



# Removal of Chemical and Biological Contaminates From the Industrial Zone in Menoufia North Egypt Using a Modified Sponge Reactor

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## Abstract

Although water constitutes about 71% of the earth, only 1.2% is allowed to us as drinking water and agriculture, while the bulk portion of the earth's water is saline ocean water. Due to the unjustified human interference with the environment, the major portion of water available for drinking and agriculture is now rapidly getting polluted. Adverse impact of water pollution causes multiple life threatening diseases as diarrhea, cholera, typhoid, dysentery and polio. Conventional technologies like physiochemical and biological methods have developed to treat the contaminated water, however, treatment method which maximum efficiency in removal all kinds of pollutants in still for being realized. Novel water treatment technology using a Hanging Sponge Reactor has developed. Study has focus on modeling and experiment measurement under laboratory and field conditions. The heavy metal ions present in industrial wastewater were copper(II), nickel(II), cadmium(II), Cobalt(II), zinc(II), ferric(III), lead(II) and chromium(III). Firstly, the laboratory study was held at 27°C using above metal ions at different concentration ratios of the ligand (L) and metal salts(M) as [2L: 1M] and [2L: 5M]. The results revealed that, the efficiency of heavy metals and bacterial removal were enhanced by increasing concentration of the organic ligand to the metal salts .At [2 L:1M] molar ratio at 27° C, the removal efficiency of heavy metals were in the range of [10% - 22%] after 30 min and it was elevated to [13% - 46%] after 60 min, while at 27 °C and(2L:5M) molar ratio .the removal efficiency elevated to (6.57%-33%) after 30 min and to (15%-70%) at 60 min. using a Hanging Sponge Reactor without organic ligand the result showed , the removal of chemical, biological parameters and also heavy metal increased with time. Also, using Hanging Sponge Reactor the result showed that. In presence 2.0 mg/L for one hour, the COD decreased 73.95%, TSS decreased 96.6%, BOD decreased 65.1% at 27°C, TS decreased 89.54%, TN decreased 71.43, TB decreased 54.43%, DO decreased 43.33%, VSS decreased 66.52% and TKN decreased 69.4% and the heavy metals decreased (75.0%-94.29%) range. However, using 2.0 mg/L for three hours, the results showed COD decreased 78.6%, TSS decreased 97.1%, BOD decreased 68.5%, at 27°C, TS decreased 92.0%, TN decreased 77.14, TB decreased 58.23%, DO decreased 56.7%, VSS decreased 70.9% and TKN decreased 75.31%, respectively and at one hour the heavy metals decreased (80.95%-95.99%) range and fecal coliforms decreased in both cases decreased (99.9%). In the case of using 4.0 mg /L for three hours the result showed COD decreased 86.84%, TSS decreased 97.35%, BOD decreased 76.8% at 27°C, TS decreased 95.7%, TN decreased 85.14, TP decreased 73.42%, DO

decreased 73.3%, VSS decreased 82.8% and TKN decreased 86.6% and the heavy metal decreased (84.64-98.1%) range, and for fecal coliforms decreased in both cases (99.9 %).

## Keywords

Organic Ligand, Hanging Sponge Reactor, Removal of Notorious Heavy Metal, Fecal Coliforms

## 1. Introduction

There are direct relations between water uses and is required quality. The most diamonding use can be consider domestic water supply , which requires than satisfaction of various quality criteria , conversely , the less diamonding uses are simples dilution and transportation of water which don't have any specific requirements in terms of quality . Water pollution is the addition of substance or energy forms that directly or indirectly alter the nature of the water body in such manner than negatively affects its legitimate uses. The basic pollution problems still need to be react with and the whole array of pollutants needs to be take lead [1-2].Wastewater treatment is a processes which removes and illuminate contaminate from wastewater and converts this into an effluent that can be returned to the water cycle, once returned the water cycle, the effluent creates an acceptable impact on environment to be reused for various purposes [1]. There are several kinds of wastewater which are treated at the aproperat type of wastewater plant. For domestic water, the treatment plant is called sewage treatment. For in dusterial wastewater, treatment takes place in dusterial wastewater treatment. A processes commonly used in wastewater treatment include biologic and chemical processes [3-5]. The main purpose of wastewater treatment is for the treated wastewater to be able to be purposed or reused safely [6-8].Waste water is treated in three phases, primary (solid removal), secondary (bacterial decomposition) and tertiary (extra filtration). There are thousands components of waste water that remains undetected disposed from modern society that also end up in sludge which has been proven to be hazards to both human and ecological health [9-10]. The main purpose of the manuscript is directed to use Hanging Sponge Reactor in presence of friendly organic ligand for treatment chemical and biological industrial waste water pollutants.

## 2. Materials and Instruments

### 2.1 Chemicals

All reagents employed for the preparation of organic ligand and its metal complexes in the laboratory were of the analytical grade and used without further purification. Metal salts were provided from Sigma-Aldrich Company. 4-amino salicylic acid (Assay  $\geq 99.99$  %), ethylenediamine (Assay  $\geq 98$  %),  $H_2SO_4$  (Assay 99.7%) and ethanol (Assay  $\geq 99.8$  %) were also obtained from Sigma-Aldrich Company.

### 2.2 Instrumentation and Measurements

The ligand and its metal complexes were analyzed for C, H, N, Cl and M at the Micro Analytical Center, Cairo University, Egypt. Standard analytical methods were used to determine the metal ion content [11].  $^1H$ -NMR spectra were obtained on bruker 400 MHz spectrometer. Chemical shifts (ppm) were reported relative to TMS. FT-IR spectra of the ligand and its metal complexes were measured using KBr discs by a Jasco FT/IR 270E Fourier transform infrared spectrophotometer covering the range  $4000-400\text{ cm}^{-1}$ . Electronic spectra in the 200-900 nm regions was recorded on a Perkin-Elmer 550 spectrophotometer. Magnetic susceptibilities were measured at  $27^\circ\text{C}$  by the Gouy method using mercuric tetrathiocyanatocobaltate(II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal's constant. The magnetic moments were calculated from the equation:

$$(\mu_{\text{eff}} = 2.828 (\chi_n \times T)^{1/2})$$

The molar conductance of  $10^{-3}$  M solution of the complexes in DMSO was measured at  $27^\circ\text{C}$  with a Bibby conductometer type MCl. The ESR spectra of solid complexes at room temperature were recorded using a varian E-109 spectrophotometer; DPPH was used as a standard material. The TLC of all compounds confirmed their purity.

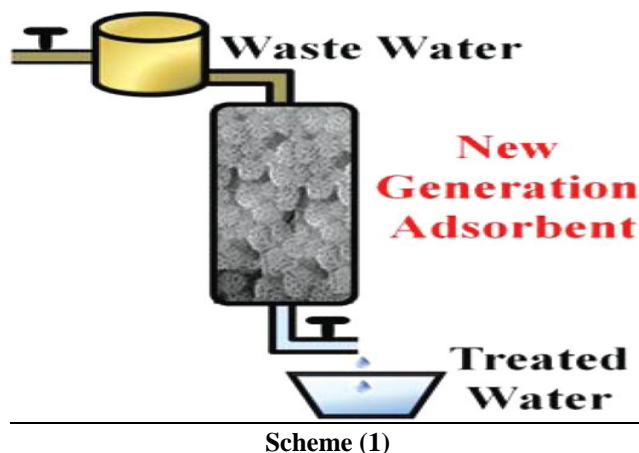
### 2.3 Laboratory Preparation

The ligand, ( $H_2L$ ) was synthesized by boiling (10.0 g, 0.6 mol) of 4-aminosalicylic acid in  $50\text{ cm}^3$  of ethanol solution in the presence of 5 drops of conc.  $H_2SO_4$  for two hours. Leave it to cool at room temperature to give 4-aminosalicylic ester that was mixed with (8.0 g, 0.4 mol) ethylenediamine. The solution was refluxed with stirring for another two hours at  $80^\circ\text{C}$ , then left to cool at room temperature. The precipitated product was filtered off then dried in air. (Figure 1) and the metal complexes were prepared using (2L: 1M) and (2L: 5M) molar ratios, in ethanol using metal acetates, chlorides, nitrates and sulphates.

### 2.4 Hanging Sponge Reactor System

The Hanging Sponge Reactor module column as shown below in scheme (1) consists of four identical segments connected vertically, each segment will be equipped with 27 L of polyurethane foam (PF) warped with plastic material randomly distributed in the whole reactor. The Hanging Sponge Reactor system was made of PVC, with a capacity of  $0.3\text{ m}^3$  and has an internal diameter of 0.16 m. The height of the reactor is 0.88 m. The reactor was filled with PF which represents 34% of the total liquid reactor volume. The characteristics of the PF (sponge) are surface area  $276\text{ m}^2/\text{m}^3$ ,

density  $27 \text{ kg/m}^3$ , void ratio 0.9, and pore size of 0.63 mm. The total volume of the PF will be 100 L. The dimensions of the used sponge (PF) (cylindrical shape) will be 27 mm height  $\times$  4mm diameter. The wastewater effluent was flowed by gravity to the distributor which will be located on the top of the Hanging Sponge Reactor module and will be rotated at 15 rpm. Chemical and biological parameters will be monitored at retention time one and three hrs according to APHA (2005) "Standard Methods for the examination of water and waste water".



### 2.5 Preparation of metal ligand complexes in the laboratory

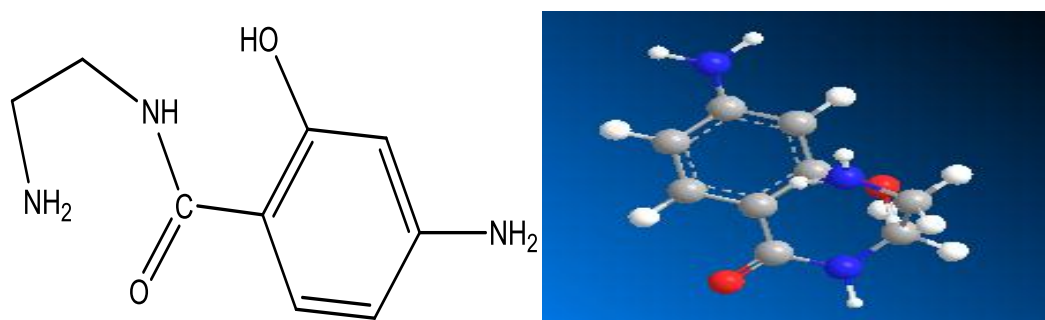
**Ligand ( $H_2L$ )** : Chemical Formula :  $C_9H_{13}N_9O_2$  , M.Wt : 195 , Color : yellowish white , M.P :  $275 \text{ }^\circ\text{C}$  , Cond :  $3.45 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$ ; Elemental analysis; Calc, C 55.38, H, 6.67, N, 21.54, Found (%), C, 55.12, H, 6.42, N, 21.13

**IR spectra** :  $\nu(\text{H-Bond}) = 3060\text{-}3320 \text{ cm}^{-1}$  ,  $\nu(\text{OH}) = 3490, 1280 \text{ cm}^{-1}$  ,  $\nu(\text{C=O}) = 1605 \text{ cm}^{-1}$  ,  $\nu(\text{Ar}) = 1497, 750 \text{ cm}^{-1}$  ,  $\nu(\text{NH}) = 3195 \text{ cm}^{-1}$   $\nu(\text{NH}_2) = 3440, 3415 \text{ cm}^{-1}$

**$^1\text{H-NMR}$** : N-CH<sub>2</sub> 3.52 ppm, Ar 6.1-8.1 ppm rang, OH 11.3 ppm NH-CO 5.32 ppm NH<sub>2</sub> 2.5 ppm

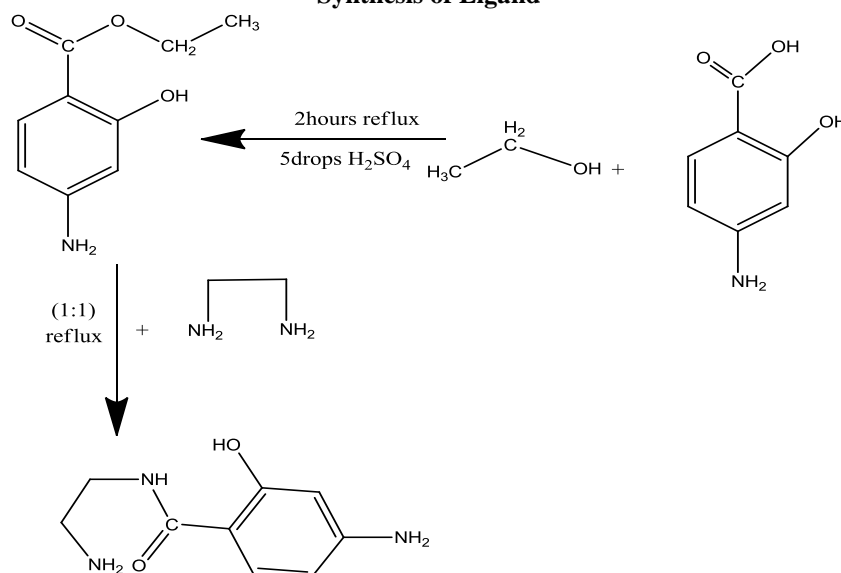
**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub>= 30 amu, m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> =74 amu , m/z, H<sub>3</sub>NO =33 amu , m/z, C<sub>2</sub>H<sub>7</sub>N<sub>2</sub>O =108 amu , m/z, C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> =95 amu

**UV-vis** : 280 nm, 315 nm due to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and charge transfer transitions.

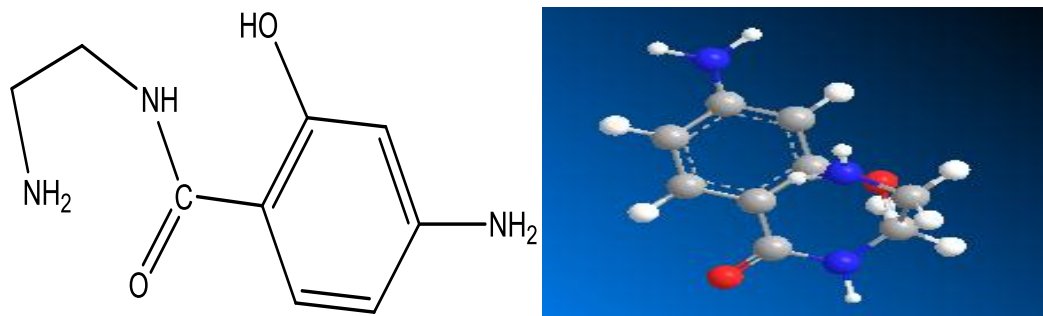


The ligand and 3D are shown in **Fig. (1)**

### Synthesis of Ligand



The structure of the organic ligand



The structure of the organic ligand and 3D are shown in **Fig. (2)**

**Complex (1), (2L: 1 M) Cu(OAc)<sub>2</sub> · H<sub>2</sub>O**

**Chemical Formula** : C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>10</sub>Cu , M.Wt : 608 , Color : yellowish brown , M.P : >300 °C, Cond : 7.45 Ω<sup>-1</sup> mol<sup>-1</sup>cm<sup>-1</sup>; Elemental analysis; Calc, C 43.42, H, 5.92, N, 15.91, Cu, 11.99 Found (%), C, 40.23, H, 3.51, N, 15.52, Cu, 10.52

**IR spectra** : ν(H<sub>2</sub>O) = 3060 - 3210 cm<sup>-1</sup> , ν(H-Bond) = 3070 - 3210 cm<sup>-1</sup> , ν(OH) = 3445,3375 ,1260,127 cm<sup>-1</sup> , ν(C=O) = 1637 cm<sup>-1</sup> , ν(Ar) = 1427,1402 cm<sup>-1</sup> , 770,750 cm<sup>-1</sup> , ν(OAc) = 1420,133 cm<sup>-1</sup> , ν(CuO) = 615 cm<sup>-1</sup> , ν(CuN) = 560 cm<sup>-1</sup>

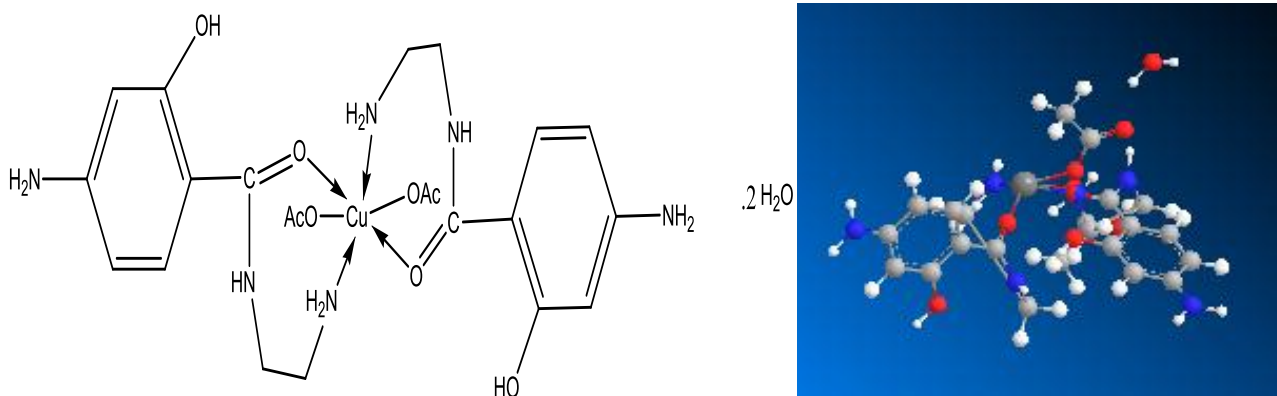
**μ<sub>eff</sub>** : 1.71 B.M

**Mass spectrum** : m/z, H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> = 66 amu , m/z, C<sub>6</sub>H<sub>6</sub>NO =108 amu , m/z, C<sub>9</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub> =195 amu , m/z, C<sub>22</sub>H<sub>16</sub>N<sub>6</sub>O<sub>10</sub> = 608 amu .

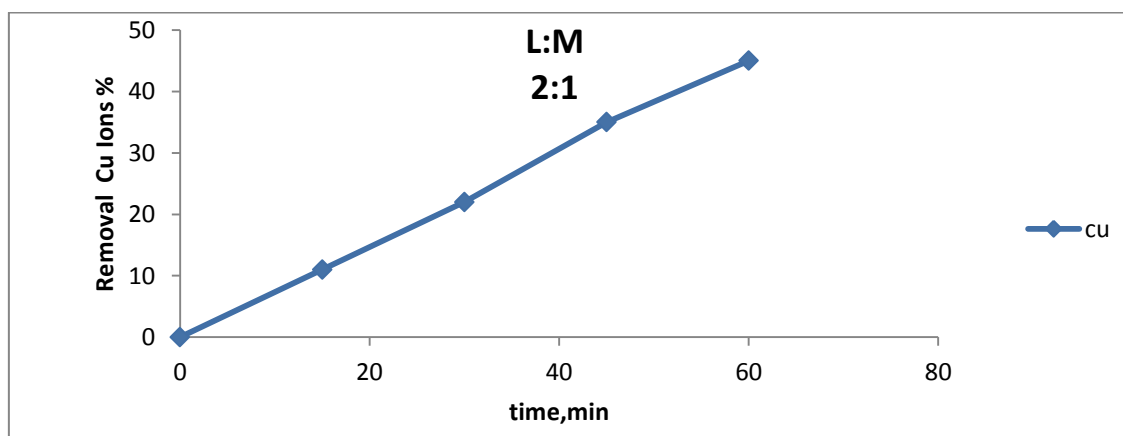
**UV-vis** : 290 nm , 310 , 415 , 570 , 610 nm due to π→π\* , n→π\* and d-d transitions .

