Section A-Research paper

Removal of wastewater contaminants from El-Dakhala polluted by anthropogenic sources using modified downflow hanging sponge system

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ABSTRACT

The presence of organic ,inorganic and biological pollutants in Waste water leads to several environmental and health impact .Exposure of humans and animals to toxic pollutants cause severe effects include reduced animal growth and development for human .To mitigate the negative impacts of toxic pollutants on the health of humans , animals and the environment ,a variety of remediation processes have been developed . These remediation processes are classified into chemical and biological which are indicated to effective in treatment of toxic pollutants in Waste water. A new technology consists of mixing new polydentat organic ligand with Waste water under different conditions and allowed Waste water to pass through modified Bio-active Sorbent System . The main objective of the present study was carried out using polydentat ligand for the removal of notorious heavy metal and fecal coliforms .The metal ions were Cu (II) , Mn (II), Ni (II) , Cd (II), Fe (III), Pb (II) and Cr(III). Firstly, the study was held at 25ºC in the laboratory using Waste water metal ions and 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 ligand to the metal salts .At [2 L:1M] molar ratio at 25º 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 25 ºC and(2L:5M) molar ratio .the removal efficiency elevated to (6.57%-33%) after 30 min and to (15%-70%) at 60 min . Also, using the Bio-active Sorbent System showed that . In presence 2g L for 1 hour the result showed

the COD decreased 95.7% , TDS decreased 90.2 % PH decrease 3.7 % and POD deceased 95.5 % at 25 C . However , the **Cu** amount decreased from 4.29 to 0.64 mgL^{-1} (84.0 %) . The **Cr** amount decreased from 5.22 to 0.35 mgL^{-1} (93.0 %) .The **Fe** amount decreased from 5.02 to 1.15mgL^{-1} (77.3%). The **Ni** amount decreased from2.23 to 0.45mgL^{-1} (80.%) .The **Zn** amount decreased from 1.87 to 0.32 mgL^{-1} (82.0%) and the **Cd** amount decreased from 4.01 to 1.18 mgL^{-1} (70.1%) . The **Mn** amount decreased from 2.25 to 0.43 mgL^{-1} (80.9%) and fecal coliforms decreased from $5.4x10^6$ to $3x10^3$and (99.9%).

However using 2.0 mgL^{-1} for three hours the result the result showed the COD decreased 96.1% , TDS decreased 97.1 % PH decrease 12.04 % and POD deceased 95.9 % at 25 C . However the **Cu** amount decreased from 4.26 to 0.61 mgL^{-1} (86.0%). The **Cr** amount decreased from 5.2 to 0.29 mgL^{-1} (95.0%) . The **Mn** amount decreased from 2.15 to 0.41mgL^{-1} (88.0%). however the **Fe** amount decreased from 5.01 to 0.15mgL^{-1} (77%) and the **Cd** amount decreased from 4.3 to 1.1 mgL^{-1} (85.0%) . The **Ni** amount decreased from 2.23 to 0.41 mgL^{-1} (82.0%). The **Zn** amount decreased from 1.87 to 0.21 mgL^{-1} (89.0%). finally fecal coliforms decreased from $5.4x10^6$ to $3x10^3$and (99.9%).

Keywords*: Organic ligand* ,Bio-active Sorbent System, removal of *notoriousheavy metal , fecal coliforms.*

1. INTRODUCTION

The major aim of waste water treatment to remove as much of the suspended solids as possible before the remaining water, called effluents is discharge back to the environment . waste water is treated in 3 phases : primary (solid removal), secondary (bacterial decomposition) and tertiary (extra filtration). The main waste water treatment technologies used in Egypt are trickling filter, conventional activated sludge , oxidation ditches , stabilization ponds, contracted wetlands , Rotating biological contractor, sequencing batch reactors , up-flow anaerobic sludge blanket and modified septic tank .

Wastewater treatment .the residue that accumulates in waste water treatment plants is .2 called sludge (or biosolids). waste water is the solid, semisolid, or slurry residual

material . waste water refers to the residual, semi-solid material left from industrial waste water, processes. It can also refer to the settled suspension obtained from conventional drinking water treatment and numerous other industrial processes. The term is also sometimes used as a generic term for solids separated from suspension in a liquid; this soupy material usually contains significant quantities of interstitial water (between the solid particles)[1] . In 1992, a United States ban on ocean dumping of human sewage sludge went into effect, leaving cities the expensive option of having to dispose waste water in landfills[2].Seeing sewage contains not only heavy metals[3] and disease pathogens such as Clostridium edificial but nutrients as well, companies such as Synagro embraced the nutrient idea and marketed sludge as "bio-solids" to farmers as a free fertilizer[4] .Organic matter, which constitutes approximately 50 percent of the solid fraction of most sludge, improves the physical condition of soils [6]An increase in organic matter content decreases bulk density [7] , increases aggregate stability [7,10,11], increases water holding capacity [7,9,12- 14], and promotes greater water infiltration [7,8, 15].Improving the physical properties of soil increases soil productivity [8]. In coarse-textured soils, higher productivity occurs from the increase in the amount of water available to crops. In fine textured soils, productivity increases because reduction in bulk density increases infiltration, porosity, and aeration by aggregation of soil particles. The improvement of soil productivity by treatment with waste water is shown dramatically in experiments using drastically disturbed lands [16- 18] , the term pollutant is defined as part of the EPA 503 rule. The components of waste water have pollutant limits defined by the EPA. A Pollutant is an organic substance, an inorganic substance, a combination of organic and inorganic substances, or a pathogenic organism that, after discharge and upon exposure, ingestion, inhalation, or assimilation into an organism either directly from the environment or indirectly by ingestion through the food chain, could, on the basis of information available to the Administrator of EPA, cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunction in reproduction), or physical deformations in either organisms or offspring

