Synthesis And Heavy Metal Removal Efficiency of 3H-BENZOOXAZOLE-2,2-DITHIOL and 3H-BENZOTHIAZOLE-2,2-DITHIOL Ligands

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Abstract— Two derivatives of benzo-hetreocyclic ligands (3H-Benzooxazole-2,2-dithiol and 3H-Benzothiazole-2,2-dithiol) were synthesized by refluxing one mole of 2-Amino-phenol with one mole of carbon disulphide (CS2) in acetone, then one mole of 2-Amino-benzene-thiol and one mole of carbon disulphide (CS2) in acetone for two hours respectively. The mixture were allowed to cool and then evaporated at room temperature, to afford a solid creamy precipitates which were washed with hexane, filtered, air dried and recrystallized with a mixture of acetone and hexane. The final product were filtered and allowed to dry. Infrared spectroscopy (IR) was used to confirm the functional groups associated with the ligands. The ability of the synthesized ligands to remove heavy metals (Fe, Cu, Zn and Ni) ions from aqueous solutions was investigated. This was carried out at five different pH values to monitor its effect on heavy metal removal. The metal salts and the synthesized ligands were dissolved in the same solvent (ethanol) and a ligand-metal ratio of 1:1 used in the investigation. The 3H-Benzooxazole-2,2-dithiol ligand, was observed to exhibit highest percentage metal removal efficiency for Nickel at pH value 3.00 giving the 90.76% removal. The 3H-Benzothiazole-2,2-dithiol exhibited the highest removal efficiency for zinc at pH 11.00, giving a percentage of 95.64%. (11.0) Though both ligands were effective in metal removal, the 3H-Benzothiazole-2,2-dithiol ligand showed better percentage removal efficiencies (67.96% - 95.64%).

Index Terms— Benzo-heterocycles, Metal removal, 3H-Benzooxazole-2,2-dithiol, 3H-Benzothiazole-2,2-dithiol

I. INTRODUCTION

Environment pollution as a result of heavy toxic metals has been of great concern to the society, and this has been a very serious problem due to 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, basically as a result of human activities thereby, reaching the water, air and food sources [1]. These deposited metals are known to be non-biodegradable and therefore undergo transformation reactions that have huge environmental, public health, and economic implications and impacts [5]-[7]. In addition, most of these toxic heavy metals have the ability to accumulate in the vital organs of plants or living organisms [8] and [9]. The pollutant metals of interest in this study include the following:

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Nickel, zinc, copper and iron. These metals 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 for instance 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] and [14].

Therefore, because of the effects of these heavy metals, it is necessary to see to it that these heavy metals are removed from the environment in order to protect the lives of people and the environment. In order 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] and [6], [15]-[19].

The use of ligands is also one of the methods that have been extensively used to effectively remove heavy metals from solution and benzo-heterocycles are one of such ligands.

Finding new ways of removing heavy metals from water is an important field of the modern scientific research race and benzo-heterocyclic ligands are one of the most fruitful research materials in this area [1]. The ligands in this study and other derivatives 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].

Benzo-heterocycles like those in this study are able to stabilize transition metals in a variety of oxidation states [24]. This ability to stabilize high oxidation states in metal complexes reflects strong o-bonding characteristic of these ligands [25]. Although the sulphur atoms of this ligands possess o-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]:
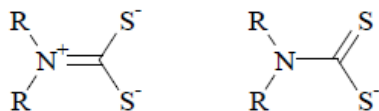
The effect of the delocalized π- orbital system results in a strong electron donation and hence a high electron density on the metal leading to its next higher oxidation state [26]. While some complexes have been known for over the years, with many having been synthesized, the majority of these contain only simple alkyl substituent such as methyl and ethyl [25]. A developing interest in the area of some benzo-heterocyclic 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 some benzo-hectrocycles containing supramolecular systems which can be used for anion binding and development of technetium radiopharmaceuticals [24].