**ESR** : g<sub>iso</sub> =2.09

**Octahedral structure with covalent bond character**



**Fig. (3)** Complex (1)



**Chart (1)** Removal of Cu ions % against time using (2L:1M)

At 27 °C (2L : 1M)

|        |       |
|--------|-------|
| 15 min | 3.5 % |
| 27 min | 7 %   |
| 45 min | 10.5% |
| 60 min | 13 %  |

**Complex (2), (2L: 5 M)  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$** 

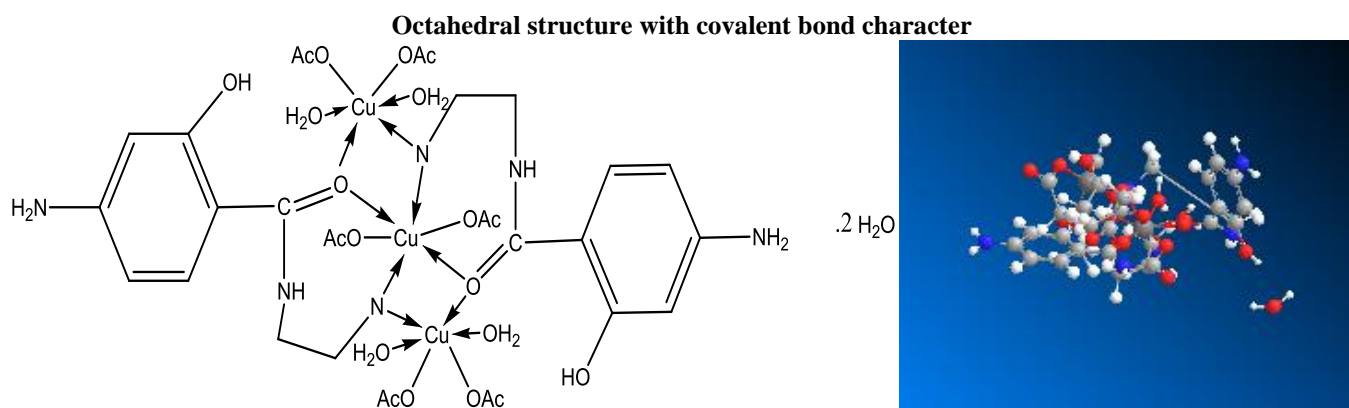
**Chemical Formula** :  $\text{C}_{27}\text{H}_{52}\text{N}_6\text{O}_{22}\text{Cu}$  , M.Wt : 1040 , Color : Brown , M.P :  $>300\text{ C}$  , Cond :  $8.45\ \Omega^{-1}\ \text{mol}^{-1}\text{cm}^{-1}$  ; Elemental analysis; Calc., C 34.62, H, 5.0, N, 8.19, Cu, 18.26 Found (%), C, 34.52, H, 4.81, N, 7.71, Cu, 17.52

**IR spectra** :  $\nu(\text{H}_2\text{O}) = 3065 - 3320\ \text{cm}^{-1}$  ,  $\nu(\text{H-Bond}) = 3600 - 3310\ \text{cm}^{-1}$  ,  $\nu(\text{OH}) = 3420, 3392, 1310, 1265\ \text{cm}^{-1}$  ,  $\nu(\text{Ar}) = 1520, 1492, 780, 730\ \text{cm}^{-1}$  ,  $\nu(\text{NO}_3) = 1327, 1230\ \text{cm}^{-1}$  ,  $\nu(\text{Cu O}) = 605\ \text{cm}^{-1}$  ,  $\nu(\text{CuN}) = 592\ \text{cm}^{-1}$

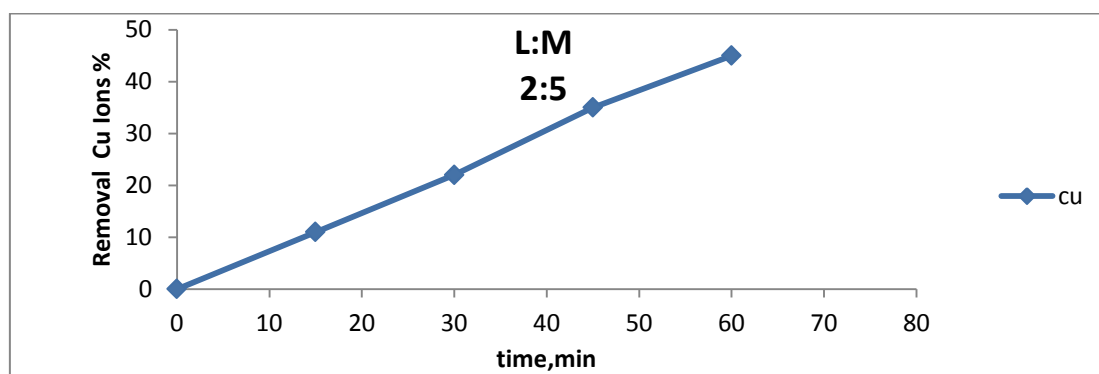
$\mu_{\text{eff}}$  : VDV 1.63B.M

**Mass spectrum** :  $m/z\ \text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_8 = 324\ \text{amu}$  ,  $m/z\ \text{C}_{18}\text{H}_{34}\text{N}_6\text{O}_{10} = 342\ \text{amu}$  ,  $m/z\ \text{C}_{18}\text{H}_{34}\text{N}_2\text{O}_4 = 728\ \text{amu}$  ,  $m/z\ \text{C}_{12}\text{H}_{24}\text{N}_8\text{O}_{28} = 1058\ \text{amu}$  ,

**UV-vis** : 290 nm, 315, 476, 605 nm due to  $\pi \rightarrow \pi^*$  ,  $n \rightarrow \pi^*$  and d-d transitions .



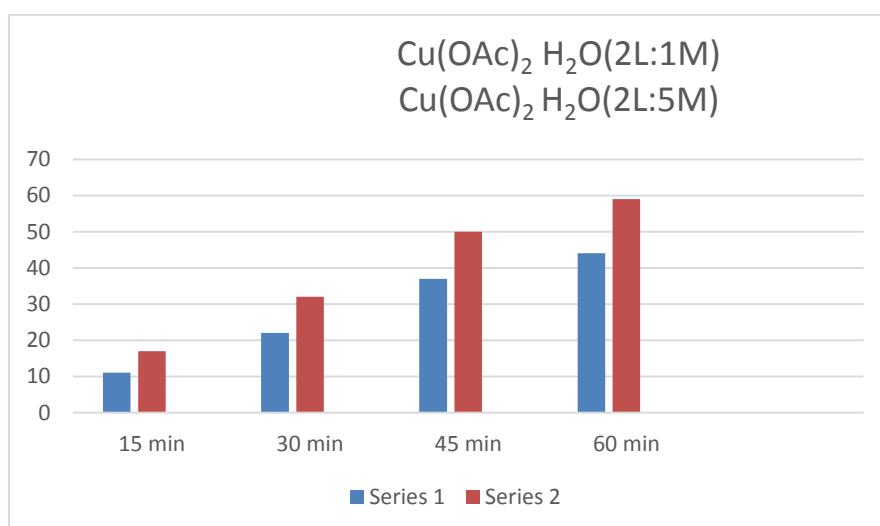
**Fig. (4)** Complex (2)



**Chart (2)** Removal of Cu ions % against time using (2L: 5M)

At  $27\text{ }^\circ\text{C}$  (2L : 1M)

|        |        |
|--------|--------|
| 15 min | 6.5 %  |
| 27 min | 12.5 % |
| 45 min | 17.5%  |
| 60 min | 23 %   |



**Chart (3)** Removal of Cu ions % for complexes (1) and (2)



**Complex (3), (2L: 1M), Cu(Cl)<sub>2</sub> · 2H<sub>2</sub>O**

**Chemical Formula** : C<sub>18</sub>H<sub>27</sub>N<sub>6</sub>O<sub>6</sub>Cl<sub>2</sub>Cu , M.Wt : 558 , Color : Brown , M.P : >300 C , Cond : 6.75 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis; Calc. C, 38.71, H, 4.84, N, 12.72, Cu, 11.34 , Found (%), C, 38.52, H, 4.61, N, 12.11, Cu, 11.01

**IR spectra** : ν(H<sub>2</sub>O) = 3070 - 3327 cm<sup>-1</sup>, 3320-3127 cm<sup>-1</sup>, ν(H-Bond) = 3600 - 3360 cm<sup>-1</sup>, 3300 - 2865 cm<sup>-1</sup>, ν(OH) = 3410, 3400 cm<sup>-1</sup>, ν(C=O) = 1646, 1615 cm<sup>-1</sup>, ν(NH) = 3275 cm<sup>-1</sup>, ν(OH) = 3300, 1290 cm<sup>-1</sup>, ν(CuO) = 620 cm<sup>-1</sup>

$\mu_{eff}$  : 1.70 B.M

**Mass spectrum** : m/z, C<sub>7</sub>H<sub>6</sub>NO<sub>2</sub> = 136 amu , m/z, C<sub>9</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub> = 195 amu , m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> = 131 amu , m/z, C<sub>18</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>C<sub>12</sub>Cu = 558 amu ,

**UV-vis** : 296 nm , 317 , 456 , 580 , 605 nm due to π→π\* , n→π\* and d-d transitions .

**ESR** : g<sub>11</sub> = 2.14 g<sub>1</sub> = 2.05 g<sub>iso</sub> = 2.08

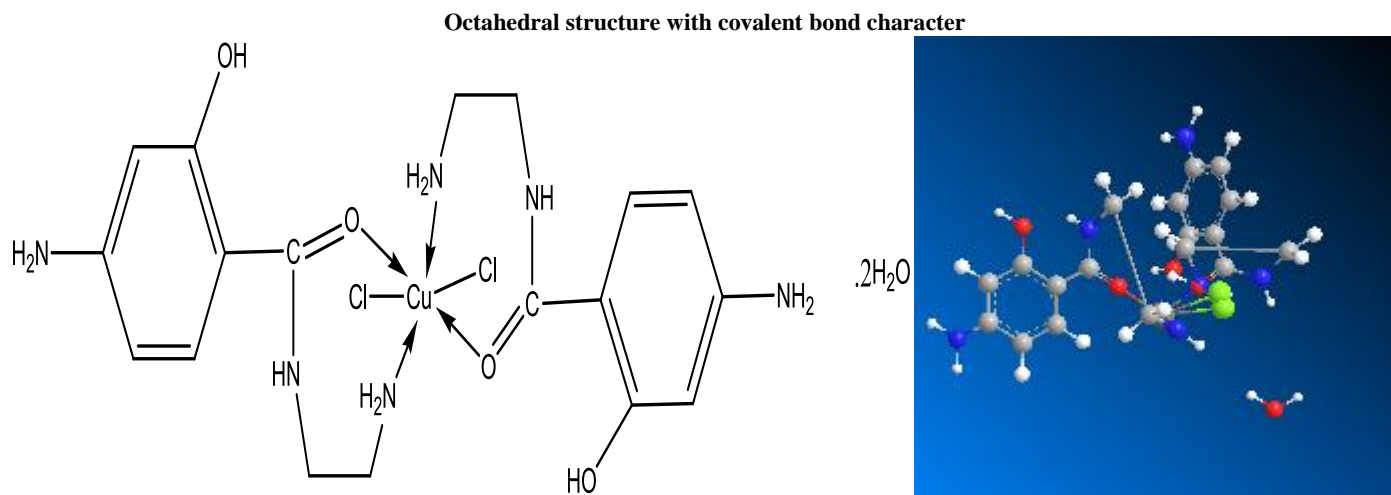


Fig. (5) Complex (3)

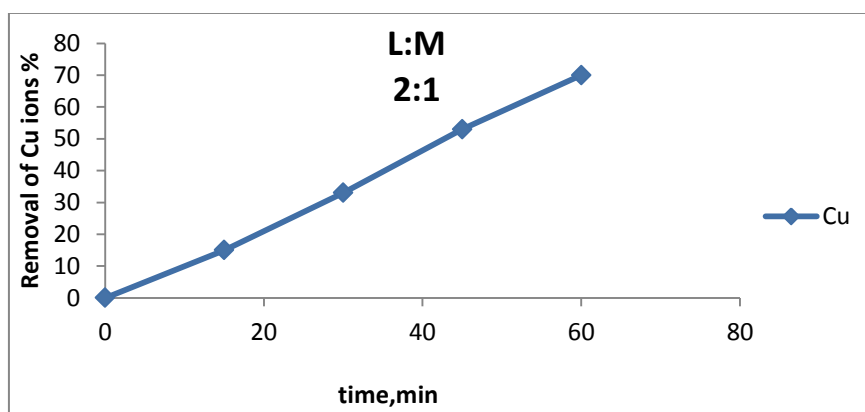


Chart (4) Removal of Cu ions % against time using (2L:1M)

At 27 °C (2L : 1M)

|        |       |
|--------|-------|
| 15 min | 4 %   |
| 30 min | 8.5 % |
| 45 min | 12 %  |
| 60 min | 15 %  |

**Complex (4), (2L:5M) Cu (Cl)<sub>2</sub> · 2H<sub>2</sub>O**

**Chemical Formula** : C<sub>18</sub>H<sub>30</sub>N<sub>6</sub>O<sub>10</sub>Cl<sub>6</sub>Cu<sub>3</sub> , M.Wt : 900 , Color : Brown , M.P : >300 C , Cond : 8.49 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis; Calc.; C, 24.0, H, 3.81, N, 9.33, Cu, 21.67 , Found (%); C, 23.56, H, 3.62, N, 8.82, Cu, 21.45,

**IR spect** : ν(H<sub>2</sub>O) = 3080 - 3332 cm<sup>-1</sup>, 3320-3150 cm<sup>-1</sup>, ν(H-Bond) = 3600 - 3327 cm<sup>-1</sup>, 3315 - 2830 cm<sup>-1</sup>, ν(OH) = 3410, 3315 cm<sup>-1</sup>, ν(C=O) = 1639, 1619 cm<sup>-1</sup>, ν(NH) = 3275 cm<sup>-1</sup>, ν(NH<sub>2</sub>) = 3376, 3305 cm<sup>-1</sup>, ν(OAc) = 1511, 1410 cm<sup>-1</sup>, ν(OH) = 1305, 1295 cm<sup>-1</sup>, ν(CuO) = 629 cm<sup>-1</sup>

$\mu_{eff}$  : 1.71 B.M

**Mass spectrum** : m/z, C<sub>7</sub>H<sub>10</sub>NO<sub>2</sub> = 140 amu, m/z, C<sub>8</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> = 185 amu, m/z, C<sub>9</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub> = 195 amu, m/z, C<sub>12</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub> = 800 amu.

**UV-vis** : 290 nm, 315, 458, 590, 603 nm due to π→π\* , n→π\* and d-d transitions.

**ESR** : g<sub>iso</sub> = 2.08

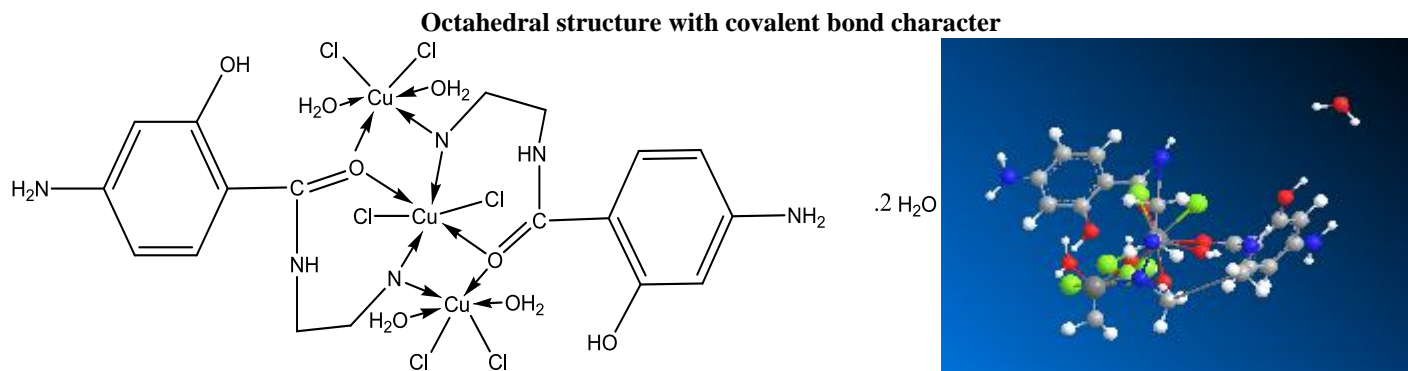


Fig. (6) Complex (4)

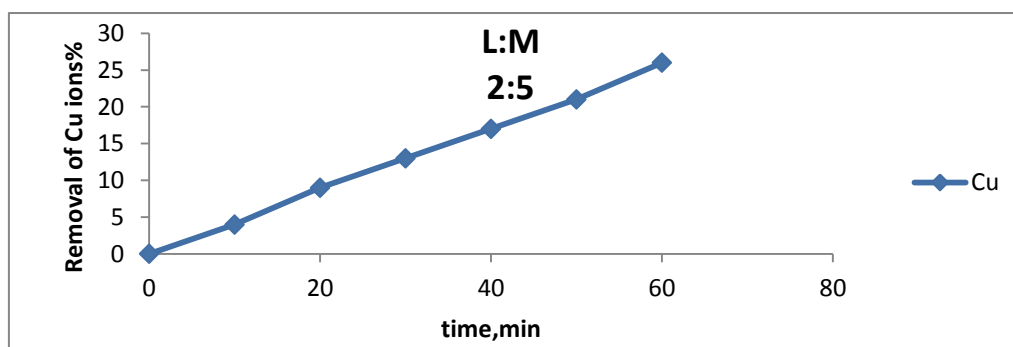


Chart (5) Removal of Cu ions % against time using (2L: 5M)

At 27 °C (2L: 5M)

|        |       |
|--------|-------|
| 15 min | 7.5 % |
| 30 min | 13 %  |
| 45 min | 20 %  |
| 60 min | 26 %  |

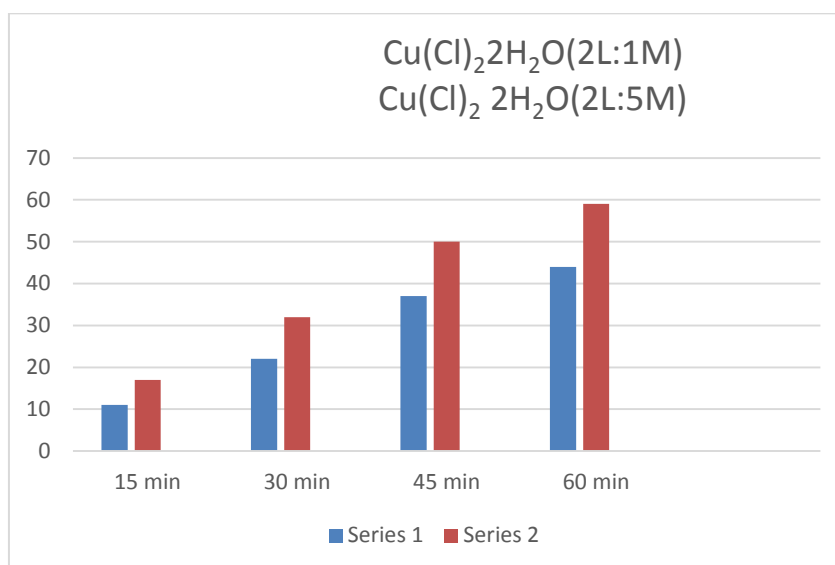


Chart (6) Removal Cu ions % complex (3) and (4)

**Complex (5), (2L: 1M) CuSO<sub>4</sub> .5H<sub>2</sub>O**

**Chemical Formula** : C<sub>18</sub>H<sub>36</sub>N<sub>6</sub>O<sub>9</sub>SCu , M.Wt : 538 , Color : yellowish Brown , , M.P : >300°C , Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis Calc. , C , 31.23, H, 4.83, N, 10.41, Cu ,11.71 , Found (%) , C,31.18 , H , 4.51 , N ,10.52 , Cu , 11.52

**IR spectra** : ν(H<sub>2</sub>O) = 3010 - 3310 cm<sup>-1</sup> , ν(H-Bond)= 3060 - 3250 cm<sup>-1</sup> , 3240- 2550 cm<sup>-1</sup> , ν(OH) = 3480 cm<sup>-1</sup> , ν(C=O)= 1650 cm<sup>-1</sup> , ν(Ar) = 1540,1490 cm<sup>-1</sup> , ν(Cu O) = 610,727 cm<sup>-1</sup> , ν(OH)= 1242,1315 cm<sup>-1</sup> , ν(CuO)= 605 cm<sup>-1</sup> , ν(CuN)= 545 cm<sup>-1</sup>

**μ<sub>eff</sub>** :1.69B.M

**Mass spectrum** : m/z H<sub>2</sub>N<sub>2</sub> , = 32 amu , m/z C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> =74 amu , m/z H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> =98amu , m/z C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> =131 amu , m/z C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> =189 amu , m/z C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> =262 amu

**UV-vis** : 295 nm , 320 , 434 , 559 , 602 nm due to π→π\* , n→π\* and d-d transitions .

**ESR** : g<sub>iso</sub> : 2.08

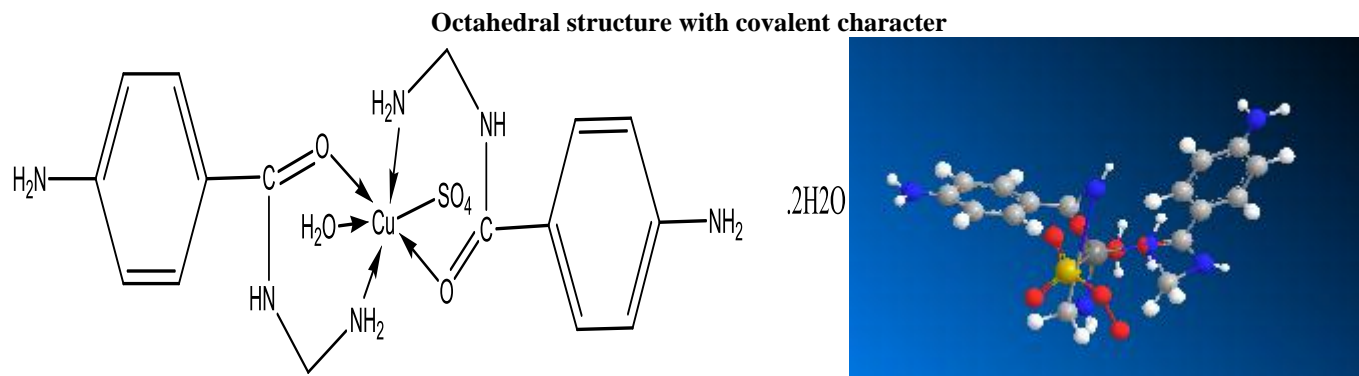


Fig. (7) Complex (5)

**Complex (6), (2L: 5M) Cu SO4.5H2O**

**Chemical Formula :**  $C_{14}H_{34}N_4O_{24}S_3Cu_3$ , M.Wt : 929 , Color : Yellowish brown , M.P :  $>300\text{ }^\circ\text{C}$  , Cond :  $9.45\ \Omega^{-1}\ \text{mol}^{-1}\ \text{cm}^{-1}$  , Elemental analysis Calc., C, 18.1, H, 3.66, N, 6.03, Cu, 20.6, Found (%)C 18.23 , H ,3.51 ,N 6.52 ,Cu ,20.52

**IR spectra :**  $\nu(\text{H}_2\text{O}) = 3010 - 3310\ \text{cm}^{-1}$  ,  $\nu(\text{H-Bond}) = 3060 - 3250\ \text{cm}^{-1}$  -  $3240 - 2550\ \text{cm}^{-1}$  ,  $\nu(\text{OH}) = 3480\ \text{cm}^{-1}$  ,  $\nu(\text{C=O}) = 1650\ \text{cm}^{-1}$  ,  $\nu(\text{Ar}) = 1540, 1490\ \text{cm}^{-1}$  ,  $\nu(\text{Cu O}) = 610, 727\ \text{cm}^{-1}$  ,  $\nu(\text{OH}) = 1242, 1315\ \text{cm}^{-1}$  ,  $\nu(\text{CuO}) = 605\ \text{cm}^{-1}$  ,  $\nu(\text{CuN}) = 545\ \text{cm}^{-1}$

$\mu_{\text{eff}} : 1.69\ \text{B.M}$

**Mass spectrum :**  $m/z\ \text{H}_2\text{N}_2 = 32\ \text{amu}$  ,  $m/z\ \text{C}_3\text{H}_{10}\text{N}_2 = 74\ \text{amu}$  ,  $m/z\ \text{H}_6\text{N}_2\text{O}_4 = 98\ \text{amu}$  ,  $m/z\ \text{C}_5\text{H}_{11}\text{N}_2\text{O}_2 = 131\ \text{amu}$  ,  $m/z\ \text{C}_7\text{H}_{13}\text{N}_2\text{O}_2 = 189\ \text{amu}$  ,  $m/z\ \text{C}_{10}\text{H}_{22}\text{N}_4\text{O}_4 = 262\ \text{amu}$

**UV-vis :** 295 nm, 320, 434, 559, 602 nm due to  $\pi \rightarrow \pi^*$  ,  $n \rightarrow \pi^*$  and d-d transitions.

