to ensure homogeneity. The average metal extraction was studied by observing the reduction in concentration measurement using an atomic absorption spectrophotometer and applying dilution factor to the observed values.

## Results and Discussion

The process of extracting each of the metal from aqueous solution using the two ligand derivatives was done using ligand to metal ratio of 1:1 at five different pH values of 3.00, 5.30, 7.30, 8.50 and 11.00. The result as shown in Tables 1 and 4 indicates that both ligands have different percentage heavy metal extractive abilities. Tables 1 and 4 also show that the pH value of the solution plays a vital role in the metal extraction as reported in similar studies [15-17].

**Table 1:** Metal Extractive Ability of Sodium phenyldithiocarbamate Salt

Metal	Initial Conc. (ppm)	Final Conc. (ppm)	pH	Extractive Ability (%)
Fe	5.00	2.636	3.00	47.28
		1.864	5.30	62.72
		0.496	7.30	90.08
		0.447	8.50	91.06
		0.321	11.00	93.58
Cu	5.00	0.201	3.00	95.98
		0.392	5.30	92.16
		0.250	7.30	95.00
		0.241	8.50	95.18
		0.216	11.00	95.68
Zn	5.00	0.966	3.00	80.68
		1.233	5.30	75.34
		0.674	7.30	86.52
		0.668	8.50	86.64
		0.496	11.00	90.08
Pb	5.00	0.899	3.00	82.02
		1.328	5.30	73.44
		0.782	7.30	84.36
		0.698	8.50	86.04
		0.674	11.00	86.52

Experiments were performed in triplicates; final concentration values are mean values

As observed from Table 1, sodium phenyldithiocarbamate ligand has higher extractive ability for copper. However, this ability was observed at pH 3.00 with percentage extractive ability of 95.98%. The lowest extraction was observed for iron at pH 3.0 with extractive ability of 47.28%. This indicates that heavy metal extractive ability of the ligand depends on the type of metal. Extractive ability range of 75.34% - 90.08 % was observed for Zn and 73.44 % - 86.52% for Pb.

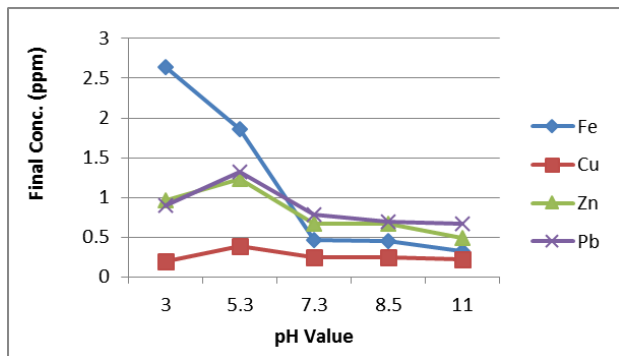


Fig 1: Variation of final concentration of metal with pH for sodium phenyldithiocarbamate ligand

The result as presented in Figure 1 shows that the ability of sodium phenyldithiocarbamate (aromatic ligand) to extract selected heavy metals was more effective in the extraction of copper at pH 3.00 with a final concentration of 0.201 ppm while the lowest extraction was observed for iron with a final concentration of 2.636 ppm at pH 3.00. Zinc and lead had approximately the same final concentration (0.668 ppm and 0.698 ppm) at same pH (8.50); and 1.233 ppm and 1.328 ppm

at pH 5.30 respectively.