of the organisms[19]. Trace elements have been defined as the elements that occur in natural systems in small amounts and that, when present in excessive concentrations, are toxic to living organisms[20] .The plant soil system has three protective mechanisms that can limit these potentially toxic trace elements in the aerial portions of a plant, and so minimize health problems to animals or humans. There are thousands other components of waste water that remain untested/undetected disposed of from modern society that also end up in sludge (pharmaceuticals, nano particles, etc.) which has been proven to be hazardous to both human and ecological health[21].Land application of waste water can have many beneficial effects. Supplying nutrients (N, P, secondary nutrients, and micronutrients) to the crops, improving soil physical properties, and increasing soil organic matter content are several advantages of land application of municipal waste water. Although these are obvious benefits, there are also concerns that must be addressed to insure a safe, economical, and environmentally sound approach to applying waste water to the soil. The most commonly voiced concerns include: 1) the potential for damage to soils, plants, animals, and humans because of possible toxic metal applications; and 2) the potential for pathogen transfer .A change in soil pH can result from application of waste water. Increased soil pH occurred when municipal waste water was added to soils [22, 23]. Metals exist in different forms in municipal waste water. Their form depends on the chemical properties of the sludge and on the chemistry of the metal [24, 25]. Cadmium concentration increased in plant tissue as soil Cu levels increased [63]; the levels of Cr, Cd, and Zn also affected the magnitude of the increase. These interactions are extremely complex and are not well understood. The presence and the concentrations of other metals can have a pronounced effect on the uptake of the metal in question [27].In 2009 the EPA released the Targeted National waste water Study, which reports on the level of metals, chemicals, hormones, and other materials present in a statistical sample of waste water .Some highlights include: Silver is present to the degree of 20 mg/kg of waste water, on average, a near economically recoverable level, while some sludge of exceptionally high quality have up to 200 milligrams of silver per

kilogram of sludge; one outlier demonstrated a silver lode of 800–900 mg per kg of sludge. Lead, arsenic, chromium, and cadmium are estimated by the EPA to be present in detectable quantities in 100% of national waste water in the US, while thallium is only estimated to be present in 94.1% of sludge[28]. The chemicals remain adsorbed to surface soil particles, making them more susceptible to surface erosion than infiltration[29].

2.Materials and Instruments

Chemicals : All reagents employed for the preparation of ligand and its metal complexes were of the analytical grade and used without further purification. Metal salts were provided from Sigma-Aldrich Company. 4-Amino salicylic Acid (Assay ≥ 99.99 %), Hydrazine Hydrate (Assay ≥ 98 %), H_2SO_4 (Assay 99.7%) and ethanol (Assay ≥ 99.8 %) were also obtained from Sigma-Aldrich Company

Instrumentation and measurements: The ligand and its metal complexes were analyzed for C, H, N 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) are reported relative to TMS. FT-IR spectra of the ligand and its metal complexes were measured using KBr discs by a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 4000-400 cm-1. Electronic spectra in the 200-900 nm regions was recorded on a Perkin-Elmer 550 spectrophotometer. The thermal analyses (DTA and TGA) were carried out on a Shimadzu DT-30 thermal analyzer from room temperature to 800 ºC at a heating rate of 10 ºC/min. Magnetic susceptibilities were measured at 25oC by the Gouy method using mercuric tetrathiocyanatocobaltate(II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal's constant 30. The magnetic moments were calculated from the equation:

$$(\mu_{eff} = 2.828 (\chi n \times T)\ 1/2)$$

(1) The molar conductance of 10-3 M solution of the complexes in DMSO was measured at 25ºC with a Bibbyconductometer 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.

Laboratory Preparation : The ligand, (**H_3L**) was synthesized by boiling (10.0 g, 1.4 mol) of 4-Aminosalicylic acid (10.0 g, 0.6mol) in 50 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) Hydrazine hydrate. The solution was refluxed with stirring for two hours at 80 ^oC, then left to cool at room temperature. The

precipitated product was filtered off then dried under vacuum over anhydrous $CaCl_2$ or dried in air. (Figure 1) and the Metal complexes had prepared from ligand (2L : 1M) or (2L : 5M)

2.1. Bio-active Sorbent System: The Bio-active Sorbent module column as shown below in scheme (1) consists of four identical segments connected vertically, each segment will be equipped with 25 L of polyurethane foam (PF) warped with plastic material randomly distributed in the whole reactor. The Bio-active Sorbent System was made of PVC, with a capacity of 0.3 m3 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 256m2/m3, density 30 kg/m3, 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 27mm height × 4mm diameter. The wastewater effluent was flowed by gravity to the distributor which will be located on the top of the Bio-active Sorbent module and will be rotated at 15 rpm. Chemical parameters such as COD, BOD, TSS, TDS, NO2 and NO3 will be monitored at retention time 3hrs according to APHA (2005) "Standard Methods for the Examination of Water and Wastewater".