**ESR :**  $g_{\text{iso}} : 2.08$

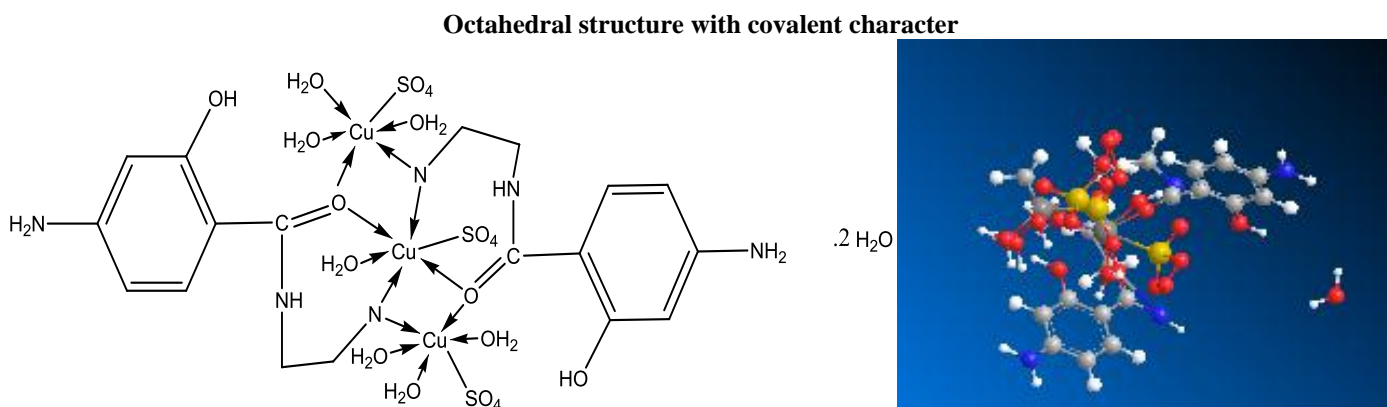


Fig. (8) Complex (6)

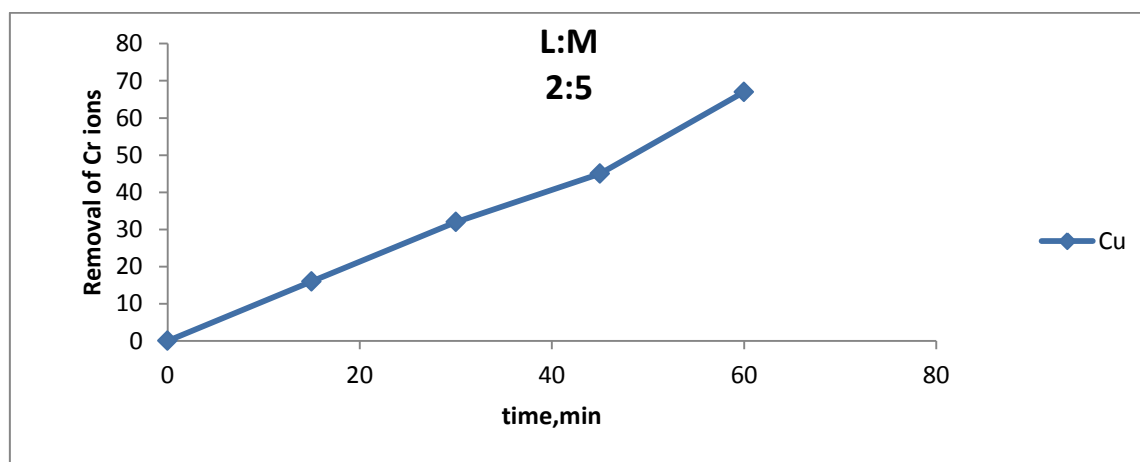


Chart (7) Removal of Cu ions % against time using (2L: 5M)

At  $27\text{ }^\circ\text{C}$  (2L: 5M)

|        |        |
|--------|--------|
| 15 min | 7.5 %  |
| 30 min | 13.5 % |
| 45 min | 20.5 % |
| 60 min | 27 %   |



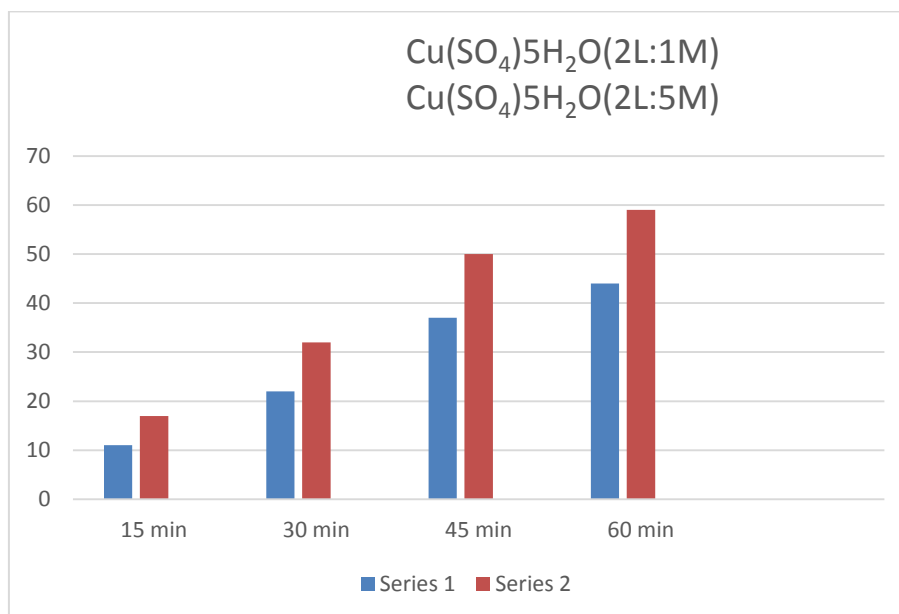


Chart (8) Removal of Cu ions % for complexes (5) and (6)

### Complex (7), (2L: 1M), Cu(NO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O

**Chemical Formula** : C<sub>14</sub>H<sub>22</sub>N<sub>6</sub>O<sub>12</sub>Cu , M.Wt : 527, Color : yellowish brown , , M.P : >300 C , Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup>, Elemental analysis Calc. ,C , 31.7, H, 4.15, N , 15.85, Cu, 11.94, Found (%) C, 31.30, H, 3.98, N, 15.56, Cu, 11.58

**IR spectra** : ν(H<sub>2</sub>O) = 3027 - 3321 cm<sup>-1</sup>, 3320-3151cm<sup>-1</sup>, ν(H-Bond)= 3600 - 3321 cm<sup>-1</sup>, 3312 - 2822 cm<sup>-1</sup>, ν(OH) = 3471, 3410 cm<sup>-1</sup>, ν(C=O)= 1637, 1617 cm<sup>-1</sup>, ν(NH) = 3271 cm<sup>-1</sup>, ν(NH<sub>2</sub>) = 3377, 3302 cm<sup>-1</sup>, ν(NO<sub>3</sub>)=1368-1210, 870 cm<sup>-1</sup>, ν(OH)= 1300, 1296 cm<sup>-1</sup>, ν(CuO)= 620 cm<sup>-1</sup>

**μ<sub>eff</sub>** : 1.70 B.M

**Mass spectrum** : m/z =273 amu C<sub>9</sub>H<sub>13</sub>N<sub>5</sub> m/z =394 amu<sup>7</sup>, m/z C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> =131 amu , m/z C<sub>18</sub>H<sub>36</sub>N<sub>6</sub>O<sub>4</sub> =466 amu , m/z C<sub>18</sub>H<sub>26</sub>N<sub>8</sub>O<sub>7</sub> =614 amu

**UV-vis**: 297 nm, 318, 457, 581, 606 nm due to π→π\*, n→π\* and d-d transitions.

**ESR** : g<sub>11</sub> = 2.16 g<sub>⊥</sub> = 2.05 and g<sub>iso</sub> = 2.08

### Octahedral structure with covalent character

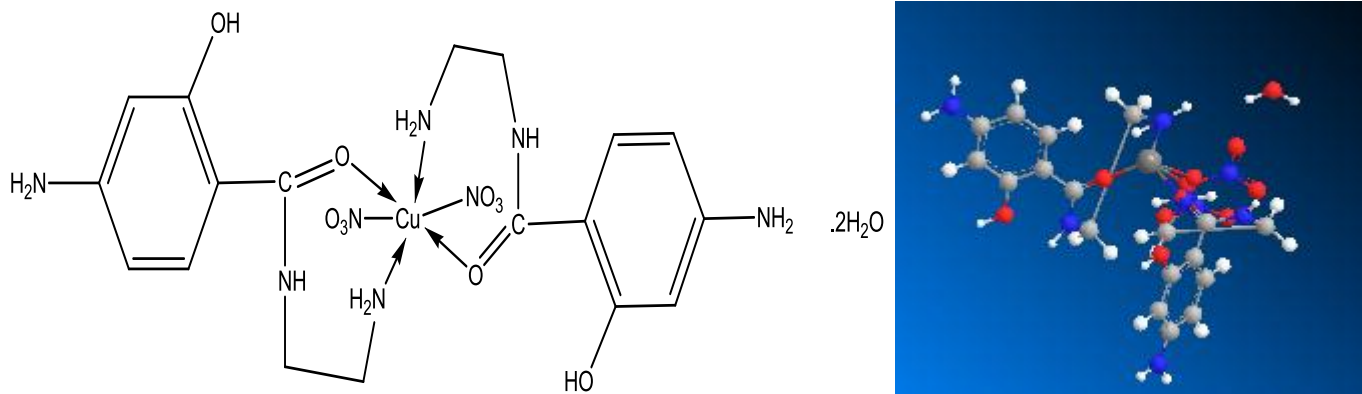


Fig. (9) Complex (7)

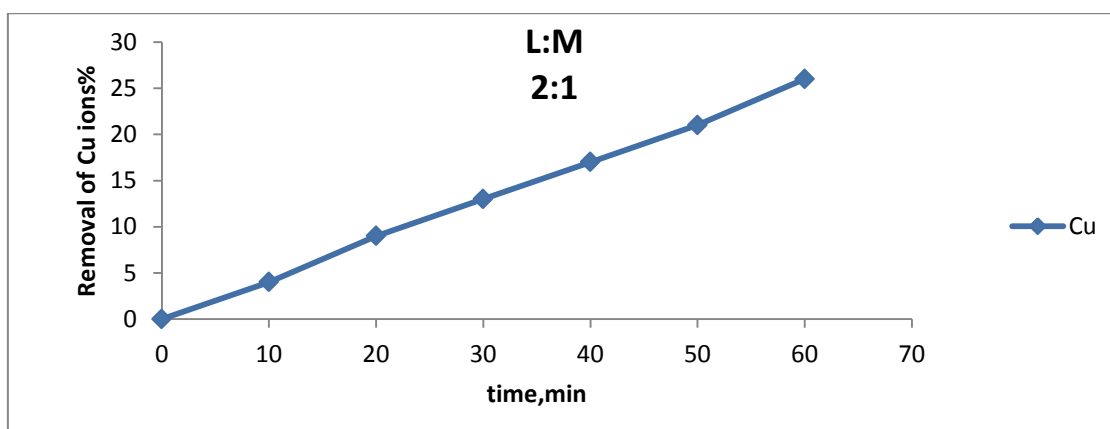


Chart (9) Removal of Cu ions % against time using (2L:1M)

At 27 °C (2L : 1M)

|        |       |
|--------|-------|
| 15 min | 3.5 % |
| 30 min | 7.5%  |
| 45 min | 12 %  |
| 60 min | 15 %  |

**Complex (8), (2L: 5M), Cu(NO<sub>3</sub>)<sub>2</sub> · 2H<sub>2</sub>O**

**Chemical Formula** : C<sub>18</sub>H<sub>34</sub>N<sub>12</sub>O<sub>28</sub>Cu<sub>3</sub>, M.Wt : 1058, Color : Brown, M.P : >300 °C, Cond : 8.15 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup>, Elemental analysis ;Calc., C, 20.42, H, 3.21, N, 15.88 Cu, 18.0, Found (%) C 20.11, H, 3.0, N, 15.65, Cu, 17.78

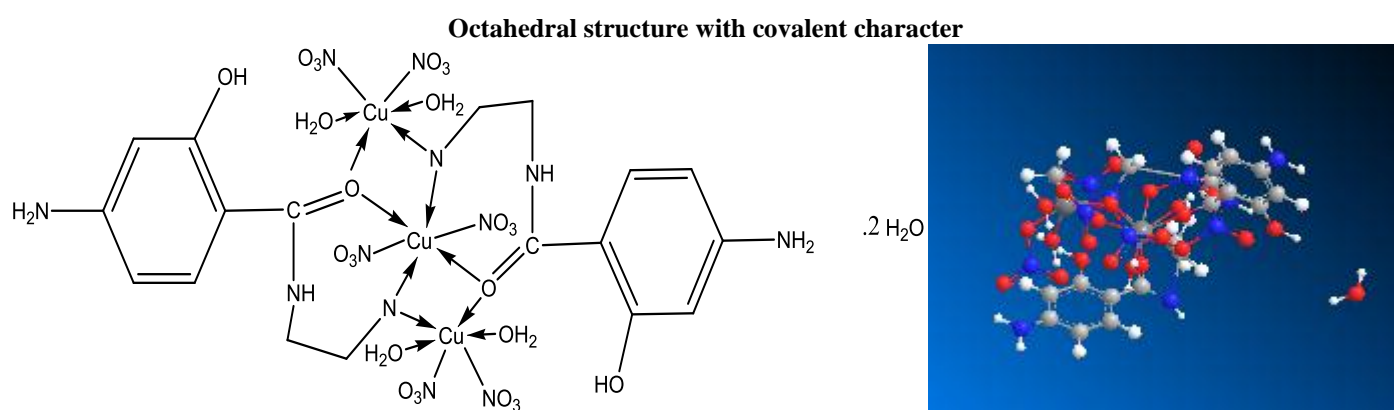
**IR spectra** :  $\nu(\text{H}_2\text{O}) = 3027 - 3321 \text{ cm}^{-1}, 3320-3151\text{cm}^{-1}, \nu(\text{H-Bond}) = 3600 - 3321 \text{ cm}^{-1}, 3312 - 2822 \text{ cm}^{-1}, \nu(\text{OH}) = 3471, 3410 \text{ cm}^{-1}, \nu(\text{C=O}) = 1637, 1617 \text{ cm}^{-1}, \nu(\text{NH}) = 3271 \text{ cm}^{-1}, \nu(\text{NH}_2) = 3377, 3302 \text{ cm}^{-1}, \nu(\text{NO}_3) = 1368-1210, 870 \text{ cm}^{-1}, \nu(\text{OH}) = 1300, 1296 \text{ cm}^{-1}, \nu(\text{CuO}) = 620 \text{ cm}^{-1}$

$\mu_{\text{eff}}$  : 1.70 B.M

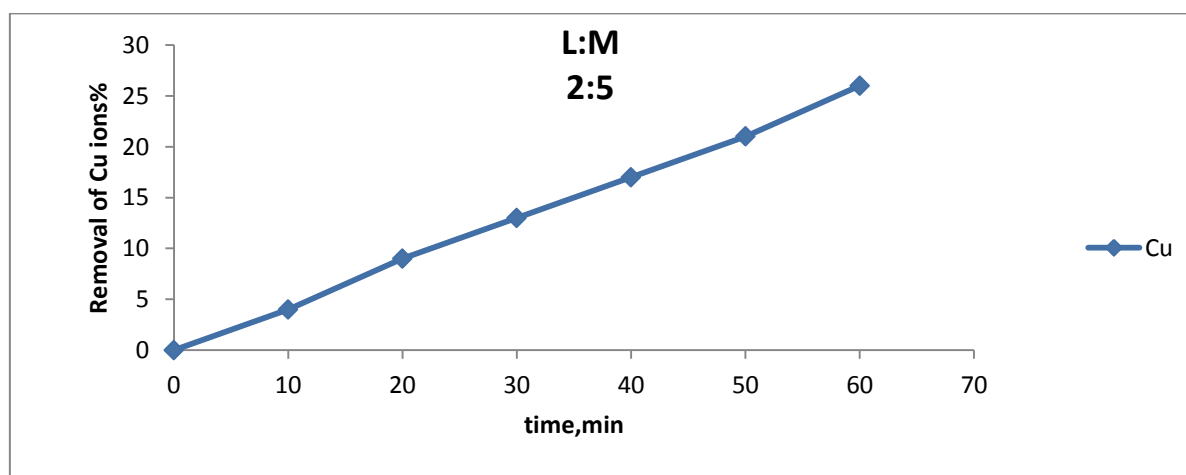
**Mass spectrum** : m/z =273 amu C<sub>9</sub>H<sub>13</sub> N<sub>5</sub> m/z =394 amu, m/z C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> =131 amu, m/z C<sub>18</sub>H<sub>36</sub>N<sub>6</sub>O<sub>4</sub> =466 amu, m/z C<sub>18</sub>H<sub>26</sub>N<sub>8</sub>O<sub>7</sub> =614 amu

**UV-vis** : 297 nm, 318, 457, 581, 606 nm due to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and d-d transitions.