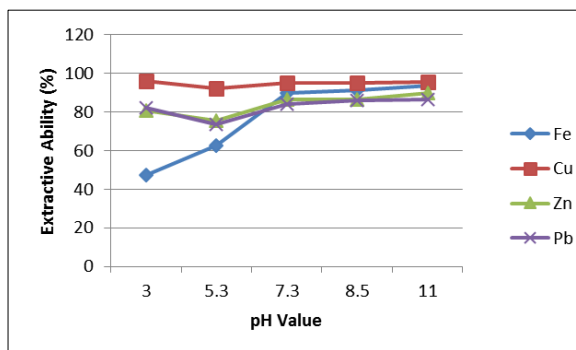


Fig 2: Effect of pH on metal extractive ability of sodium phenyldithiocarbamate ligand

Figure 2 shows the plot of percentage extractive ability against the various pH used in this study. The result as shown indicates the effect of pH on the ligand’s ability to extract selected heavy metals. The highest percentage extractive ability (93.58%) of the aromatic ligand in the extraction of iron was observed at pH 11.00 while the lowest extractive ability (47.28%) for the same metal was observed at pH 3.00. Thus, extractive ability of the ligand depends on the pH of the medium.

Statistical analysis was carried out on the results obtained from the metal extractive abilities of both ligands (Tables 1 and 4). Table 2 shows the statistical ANOVA result of sodium phenyldithiocarbamate ligand showing the means of each of the selected metal, the means of the final concentrations at the different pH and their corresponding standard deviation while Table 5 shows that of the cyclohexyldithiocarbamate ligand.

Table 2: ANOVA Result for Metals and Final Concentration at Different pH Values for the Aromatic Ligand

Variable	Sub-variable	Mean	ANOVA F-ratio (P-values)	Remark
pH	3.0	1.1755±0.5166	2.660 (0.085)	Not significant
	5.3	1.2042±0.3043		
	7.3	0.5505±0.1162		
	8.5	0.5135±0.1067		
	11.0	0.4268±0.1006		
Metal	Fe	1.1528±0.4651	2.778 (0.046)	Significant
	Cu	0.2600±0.0341		
	Zn	0.8074±0.1305		
	Pb	0.8762±0.1196		

Significant at the 0.05 level

Table 2 shows significant difference among the metal, whereas there is no significant difference among pH values, since the p-value of the metal (0.046) is less than the critical value of 0.05 and the p-values of pH values (0.085) is greater

than the critical value of 0.05 respectively. Then, using the least square difference (LSD) of multiple comparisons for metal, the difference was identified as shown in Table 3.

Table 3: Least Square Difference (LSD) Result for Metal for the Aromatic Ligand

(I) Metal	(J) Metal	Mean Difference (I-J)	Std. Error	Sig.
A	B	0.89280*	0.35274	0.022
	C	0.34540	0.35274	0.342
	D	0.27660	0.35274	0.444
B	A	-0.89280*	0.35274	0.022
	C	-0.54740	0.35274	0.140
	D	-0.61620	0.35274	0.100
C	A	-0.34540	0.35274	0.342
	B	0.54740	0.35274	0.140
	D	-0.06880	0.35274	0.848
D	A	-0.27660	0.35274	0.444
	B	0.61620	0.35274	0.100
	C	0.06880	0.35274	0.848

The mean difference is significant at the 0.05 level; A = Fe, B = Cu, C = Zn, D = Pb

Table 3 indicates that the process of extracting each of the metal from the solution using sodium phenylthiocarbamate ligand is significant with iron and copper while others (Zn and

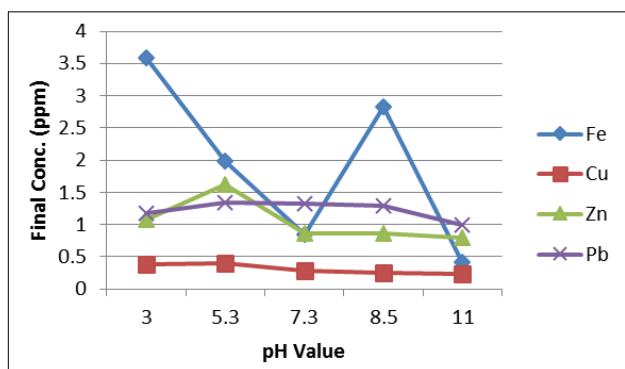
Pb) are not significant. As indicated, the significant difference observed in the heavy metal extraction is shown in the extraction of iron and copper.

