

Synthesis and Metal Removal Efficiency of Sodium Phenylthiocarbamate and Sodium Cyclohexylthiocarbamate Ligands

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Abstract: Two derivatives of dithiocarbamate ligand (sodium phenylthiocarbamate and sodium cyclohexylthiocarbamate) were synthesized and infrared spectroscopy was used to confirm the functional groups associated with the ligands. The synthesized ligands' ability to extract metal (Fe, Cu, Zn and Pb) ions from aqueous solutions were investigated. The analyses were carried out in five different pH to monitor the effect of pH on heavy metal removal. Metal salts and synthesized ligands were dissolved in the same solvent (ethanol for Fe, Cu and Zn salts and dimethylsulphoxide for Pb salt) and a ligand-metal ratio of 2:1 used in the experiment. The ligands showed effective metal removal efficiency of up to 97.96%. It was observed that both ligands exhibited highest percentage metal removal efficiency at the same pH value (11.0) for all the metals used with the exception of copper (pH 8.5). Though both ligands were effective in metal removal, the aromatic derivative of the ligand showed better percentage removal efficiencies (71.20% - 97.96%). Statistical analysis carried out on the data generated showed significant difference in the metal removal for both ligands particularly in respect of copper and iron.

Keywords: Dithiocarbamate, ligands, metal removal, water pollution, heavy metal.

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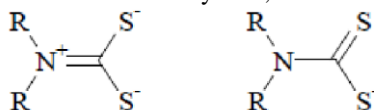
I. Introduction

Pollution of the environment by heavy toxic metals has been of great concern recently and is a very serious problem because of the adverse and discharge effect of these metals [1]. These metals occur globally through anthropogenic activities [2-4] and are deposited into the environment directly or indirectly, thereby, reaching water, air and food sources [1]. These deposited metals are non-biodegradable and therefore undergo transformation reactions that have huge environmental, public health, and economic impacts [5-7]. In addition, most of the toxic heavy metals have the tendency to accumulate in the vital organs of plants or living organisms [8, 9]. The pollutant metals of interest in this study include lead, Iron, zinc and copper. These are known to find wide use and applications in common consumer products and some basic engineering works, paper and pulp industries, tanning of leather, plastics stabilizers, photographic materials, fertilizers, pigments and batteries [1]. Lead and some other metals are known to have toxicological effects on the health of humans and living organisms [10-12]. At a reduced dosage, copper and zinc are known to be relatively non-toxic to humans and animals. They are in fact necessary for proper functioning of living organisms and they are involved in the metabolism of proteins and carbohydrates. Exposure to high dosage by these metals however can be very harmful and bring about many adverse health impact and damage to many biochemical processes [13, 14].

Due to the effects of these heavy metals, it is therefore necessary to see to it that these heavy metals are removed from water in order to protect the lives of people and the environment. To achieve this, different methods have been used for the removal of heavy metal from polluted water [1]. These methods include chemical precipitation-filtration, ion exchange, reverse osmosis, oxidation-reduction, solvent extraction, adsorption, cementation, plant leaf extraction, electrochemical treatment technologies and membrane separation [5, 6, 15-19].

Finding new ways of removing heavy metals from water is an important field of modern scientific research and dithiocarbamate ligands are one of the most fruitful research materials in this area [1]. Dithiocarbamate ligands are a type of dithiolate ligands, which contain a number of mono and di-negative charge ligand groups [20] and they are known to have versatile binding abilities and form complexes with most of the transition metals [21-23].

Dithiocarbamates can stabilize transition metals in a variety of oxidation states [24]. This ability of stabilizing high oxidation states in metal complexes reflects strong σ -bonding characteristic of these ligands [25]. Although the sulphur atoms of dithiocarbamate ligands possess σ -donor and n -back-donation characteristics of the same order of magnitude, these ligands have a special characteristic in that there is an additional n -electron flow from nitrogen to sulphur *via* a planar delocalized π -orbital system, as shown below[25]:



The effect of the delocalized π -orbital system results in a strong electron donation and hence a high electron density on the metal leading to its next higher oxidation state [26]. While dithiocarbamate complexes have been known for over the years, with many having been synthesized, the majority of these contain only simple alkyl substituents such as methyl and ethyl [25]. A developing interest in the area of dithiocarbamate chemistry is the functionalization of the backbone such that new applications and interactions can be developed. This area is still in its early stages, but already interesting potential applications have been noted including functionalization of gold nanoparticles, stepwise build-up of multimetallic arrays, synthesis of dithiocarbamate-containing supramolecular systems which can be used for anion binding and development of technetium radiopharmaceuticals [24].