**ESR** :  $g_{11} = 2.16$   $g_{\perp} = 2.05$  and  $g_{\text{iso}} = 2.08$



**Fig. (10)** Complex (8)



**Chart (10)** Removal Cu ions % against time

At 27 °C (2L : 5M)

|        |        |
|--------|--------|
| 15 min | 7.5 %  |
| 30 min | 14.5 % |
| 45 min | 22 %   |
| 60 min | 28 %   |

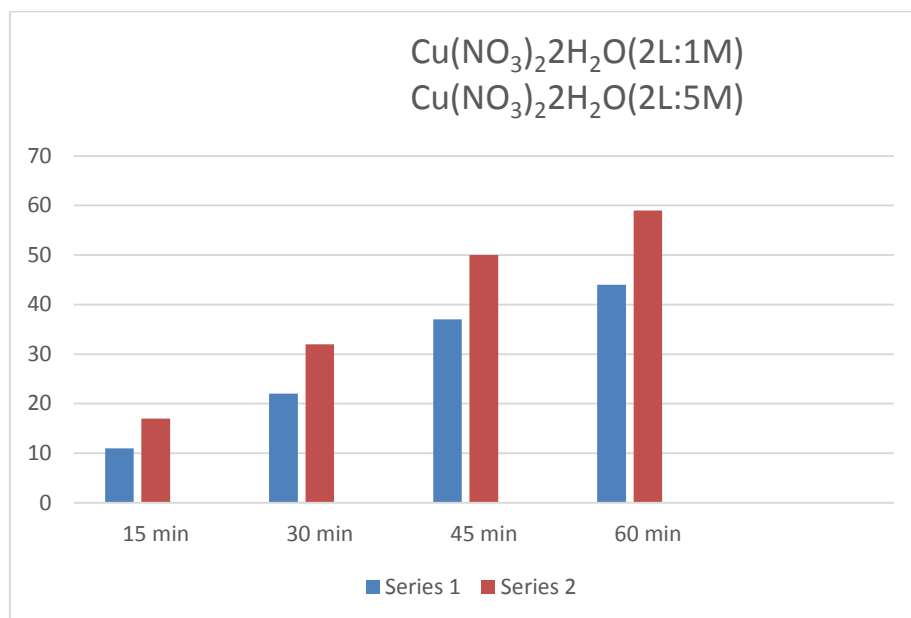


Chart (11) Removal of Cu ions % for complexes (7) and (8)

### Complex (9), (2L: 1M) Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O

**Chemical Formula** : C<sub>18</sub>H<sub>28</sub>N<sub>6</sub>O<sub>10</sub>Cd , M.Wt : 600 , Color : Brown , M.P : >300 °C , Cond : 9.15 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis ; Calc. C, 36.0, H, 4.67, N, 14.0, Cd, 18.7 , Found (%), C, 30.826, H, 4.52, N, 13.75, Cd, 18.7

**IR spectra** : ν(H<sub>2</sub>O) = 3027 - 3321 cm<sup>-1</sup>, 3320-3151 cm<sup>-1</sup>, ν(H-Bond) = 3600 - 3321 cm<sup>-1</sup>, 3312 - 2822 cm<sup>-1</sup>, ν(OH) = 3471, 3410 cm<sup>-1</sup>, ν(C=O) = 1637, 1617 cm<sup>-1</sup>, ν(NH) = 3271 cm<sup>-1</sup>, ν(NH<sub>2</sub>) = 3377, 3302 cm<sup>-1</sup>, ν(NO<sub>3</sub>) = 1368-1210, 870 cm<sup>-1</sup>, ν(OH) = 1300, 1296 cm<sup>-1</sup>, ν(CuO) = 620 cm<sup>-1</sup>

$\mu_{eff}$  : 1.70 B.M

**Mass spectrum** : m/z = 273 amu C<sub>9</sub>H<sub>13</sub>N<sub>5</sub> m/z = 394 amu, m/z C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> = 131 amu , m/z C<sub>18</sub>H<sub>36</sub>N<sub>6</sub>O<sub>4</sub> = 466 amu , m/z C<sub>18</sub>H<sub>26</sub>N<sub>8</sub>O<sub>7</sub> = 614 amu

**UV-vis** : 297 nm, 318, 420 nm due to π→π\* and n→π\* transitions

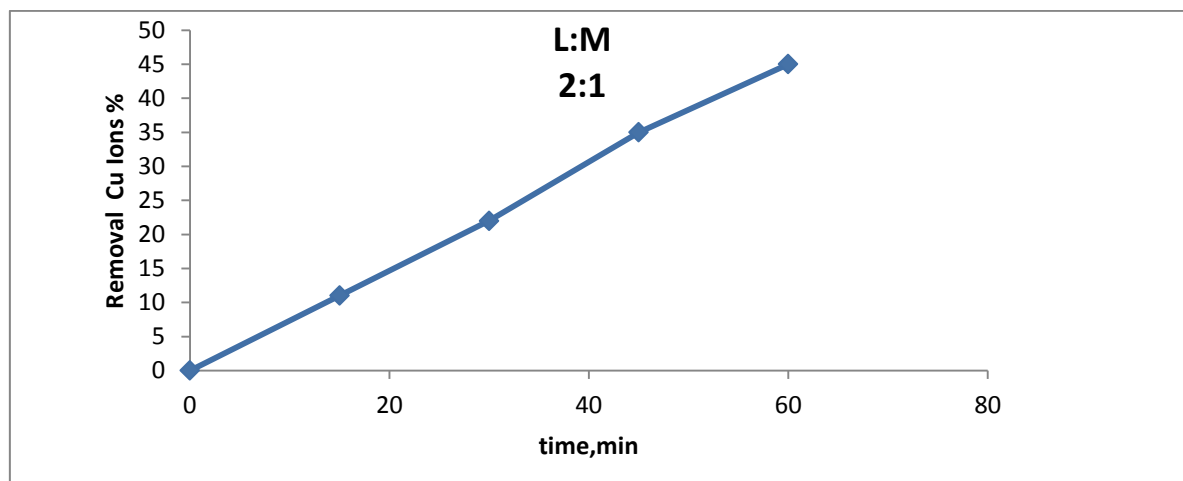
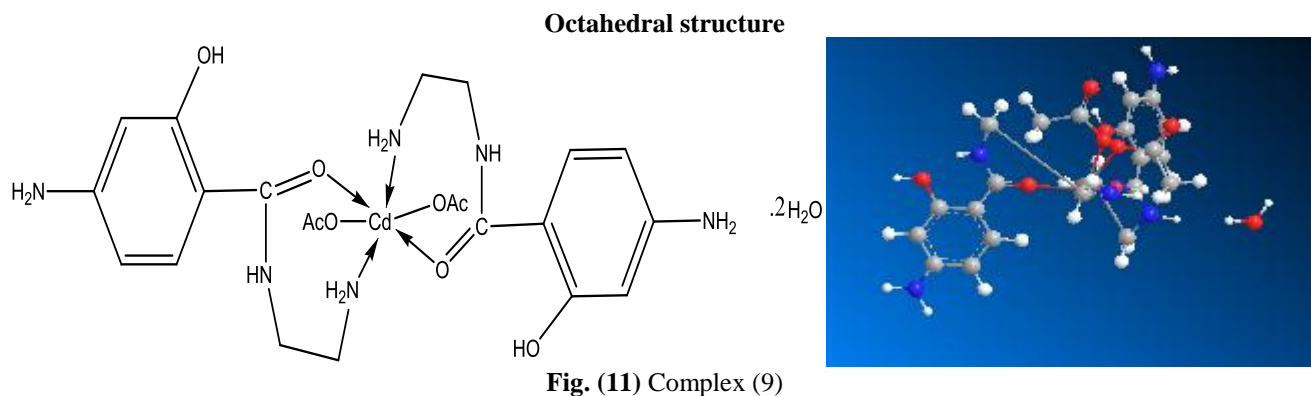


Chart (12) Removal of Cd ions % against time using (2L: 1M)

At 27 °C (2L : 1M )

|        |      |
|--------|------|
| 15 min | 6 %  |
| 30 min | 12 % |
| 45 min | 15 % |
| 60 min | 20 % |

### Complex (10), (2L: 5M), Cd (OAc)<sub>2</sub> 2H<sub>2</sub>O

**Chemical Formula** : C<sub>26</sub>H<sub>44</sub>N<sub>6</sub>O<sub>20</sub>Cd<sub>3</sub> , M.Wt : 1096 , Color : Brown , M.P : >300 °C , Cond : 9.40 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis: Calc. C, 28.47, H, 4.01 , N, 7.66, Cd, 27.77 , Found (%), C, 28.0, H, 3.75 , N, 7.32 , Cd, 27.11

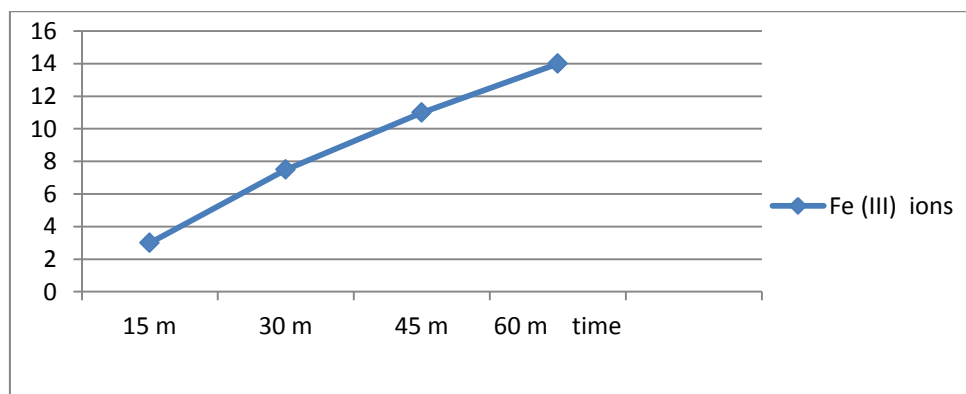
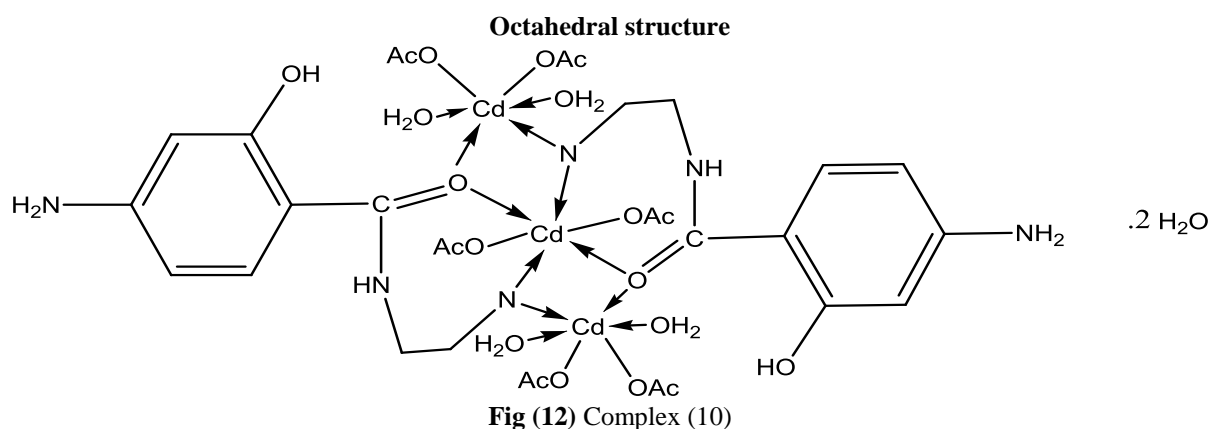
**IR spectra** :  $\nu(\text{H}_2\text{O}) = 3033 - 3323 \text{ cm}^{-1}, 3320-3153 \text{ cm}^{-1}, \nu(\text{H-Bond}) = 3603 - 3323 \text{ cm}^{-1}, 3310 - 2828 \text{ cm}^{-1}, \nu(\text{OH}) = 3478, 3418 \text{ cm}^{-1}, \nu(\text{C=O}) = 1638, 1618 \text{ cm}^{-1}, \nu(\text{NH}) = 3270 \text{ cm}^{-1}, \nu(\text{NH}_2) = 3378, 3308 \text{ cm}^{-1}, \nu(\text{OAc}) = 1511, 1410 \text{ cm}^{-1}, \nu(\text{OH}) = 1300, 1298 \text{ cm}^{-1}, \nu(\text{CdO}) = 620 \text{ cm}^{-1}, \nu(\text{CdN}) = 588 \text{ cm}^{-1}$

$\mu_{\text{eff}}$  : Diamagnetic

**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu , m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> = 74 amu , m/z, H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98 amu , C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>, m/z = 131 amu , C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>, m/z = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> = 262 amu

**UV-vis** : 290 nm, 317, 327 nm due to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and charge transfer transitions.

**<sup>1</sup>H-nmr (deuterated DMSO)** : NH = 7.3 ppm, NH<sub>2</sub> = 4.5 ppm, CH<sub>a</sub> group 2.70 - 3.15 ppm, CH 2.2 ppm, OH 5.1 ppm



**Chart (13)** Removal of Cd ions % against time using (2L: 5M)

At 27 °C (2L : 5M )

|        |        |
|--------|--------|
| 15 min | 8.5 %  |
| 30 min | 17.5 % |
| 45 min | 26 %   |
| 60 min | 34 %   |

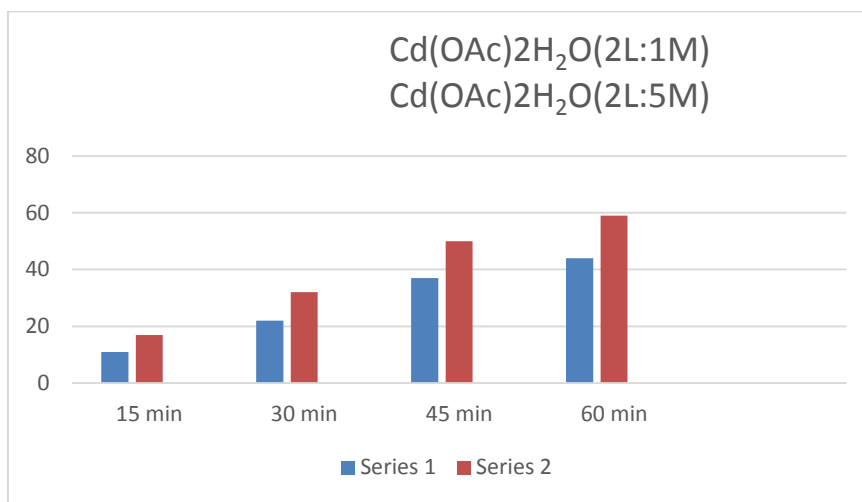


Chart (14) Removal of Cu ions % for complexes (9) and (10)

### Complex (11), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (2L : 1M)

**Chemical Formula** : C<sub>18</sub>H<sub>28</sub>N<sub>4</sub>O<sub>10</sub>Zn , M.Wt : 553 , Color : Brown , M.P : >300 °C , Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis; Calc, C, 39.06, H, 5.06, N, 11.38, Zn, 11.83 , Found (%), C, 38.82, H, 4.92, N, 14.75, Zn, 11.65

**IR spectra** : ν(H<sub>2</sub>O) = 3027 - 3320 cm<sup>-1</sup>, 3320-3155 cm<sup>-1</sup>, ν(H-Bond) = 3604 - 3324 cm<sup>-1</sup>, 3310 - 2824 cm<sup>-1</sup>, ν(OH) = 3470, 3414 cm<sup>-1</sup>, ν(C=O) = 1630, 1615 cm<sup>-1</sup>, ν(NH) = 3270 cm<sup>-1</sup>, ν(NH<sub>2</sub>) = 3376, 3300 cm<sup>-1</sup>, ν(OAc) = 1515, 1414 cm<sup>-1</sup>, ν(OH) = 1304, 1295 cm<sup>-1</sup>, ν(ZnO) = 624 cm<sup>-1</sup>, ν(ZnN) = 584 cm<sup>-1</sup>

**μ<sub>eff</sub>**: Diamagnetic

**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu, m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> = 74 amu, m/z, H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98 amu, m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> = 131 amu , m/z, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> = 262 amu

**UV-vis** : 299 nm, 318, 424, nm due to π→π\*, n→π\* and charge transfer transitions.

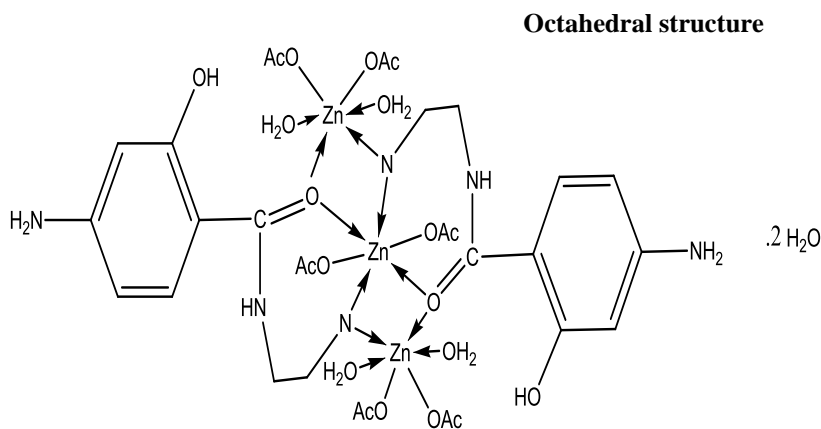


Fig (13) Complex (11)

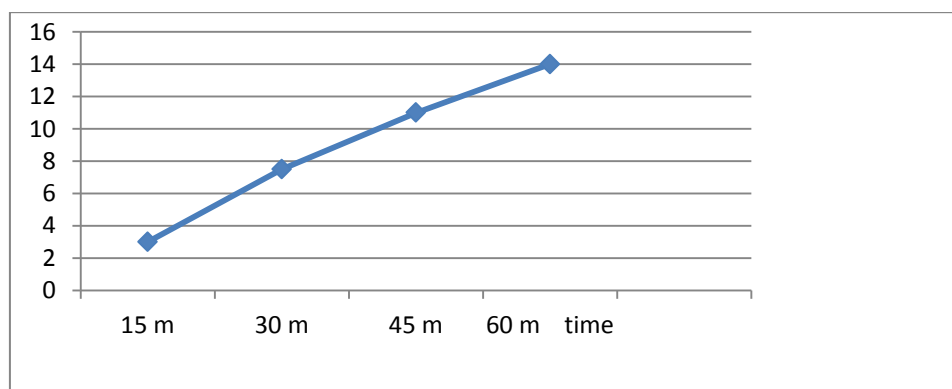


Chart (15) Removal Zn ions % against time using (2L:1M)

At 27 °C (2L : 5M )

|        |       |
|--------|-------|
| 15 min | 4.5 % |
| 30 min | 7.5 % |
| 45 min | 12 %  |
| 60 min | 15 %  |

**Complex (12), Zn(OAc)<sub>2</sub>·H<sub>2</sub>O (2L : 5M)**

**Chemical Formula :** C<sub>27</sub>H<sub>52</sub>N<sub>6</sub>O<sub>22</sub>Zn, M.Wt : 1060, Color : Brown, M.P : >270 C, Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup>, Elemental Analysis, calc, C, 32.67, H, 4.61, N, 8.79, Zn, 20.54, Found (%), C, 32.21, H, 4.52, N, 8.56, Zn, 20.21

**IR Spectra :** ν(H<sub>2</sub>O) = 3066 - 3326 cm<sup>-1</sup>, 3326-3156 cm<sup>-1</sup>, ν(H-Bond) = 3606 - 3326 cm<sup>-1</sup>, 3316 - 2820 cm<sup>-1</sup>, ν(OH) = 3456, 3426 cm<sup>-1</sup>, ν(C=O) = 1636, 1616 cm<sup>-1</sup>, ν(NH) = 3276 cm<sup>-1</sup>, ν(NH<sub>2</sub>) = 3376, 3300 cm<sup>-1</sup>, ν(OAc) = 1516, 1416 cm<sup>-1</sup>, ν(OH) = 1346, 1296 cm<sup>-1</sup>, ν(ZnO) = 621 cm<sup>-1</sup>, ν(ZnN) = 585 cm<sup>-1</sup>

**μ<sub>eff</sub> :** Diamagnetic

**Mass spectrum :** H<sub>2</sub>N<sup>+</sup>, m/z = 32 amu, C<sub>3</sub>H<sub>10</sub>N<sup>+</sup>, m/z = 74 amu, H<sub>6</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>, m/z = 98 amu, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, m/z = 131 amu, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, m/z = 189 amu, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub><sup>+</sup>, m/z = 262 amu

**UV-vis :** 296 nm, 318, 418 nm due to π→π\* and n→π\* transitions.

**<sup>1</sup>H-nmr<sup>-1</sup> (deuterated DMSO) :** NH = 7.0 ppm, NH<sub>2</sub> = 4.2 ppm, CH<sub>2</sub> group 2.60 - 3.27 ppm, CH 2.1 ppm, OH 5.7 ppm

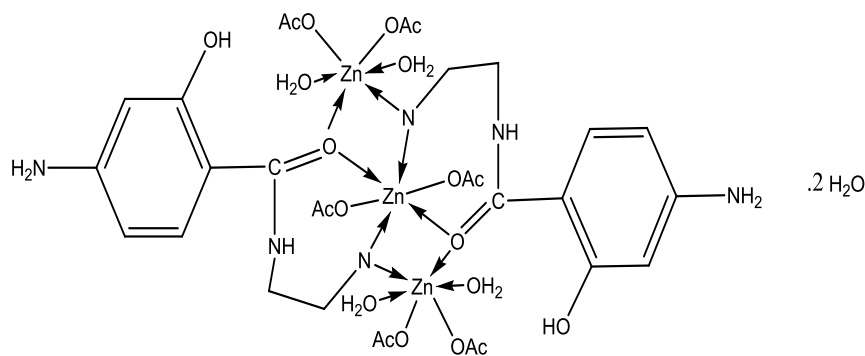


Fig. (14) Complex (12)

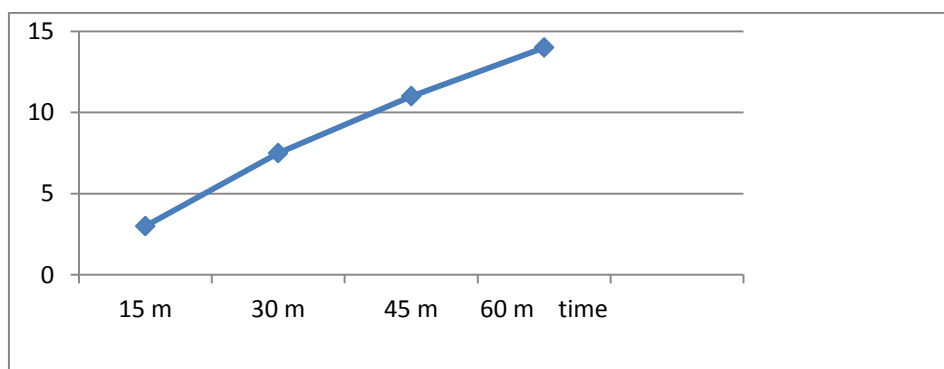


Chart (16) Removal Zn ions % against time using (2L:5M)

At 27 °C (2L : 5M)

|        |        |
|--------|--------|
| 15 min | 6.5 %  |
| 30 min | 12.5 % |
| 45 min | 16.5 % |
| 60 min | 27 %   |