Some researchers have successfully used some derivatives of benzo-heterocycles like the benzo-dithiocarbamate derivatives as ligands for the removal of some metal ions from aqueous solutions [1] and [16], [27]-[30]. Gaur *et al.* [30] successfully used a copolymer containing a benzo-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 beno-heterocyclic ligands (*3H-Benzooxazole-2,2-dithiol and 3H-Benzothiazole-2,2-dithiol*). These ligands were used for the treatment of polluted water containing 5.0 ppm concentrations of selected metals (Ni, Cu, Zn and Fe). The metal removal efficiencies of the ligands were monitored and compared.

$$C_6H_7NO + CS_2 \longrightarrow C_7H_7NOS_2 \qquad (1)$$

II. MATERIALS AND METHODS

A. Chemicals

The chemicals used in carrying out this study were of high purity. 2-Amino-phenol (99.5%) was obtained from Sigma Aldrich, 2-Amino-benzene-thiol (99.5%) obtained from Sigma Aldrich, carbon disulphide (99.5%) was supplied by Riedel-deHaen, acetone (99.0%) by Fluka and hexane (98%) by May and Baker,

B. 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.

C. Syntheses of Ligands
### C.1 Synthesis of 3H-Benzooxazole-2,2-dithiol

One mole of 2-Amino-phenol C_6H_7NO (10.0g) was dissolved in acetone using a round bottom flask and stirred under reflux for about 1hour. In a drop-wise manner, an equimolar amount of carbon disulphide (6.97g) was added and allowed to reflux for another 2hours. The mixture was allowed to cool at room temperature and allowed to evaporate, resulting in the precipitation of a solid creamy product which was washed with hexane, filtered and air dried (Equation 1 and Scheme 1 below). The solid product was then recrystallized using a mixture of acetone and hexane. The product was filtered and allowed to dry. The product gave a melting point range of 147-148°C with a percentage yield of 75%.

Mechanism of reaction:

Scheme 1: Synthesis of 3H-Benzooxazole-2,2-dithiol [$C_7H_7NOS_2$]
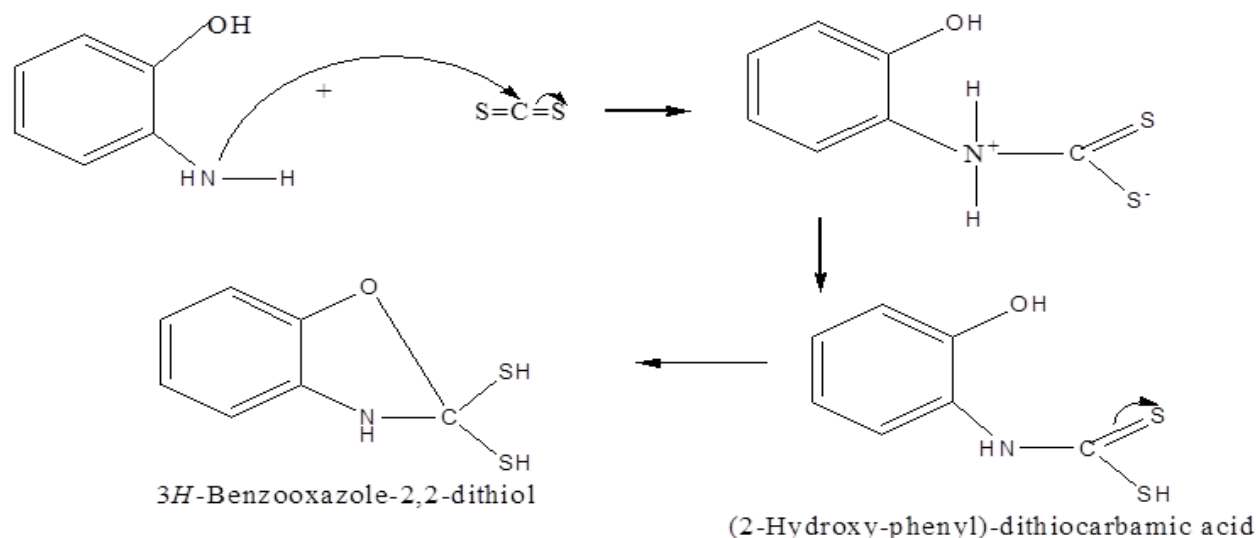
C.2 Synthesis of 3H-Benzothiazole-2,2dithiol