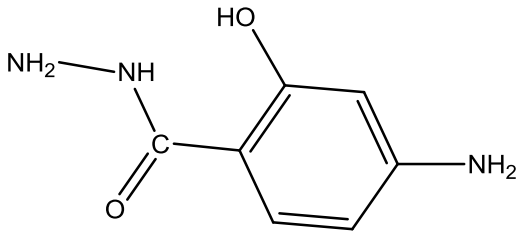
Scheme (1)

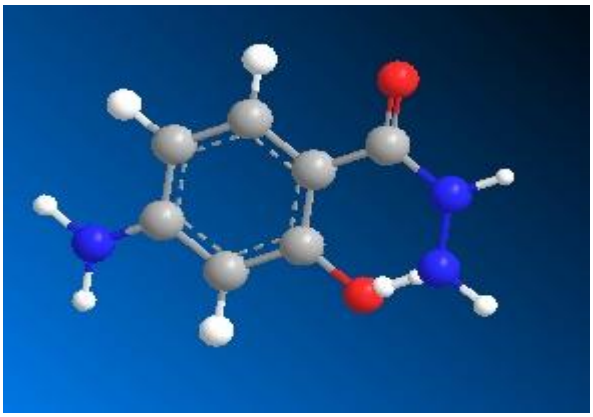
Synthesis of the organic Ligand.

4-Amino salicylic acid (10.0 g, 0.5mol) was boiled in ethanol for 1h and few drops of conc. H_2SO_4 were added , the reaction solution was refluxed with continuous stirring for 3hrs at 60-70 ºC. (4.27 g, 1.33mol) of Hydrazine hydrate was added. The mixture was refluxed with stirring for more 2hrs and the yellowish precipitate which formed was filtered off, washed with ethanol and dried in air.

The structure of the (Ligand) and 3D are shown in Fig (1).

Chemical Formula : $C_7H_9N_3O_2$, M.Wt : 167 , Color : Off-whit , M.P : >300, Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1}Analy Elemental Analysis calc :C ,45.7, H, 8.38, N , 21.36 ,. Found (%), C, 45.22, H ,8.10,N, 20.97





The structure of the Ligand and 3D are shown in Fig (1)

IR Spect

υ(H-Bond)= 3579 - 3200 Cm^{-1} , 3191 - 2560 Cm^{-1}, υ(OH) = 3411 , 3378 Cm^{-1} , υ(C=O)= 1664,1620 Cm^{-1} , υ(NH)= 3185 Cm^{-1} ,υ(CH2)= 3125,2890 Cm^{-1} ,υ(NH2)= 3310, 2891 Cm^{-1}, υ(OH) = 1330,1285 Cm^{-1}

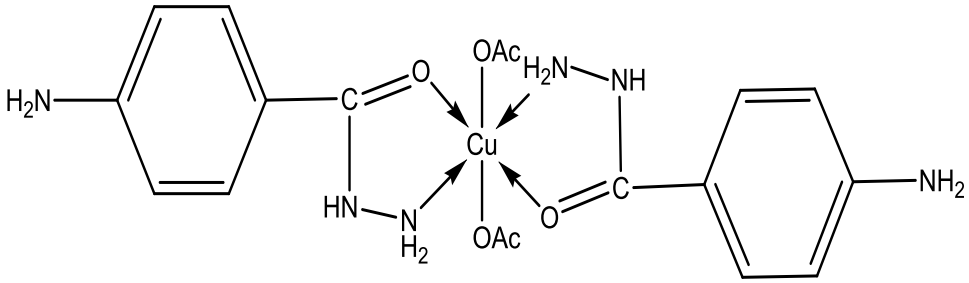
Mass spectrum :H_4N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

UV-vis : 290 nm , 315 due to $\pi \rightarrow \pi^*$,$n \rightarrow \pi^*$ transitions

[1]**H-nmr** (deuterated DMSO) : NH = 7.5 ppm , NH_2= 4.7 ppm , CH_2 group 2.72 -3.35 ppm , CH 2.1 ppm , OH 5.3 ppm

Complex (1) (2L : 1 M) $Cu(OAc)_2$

Chemical Formula : $C_{18}H_{26}N_6O_9Cu$, M.Wt : 528 , Color : yellowish Brown , M.P : >300 C , Cond : 9.45 Ω^{-1} $mol^{-1}Cm^{-1}$; Elemental Analysis calc C 40.91 , H, 3.79, N, 15.91, Cu, 11.99 Found (%), C, 40.23 , H, 3.51, N , 15.52, Cu , 10.52



.2H2O

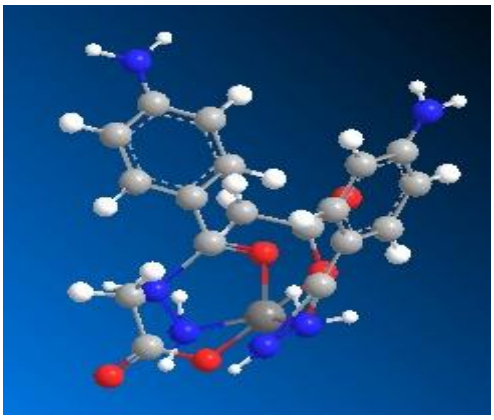


Fig (2) the structure of and 3D of complex (1)

IR Spect :

υ(H_2O) = 3500 - 3280 Cm^{-1} , υ(H-Bond)= 3550 - 3210 Cm^{-1} , υ(OH) = 3430,3345 Cm^{-1} , υ(C=O)= 1647 Cm^{-1} , υ(Ar)= 1530,1492 Cm^{-1} , 770,750 Cm^{-1} , υ(OAc) = 1430,1315 Cm^{-1} , υ(OH)= 1242,1315 Cm^{-1} , υ(Cu O)= 605 Cm^{-1} , υ(Cu N)= 565 Cm^{-1}

μ eff : 1.69 B.M

Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

UV-vis : 293 nm , 319 , 736 , 576 , 611 nm due to $\pi \rightarrow \pi^*$,$n \rightarrow \pi^*$ and d-d transitions .