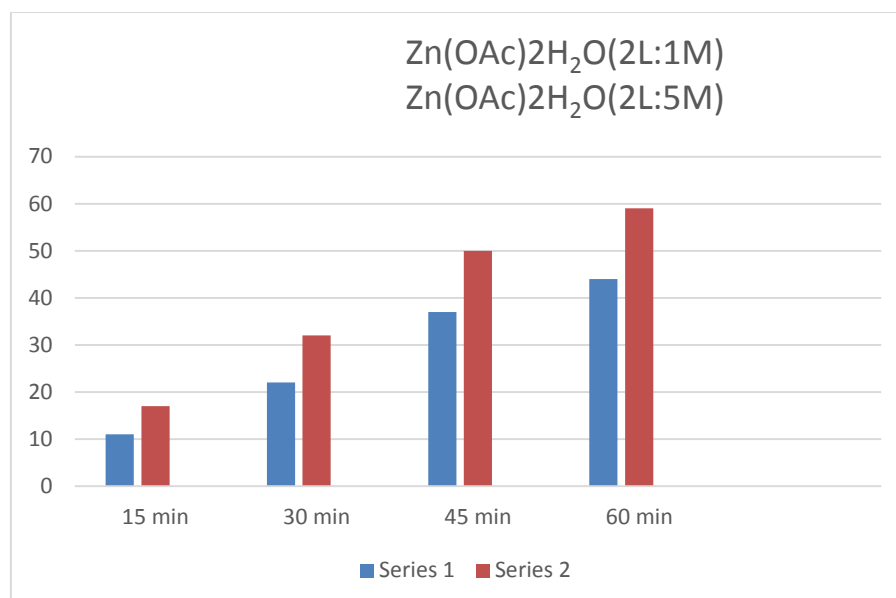


Chart (17) Removal of Zn ions % for complexes (11) and (12)



**Complex (13), Ni(OAc)<sub>2</sub>·2H<sub>2</sub>O (2L:1M)**

**Chemical Formula** : C<sub>18</sub>H<sub>28</sub>N<sub>6</sub>O<sub>10</sub>Ni , M.Wt : 547 , Color : Brown ,M.P : >300 °C ,Cond : 9.45 Ω<sup>-1</sup>mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis, calc, C,39.49, H, 5.12 , N ,15.30, Ni,10.72 , Found (%), C , 39.23, H , 4.85 , N , 14.85 , Ni 10.58

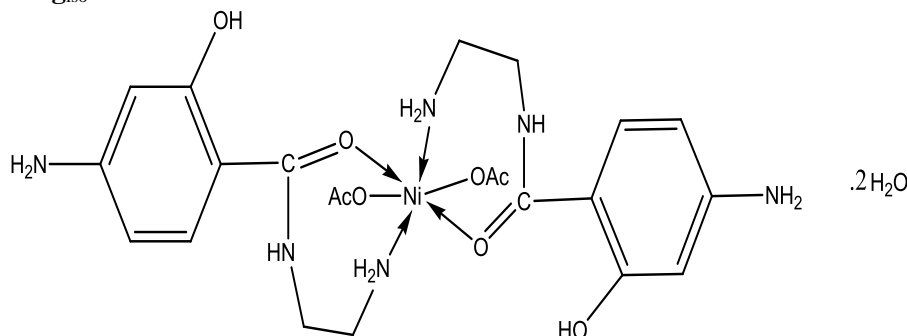
**IR Spectra** : ν(H<sub>2</sub>O) = 3027 - 3320 cm<sup>-1</sup> ,3320-3150 cm<sup>-1</sup>,ν(H-Bond) = 3600 – 3320 cm<sup>-1</sup>,3310 - 2820 cm<sup>-1</sup>,ν(OH) = 3470,3410 cm<sup>-1</sup> ,ν(C=O) = 1630,1615 cm<sup>-1</sup>,ν(NH) = 3270 cm<sup>-1</sup>,ν(NH<sub>2</sub>) = 3376, 3300 cm<sup>-1</sup>,ν(OAc) = 1511,1410 cm<sup>-1</sup>,ν(OH) = 1305,1295 cm<sup>-1</sup>,ν(Mn O) = 627 cm<sup>-1</sup> , ν(MnN) =579 cm<sup>-1</sup>

**μ<sub>eff</sub>** : 6.1 B.M

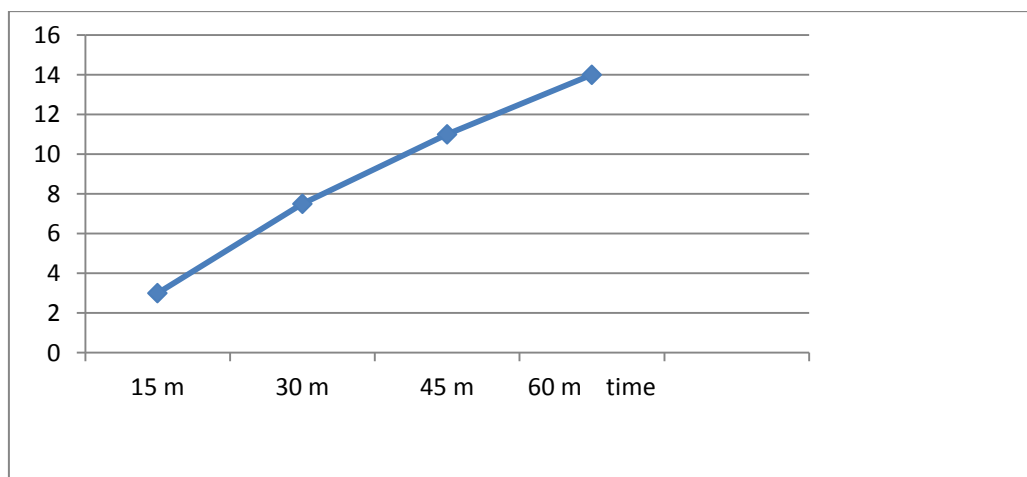
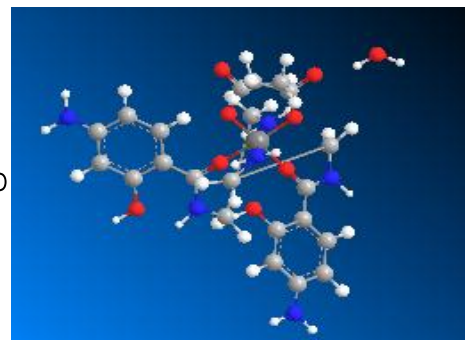
**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu , m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>, m/z = 74 amu , m/z, H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98amu , m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> = 131 amu , m/z, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> = 262 amu

**UV-vis** : 295 nm , 315, 455 , 565 , 605 nm due to π→π\* , n→π\* and d-d transitions .

**ESR** : g<sub>iso</sub> = 2.05



**Fig. (15)** Complex (12)



**Chart (18)** Removal of Ni ions % against time using (2L:1M)

At 27 °C (2L : 5M)

|        |       |
|--------|-------|
| 15 min | 4 %   |
| 30 min | 7.5 % |
| 45 min | 12 %  |
| 60 min | 23 %  |

**Complex (13), Ni(OAc)<sub>2</sub>·2H<sub>2</sub>O (2L:5M)**

**Chemical Formula** : C<sub>26</sub>H<sub>44</sub>N<sub>6</sub>O<sub>20</sub>Ni<sub>3</sub> , M.Wt : 937 , Color : Brown , M.P : >300 °C ,Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup>cm<sup>-1</sup> , Elemental Analysis, calc, C,39.49, H, 5.12 , N ,15.30, Ni,10.72 , Found (%), C , 39.23, H , 4.85 , N , 14.85 , Ni 10.58

**IR Spectra** : ν(H<sub>2</sub>O) = 3027 - 3320 cm<sup>-1</sup> ,3320-3150 cm<sup>-1</sup>,ν(H-Bond)= 3600 - 3320 cm<sup>-1</sup>,3310 - 2820 cm<sup>-1</sup>,ν(OH) = 3470,3410 cm<sup>-1</sup> ,ν(C=O)= 1630,1615 cm<sup>-1</sup>,ν(NH) = 3270 cm<sup>-1</sup>,ν(NH<sub>2</sub>) = 3376, 3300 cm<sup>-1</sup>,ν(OAc) = 1511,1410 cm<sup>-1</sup>,ν(OH)= 1305,1295 cm<sup>-1</sup>,ν(Ni O)= 627 cm<sup>-1</sup> , ν(NiN)=579 cm<sup>-1</sup>

**μ<sub>eff</sub>** : 2.62 B.M

**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu , m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>, m/z = 74 amu , m/z, H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98amu , m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> = 131 amu , m/z, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> = 262 amu

**UV-vis** : 295 nm , 315, 455, 565, 605, 748 nm due to π→π\* , n→π\* and d-d transitions.

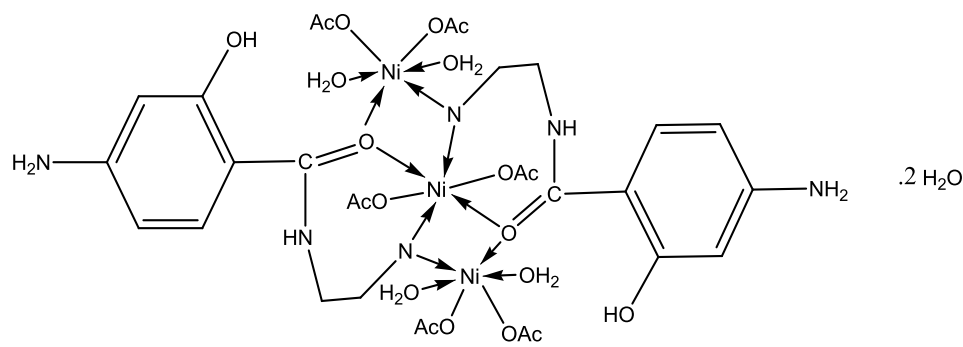


Fig. (16) Complex (13)

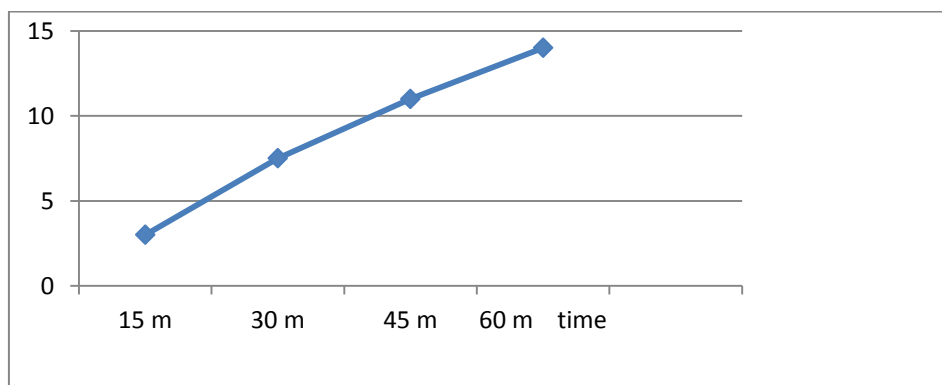
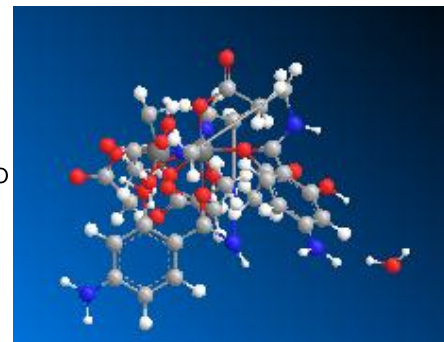


Chart (19) Removal of Ni ions % against time using (2L:1M)

At 27 °C (2L : 5M)

|        |       |
|--------|-------|
| 15 min | 3 %   |
| 30 min | 7.5 % |
| 45 min | 10 %  |
| 60 min | 13 %  |

#### Complex (14), Co(OAc)<sub>2</sub> (2L:1M)

**Chemical Formula** : C<sub>18</sub>H<sub>28</sub>N<sub>6</sub>O<sub>10</sub>Co , M.Wt : 543 , Color : Brown , M.P : >300 °C , Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis; Calc, C,39.78, H, 5.16, N,15.47, Co ,10.13 , Found (%), C, 39.56, H, 5.0, N,15.16 , Co 9.98  
**IR Spectra** : ν(H<sub>2</sub>O) = 3027 - 3320 cm<sup>-1</sup> ,3320-3150 cm<sup>-1</sup>,ν(H-Bond) = 3600 - 3320 cm<sup>-1</sup>,3310 - 2820 cm<sup>-1</sup>,ν(OH) = 3470,3410 cm<sup>-1</sup> ,ν(C=O) = 1630,1615 cm<sup>-1</sup>,ν(NH) = 3270 cm<sup>-1</sup>,ν(NH<sub>2</sub>) = 3376, 3300 cm<sup>-1</sup>,ν(OAc) = 1511,1410 cm<sup>-1</sup>,ν(OH)= 1305,1295 cm<sup>-1</sup>,ν(Co O)= 627 cm<sup>-1</sup> , ν(CoN)=579 cm<sup>-1</sup>

**μ<sub>eff</sub>** : 4.36 B.M

**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu , m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub>, m/z = 74 amu , m/z, H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98amu , m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> = 131 amu , m/z, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> = 262 amu

**UV-vis** : 295 nm, 315, 455, 565, 605 nm due to π→π\*, n→π\* and d-d transitions.

**ESR** : g<sub>iso</sub> = 2.05; Octahedral structure with covalent bond character.

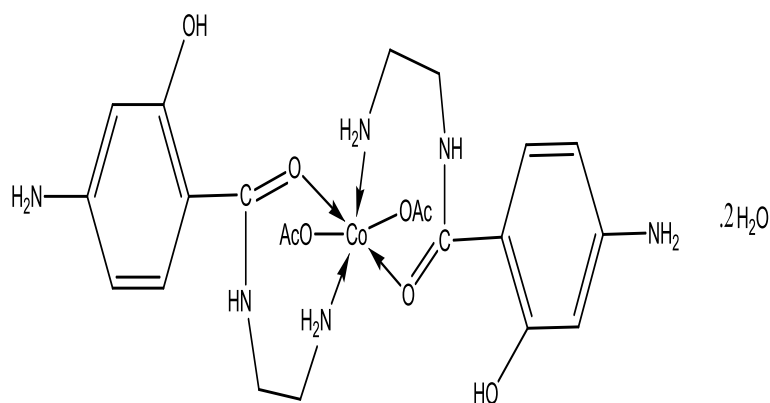


Fig. (17) Complex (14)



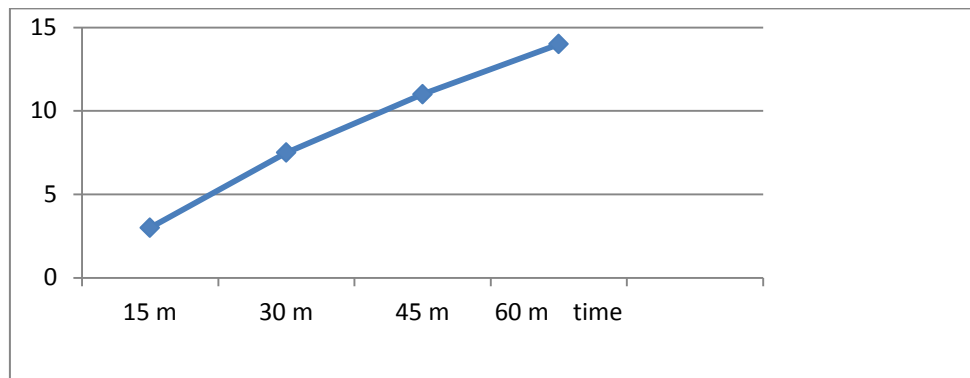


Chart (19) Removal of Co ions % against time using (2L:1M)

At 27 °C (2L : 5M )

|        |       |
|--------|-------|
| 15 min | 3 %   |
| 30 min | 7.5 % |
| 45 min | 10 %  |
| 60 min | 13 %  |

**Complex (15),**  $\text{Co}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (2L:5M)

**Chemical Formula :**  $\text{C}_{26}\text{H}_{44}\text{N}_6\text{O}_{20}\text{Co}_3$  , M.Wt : 937 , Color : Brown , M.P :  $>300$  °C , Cond :  $9.45 \Omega^{-1} \text{mol}^{-1}\text{cm}^{-1}$  , Elemental Analysis, calc, C,39.49, H, 5.12, N,15.30, Ni,10.72 , Found (%), C, 39.23, H, 4.85, N, 14.85, Co 10.58

**IR Spectra :**  $\nu(\text{H}_2\text{O}) = 3027 - 3320 \text{ cm}^{-1}$  ,  $3320-3150 \text{ cm}^{-1}$  ,  $\nu(\text{H-Bond}) = 3600 - 3320 \text{ cm}^{-1}$  ,  $3310 - 2820 \text{ cm}^{-1}$  ,  $\nu(\text{OH}) = 3470,3410 \text{ cm}^{-1}$  ,  $\nu(\text{C=O}) = 1630,1615 \text{ cm}^{-1}$  ,  $\nu(\text{NH}) = 3270 \text{ cm}^{-1}$  ,  $\nu(\text{NH}_2) = 3376, 3300 \text{ cm}^{-1}$  ,  $\nu(\text{OAc}) = 1511,1410 \text{ cm}^{-1}$  ,  $\nu(\text{OH}) = 1305,1295 \text{ cm}^{-1}$  ,  $\nu(\text{CoO}) = 627 \text{ cm}^{-1}$  ,  $\nu(\text{CoN}) = 579 \text{ cm}^{-1}$

$\mu_{\text{eff}}$  : 2.02 B.M

**Mass spectrum :**  $m/z$ ,  $\text{H}_2\text{N}_2 = 32 \text{ amu}$  ,  $m/z$ ,  $\text{C}_3\text{H}_{10}\text{N}_2$ ,  $m/z = 74 \text{ amu}$  ,  $m/z$ ,  $\text{H}_6\text{N}_2\text{O}_4 = 98 \text{ amu}$  ,  $m/z$ ,  $\text{C}_5\text{H}_{11}\text{N}_2\text{O}_2 = 131 \text{ amu}$  ,  $m/z$ ,  $\text{C}_7\text{H}_{13}\text{N}_2\text{O}_2 = 189 \text{ amu}$  ,  $m/z$ ,  $\text{C}_{10}\text{H}_{22}\text{N}_4\text{O}_4 = 262 \text{ amu}$

**UV-vis :** 295 nm, 315, 455, 565, 605 nm due to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and d-d transitions.