**Table 4:** Metal Extractive Ability of Sodium cyclohexyldithiocarbamate Salt

Metal	Initial Conc. (ppm)	Final Conc. (ppm)	pH	Extractive Ability (%)
Fe	5.00	3.584	3.00	28.32
		1.982	5.30	60.36
		0.848	7.30	83.04
		2.834	8.50	43.32
		0.412	11.00	91.76
Cu	5.00	0.384	3.00	92.32
		0.397	5.30	92.06
		0.284	7.30	94.32
		0.258	8.50	94.84
		0.229	11.00	95.42
Zn	5.00	1.074	3.00	78.52
		1.627	5.30	67.46
		0.859	7.30	82.82
		0.861	8.50	82.78
		0.793	11.00	84.14
Pb	5.00	1.184	3.00	76.32
		1.345	5.30	73.10
		1.317	7.30	73.66
		1.284	8.50	74.32
		0.996	11.00	80.08

Experiments were performed in triplicates; final concentration values are mean values

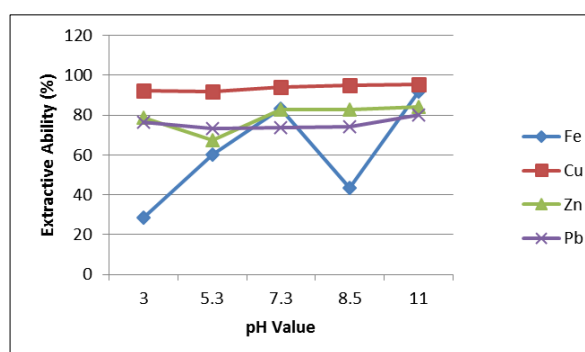
Sodium cyclohexyldithiocarbamate ligand as observed from Table 4 had the highest extractive ability for copper at pH 11.0 with percentage ability of 95.42%, and the lowest extraction for iron at pH 3.00 with percentage ability of 28.32%. Highest extractive abilities of the ligand were observed at pH 11.0 for all the metals. The ligand's ability in extracting Zn was in the range of 67.46% - 84.14% and 73.10% - 80.08 % for Pb.



**Fig 3:** Variation of final concentration of metal with pH for sodium cyclohexyldithiocarbamate ligand

The ability of sodium cyclohexyldithiocarbamate ligand to extract the selected heavy metals was observed to be more evident in the extraction of copper at pH of 11.0 with a final

concentration of 0.229 ppm while the lowest extraction was recorded for iron with a final concentration of 3.584 ppm at pH 3.00 (Figure 3). Zinc and Lead showed final concentrations of 0.793 ppm and 0.996 ppm respectively at same pH (11.0). The result as displayed in Figure 4 reveals the effect of pH on sodium cyclohexyldithiocarbamate ligand's ability to extract heavy metals. The highest percentage extractive ability (95.42%) was observed in the extraction of copper at pH 11.0, while the lowest extractive ability of 28.32% at pH 3.00 was recorded for iron. The observed low ability (28.32%) may be attributed to the unstable nature of most dithiocarbamate compounds at pH values less than four<sup>[18]</sup>.



**Fig 4:** Effect of pH on metal extractive ability of sodium cyclohexyldithiocarbamate ligand

**Table 5:** ANOVA Result for Metals and Final Concentration at Different pH Values for the Cyclohexyl Ligand

Variable	Sub-variable	Mean	ANOVA F-ratio (P-values)	Remark
pH	3	1.5565±0.6986	1.458 (0.275)	Not significant
	5.3	1.3378±0.3395		
	7.3	0.8270±0.2114		
	8.5	1.3092±0.5501		
	11	0.6075±0.1748		
Metal	Fe	1.9320±0.5929	5.204 (0.016)	Significant
	Cu	0.3104±0.0339		

	Zn	1.0428±0.1525	
	Pb	1.2252±0.1937	

Significant at the 0.05 level

ANOVA result (Table 5) shows significant difference among the metals and no significant difference among the pH values; since the p-value of the metal (0.016) is less than the critical value of 0.05 and the p-values of pH values (0.275) is greater

than the critical value of 0.05 respectively. Using the least square difference (LSD) of multiple comparisons for metals, the difference was identified as shown in Table 6.