ESR : g_{11}=2.13 , $g_{\perp}$ =2.07 , g_{iso} =2.09

Octahedral structure with covalent bond character

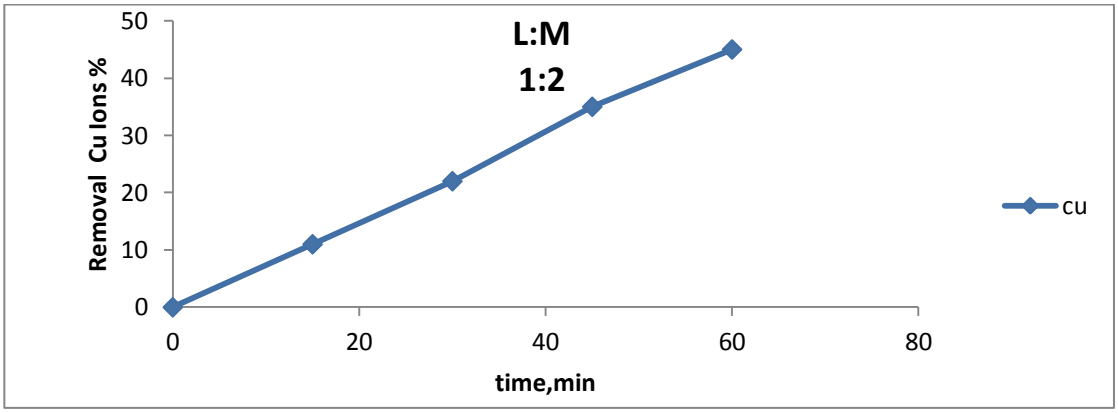


Chart (1) Removal Cu ions % complex (1) of Wast water

At 30 ºC (2L : 1M)

15 min	11 %
30 min	22 %
45 min	37 %
60 min	45 %

Complex (2) (2L:5M) $Cu(OAc)_2$

Chemical Formula: $C_{26}H_{44}N_6O_{20}Cu_3$, M.Wt : 951 , Color : Brown , M.P : >300 C , Cond : 9.45 Ω-1 mol-1 Cm-1 Elemental Analysis calc , C , 32.8, H, 4.63, N, 8.83, Cu, 20.1 ,.Found (%) C ,32.51 H, 4.21, N, 8.33, Cu, 19.75

IR Spect :

υ(H-Bond)= 3550 - 3320 Cm-3310 - 2780 Cm^{-1},υ(OH) = 3445 , 3400 Cm^{-1},υ(C=O)= 1638,1626 Cm-1,υ(NH)= 3200 Cm^{-1},υ(CH_2)= 3120,2890 Cm^{-1},υ(NH_2)= 3380,2890 Cm^{-1},υ(OH) = 1325,1295 Cm^{-1}

μ eff 1.53 B.M

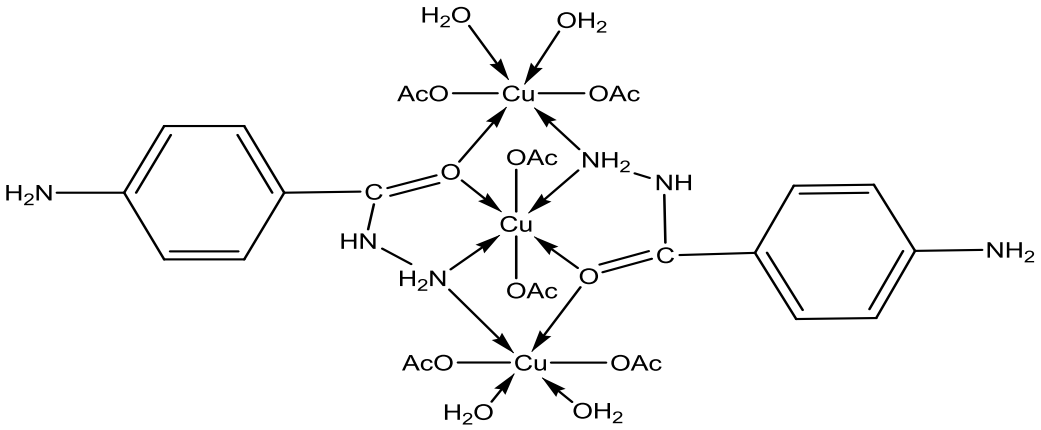
Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

UV-vis : 296 nm , 321 , 476 , 606 nm due to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and d-d transitions .