The same procedure for the synthesis is 3H-Benzooxazole-2,2dithiol above was also employed in the synthesis of 3H-Benzothiazole-2,2-dithiol. The product gave a melting point of 87-90°C with a percentage yield of 80%.

$$C_6H_7NS + CS_2 \longrightarrow C_7H_7NS_3 \qquad (2)$$

Scheme 2: Synthesis of 3H-Benzothiazole-2,2dithiol [$C_7H_7NS_3$].
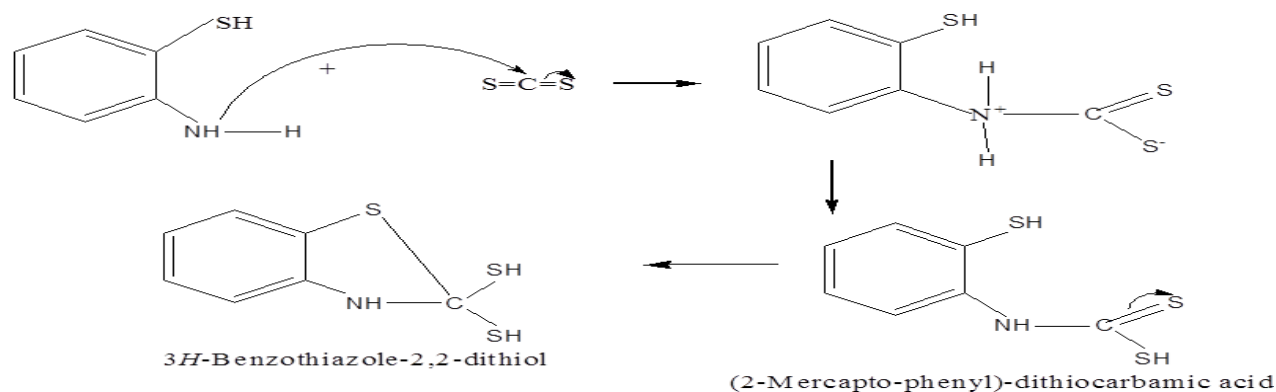
D. Preparation of Stock Solutions

The solutions (5ppm) of the metals (Nickel, 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 dissolved in ethanol.

E. Removal of Heavy Metals from Solution

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

$$V_1 = \frac{C_2V_2}{C_1}$$

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 5 ml of 5 ppm of each metal solution in a glass vial was added 5 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 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 3H-Benzooxazole-2,2-dithiol and 3H-Benzothiazole-2,2-dithiol were successfully synthesized; as a creamy solid with melting points 147-148°C with a percentage yield of 75% and 87-90°C with a percentage yield of 80% respectively. The FTIR spectra of the ligands indicated the presence of the following functional groups: NH(3200), CN(1480), C=S(990), C-H due to aromatic (3040), C-N (1470) which were in agreement with works of [33, 35 and 25].

The metal removal from the solution using the two synthesized ligand derivatives was performed 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 results (Tables 1 and 2) 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 1: Removal Efficiency of the **3H-Benzooxazole-2,2-dithiol Ligand**

Metal	Initial Conc (ppm)	Final Conc (ppm)	pH	Removal Efficiency (%)
Cu	5.00	1.928	3.00	61.44
	5.00	1.872	5.30	62.56
	5.00	1.861	7.30	62.78
	5.00	1.421	8.50	71.58
	5.00	1.421	11.00	74.98
Fe	5.00	2.012	3.00	59.76
	5.00	1.905	5.30	61.90
	5.00	1.982	7.30	60.36
	5.00	1.204	8.50	75.92
	5.00	0.912	11.00	81.76
Zn	5.00	0.722	3.00	85.56
	5.00	0.821	5.30	83.58
	5.00	1.752	7.30	64.96
	5.00	0.625	8.50	87.50
	5.00	0.612	11.00	87.76
Ni	5.00	0.462	3.00	90.76
	5.00	0.924	5.30	81.52
	5.00	1.526	7.30	69.48
	5.00	0.782	8.50	84.36
	5.00	0.762	11.00	84.76