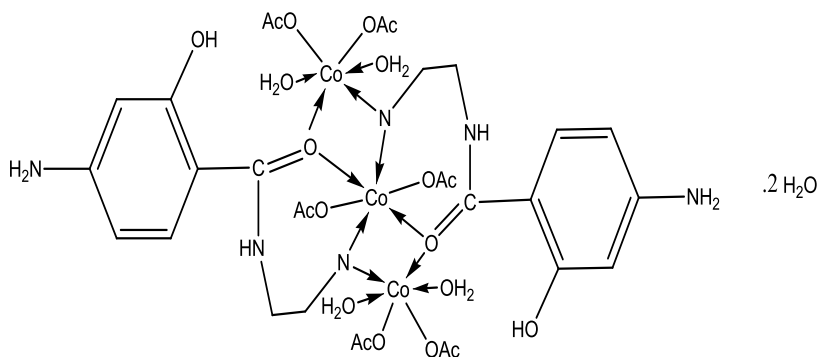


Fig (16) Complex (13)

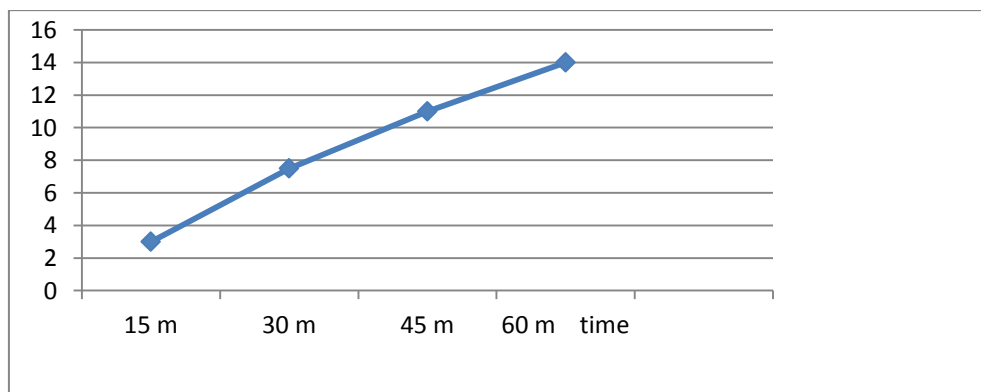
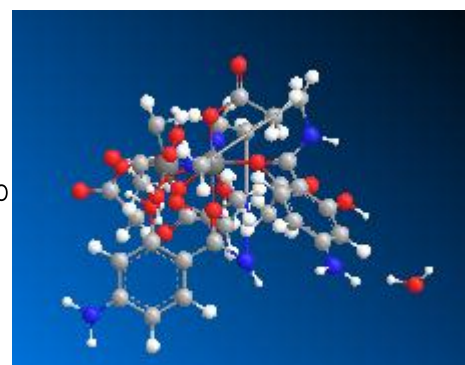


Chart (20) Removal of Co ions % against time using (2L:1M)

At 27 °C (2L : 5M )

|        |       |
|--------|-------|
| 15 min | 3 %   |
| 30 min | 7.5 % |
| 45 min | 10 %  |
| 60 min | 13 %  |

**Complex (16), Fe(SO<sub>4</sub>)<sub>2</sub>·7H<sub>2</sub>O (2L:1M)**

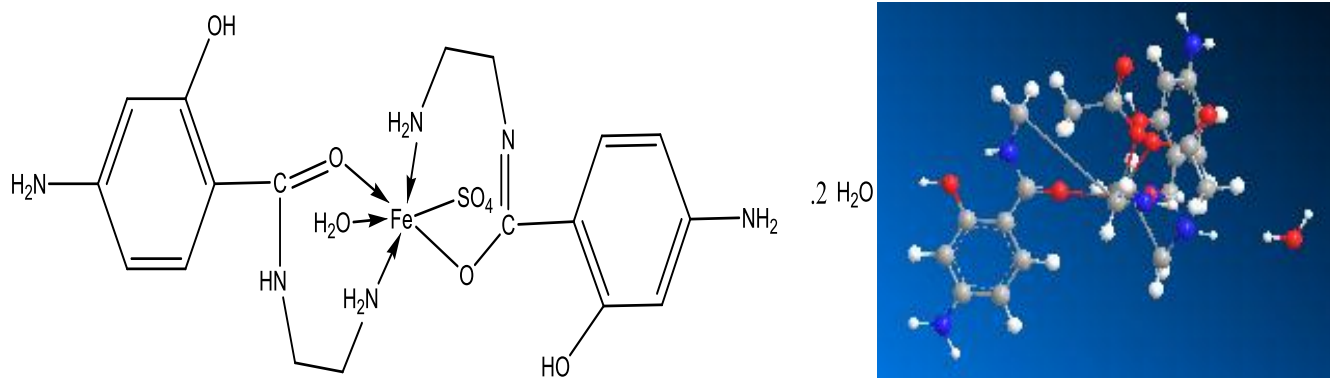
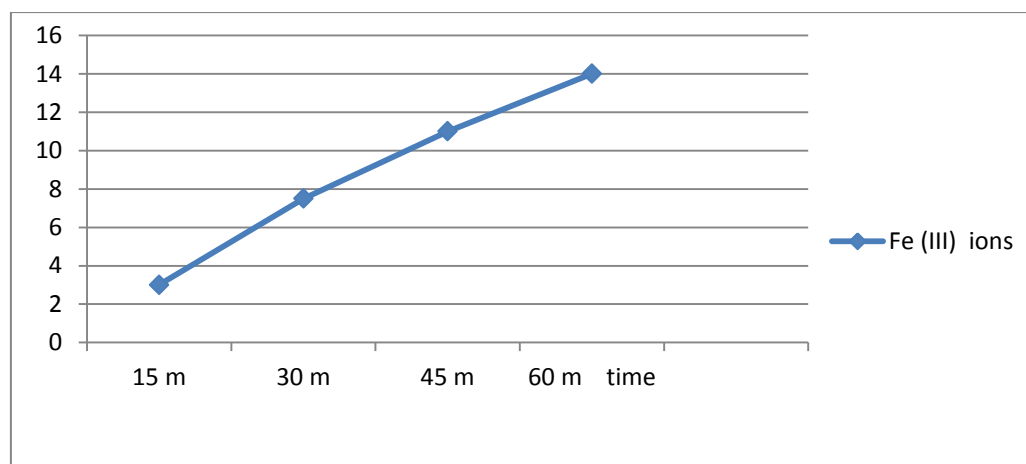
**Chemical Formula** : C<sub>14</sub>H<sub>23</sub>N<sub>4</sub>O<sub>11</sub>Fe , M.Wt : 510 , Color : Brown , M.P : >300 C , Cond : 9.45 Ω<sup>-1</sup>mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis, calc, C,32.94, H, 4.51 , N ,10.98, Fe ,10.56 , Found (%), C , 32.65, H , 4.23 , N , 9.72 , Fe 10.78

**IR Spectra** : ν(H<sub>2</sub>O) = 3031 - 3311 cm<sup>-1</sup>, 3321-3151 cm<sup>-1</sup>, ν(H-Bond) = 3601 - 3321 cm<sup>-1</sup>, 3311 - 2821 cm<sup>-1</sup>, ν(OH) = 3471, 3411 cm<sup>-1</sup>, ν(C=O) = 1631, 1611 cm<sup>-1</sup>, ν(NH) = 3271 cm<sup>-1</sup>, ν(NH<sub>2</sub>) = 3371, 3301 cm<sup>-1</sup>, ν(OAc) = 1511, 1411 cm<sup>-1</sup>, ν(OH) = 1301, 1291 cm<sup>-1</sup>, ν(Fe O) = 621 cm<sup>-1</sup>, SO<sub>4</sub> = 1271, 1181, 1021, 681 cm<sup>-1</sup>

**μ<sub>eff</sub>** : 5.81 B.M

**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu , m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> = 74 amu , m/z, H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98 amu , m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> = 131 amu , m/z, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> = 262 amu

**UV-vis** : 291 nm, 311, 441, 571 , nm due to π→π\* , n→π\* and Charge transfer transitions .

**Octahedral structure with covalent bond character****Fig. (19)** Complex (15)

Removal Fe(III) ions (%)

**Chart (21)** Removal Fe ions % against time using (2L:1M)

At 27 °C (2L : 1M )

|        |       |
|--------|-------|
| 15 min | 3 %   |
| 30 min | 7.5 % |
| 45 min | 11 %  |
| 60 min | 14 %  |

**Complex (17), Fe SO<sub>4</sub> 2H<sub>2</sub>O (2L:5M)**

**Chemical Formula** : C<sub>14</sub>H<sub>27</sub>N<sub>4</sub>O<sub>23</sub>S<sub>2</sub>Fe<sub>3</sub> , M.Wt : 850 , Color : Brown , M.P : >270 C , Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental Analysis, calc, C,19.76, H, 3.41 , N ,6.59, Fe ,19.41 , Found (%), C , 19.21, H , 3.11 , N , 6.31 , Fe 18.92

**IR spectra** : ν(H<sub>2</sub>O) = 3032 - 3322 cm<sup>-1</sup>, 3322-3152 cm<sup>-1</sup>, ν(H-Bond) = 3602 - 3322 cm<sup>-1</sup>, 3312 - 2822 cm<sup>-1</sup>, ν(OH) = 3472, 3412 cm<sup>-1</sup>, ν(C=O) = 1632, 1612 cm<sup>-1</sup>, ν(NH) = 3272 cm<sup>-1</sup>, ν(NH<sub>2</sub>) = 3372, 3302 cm<sup>-1</sup>, ν(OAc) = 1512, 1412 cm<sup>-1</sup>, ν(OH) = 1302, 1292 cm<sup>-1</sup>, ν(Fe O) = 622 cm<sup>-1</sup>, ν(SO<sub>4</sub>) = 1272, 1182, 1032, 672 cm<sup>-1</sup>

**μ<sub>eff</sub>** : 3.62 B.M

**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu , m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> = 74 amu , m/z, H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98 amu , m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> = 131 amu , m/z, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> = 262 amu

**UV-vis** : 292 nm, 312, 432, 552 , nm due to π→π\* , n→π\* and Charge transfer transitions .

Octahedral structure

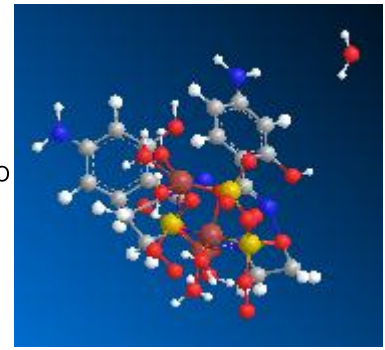
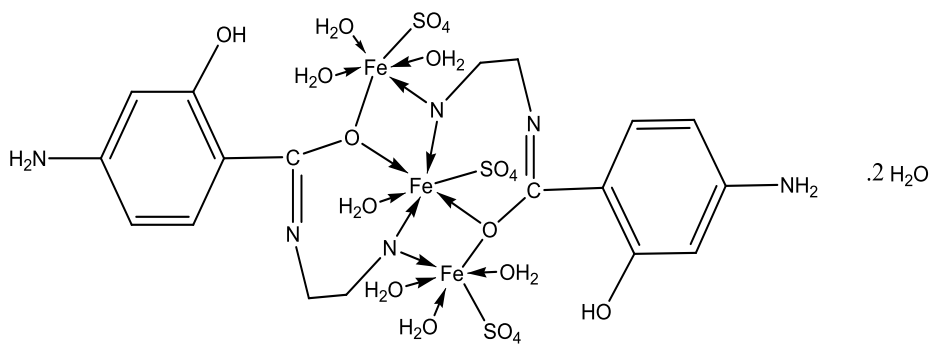
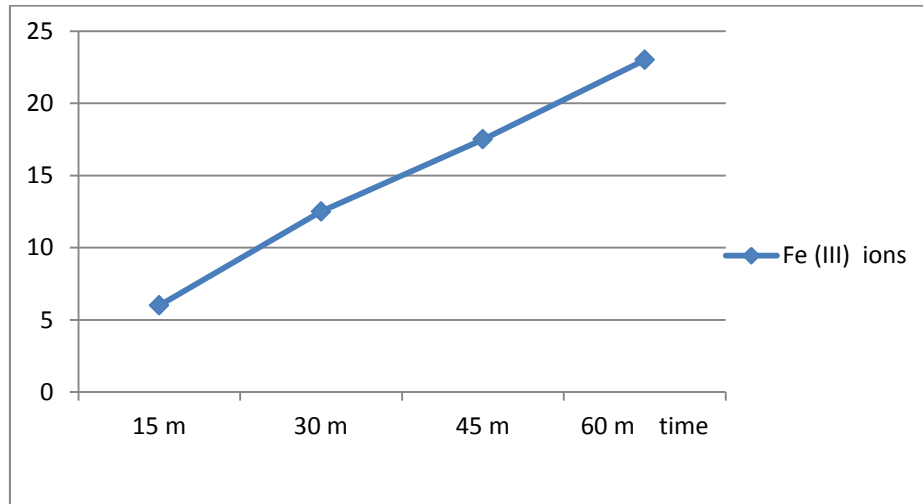


Fig. 20 Complex (17)



Removal Fe(III) ions (%) 1

Chart (22) Removal Fe ions % against time using (2L:5M)

At 27 °C (2L : 5M)

|        |        |
|--------|--------|
| 15 min | 6 %    |
| 30 min | 12.5 % |
| 45 min | 17.5 % |
| 60 min | 23 %   |

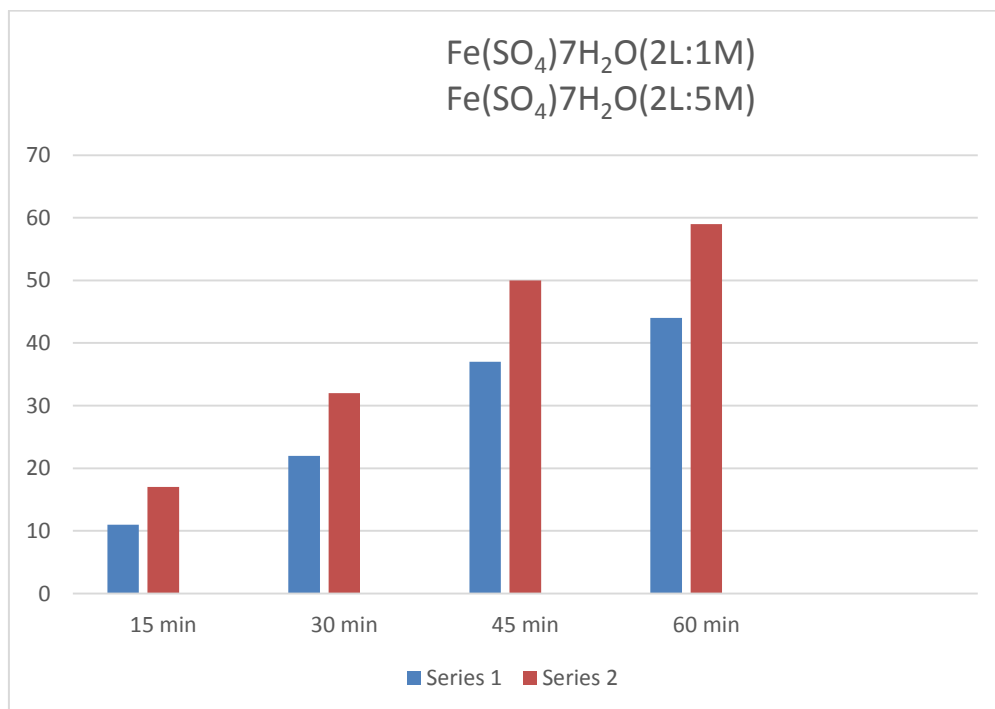


Chart (23) Removal of Fe ions % for complexes (16) and (17)

**Complex (18), CrSO<sub>4</sub> 2H<sub>2</sub>O (2L:1M)**

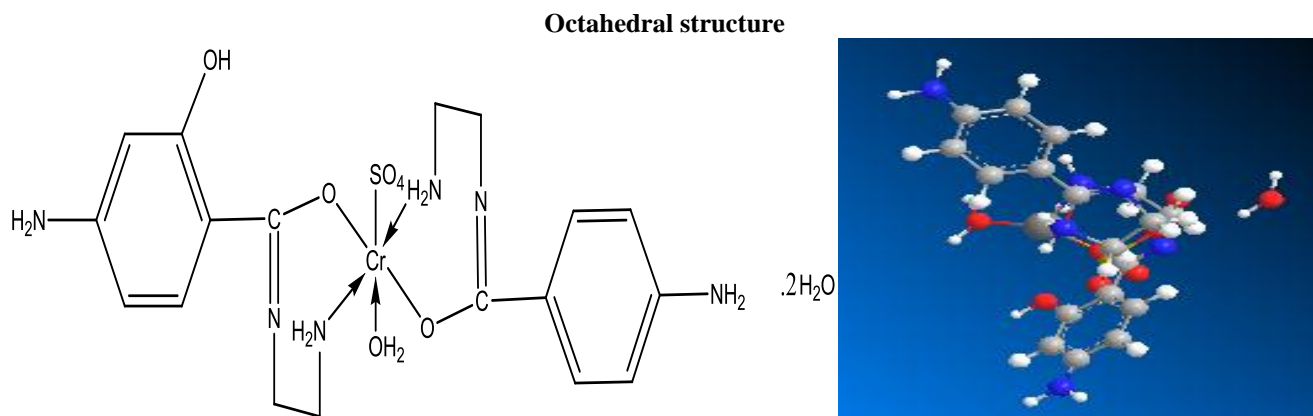
**Chemical Formula** : C<sub>14</sub>H<sub>23</sub>N<sub>4</sub>O<sub>11</sub>SCr , M.Wt : 507 , Color : Brown , M.P : >300 C , Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental analysis, calc, C, 33.14, H, 4.53, N, 11.04, Cr 10.27 , Found (%), C, 32.86, H, 4.22, N, 10.75 , Cr 9.82

**IR spectra** :  $\nu(\text{H}_2\text{O}) = 3032 - 3322 \text{ cm}^{-1}, 3322-3152 \text{ cm}^{-1}, \nu(\text{H-Bond}) = 3602 - 3322 \text{ cm}^{-1}, 3312 - 2822 \text{ cm}^{-1}, \nu(\text{OH}) = 3472, 3412 \text{ cm}^{-1}, \nu(\text{C=O}) = 1632, 1612 \text{ cm}^{-1}, \nu(\text{NH}) = 3272 \text{ cm}^{-1}, \nu(\text{NH}_2) = 3372, 3302 \text{ cm}^{-1}, \nu(\text{OAc}) = 1512, 1412 \text{ cm}^{-1}, \nu(\text{OH}) = 1302, 1292 \text{ cm}^{-1}, \nu(\text{Cr O}) = 622 \text{ cm}^{-1}, \nu(\text{SO}_4) = 1272, 1182, 1032, 672 \text{ cm}^{-1}$

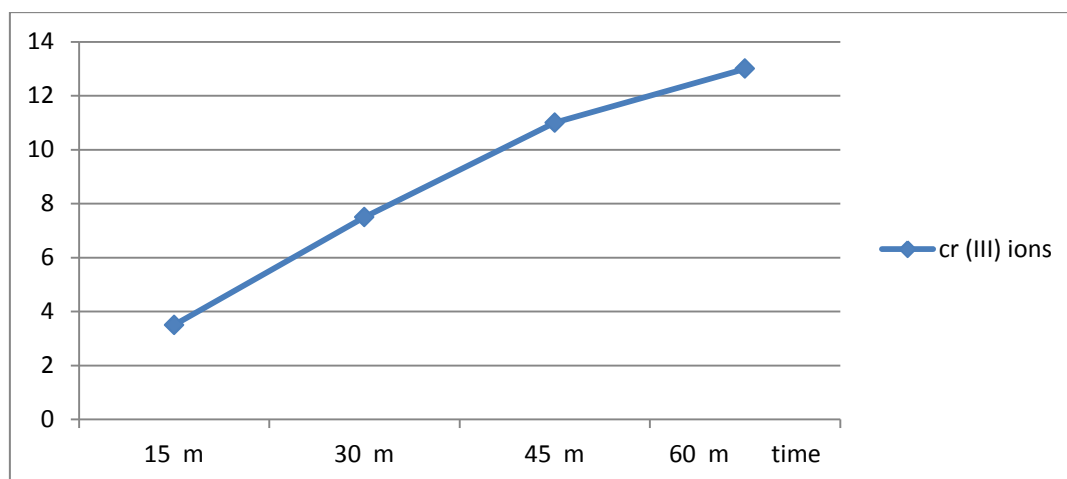
$\mu_{\text{eff}}$  : 3.62 B.M

**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu , m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> = 74 amu , H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98 amu , m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> , = 131 amu , m/z, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> , = 262 amu

**UV-vis** : 292 nm , 312 , 432 , 552 , nm due to  $\pi \rightarrow \pi^*$  ,  $n \rightarrow \pi^*$  and Charge transfer transitions .



**Fig. 21** Complex (18)



**Chart (24)** Removal Cr ions % against time using (2L: 1M)

At 27 °C (2L: 5M)

|        |       |
|--------|-------|
| 15 min | 3.5 % |
| 30 min | 7.5 % |
| 45 min | 11 %  |
| 60 min | 13 %  |

**Complex (19), CrSO<sub>4</sub> 2H<sub>2</sub>O (2L: 5M)**

**Chemical Formula** : C<sub>14</sub>H<sub>27</sub>N<sub>4</sub>O<sub>23</sub>SCr<sub>3</sub> , M.Wt : 841 , Color : Brown , M.P : >300 C , Cond : 9.45 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>-1</sup> , Elemental Analysis; Calc, C, 19.97, H, 4.45, N, 6.66, Cr 18.55 , Found (%), C, 19.72, H, 4.31, N, 6.13 , Cr 18.23

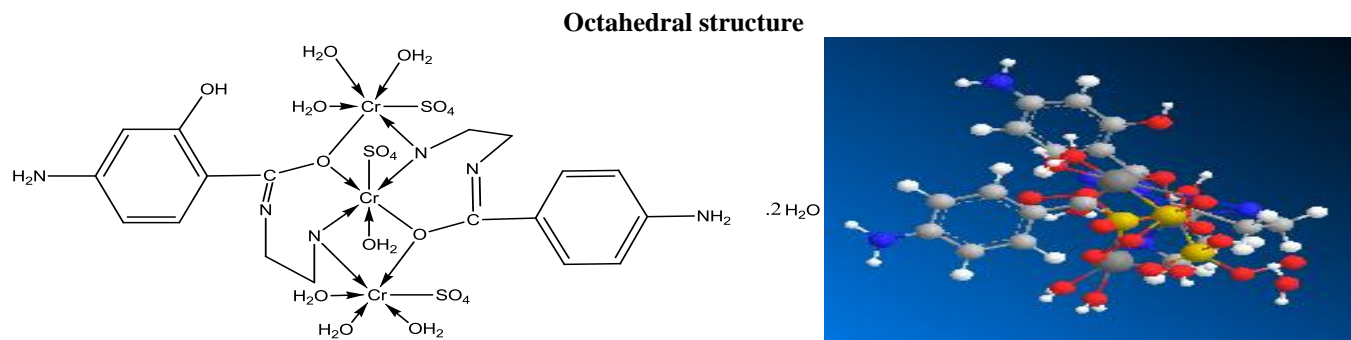
**IR spectra** :  $\nu(\text{H}_2\text{O}) = 3032 - 3322 \text{ cm}^{-1}, 3322-3152 \text{ cm}^{-1}, \nu(\text{H-Bond}) = 3602 - 3322 \text{ cm}^{-1}, 3312 - 2822 \text{ cm}^{-1}, \nu(\text{OH}) = 3472, 3412 \text{ cm}^{-1}, \nu(\text{C=O}) = 1632, 1612 \text{ cm}^{-1}, \nu(\text{NH}) = 3272 \text{ cm}^{-1}, \nu(\text{NH}_2) = 3372, 3302 \text{ cm}^{-1}, \nu(\text{OAc}) = 1512, 1412 \text{ cm}^{-1}, \nu(\text{OH}) = 1302, 1292 \text{ cm}^{-1}, \nu(\text{Cr O}) = 622 \text{ cm}^{-1}, \nu(\text{SO}_4) = 1272, 1182, 1032, 672 \text{ cm}^{-1}$

$\mu_{\text{eff}}$  : 3.62 B.M

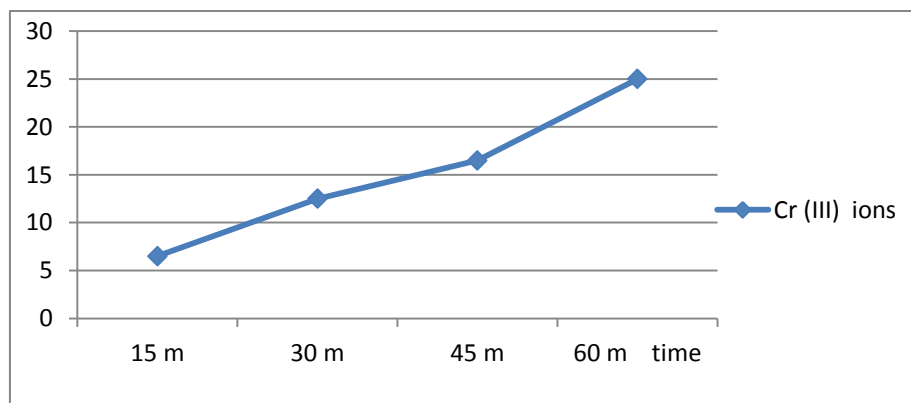
**Mass spectrum** : m/z, H<sub>2</sub>N<sub>2</sub> = 32 amu , m/z, C<sub>3</sub>H<sub>10</sub>N<sub>2</sub> = 74 amu , H<sub>6</sub>N<sub>2</sub>O<sub>4</sub> = 98 amu , m/z, C<sub>5</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> , = 131 amu , m/z, C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> = 189 amu , m/z, C<sub>10</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub> , = 262 amu

**UV-vis** : 292 nm , 312 , 432 , 552 , nm due to  $\pi \rightarrow \pi^*$  ,  $n \rightarrow \pi^*$  and charge transfer transitions .