ESR g_{iso} : 2.10

Covalent bond character with Octahedral geometry



.2H2O

Fig (3) the structure of and 3D of complex (2)

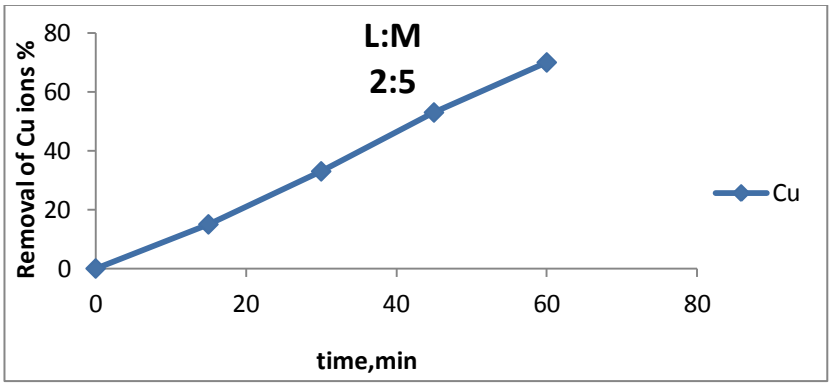


Chart (2) Removal Cu ions % versus time complex (2) of Wast water

At 30 ºC (2L : 5M)

15 min 17 %

30 min 33 %

45 min 53 %

60 min 70 %

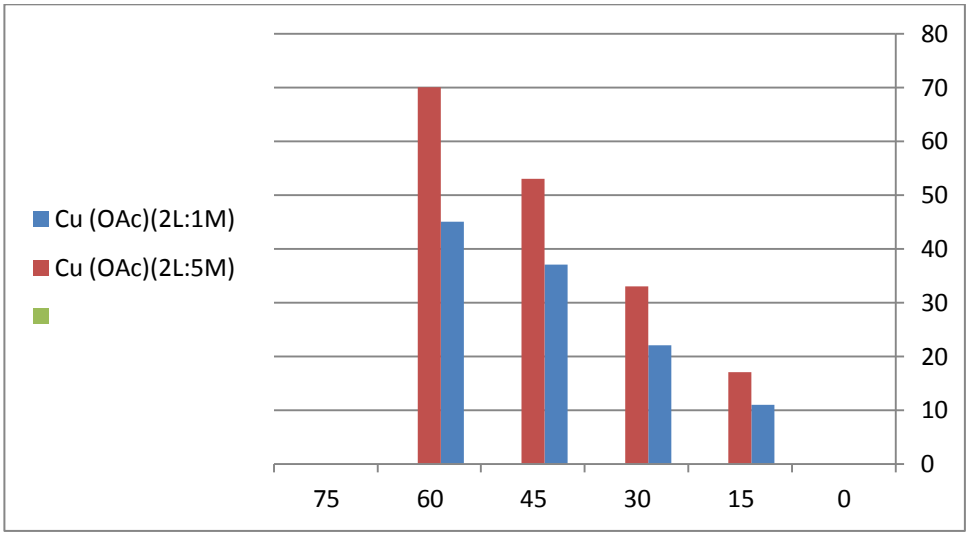
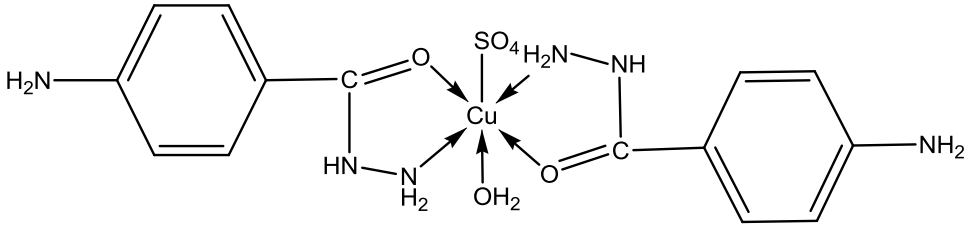


Chart (3) Removal Cu ions % complex (1,2) of Wast water

Complex (3) (2L:1M) $Cu(SO_4)_2$

Chemical Formula: $C_{14}H_{26}N_4O_{12}SCu$, M.Wt : 538 , Color : yellowish Brown , , M.P : >300 C , Cond : 9.45 Ω^{-1} mol-1 Cm^{-1}, 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



.2H2O

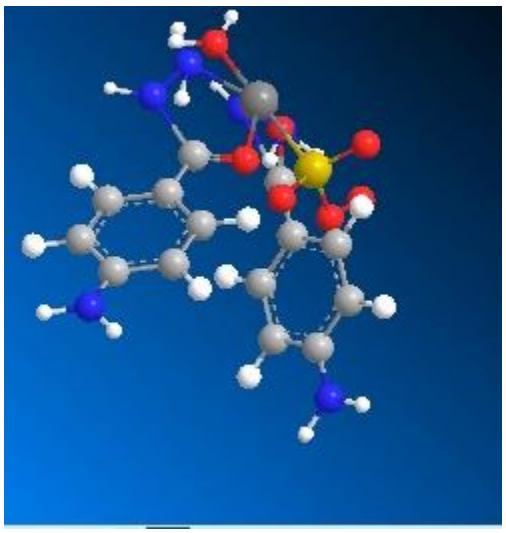


Fig (4) the structure of and 3D of complex (3)

IR Spect :

υ(H2O) = 3510 - 3310 Cm^{-1} , υ(H-Bond)= 3560 - 3250 Cm^{-1},-3240- 2550 Cm^{-1} , υ(OH) = 3480 Cm^{-1}