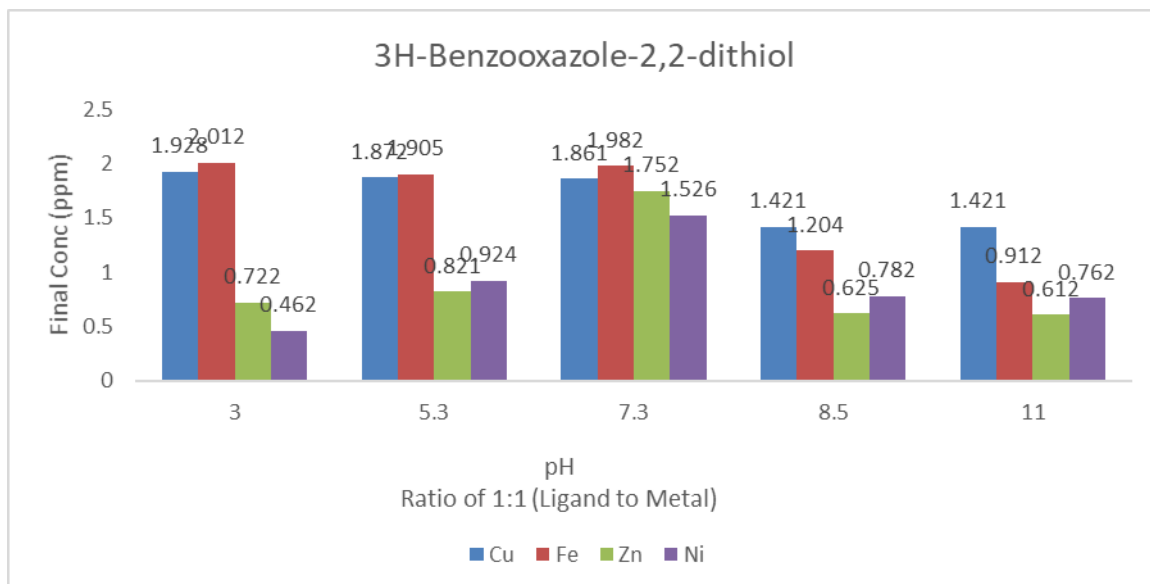Experiments were performed in triplicates; final concentration values are mean value

Fig 1: Variation of final concentration of metal with pH for **3H-Benzooxazole-2,2-dithiol Ligand**

The result as presented in Fig.1, shows that the ability of **3H-Benzooxazole-2,2-dithiol Ligand** to remove the selected heavy metals was more effective in the removal of Nickel at pH of 3.00 with a final concentration of 0.462 ppm. The lowest removal was observed for iron with a final concentration of 2.012 ppm. Zinc showed its highest removal at pH11.00 with final concentration of 0.612 ppm, whereas copper showed its highest removal also at pH 11.00 with the final concentration of 1.421ppm.

The plot of percentage removal efficiency of **3H-Benzooxazole-2,2-dithiol** at the various pH values (Fig. 2) indicates that the highest percentage removal efficiency (90.76%) was observed for Nickel at pH of 3.00 while recording the lowest removal efficiency of 59.76% at the pH of 3.00 with iron. Zinc experienced highest removal at pH 11.00 with 87.76% whereas Copper did at pH 11.00 with the % removal of 74.98%. This suggests that the metal removal efficiency of **3H-Benzooxazole-2,2-dithiol** may depend on the pH of the medium.
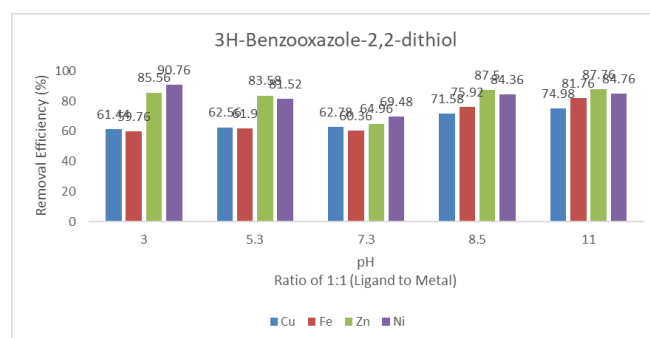