Some researchers have successfully used dithiocarbamate derivatives as ligands for the removal of some metal ions from aqueous solutions [1, 16, 27-30]. Gaur *et al.* [30] successfully used a copolymer containing a dithiocarbamate moiety to efficiently remove some selected metal ions from aqueous solutions, while Abu-El-Halawa *et al.* [1] prepared two types of dithiocarbamate ligands, one of which is aliphatic (diethyldithiocarbamate) and the other aromatic (diphenyldithiocarbamate). Their investigation results showed that the diphenyldithiocarbamate ligand was more efficient in removing Pb, Cd, Cu and Zn than the diethyldithiocarbamate analogue. They also reported that the metal removal efficiency of the diphenyldithiocarbamate ligand was more effective than using the activated carbon method.

The purpose of this research is to monitor heavy metal removal efficiency of two derivatives of dithiocarbamate (aromatic and cyclohexyl derivatives). These ligands were used for the treatment of polluted water containing 5.0 ppm concentrations of selected metals (Pd, Fe, Cu and Zn). The metal removal efficiencies of the ligands were monitored and compared.

II. Materials and Methods

2.1 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, and aniline (99.5%) by Fluka.

2.2 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 while melting points of the synthesized ligands were determined using an electro-thermal series digital melting point apparatus. Infrared (IR) spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR spectrometer with KBr pellets.

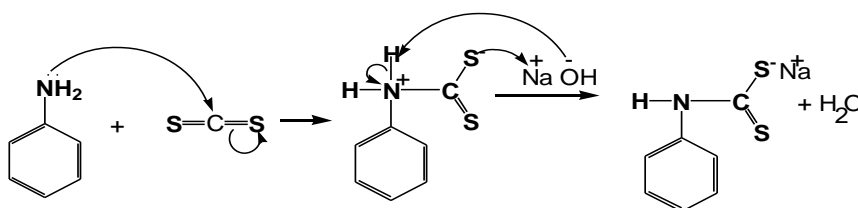
2.3 Statistical Analysis

Analysis of variance (ANOVA) was used to analyze the data obtained from the study.

2.4 Syntheses of Ligands

2.4.1 Synthesis of Sodium phenyldithiocarbamate Salt

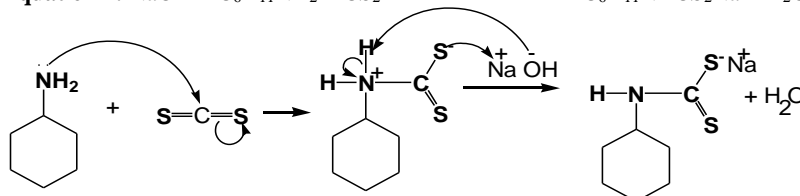
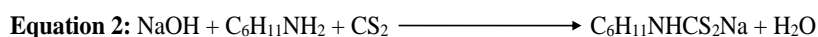
Sodium phenyldithiocarbamate salt was synthesized according to established methods with slight modification [31, 32, 1]. A 0.05M concentration of sodium hydroxide solution was prepared by dissolving 2g of NaOH in 10ml of deionised water and mixed with 1mol equivalent (4.5664ml) of aniline in a round bottom flask. The mixture was stirred for 10 minutes using a magnetic stirrer. A 1mol equivalent (3.02ml) of carbon disulphide solution was added to the mixture in a drop-wise manner until a reddish colour appeared. The mixture was further stirred for three hours and heated to evaporate water. The mixture was allowed to cool at room temperature for 24 hours. The precipitate was subsequently washed with diethyl ether – ethanol (3:1); filtered and air dried to give a shiny cream solid (Equation 1 and Scheme 1). The solid product was recrystallized from ethanol. The percentage yield was 77.27% with melting point of $\sim 182^{\circ}\text{C}$.



Scheme 1: Synthesis of sodium phenylthiocarbamate ligand $\text{Na}[\text{C}_6\text{H}_5\text{NHCS}_2]$

2.4.2 Synthesis of Sodium Cyclohexylthiocarbamate Salt

Sodium salt of cyclohexylthiocarbamate was prepared using a slightly modified version of an already reported method [33]. The ligand was synthesized by dissolving 2g of NaOH in 15ml of deionised water and mixed with an equimolar amount of cyclohexylamine. After stirring for 10 minutes, an equimolar amount of solution of 0.1M carbondisulphide was added dropwise. The mixture was stirred for three hours and a pale-yellow solid was formed (Equation 2 and Scheme 2). The solid product was washed with cold water-ethanol (1:1) solution and filtered giving a white product which was recrystallized from ethanol [33]. Percentage yield was 62% with melting point of $\sim 130^\circ\text{C}$ which corresponds with that reported by Alshamaileh *et al.* [33].