υ(C=O)= 1650 Cm^{-1}, ,υ(Ar) = 1540,1490 Cm^{-1} , υ(Cu O) = 610,730 Cm^{-1} , υ(OH)= 1242,1315 Cm^{-1} , υ(Cu O)= 605 Cm^{-1} , υ(Cu N)= 545 Cm^{-1}

μ eff 1.68 B.M

Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

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

H-nmr (deuterated DMSO) : NH = 7.4 ppm , NH_2= 4.8 ppm , CH_2 group 2.73 -3.36 ppm , CH 2-1 ppm , OH 5.4 ppm

ESR g_{iso} : 2.08

Octahedral structure with covalent character

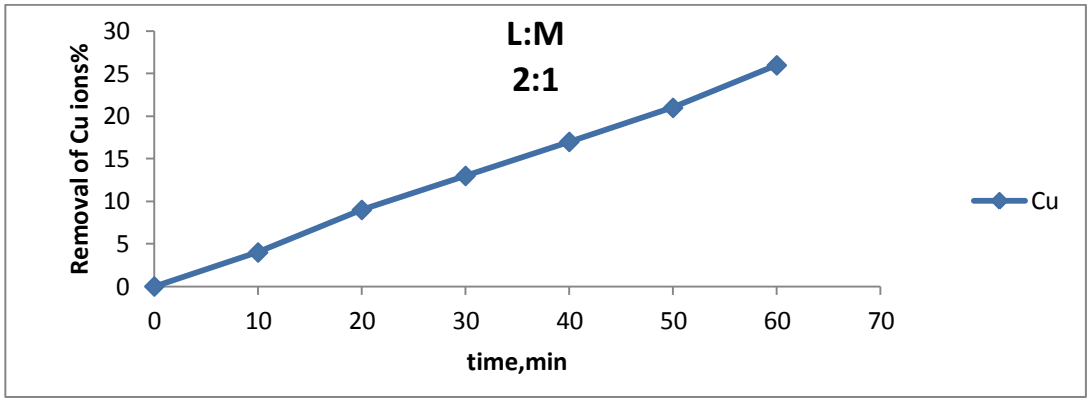


Chart (4) Removal Cu ions % complex (3) of Wast water

Complex (4) (2L:5M) Cu SO_4

Chemical Formula: $C_{14}H_{34}N_4O_{24}S_3Cu_3$, M.Wt : 929 , Color : yellowish Brown , M.P : >300 C, Cond : 9.45 Ω^{-1} mol^{-1} 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

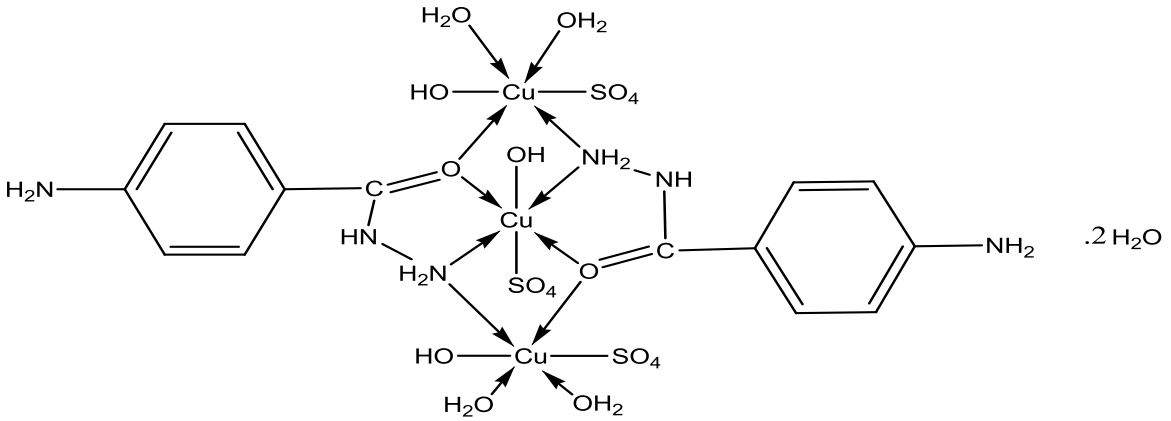


Fig (5) the structure of and 3D of complex (4)

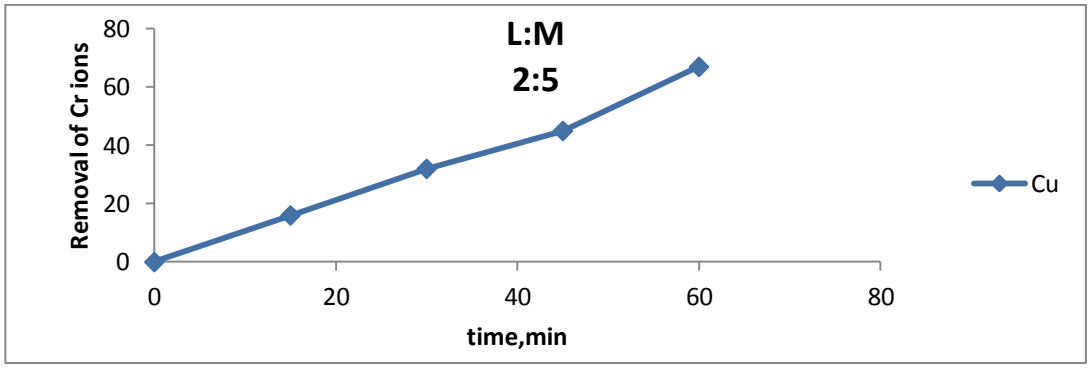


Chart (5) Removal Cu ions % complex (4) of Wast water

At 30 °C (2L : 5M)