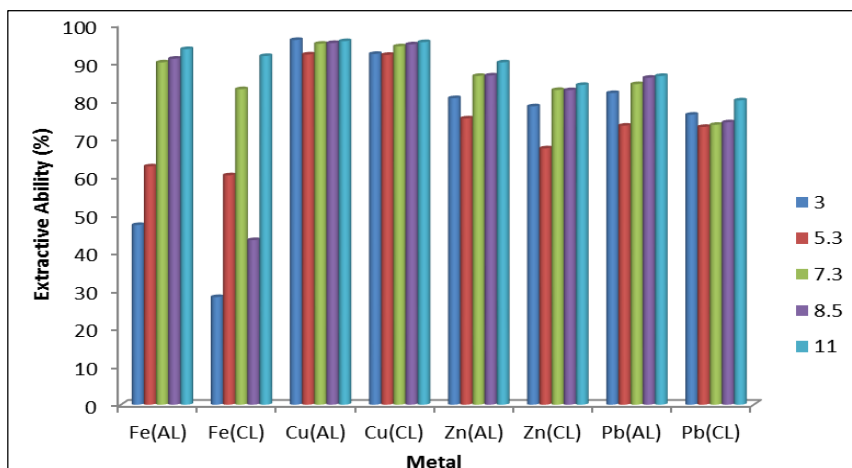
**Table 6:** Least Square Difference (LSD) Result for Metals for the cyclohexyl Ligand

(I) Metal	(J) Metal	Mean Difference (I-J)	Std. Error	Sig.
A	B	1.62160*	0.43605	0.002
	C	0.88920	0.43605	0.058
	D	0.70680	0.43605	0.125
B	A	-1.62160*	0.43605	0.002
	C	-0.73240	0.43605	0.112
	D	-0.91480	0.43605	0.052
C	A	-0.88920	0.43605	0.058
	B	0.73240	0.43605	0.112
	D	-0.18240	0.43605	0.681
D	A	-0.70680	0.43605	0.125
	B	0.91480	0.43605	0.052
	C	0.18240	0.43605	0.681

The mean difference is significant at the 0.05 level; A = Fe, B = Cu, C = Zn, D = Pb

The process of extracting each of the metal from aqueous solutions using sodium cyclohexyldithiocarbamate ligand was

significant for Fe and Cu while no significant difference was observed for Zn and Pb (Table 6).

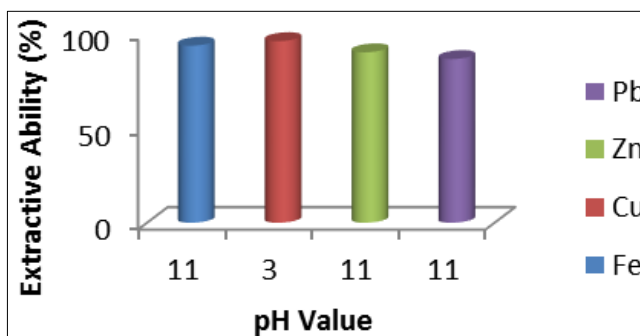


**Key:** AL= Phenylthiocarbamate (aromatic) Ligand, CL = Cyclohexyldithiocarbamate Ligand

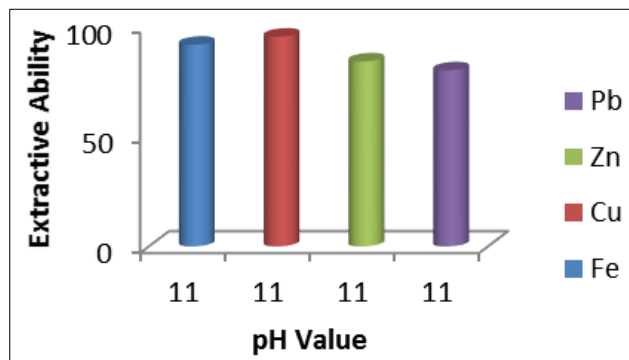
**Fig 5:** Comparison of metal extractive ability of both ligands