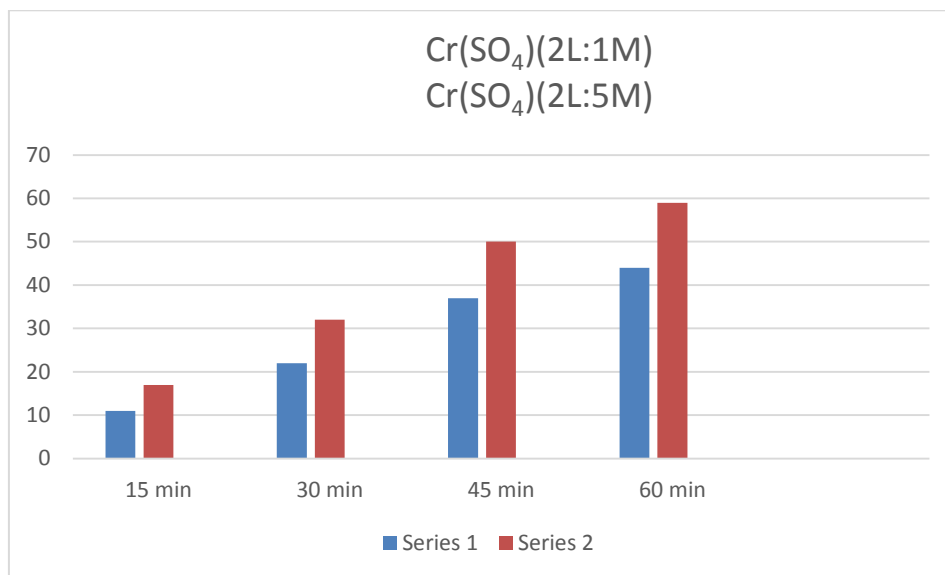
**Fig. 22** complex (19)



**Chart (25)** Removal of Cr ions % against time using (2L: 5M)

At 27 °C (2L: 5M)

|        |        |
|--------|--------|
| 15 min | 6.5 %  |
| 30 min | 12.5 % |
| 45 min | 16.5 % |
| 60 min | 19 %   |



**Chart (26)** Removal of Cr ions % for complexes (18) and (19)

### 3. Result and Discussion

#### 3.1 Measuring of the Capacity of the Organic Ligand (Metal Removal Efficiency)

Bio sorption capacity ( $q_e$ ), the amount of metal adsorbed per gram of bio-sorbent, can be calculated in mg/g as follows:

$$Q_e = (C_o - C_e) V / m$$

Where  $C_o$  is the initial metal ions concentration (mg/L),  $C_e$  is the equilibrium concentration of metal ions (mg / L),  $V$  is the volume of solution (L) and  $m$  is the mass of bio sorbent (g) . Percentage of metal removal can also be displayed by the percentage of metal removal as follows:

$$\text{Metal removal (\%)} = 100 (C_o - C_e) / C_o$$

When the organic ligand was treated with the metal ions in (2 L : 1 M) and ( 2 L : 5 M ) molar ratios, and the removal efficiency after 30 min and 60 min at 27 °c were recorded.

### 3.2 Preparation of the Ligand Metal Complexes in Laboratory

Waste water contains notorious metal ions such as Cu(II), Ni(II), Cd(II), Fe (III), Pb(II), Zn(II), Mn(II) and Cr(III). In order to know the capacity of the ligand to remove these ions, metal complexes of these ions have been prepared in the laboratory using reflux(70°C) with continuous stirring for 1-3 hrs, then left to cool at room temperature, filtered off, washed the precipitate formed with ethanol and dried in desiccators in the presence of CaCl<sub>2</sub>. Using (2L: 1M) and (2L: 5M) molar ratios.

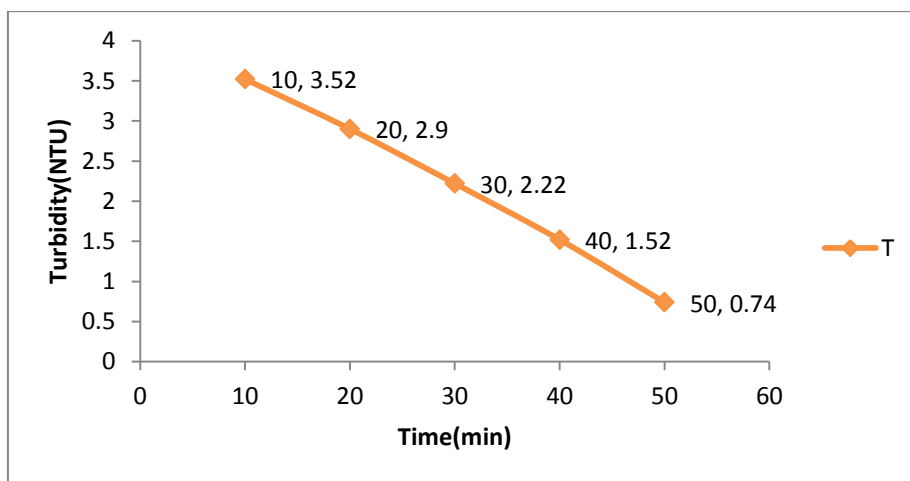
### 3.3 Effect of the Organic Ligand on Turbidity at Different Conditions on Industrial Waste Water

#### 3.3.1 Turbidity with time at 27 °C

The results showed turbidity decreased when the time increased at temperature 27 °C After 10 min turbidity was 3.52 NTU while after 50 min turbidity was 0.74 as shown in table(1)

**Table (1)** Turbidity with time At Volume = 15 ml wastewater, Temperature=27 °C, Wt. of organic ligand (1) = 0.5g

| Turbidity | Time (min) |
|-----------|------------|
| 3.52 NTU  | 10         |
| 2.9 NTU   | 20         |
| 2.22 NTU  | 27         |
| 1.52 NTU  | 40         |
| 0.74 NTU  | 50         |



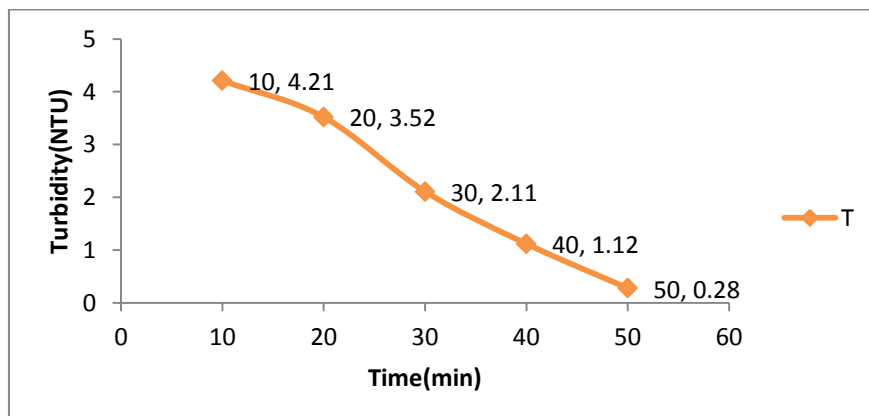
**Chart (27)** Relationship between turbidity and time

#### 3.3.2 Turbidity with time at 27 °C

The result showed turbidity decreased when time increased at temperature 27 °C After 10 min, turbidity was 4.21 NTU while after 50 min turbidity was 0.28 as shown in table (2)

**Table (2)** Turbidity with time t Volume= 15 ml wastewater, Temperature=27°C, Wt of ligand (1) = 0.5g

| Turbidity | Time (min) |
|-----------|------------|
| 4.21 NTU  | 10         |
| 3.52 NTU  | 20         |
| 2.11 NTU  | 27         |
| 1.12 NTU  | 40         |
| 0.28 NTU  | 50         |



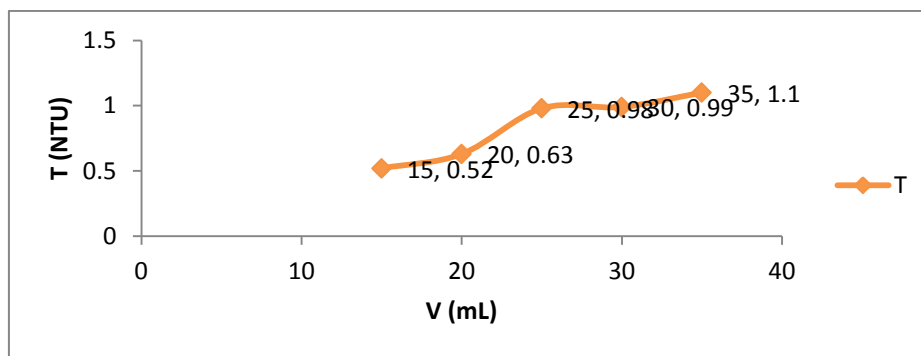
**Chart (28)** Relationship between turbidity and time at 27°C

### 3.3.3 Turbidity with volume at 27 °C

The results showed the turbidity decreased when the volume increased at temperature 27 °C at volume 15 ml turbidity is 0.52 NTU while at 30 ml turbidity is 1.10 as shown in table (3)

**Table (3)** Turbidity with time at Time = 27 minutes, Temperature = 27 °C, Wt. of organic ligand (1) = 0.5g

| Turbidity | Volume (mL) |
|-----------|-------------|
| 0.52 NTU  | 15          |
| 0.63 NTU  | 20          |
| 0.98 NTU  | 27          |
| 0.99 NTU  | 27          |
| 1.10 NTU  | 30          |



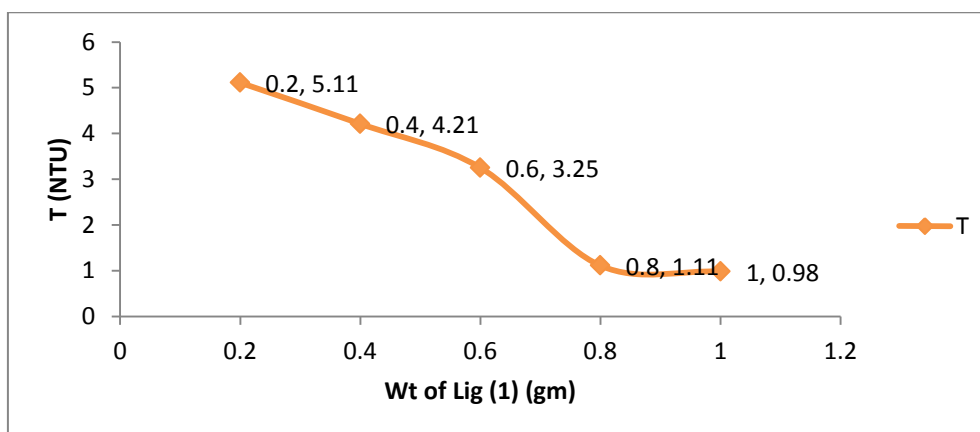
**Chart (29)** Relationship between turbidity and volume at 27 °C

### 3.3.4 Turbidity with different weights of the organic ligand at 27 °C

The results showed the turbidity decreased when the weight of the organic ligand increased at temperature 27°C at time 30 min. At weight 0.2 g turbidity is 5.11 NTU while weight 2.0 g turbidity is 0.98 NTU as shown as in table (4)

**Table (4)** Turbidity with time at time= 30 minutes, temperature=27 °C Volume = 15ml

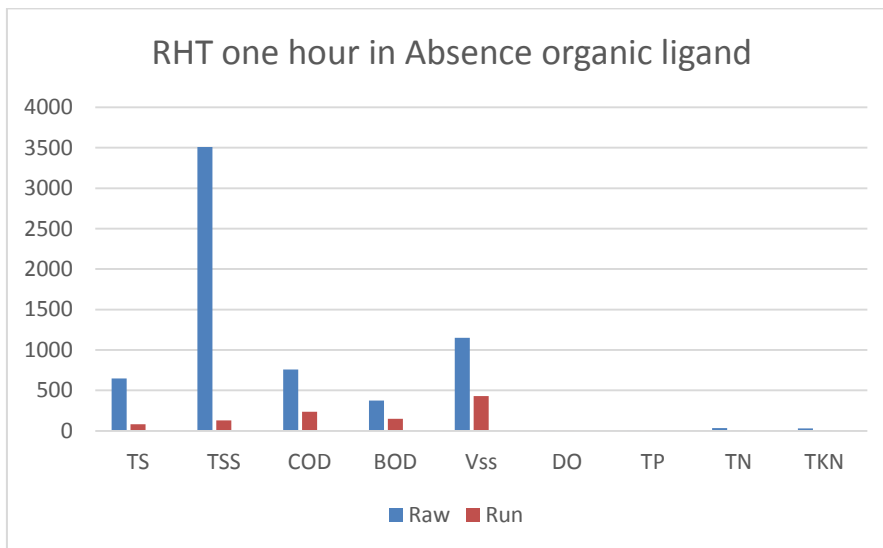
| Turbidity | Wt of ligand (1) g |
|-----------|--------------------|
| 5.11 NTU  | 0.2                |
| 4.21 NTU  | 0.4                |
| 3.27 NTU  | 0.6                |
| 1.11 NTU  | 0.8                |
| 0.98 NTU  | 1.0                |



**Chart (30)** Relationship between turbidity and different weights of the organic ligand at 27 °C using 15 ml of industrial wastewater

### 3.4 Post-Treatment of Industrial Wastewater at RHT One Hour in Absence of the Organic Ligand. (Table 5)

| COD    | TSS    | TS     | TKN    | VSS    | pH   | DO     | TP    | TN     | BOD    | Tem   | E.X.P |
|--------|--------|--------|--------|--------|------|--------|-------|--------|--------|-------|-------|
| 760    | 3510   | 650    | 32     | 1150   | 7.79 | 1.2    | 1.58  | 35     | 375    | 27 °C | Raw   |
| 300    | 162    | 96     | 14     | 520    | 7.76 | 0.92   | 1.1   | 18     | 182    | 27 °C | Run   |
| 60.53% | 95.38% | 85.23% | 56.25% | 54.78% | -    | 23.33% | 48.0% | 48.57% | 51.47% |       |       |



| Parameters           | Unit       | Raw                 | Run                  | Efficiency |        |
|----------------------|------------|---------------------|----------------------|------------|--------|
| Heavy metals removal | Cu(II)     | mgL <sup>-1</sup>   | 4.27                 | 3.12       | 26.93% |
|                      | Cr(II)     | mgL <sup>-1</sup>   | 5.27                 | 4.1        | 22.2%  |
|                      | Fe(II)     | mgL <sup>-1</sup>   | 5.99                 | 4.22       | 29.55% |
|                      | Ni(II)     | mgL <sup>-1</sup>   | 3.2                  | 2.75       | 8.19%  |
|                      | Zn(II)     | mgL <sup>-1</sup>   | 1.97                 | 1.82       | 7.61%  |
|                      | Co(II)     | mgL <sup>-1</sup>   | 2.5                  | 2.32       | 7.2%   |
|                      | Cd(II)     | mgL <sup>-1</sup>   | 2.1                  | 1.98       | 5.71%  |
|                      | Pb(II)     | mgL <sup>-1</sup>   | 1.9                  | 1.87       | 5.79%  |
| Fecal Coliform       | unit/100ml | 5.4x10 <sup>6</sup> | 4.5 x10 <sup>5</sup> | 91.7%      |        |

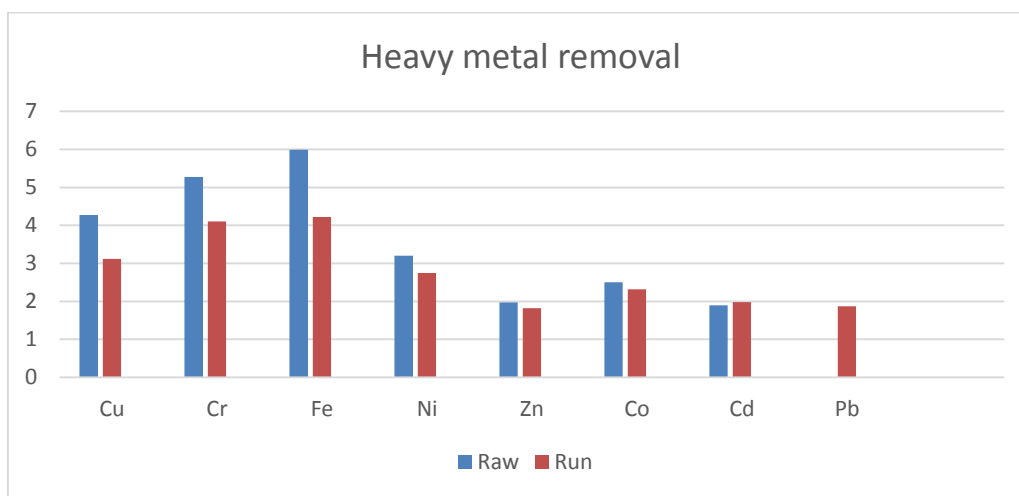
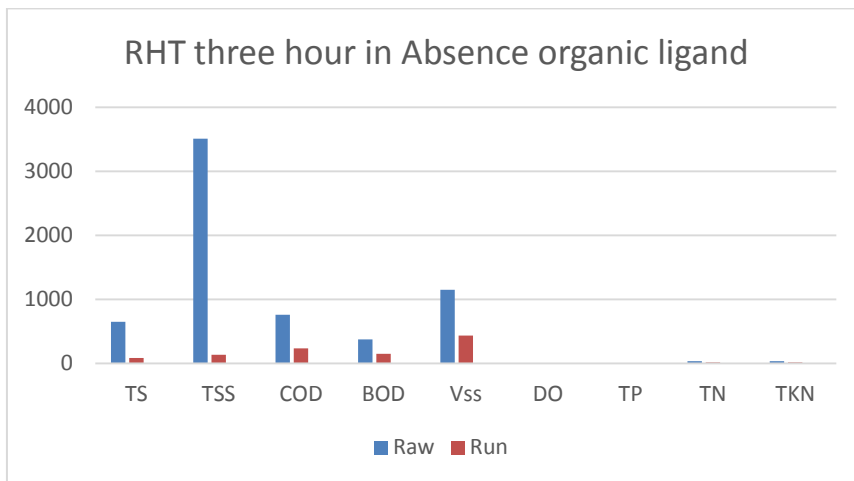


Chart (31) The results of heavy metal decreases as HRT 1 hr. in absence of the organic ligand

3.5 Post-Treatment of Industrial Wastewater at RHT Three Hour in Absence of Organic Ligand. (Table 6)

| COD   | TSS    | TS     | TKN   | VSS   | pH   | DO    | TP     | TN     | BOD    | Tem   | E.X.P |
|-------|--------|--------|-------|-------|------|-------|--------|--------|--------|-------|-------|
| 760   | 3510   | 650    | 32    | 1150  | 7.79 | 1.2   | 1.58   | 35     | 375    | 27 °C | Raw   |
| 235   | 131    | 81     | 12    | 431   | 7.73 | 0.82  | 0.98   | 13     | 148    | 27 °C | Run   |
| 69.1% | 96.27% | 87.54% | 62.5% | 62.5% | -    | 31.7% | 37.97% | 62.86% | 60.53% | -     |       |



| Parameters           | Unit              | Raw                 | Run                  | Efficiency |        |
|----------------------|-------------------|---------------------|----------------------|------------|--------|
| Heavy metals removal | Cu(II)            | mgL <sup>-1</sup>   | 4.27                 | 2.95       | 30.91% |
|                      | Cr(III)           | mgL <sup>-1</sup>   | 5.27                 | 3.87       | 26.57% |
|                      | Fe(III)           | mgL <sup>-1</sup>   | 5.99                 | 3.65       | 39.1%  |
|                      | Ni(II)            | mgL <sup>-1</sup>   | 3.2                  | 2.11       | 34.1%  |
|                      | Zn(II)            | mgL <sup>-1</sup>   | 1.97                 | 1.31       | 33.5%  |
|                      | Co(II)            | mgL <sup>-1</sup>   | 2.5                  | 1.99       | 20.4%  |
|                      | Cd(II)            | mgL <sup>-1</sup>   | 2.1                  | 1.68       | 20.0%  |
| Pb(II)               | mgL <sup>-1</sup> | 1.9                 | 1.35                 | 28.95%     |        |
| Fecal Coliform       | unit/100ml        | 5.4x10 <sup>6</sup> | 4.7 x10 <sup>4</sup> | 99.13%     |        |