15 min	16 %
30 min	32 %
45 min	48 %
60 min	67 %

Complex (5) (2L:1M) $Cu(NO_3)_2$

Chemical Formula : $C_{14}H_{22}N_6O_{12}Cu$, M.Wt : 530, Color : yellowish Brown , , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1}, Elemental Analysis calc ,C , 31.7, H, 4.15, N , 15.85, Cu, 11.94, Found (%) C, 31.35,H, 3.98, N, 15.56,Cu, 11.58

IR Spect : $\upsilon(H_2O)$ = 3530 - 3321 Cm^{-1},3320-3151Cm^{-1},υ(H-Bond)= 3600 - 3321 Cm^{-1},3312 - 2822 Cm^{-1},υ(OH) = 3471,3410 Cm^{-1},υ(C=O)= 1637,1617 Cm^{-1},υ(NH) = 3271 Cm^{-1},$\upsilon(NH_2)$ = 3377, 3352 Cm^{-1},υ(OAc) = 1511,1410 Cm^{-1},υ(OH)= 1350,1296Cm^{-1},υ(Cu O)= 629 Cm^{-1}

$\upsilon(NO_3)$=1368-1210,870 Cm^{-1}

μ eff 1.17 B.M

Mass spectrum :

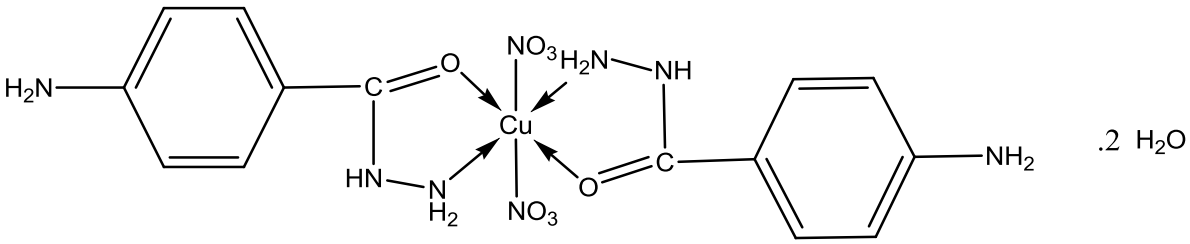
H_4N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

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

ESR g_{11} = 2.15 g_1 = 2.06 and g_{iso} = 2.09

A_{11} = 102G A_1 = 11 G and A_{iso} = 41 G

Octahedral structure with covalent character



.2 H_2O

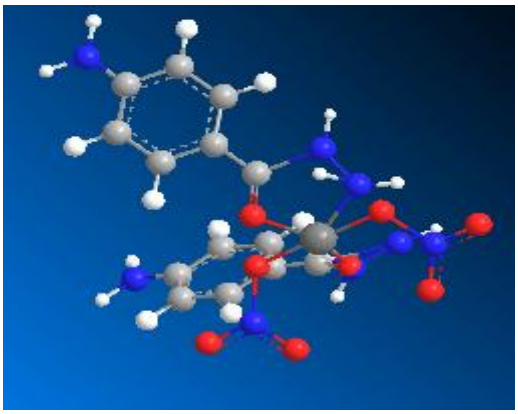


Fig (6) the structure of and 3D of complex (5)

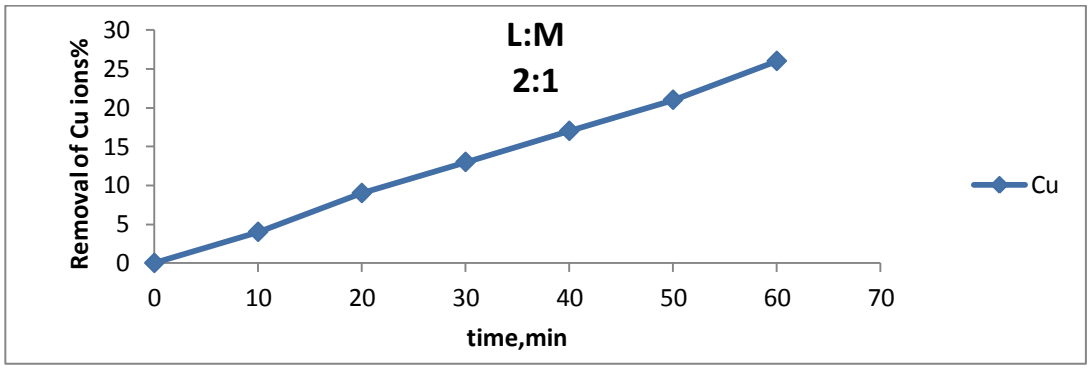


Chart (6) Removal Cu ions % complex (5) of Wast water

At 30 ℃ (2L : 1M)

15 min	6.5 %
30 min	12 %
45 min	17 %
60 min	24 %

Complex (6) (2L:5M) $Cu(NO_3)_2$

Chemical Formula: $C_{14}H_{28}N_{10}O_{26}Cu_3$, M.Wt : 944 , Color : yellowish Brown , M.P : >300 C , Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1}, Elemental Analysis calc, C 17.79, H, 2.97, N, 14.83 Cu ,20.1 , Found (%)C17.56 ,H ,1.72 , N, 14.67, Cu, 19.81