Scheme 2: Synthesis of sodium cyclohexylthiocarbamate ligand $\text{Na}[\text{C}_6\text{H}_{11}\text{NHCS}_2]$

2.5 Preparation of Stock Solutions

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

2.6 Removal of Heavy Metals from Solution

Appropriate metal concentration for each metal was prepared by diluting the reference solution using the formula:

$$V_1 = \frac{C_2 V_2}{C_1}$$

Where V_1 = Volume of the original stock solution to be diluted

V_2 = Required volume of the new concentration

C_1 = Concentration of the original stock solution

C_2 = Required concentration to be obtained after dilution

The pH of metal solutions was determined using a pH meter. The pH of the solutions was varied and adjusted using drops of 1M perchloric acid (HClO_4) and 1M NaOH [34]. To 5ml 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 2:1 (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 removal was studied by observing the reduction in concentration measurement using the atomic absorption spectrophotometer and applying dilution factor to the observed values.

III. Results and Discussion

The ligands were successfully synthesized; giving a shiny cream solid for the aromatic ligand and a shiny white solid for the cyclohexyl type of the ligand. The melting point of the aromatic ligand was $\sim 182^{\circ}\text{C}$ with a percentage yield of 77.271% which is higher than the 75% yield reported by Onwudiwee *et al.* [32]. The melting point of the cyclohexyl type was $\sim 130^{\circ}\text{C}$ with a percentage yield of 62%. This is also higher than that synthesized by Alshamaileh *et al.* [33] which gave a yield of 60%. The peaks of the infra-red spectra of both ligands were compared to established structures (Table 1). The major functional groups identified were in agreement with reported works [33, 35, 25].

Table 1: Absorption Frequencies Identified in the Infra-red spectra of the Ligands

Peak (cm^{-1})	Functional Group	Reference
3200	N-H	[33]
1480	C-N	[33]
990	C=S	[33]
3040	C-H due to aromatic ring	[35]
1470.36	C-N	[25]

The process of removing each of the metal from the solution using the two synthesized ligand derivatives was observed using ligand to metal ratio of 2:1 at five different pH values of 3.00, 5.30, 7.30, 8.50 and 11.00. The results (Tables 2 and 6) indicate that both ligands have different percentage removal efficiencies of the selected heavy metals. It was also observed for all the metals used, that the metal removal efficiency varied with change in pH even while the concentrations were kept constant. This confirms that pH of the solution plays a vital role in metal removal efficiency of ligands as reported in similar studies [36, 1, 37].

Table 2: Removal Efficiency of the Aromatic Ligand Sodium phenylthiocarbamate Salt

Metal	Initial Conc. (ppm)	Final Conc. (ppm)	pH	Removal Efficiency (%)
Fe	5.00	0.406	3.00	91.88
	5.00	1.440	5.30	71.20
	5.00	0.200	7.30	96.00
	5.00	0.166	8.50	96.68
	5.00	0.128	11.00	97.44
Cu	5.00	0.194	3.00	96.12
	5.00	0.261	5.30	94.04
	5.00	0.182	7.30	96.36
	5.00	0.102	8.50	97.96
	5.00	0.154	11.00	96.92
Zn	5.00	0.789	3.00	84.22
	5.00	0.998	5.30	80.04
	5.00	0.342	7.30	93.16
	5.00	0.398	8.50	92.04
	5.00	0.324	11.00	93.52
Pb	5.00	0.765	3.00	84.70
	5.00	0.992	5.30	80.16
	5.00	0.762	7.30	84.76
	5.00	0.637	8.50	87.26
	5.00	0.452	11.00	90.96

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

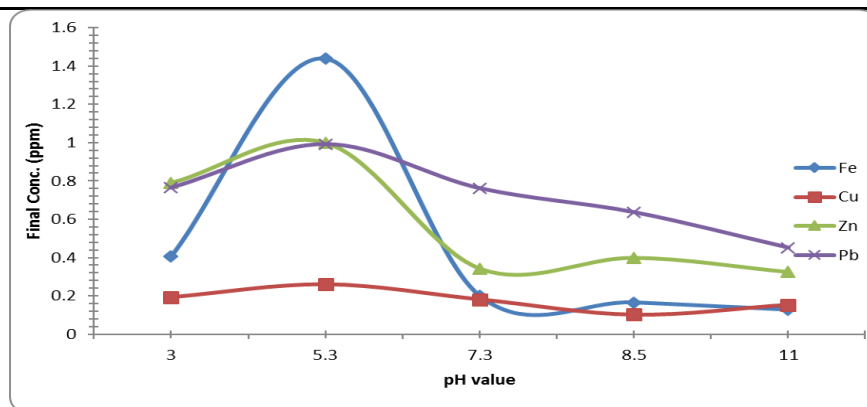


Figure 1: Variation of final concentration of metal with pH for sodium phenylthiocarbamate ligand