Metal extractive abilities of both ligands were compared. Figure 5 shows the comparison of the metal extractive abilities of the two ligands at different pH values. The chart indicates that sodium phenylthiocarbamate ligand had better percentage extractive abilities for all the selected heavy metals at different pH. The pH and type of ligand therefore

play vital roles in heavy metal extraction. The highest extractive abilities of both ligands for all the selected metals were recorded at pH 11.00; with the exception of sodium phenylthiocarbamate for copper (pH 3.00) (Figures 6 and 7).



**Fig 6:** pH values of solution having highest metal extraction for sodium phenylthiocarbamate ligand



**Fig 7:** pH values of solution having highest metal extraction for sodium cyclohexyldithiocarbamate ligand

As reported in literature, dithiocarbamate compounds are known to be unstable at pH values less than four <sup>[18]</sup>. From result obtained from this study, it was observed that the extractive ability of the ligands varied with variation of the pH for the same ligand and same metal. Comparison between the results of the two ligands showed that sodium phenyldithiocarbamate derivative of the ligand has a better percentage extractive ability of metals than sodium cyclohexyldithiocarbamate ligand. This can be attributed to its stability as well as its high bonding capacity for heavy metals <sup>[19]</sup>. The results indicated that the lowest extractive ability of sodium cyclohexyldithiocarbamate ligand was 28.32 % for Fe at pH of 3.00, while the extractive ability of sodium phenyldithiocarbamate ligand for the same metal at the same pH was 47.28 %.

Results also indicated that the highest percentage extractive ability for both ligand and for all the metals was at the same pH value (11.00). However, this observation was not true for copper as the highest extractive ability was observed at pH 3.00 for sodium phenyldithiocarbamate ligand as shown in Figures 6 and 7. This observation supports the fact that the extraction of metals by ligands depends on the type of ligand that is used <sup>[20]</sup>; because sodium phenyldithiocarbamate ligand has an aromatic system which makes it more stable as compared to sodium cyclohexyldithiocarbamate that lacks the system. Sodium phenyldithiocarbamate ligand has a pi electron system that has an empty anti-bonding orbital that may accept electrons thereby reducing the electronic charge concentrated on the metal <sup>[16]</sup>. This process may influence the stability of the complex formed. This process is known as metal-ligand charge transfer (MLCT) <sup>[21]</sup>.

From result, copper was better extracted than any of the other metal using both ligands while iron was the least extracted with extractive ability of 28.32 % for sodium cyclohexyldithiocarbamate ligand at pH 3. There is no significant difference in the extraction of lead and zinc as observed statistically, but significant difference exists in the ligands' abilities to extract iron and copper.

The results obtained in this study was also compared to those of literature and it was observed that for the aromatic ligand, the more complex the ligand or the more the aromatic group in the ligand, the more its ability to extract the selected heavy metals. This observation was seen in the study carried out by Rajab *et al.* <sup>[16]</sup>, who used dibenzylthiocarbamate as ligand in the extraction of Cd, Pb, Zn and Cu.

This result was also compared to our earlier report <sup>[13]</sup> where a ratio of 2:1 ligand to metal was reported for the same ligands (sodium phenyldithiocarbamate and sodium cyclohexyldithiocarbamate ligand) and it was observed that the higher the ratio of ligand to metal, the better the extraction

of the metals. Therefore, an increase in the ligand to metal ratio may bring about a complete extraction of all the selected heavy metals from aqueous solution depending on the pH of the medium.

### Conclusion

This study has shown that the two ligands have metal extractive abilities at ligand to metal ratio of 1:1. Sodium phenyldithiocarbamate salt was more effective in the extraction of the studied heavy metals compared to sodium cyclohexyldithiocarbamate salt at the same pH. Therefore, for better result in the extraction of metals, the use of the aromatic ligand at pH 11.00 may be considered.

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