Fig 2: Effect of pH on % metal removal efficiency of **3H-Benzooxazole-2,2-dithiol** ligand

Table 2: Removal Efficiency of the Ligand **3H-Benzothiazole-2,2-dithiol**

Metal	Initial Conc (ppm)	Final Conc (ppm)	pH	Removal Efficiency (%)
Cu	5.00	1.602	3.00	67.96
	5.00	1.416	5.30	71.68
	5.00	1.214	7.30	75.72
	5.00	0.962	8.50	80.76
	5.00	0.618	11.00	87.64
Fe	5.00	1.962	3.00	60.76
	5.00	1.624	5.30	67.52
	5.00	1.242	7.30	75.16
	5.00	0.621	8.50	87.58
	5.00	0.341	11.00	93.72
Zn	5.00	0.612	3.00	87.76
	5.00	0.422	5.30	91.56
	5.00	0.912	7.30	81.76
	5.00	0.524	8.50	89.52
	5.00	0.218	11.00	95.64
Ni	5.00	0.321	3.00	93.58
	5.00	0.532	5.30	89.36
	5.00	0.564	7.30	88.72
	5.00	0.922	8.50	81.56

	5.00		1.012	11.00	79.76

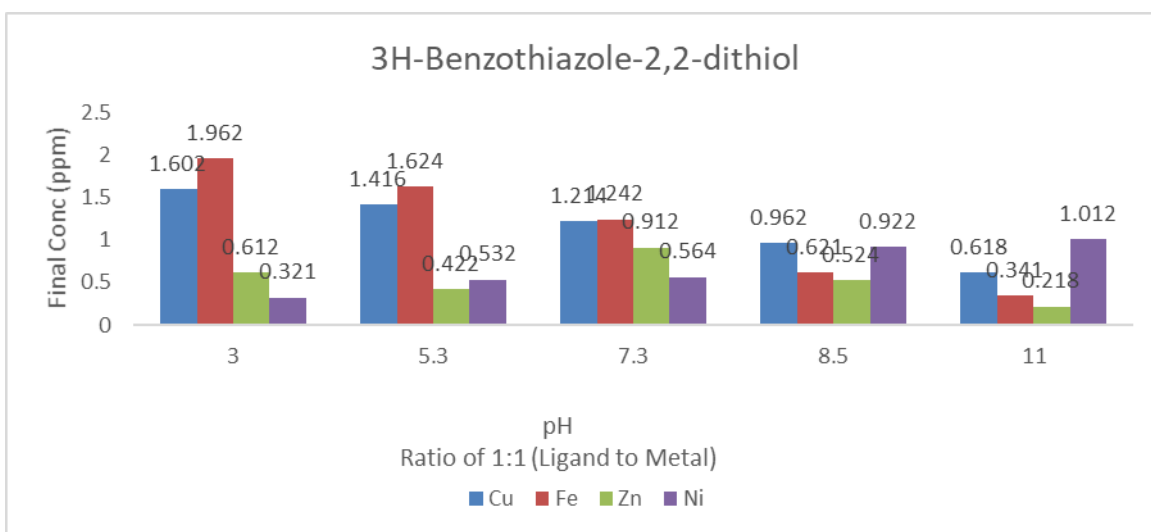Experiments were performed in triplicates; final concentration values are mean value

Fig 3: Variation of final concentration with pH values for *3H-Benzothiazole-2,2-dithiol* ligand