The result as presented in Figure 1 shows that the ability of sodium phenylthiocarbamate (aromatic ligand) to remove the selected heavy metals was more effective in the removal of copper at pH of 8.50 with a final concentration of 0.102 ppm while the lowest removal was observed for iron with a final concentration of 1.440 ppm at pH of 5.30. Zinc and lead had approximately the same final concentration (0.998 ppm and 0.992 ppm) at same pH (5.30).

Percentage removal efficiency of sodium phenylthiocarbamate plot against the various pH values (Figure 2) shows the effect of the pH on the ligand's ability to remove the selected heavy metals. Sodium phenylthiocarbamate was observed to have the highest percentage removal efficiency (97.96%) with respect to copper at pH of 8.50 while recording the lowest removal efficiency of 71.20% at the pH of 5.30 with iron. This suggests that the metal removal efficiency of sodium phenylthiocarbamate may depend on the pH of the medium.

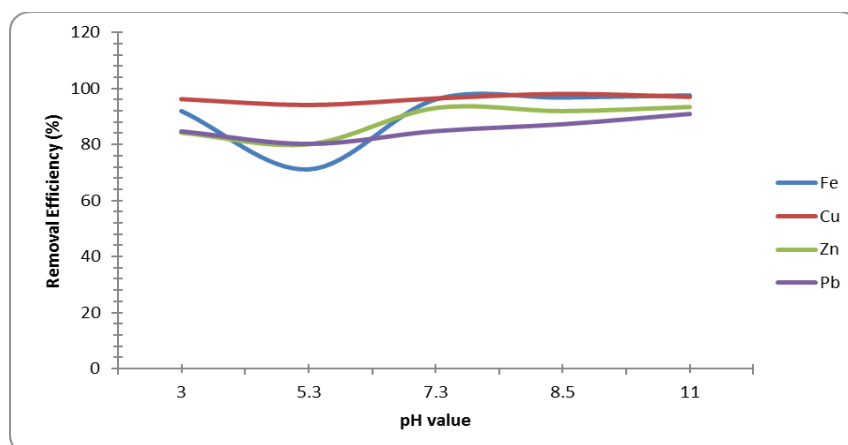


Figure 2: Effect of pH on metal removal efficiency of sodium phenylthiocarbamate ligand

Statistical analysis was carried out on the results obtained from the metal removal efficiencies (Tables 2 and 6) of both ligands. Table 3 shows the statistical ANOVA result of the aromatic ligand showing arithmetic means of the final concentrations for each of the selected metal, the means of the final concentrations at different pH and their corresponding standard deviation; while Table 7 shows those of the cyclohexyl type of the ligand. Table 3 shows significant difference among the metal and pH values, since the p-values (0.011 and 0.019) were lower than the critical value of 0.05. Because of the significant difference in the heavy metal removal as observed from Table 3 in the pH as well as in the metal, there was therefore the need to identify this difference. The difference was identified using the least square difference (LSD) of multiple comparisons shown in Tables 4 and 5. Table 4 gives the pH at which least square difference (significance) was observed while Table 5 shows the metals where the least square difference was observed. The process of removing metals from solutions using the aromatic ligand at pH of 3.00 and 5.30 for the different metals were significant while the pH of 7.30, 8.50 and 11.00 were not significant (Table 4). Table 5 indicates that the process of removing each of the metal from the solution using the aromatic ligand for Fe is significant while others (Cu, Zn, and Pb) are not significant. As indicated, the significant difference observed in the heavy metal removal is shown in the removal of iron at pH 3.00 and 5.30 while the removal of other metals showed no significant difference.