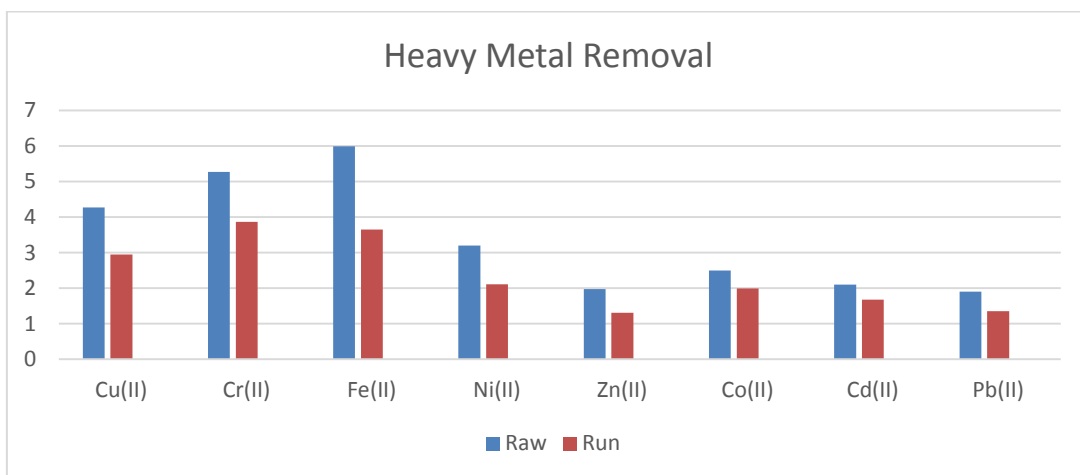
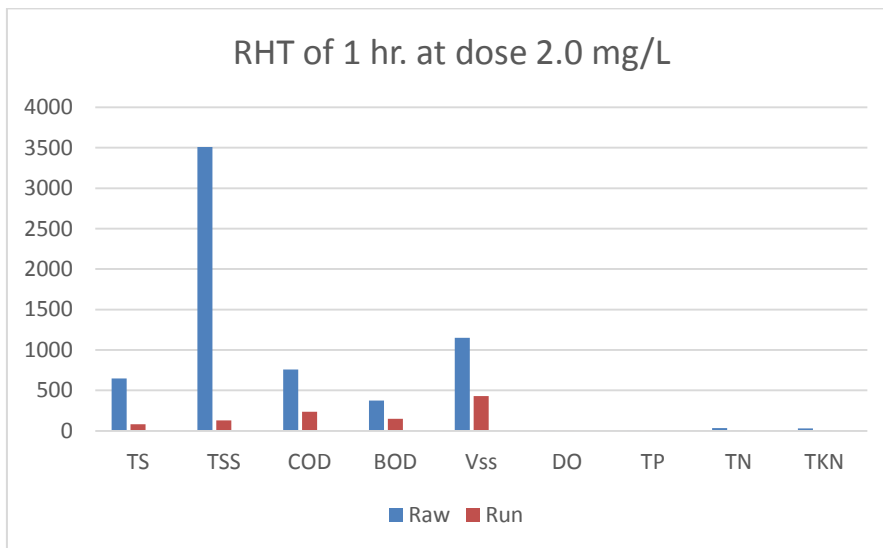


Chart (32) The results of heavy metal decreases as HRT3 hrs. in absence of the organic ligand

3.6 Post-Treatment of Industrial Wastewater at RHT One Hour at Dose 2.0 GI<sup>-1</sup> from the Organic Ligand. ( Table 7)

Table (5) Performance results in treating 5Lwastewater at a total HRT of 1hrs (at dose 2.0 gL<sup>-1</sup> from the organic ligand)

| COD    | TSS    | TS     | TKN   | VSS    | pH   | DO     | TP     | TN     | BOD    | Tem   | E.X.P |
|--------|--------|--------|-------|--------|------|--------|--------|--------|--------|-------|-------|
| 760    | 3510   | 650    | 32    | 1150   | 7.79 | 1.2    | 1.58   | 35     | 375    | 27 °C | Raw   |
| 198    | 120    | 68     | 9.8   | 385    | 7.73 | 0.68   | 0.72   | 10     | 131    | 27 °C | Run   |
| 73.95% | 96.61% | 89.54% | 69.4% | 66.52% | -    | 43.33% | 54.43% | 71.43% | 65.1%) | -     |       |



| Parameters           | Unit       | Raw                 | Run                | Efficiency |         |
|----------------------|------------|---------------------|--------------------|------------|---------|
| Heavy metals removal | Cu(II)     | mgL <sup>-1</sup>   | 4.27               | 0.67       | 84.24%  |
|                      | Cr(III)    | mgL <sup>-1</sup>   | 5.27               | 0.27       | 94.29%  |
|                      | Fe(III)    | mgL <sup>-1</sup>   | 5.99               | 1.82       | 70%     |
|                      | Ni(II)     | mgL <sup>-1</sup>   | 3.20               | 0.53       | 83.43%  |
|                      | Zn(II)     | mgL <sup>-1</sup>   | 1.97               | 0.32       | 83.43%  |
|                      | Co(II)     | mgL <sup>-1</sup>   | 2.5                | 0.4        | 80.95 % |
|                      | Cd(II)     | mgL <sup>-1</sup>   | 2.1                | 0.38       | 82.73 % |
|                      | Pb(II)     | mgL <sup>-1</sup>   | 1.9                | 0.26       | 85.56 % |
| Fecal Coliform       | unit/100ml | 5.4x10 <sup>6</sup> | 3 x10 <sup>3</sup> | 99.9%      |         |

Volume = 5L Semisolid sludge, (RT) Retention Time = 1 hours Wt. of Lig(1) = 2.0gm

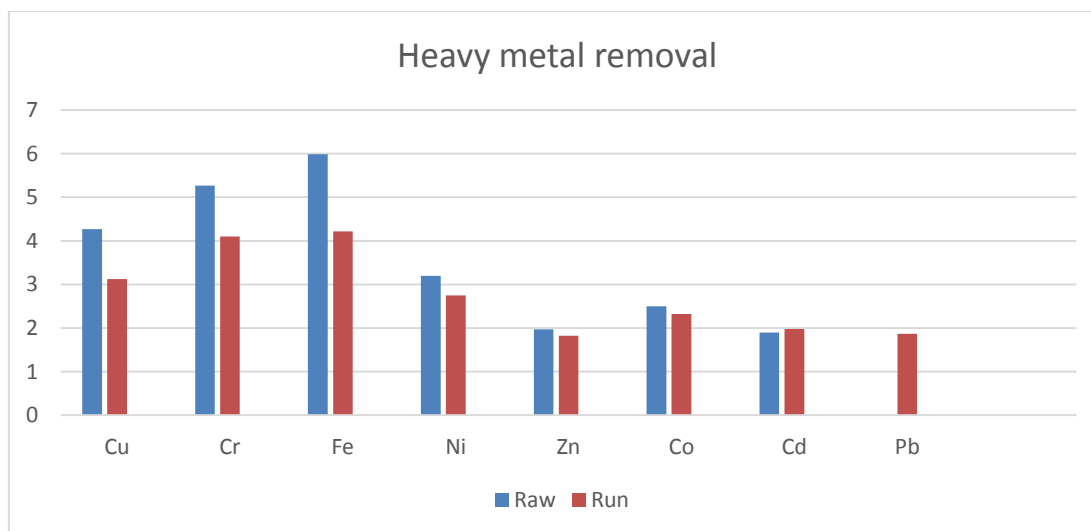


Chart (33) The results of heavy metal decreases as HRT3 hrs. (At dose 2.0 gL<sup>-1</sup>)

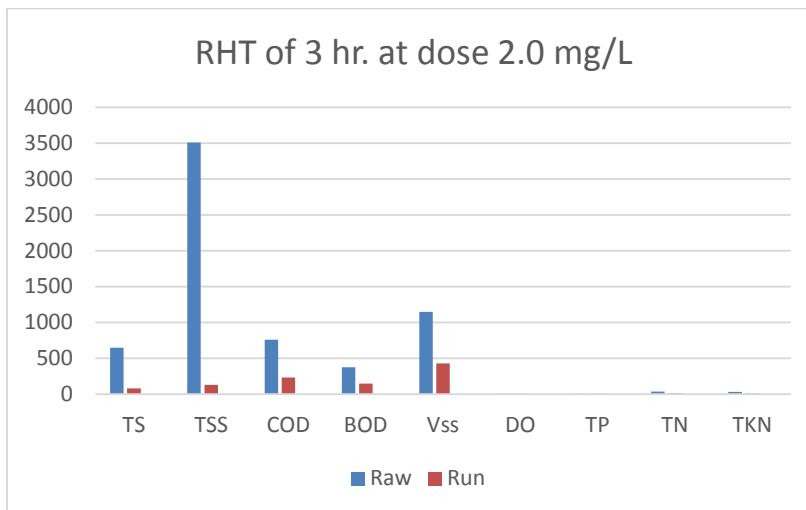
Particles of heavy metals should be absorbed and captured in the surface of the ligand surface area. Particles to be digested it should be captured first and the digestion and the biodegradation processes will be then occurred in the land. Available data indicated good performance of the ligand regarded to heavy metals removal efficiency. Also, the results also showed that, the residual values of fecal coliform when treated with the ligand , the amount decreased from 3.4x10<sup>6</sup> to 3.4x10<sup>3</sup> (99.9%).

### 3.7 Post-Treatment Of Industrial Wastewater At RHT 3hrs At Dose 2.0 GI<sup>-1</sup> From The Organic Ligand

Table (6) Performance results in treating 5L semisolid at a total HRT of 3hrs (at dose 2.0 gL<sup>-1</sup> from the organic ligand).

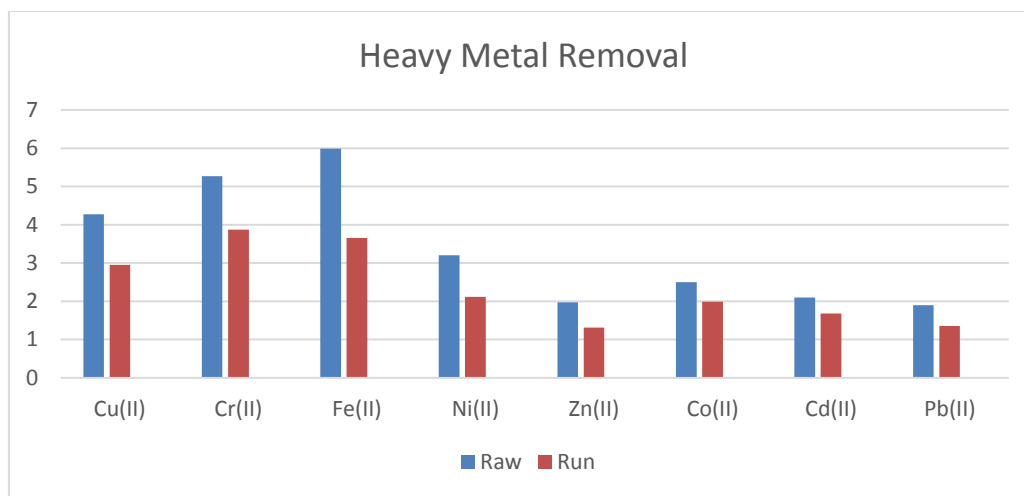
| COD   | TSS   | TS    | TKN    | VSS   | pH   | DO    | TP     | TN     | BOD   | Tem   | E.X.P |
|-------|-------|-------|--------|-------|------|-------|--------|--------|-------|-------|-------|
| 760   | 3510  | 650   | 32     | 1150  | 7.79 | 1.2   | 1.58   | 35     | 375   | 27 °C | Raw   |
| 163   | 102   | 52    | 7.9    | 335   | 7.6  | 0.52  | 0.66   | 8      | 118   | 27 °C | Run   |
| 78.6% | 97.1% | 92.0% | 75.31% | 70.9% | -    | 56.7% | 58.23% | 77.14% | 68.5% | -     |       |





| Parameters           | Unit       | Raw                 | Run                | Efficiency |         |
|----------------------|------------|---------------------|--------------------|------------|---------|
| Heavy metals removal | Cu(II)     | mgL <sup>-1</sup>   | 4.27               | 0.67       | 84.24%  |
|                      | Cr(III)    | mgL <sup>-1</sup>   | 5.27               | 0.27       | 94.29%  |
|                      | Fe(III)    | mgL <sup>-1</sup>   | 5.99               | 1.82       | 70%     |
|                      | Ni(II)     | mgL <sup>-1</sup>   | 3.20               | 0.53       | 83.43%  |
|                      | Zn(II)     | mgL <sup>-1</sup>   | 1.97               | 0.32       | 83.43%  |
|                      | Co(II)     | mgL <sup>-1</sup>   | 2.5                | 0.4        | 80.95 % |
|                      | Cd(II)     | mgL <sup>-1</sup>   | 2.1                | 0.38       | 82.73 % |
|                      | Pb(II)     | mgL <sup>-1</sup>   | 1.9                | 0.26       | 85.56 % |
| Fecal Coliform       | unit/100ml | 5.4x10 <sup>6</sup> | 3 x10 <sup>3</sup> | 99.9%      |         |

At, Volume = 5L Semisolid sludge, (RT) Retention Time = 3 hours Wt. of Ligand (1) =2.0 g.



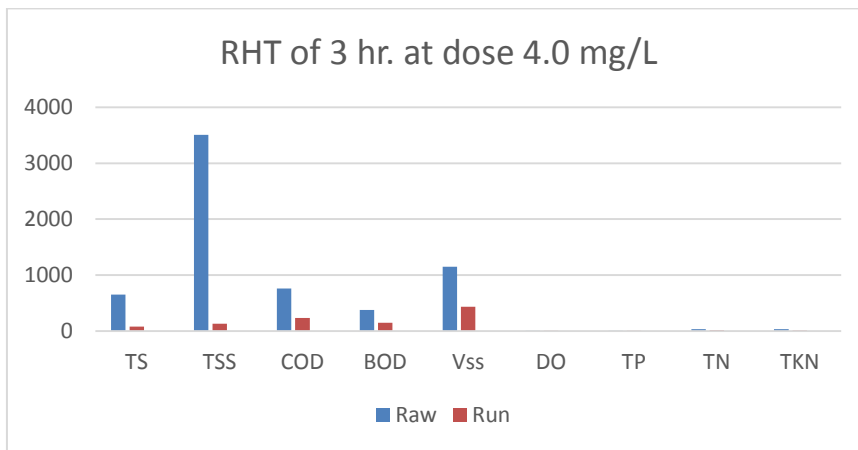
**Chart (34)** The results of heavy metal decreases as HRT3 hrs. (At dose 2.0 gL<sup>-1</sup>)

The results showed that concentration of heavy metal decreases as HRT 3hrs at dose 2.0 mg.L<sup>-1</sup> The Cu amount decrease from 4.27 to 0.27 mL<sup>-1</sup> (85.0%).The Cr amount decrease from 5.22 to 0.27 mL<sup>-1</sup> (94.0%). the Fe amount decrease from 4.98 to 0.44 mL<sup>-1</sup> (76.0%). Ni amount decrease from 2.20 to 0.40 mL<sup>-1</sup> (81.0%).The Zn amount decrease from 1.77 to 0.20 mL<sup>-1</sup> (88.0%). Particles of heavy metals should be absorbed and captured in the surface of the Ligand surface area. Particles to be digested it should be captured first and the digestion and the biodegradation processes will be then occurred in the land. Available data indicated good performance of the Ligand regarded to heavy metals removal efficiency. Also, the results also showed that, the residual values of fecal coliform when treated with the ligand, the amount decreases from 3.4x10<sup>6</sup> to 3.4x10<sup>3</sup> (99.9%).

### 3.8 Post-Treatment at RHT 3hrs in Presence of the Organic Ligand (At Dose 4.0 GI<sup>-1</sup> from the Ligand)

**Table (9)** Performance results of treating municipal wastewater at a total HRT of 3 hrs. (At dose 4.0 gL<sup>-1</sup> From the organic ligand)

| COD    | TSS    | TS    | TKN   | VSS   | pH   | DO    | TP     | TN     | BOD   | Tem   | E.X.P |
|--------|--------|-------|-------|-------|------|-------|--------|--------|-------|-------|-------|
| 760    | 3510   | 650   | 32    | 1150  | 7.79 | 1.2   | 1.58   | 35     | 375   | 27 °C | Raw   |
| 100    | 93     | 28    | 4.3   | 198   | 7.74 | 0.32  | 0.42   | 5.2    | 87    | 27 °C | Run   |
| 86.84% | 97.35% | 95.7% | 86.6% | 82.8% | -    | 73.7% | 73.42% | 85.14% | 76.8% | -     |       |



| Parameters           | Unit              | Raw                 | Run                | Efficiency |        |
|----------------------|-------------------|---------------------|--------------------|------------|--------|
| Heavy metals removal | Cu(II)            | mgL <sup>-1</sup>   | 5.2                | 0.78       | 85%    |
|                      | Cr(II)            | mgL <sup>-1</sup>   | 4.65               | 0.27       | 92%    |
|                      | Fe(II)            | mgL <sup>-1</sup>   | 4.82               | 0.38       | 92%    |
|                      | Ni(II)            | mgL <sup>-1</sup>   | 3.2                | 0.45       | 85.93% |
|                      | Zn(II)            | mgL <sup>-1</sup>   | 2.8                | 0.38       | 82.43% |
| Co(II)               | mgL <sup>-1</sup> | 2.5                 | 0.85               | 75%        |        |
| Cd(II)               | mgL <sup>-1</sup> | 4.153               | 0.68               | 79%        |        |
| Pb(II)               | mgL <sup>-1</sup> | 3.62                | 0.31               | 81.2%      |        |
| Fecal Coliform       | unit/100ml        | 5.4x10 <sup>6</sup> | 3 x10 <sup>3</sup> | 99.9%      |        |

At, Volume = 5L Semisolid sludge, (RT) Retention Time = 3 hours Wt. of the organic Ligand (1) = 4.0 g

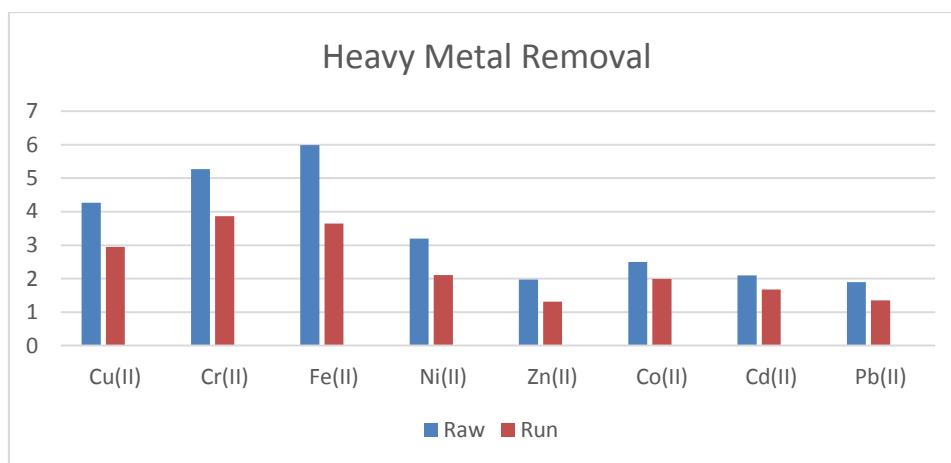


Chart (35) The results of heavy metal decreases as HRT3 hrs. (At dose 4.0 gL<sup>-1</sup>)

The results show that concentration of heavy metal decreases as HRT 3hrs at dose 4.0 mg.L<sup>-1</sup> The Cu amount decrease from 4.27 to 0.27 mL<sup>-1</sup> (91.0%).The Cr amount decrease from 5.24 to 0.11 mL<sup>-1</sup> (96.0%). The Fe amount decrease from 5.01 to 0.44 mL<sup>-1</sup> (96.0%).The Ni amount decrease from 2.23 to 0.20 mL<sup>-1</sup> (91.0%).The Zn amount decrease from 1.87 to 0.03 mgL<sup>-1</sup> (97.0%)

**Conclusion**

Cheap in cost and easy to install and operate) for removing chemical and biological parameters TS, TSS, COD, BOD, TN, TP, DO, VSS, and TKN and heavy metals ions like Cu(II), FE(III),Cr(III), Ni(II), Zn(II), Co(II), Cd(II) and PB(II) and also fecal coliform. The class results reached the highest level >90% in all removing levels.

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**Conflicts of Interest**

The authors declare no conflict of interest.

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