The ability of *3H-Benzothiazole-2,2-dithiol* ligand to remove the selected heavy metals (Table 2) was more evident in the removal of zinc at pH of 11.00 with the final concentration of 0.218 ppm while the lowest removal was recorded for iron with a final concentration of 1.962ppm at the pH of 3.00. Copper showed its highest final concentration at 1.602ppm at pH 3.00 and lowest at 0.618ppm at pH of 11.00 whereas Nickel had its highest final concentration at 1.012ppp at pH 11.00 with the lowest at 0.321ppm at pH 3.00. The result as displayed on Fig. 4 reveals the effect of pH on *3H-Benzothiazole-2,2-dithiol* ligand's ability to remove heavy metals. The highest percentage removal efficiency (95.64%) was observed in the removal of zinc at pH of 11.00 while showing the lowest removal efficiency of 60.76% at the pH of 3.00 with iron. The observed low efficiency may be attributed to the unstable nature of most of the compounds at pH values less than four [38].
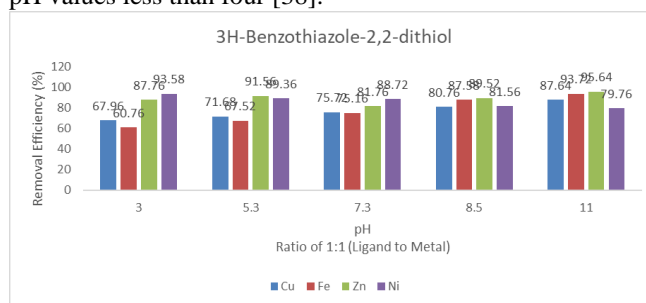

Fig 4: Effect of pH on metal removal efficiency

3H-Benzothiazole-2,2-dithiol of ligand

Table 3: Comparison of metal removal efficiencies of both Ligands

Metal	Initial Conc (ppm)	pH	% Removal of 3H-Benzooxazole-2,2-dithiol	% Removal of *3H-Benzothiazole-2,2-dithiol*
Cu	5	3.00	61.44	67.96
		5.30	62.56	71.68
		7.30	62.78	75.72
		8.50	71.58	80.76
		11.0	74.98	87.64
Fe		3.00	59.76	60.76
		5.50	61.90	67.52
		7.30	60.36	75.16
		8.50	75.92	87.58
		11.0	81.76	93.72
Zn		3.00	85.56	87.76

		5.30	83.58	91.56
		7.30	64.96	81.76
		8.50	87.50	89.52
		11.0	87.76	95.64
Ni		3.00	90.76	93.58
		5.30	81.52	89.36
		7.30	69.48	88.72
		8.50	84.36	81.56
		11.0	84.76	79.76

Comparing metal removal efficiencies of the two ligands at different pH values, it was observed that the *3H-Benzothiazole-2,2-dithiol* ligand exhibited better metal removal efficiencies at almost all the different pH values, except for Ni at pH 8.50 and 11.0. 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 *3H-Benzothiazole-2,2-dithiol* ligand has a better percentage removal efficiency of the metals than the *3H-Benzooxazole-2,2-dithiol* ligand. This may be attributed to its high bonding ability for heavy metals [39]. The results indicated that the lowest removal efficiency of the *3H-Benzooxazole-2,2-dithiol* ligand was 59.76% with Fe at a pH value of 3.00, whereas the removal efficiency of the *3H-Benzothiazole-2,2-dithiol* with same metal at the same pH was 60.76%.

Results also indicated that the highest percentage removal efficiency for both ligand and for all the metals was at the same pH value 11.0. However, this observation is not true for Nickel which gave its highest removal at pH 3.00 with a percentage of 93.58%. Coincidentally, this observation supports the fact that the removal efficiency of the metal basically depends on the type of ligand that is used [40]. It was also observed that the Zinc metal was better removed than any of the other metals using both ligands giving a % removal of 95.64% at pH 11.0 whereas iron was the least removed with efficiency of 59.76% for the *3H-Benzooxazole-2,2-dithiol* ligand at pH 3.

The results of ligand used in this study was also compared with that of dibenzyldithiocarbamate which was used in the removal of Cd, Zn, Cu and Pb as reported by Abu-El-Halawa and Zabinb [1]. It was observed that the difference in the removal is minimal. 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.

IV. CONCLUSION

This work has shown that the *3H-Benzothiazole-2,2-dithiol* ligand is more effective than the *3H-Benzooxazole-2,2-dithiol* ligand in the removal of the selected heavy metals at the same pH. Therefore, the 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 zinc at pH 11.0 using *3H-Benzothiazole-2,2-dithiol* with the % 0f 95.64% and Nickel at pH 3.00 using *Benzooxazole-2,2-dithiol* with the % of 90.76%.

This therefore, gives a viable approach for treatment of polluted water containing heavy metal ions.

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