Table 3: ANOVA Result for Metals and Final Concentrations at Different pH Values for Sodium phenylthiocarbamate Ligand

Variable	Sub-variable	Mean	ANOVA F-ratio (P-values)	Remark
pH values	3.0	0.5385±0.1444	5.234 (0.011)	Significant
	5.3	0.9228±0.2443		
	7.3	0.3715±0.13499		
	8.5	0.3258±0.12168		
	11.0	0.2645±0.07612		
Metal	Cu	0.4680±0.2477	4.880 (0.019)	Significant
	Fe	0.1786±0.0260		
	Zn	0.5702±0.1366		
	Pb	0.7216±0.0885		

Significant at 0.05 level

Table 4: Least Square Difference (LSD) Result for pH Values for Sodium phenylthiocarbamate Ligand

(I) pH values	(J) pH values	Mean Difference (I-J)	Std. Error	Sig.
3	5.3	-0.38425	0.21849	0.099
	7.3	0.16700	0.21849	0.457
	8.5	0.21275	0.21849	0.346
	11	0.27400	0.21849	0.229
5.3	3	0.38425	0.21849	0.099
	7.3	0.55125*	0.21849	0.023
	8.5	0.59700*	0.21849	0.015
7.3	3	-0.16700	0.21849	0.457
	5.3	-0.55125*	0.21849	0.023
	8.5	0.04575	0.21849	0.837
8.5	11	0.10700	0.21849	0.631
	3	-0.21275	0.21849	0.346
	5.3	-0.59700*	0.21849	0.015
11	7.3	-0.04575	0.21849	0.837
	11	0.06125	0.21849	0.783
	3	-0.27400	0.21849	0.229
11	5.3	-0.65825*	0.21849	0.009
	7.3	-0.10700	0.21849	0.631
	8.5	-0.06125	0.21849	0.783

*The mean difference is significant at 0.05 level

Table 5: Least Square Difference (LSD) Results for Metal for Sodium phenylthiocarbamate Ligand

(I) Metal	(J) Metal	Mean Difference (I-J)	Std. Error	Sig.
1	2	0.28940	0.21038	0.188
	3	-0.10220	0.21038	0.634
	4	-0.25360	0.21038	0.246
2	1	-0.28940	0.21038	0.188
	3	-0.39160	0.21038	0.081
	4	-0.54300*	0.21038	0.020
3	1	0.10220	0.21038	0.634
	2	0.39160	0.21038	0.081
	4	-0.15140	0.21038	0.482
4	1	0.25360	0.21038	0.246
	2	0.54300*	0.21038	0.020
	3	0.15140	0.21038	0.482

*The mean difference is significant at 0.05 level; 1= Cu, 2 =Fe, 3 =Zn, 4= Pb

Table 6: Removal Efficiency of the Ligand Sodium cyclohexyldithiocarbamateSalt

Metal	Initial Conc. (ppm)	Final Conc. (ppm)	pH	Removal Efficiency (%)
Fe	5.00	3.229	3.00	35.42
	5.00	1.591	5.30	68.18
	5.00	0.520	7.30	89.60
	5.00	0.343	8.50	93.14
	5.00	0.214	11.00	95.72
Cu	5.00	0.261	3.00	94.78
	5.00	0.310	5.30	93.80
	5.00	0.199	7.30	96.02
	5.00	0.176	8.50	96.48
	5.00	0.432	11.00	91.36
Zn	5.00	0.894	3.00	82.12
	5.00	1.002	5.30	79.96
	5.00	0.456	7.30	90.88
	5.00	0.421	8.50	91.58
	5.00	0.382	11.00	92.36
Pb	5.00	0.876	3.00	82.48
	5.00	1.024	5.30	79.52
	5.00	0.841	7.30	83.18
	5.00	0.782	8.50	84.36
	5.00	0.510	11.00	89.80

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

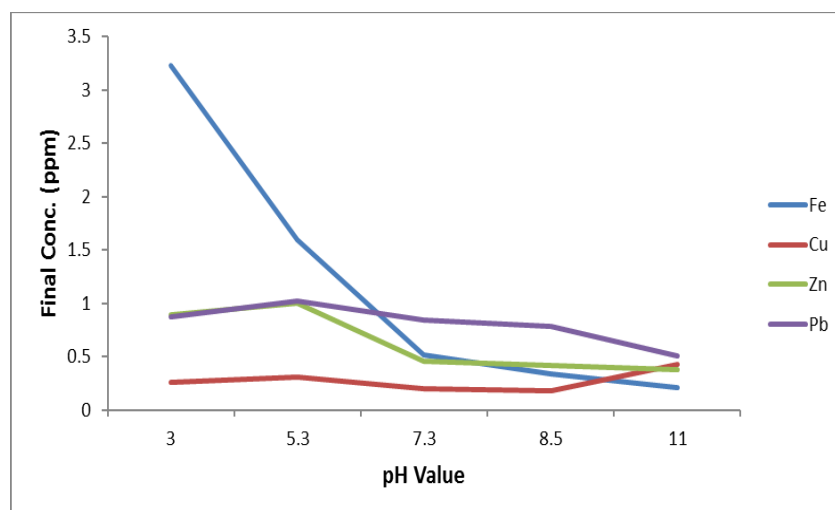


Figure 3: Variation of final concentration with pH values for sodium cyclohexyldithiocarbamateligand

The ability of sodium cyclohexyldithiocarbamate ligand to remove the selected heavy metals (Table 6 and Figure 3) was more evident in the removal of copper at pH of 8.50 with the final concentration of 0.176ppm while the lowest removal was recorded for iron with a final concentration of 3.229 ppm at pH of 3.00. Zinc and lead had approximately the same final concentration (1.002ppm and 1.024ppm respectively) at same pH (5.30). The result as displayed on Figure 4 reveals the effect of pH on sodium cyclohexyldithiocarbamate ligand's ability to remove heavy metals. The highest percentage removal efficiency(96.48%) was observed in the removal of copper at pH of 8.50 while showing the lowest removal efficiency of 35.42% at pH 3.00 with iron. The observed low efficiency (35.42%) may be attributed to the unstable nature of most dithiocarbamate compounds at pH values less than four [38].

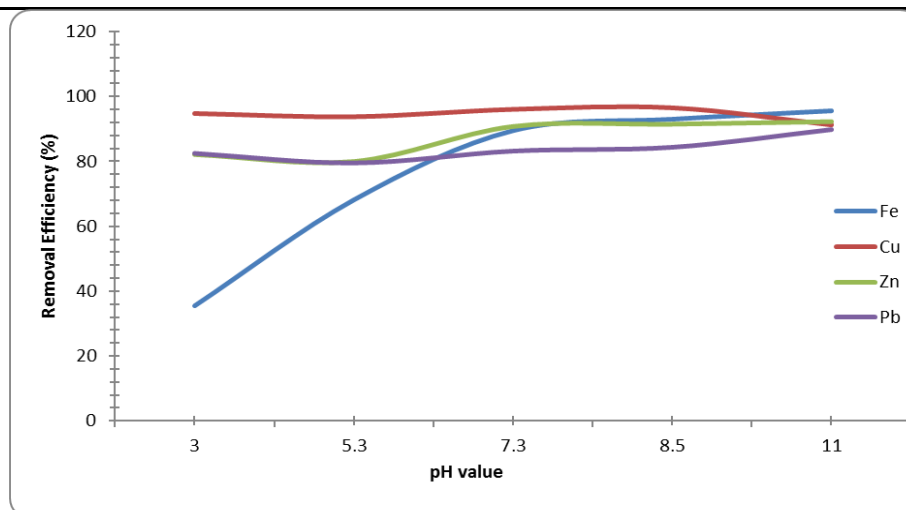


Figure 4: Effect of pH on metal removal efficiency of sodium cyclohexyldithiocarbamate ligand

Statistical analysis showed significant difference in metal removal efficiencies of sodium cyclohexyldithiocarbamate ligand with respect to the different metals, whereas there is no significant difference with respect to the different pH values; since the p-value of the metal (0.017) is less than the critical value of 0.05 and the p-values of pH values (0.183) is greater than the critical value of 0.05 (Table 7). Subsequently, using the least square difference (LSD) of multiple comparisons for metal as presented in Table 8, the difference was identified. The process of removing each of the metal from solutions using the synthesized cyclohexyl type of the ligand (sodium cyclohexyldithiocarbamate) derivative was significant for Fe and Cu while not significant for the others.

Table 7: ANOVA Result for Metals and Final Concentration at Different pH for Sodium cyclohexyldithiocarbamate Ligand

Variable	Sub-variable	Mean	ANOVA F-ratio (P-values)	Remark
pH values	3.0	1.3150±0.6547	1.857 (0.183)	Not -significant
	5.3	0.9818±0.2621		
	7.3	0.5040±0.1320		
	8.5	0.4305±0.1278		
	11.0	0.3845±0.0626		
Metal	Cu	1.1794±0.5673	2.771 (0.017)	Significant
	Fe	0.2756±0.0456		
	Zn	0.6310±0.1316		
	Pb	0.8066±0.0841		

Significant at 0.05 level

Table 8: Least Square Difference (LSD) Result for Metals for Sodium cyclohexyldithiocarbamate Ligand

(I) Metal	(J) Metal	Mean Difference (I-J)	Std. Error	Sig.
1	2	0.90380*	0.41724	0.046
	3	0.54840	0.41724	0.207
	4	0.37280	0.41724	0.385
2	1	-0.90380*	0.41724	0.046
	3	-0.35540	0.41724	0.407
	4	-0.53100	0.41724	0.221
3	1	-0.54840	0.41724	0.207
	2	0.35540	0.41724	0.407
	4	-0.17560	0.41724	0.679
4	1	-0.37280	0.41724	0.385
	2	0.53100	0.41724	0.221
	3	0.17560	0.41724	0.679

*The mean difference is significant at 0.05 level; 1= Cu, 2 = Fe, 3 = Zn, 4= Pb

In comparing metal removal efficiencies of the two ligands at different pH values (Figure 5), it was observed that the aromatic type of the ligand exhibited better metal removal efficiencies at almost all the different pH values. This observation suggests that the pH and the type of ligand have a synergistic effect on heavy metal removal.

It is interesting to note that the removal efficiency varied with variation of pH for the same ligand and same metal. Comparison between the results of the two ligands showed that the aromatic derivative of the ligand had a better percentage removal efficiency of the metals than the cyclohexyl type. This can be attributed to its stability as well as its high bonding ability for heavy metals [39]. The results indicated that the lowest removal efficiency of the cyclohexyl type of the ligand was 35.42% with Fe at a pH value of 3.00, while the removal efficiency of the aromatic ligand for the same metal at the same pH was 91.88%.

Results also indicated that the highest percentage removal efficiency for both ligand and for all the metals was at the same pH (11.0). However, this observation is not true for copper as the highest removal efficiency was observed at pH 8.50 for both ligands as clearly shown in Figures 6 and 7. Coincidentally, this observation supports the fact that the removal efficiency of the metal basically depends on the type of ligand that is used [40] because the aromatic type of the ligand has an aromatic system which makes it more stable when compared to the cyclohexyl type that lacks the system. The aromatic type of the 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 [1]. This process may have an effect on the stability of the complex formed as a whole. This process is known as metal-ligand charge transfer (MLCT) [41].

It was also observed that copper was better removed than any of the other metals using both ligands while iron was the least removed with efficiency of 35.42% for the cyclohexyl type of the ligand at pH 3. There is no significant difference in the removal of lead and zinc as observed statistically, but significant difference exists between the removal of iron and copper.

The results obtained in this study was also compared with those of literature [1] and it was observed that for the aromatic ligand, the more complex the ligand or the more the aromatic group on the ligand, the higher its metal removal efficiency. This observation was reported by Abu-El-Halawa *et al.* [1] who used dibenzylthiocarbamate as ligand in the removal of Cd, Pb, Zn and Cu. Although the difference in the metal removal between that of dibenzylthiocarbamate used in Abu-El-Halawa *et al.* and the phenylthiocarbamate used in this study is not much (96.00%-99.98% for dibenzylthiocarbamate and 94.02%-97.96% for phenylthiocarbamate). Dibenzylthiocarbamate gave a better removal efficiency for all the metals and in all the pH values than phenylthiocarbamate used in this study, except for zinc which gave 93.10% for the dibenzylthiocarbamate and 96.92% for phenylthiocarbamate at the pH of 11.00. This observation may be because of the extra pi electron system from the other phenyl group in dibenzylthiocarbamate. Therefore, for better removal of the selected heavy metal using aromatic ligand of dithiocarbamate, it may be necessary to consider those that contain more aromatic groups.

The result of cyclohexylthiocarbamate ligand used in this study was also compared with that of diethylthiocarbamate which was used in the removal of Zn, Cu and Pb as reported by Abu-El-Halawa and Zabinb [1]. It was observed that the aliphatic type of the ligand gave better removal of copper in all the pH values, although the difference in the removal is minimal. However, cyclohexylthiocarbamate ligand used in this study gave higher removal of Zn and Pb in all the pH values than that reported for diethylthiocarbamate [1] except at pH of 11.00; where the removal efficiency of the cyclohexylthiocarbamate and diethylthiocarbamate were 92.36% and 95.52% for Zn, and 89.80% and 94.86% for Pb respectively. Diethylthiocarbamate also had higher metal removal efficiency at pH of 3.00; where the removal efficiencies were 82.48% and 88.82% for cyclohexylthiocarbamate and

diethyldithiocarbamate respectively. This observation agrees with the fact that the removal ability of the selected heavy metals depends on the ligand type and on the pH of the medium.

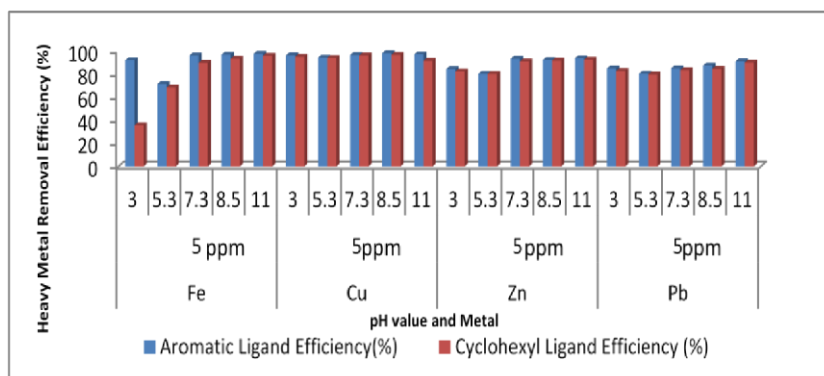


Figure 5: Comparison of metal removal efficiencies of both ligands

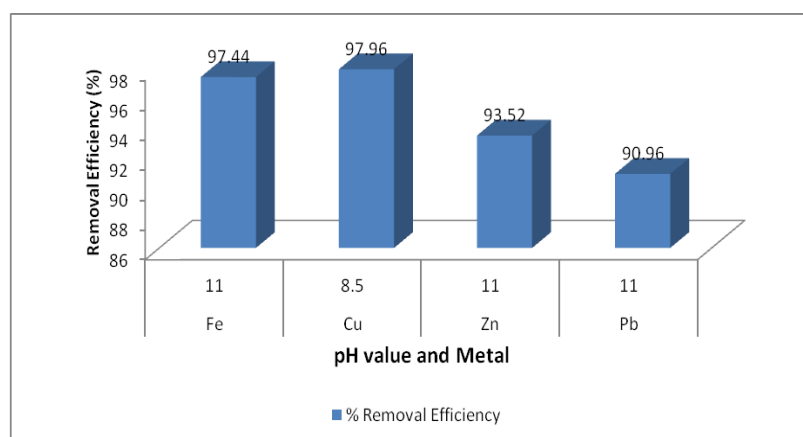


Figure 6: pH Values of solution having highest metal removal efficiency for sodium phenylthiocarbamateligan

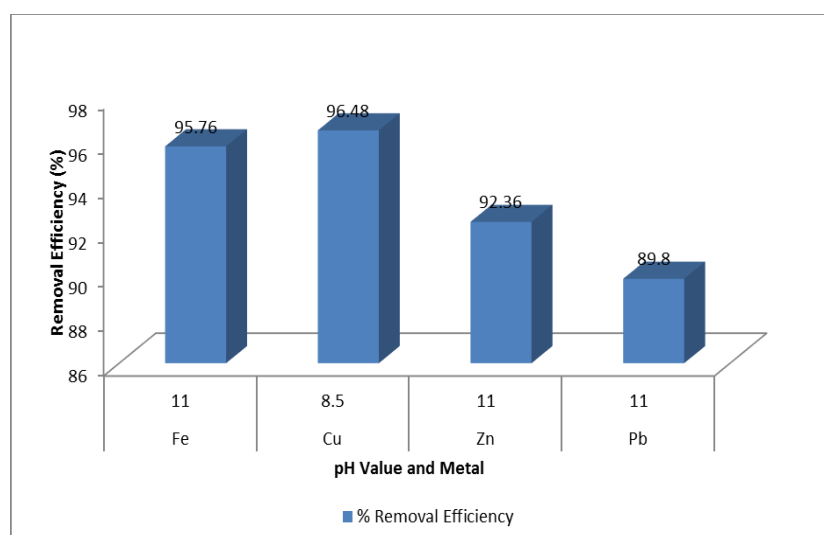


Figure 7: pH values of solution having highest metal removal efficiency for sodium cyclohexyldithiocarbamateligan

IV. Conclusion

This work has shown that aromatic type of dithiocarbamateligan is more effective than cyclohexyl type of the ligand in the removal of selected heavy metals at the same pH. Therefore, removal efficiency of heavy metals

using ligands depends on the ligand type. The pH of the solution was also observed to have played a role in the removal of the selected heavy metals with both ligands having highest removal efficiency for copper at the same pH (8.50). It was also shown statistically that there is significant difference in heavy metal removal ability of both ligands (sodium phenyldithiocarbamate and sodium cyclohexyldithiocarbamate). However, this significant difference is particular with copper and iron. This therefore, gives a viable approach for treatment of polluted water containing heavy metal ions.

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