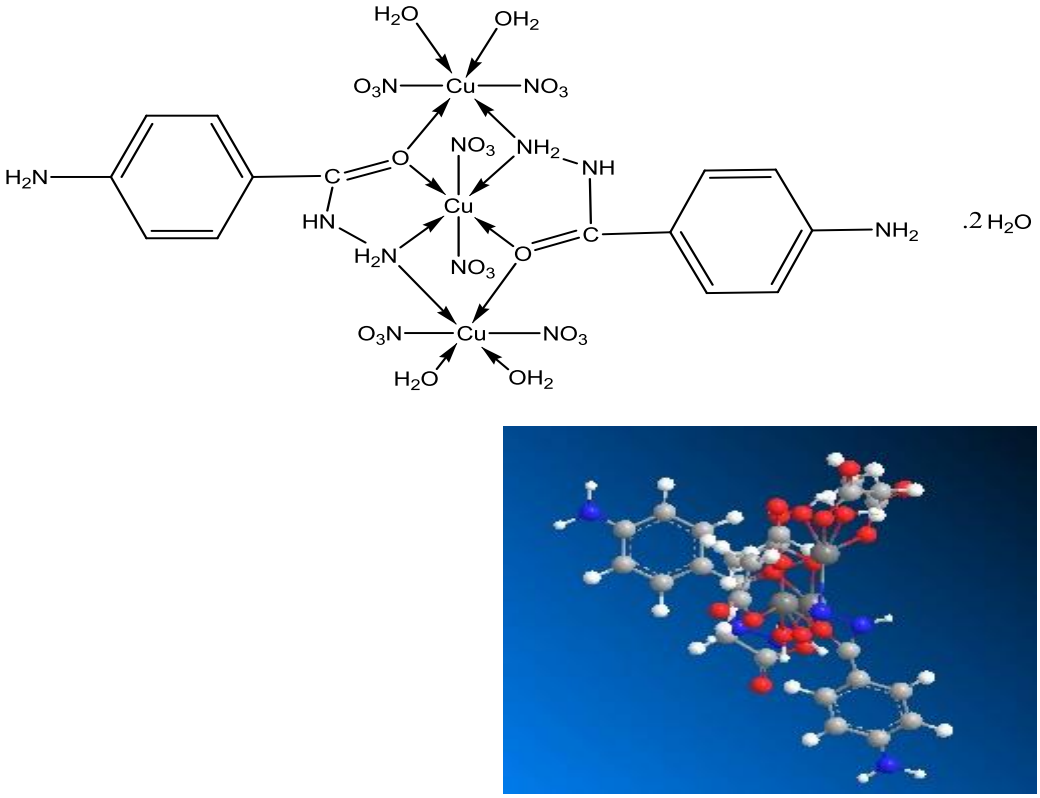


Fig (7) the structure of and 3D of complex (6)

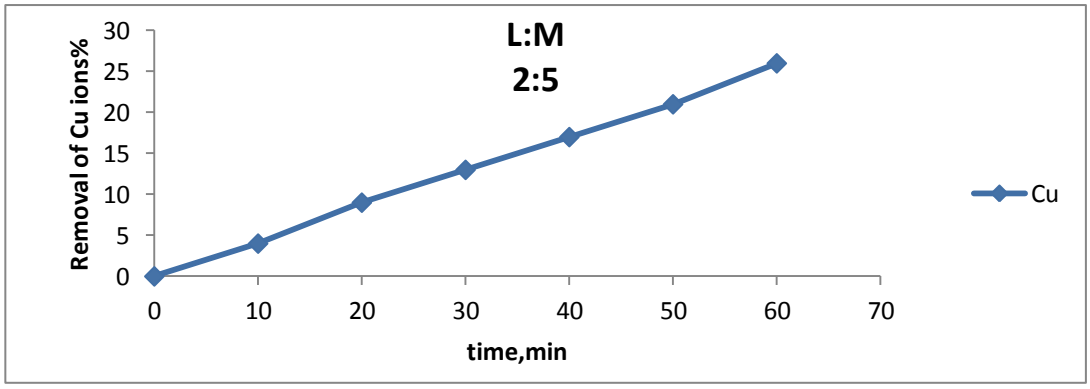


Chart (7) Removal Cu ions % complex (6) of Wast water

At 30 ºC (2L : 1M)

15 min	3.5 %
30 min	7.5 %
45 min	11 %

60 min 15 %

Complex (7) (2L:1M) $Cu(Cl)_2$

Chemical Formula : $C_{14}H_{22}N_4O_{12}Cl_2Cu$, M.Wt : 381 , Color : Brown , M.P : >300 C , Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , Elemental Analysis calc ,C, 44.1,H, 5.77, N, 14.7,Cu, 16.61 ,Found (%), C, 43.87, , H, 5.56, N, 14.41, Cu, 16.23

IR Spect : $\upsilon(H_2O)$ = 3530 - 3322 Cm^{-1},3322-3150 Cm^{-1},υ(H-Bond)= 3601 - 3320 Cm^{-1},3310 - 2825 Cm-1,υ(OH) = 3470,3415 Cm^{-1},υ(C=O)= 1636,1617 Cm^{-1},υ(NH) = 3275Cm^{-1},$\upsilon(NH_2)$ = 3376, 3355 Cm^{-1},υ(OAc) = 1511,1410 Cm^{-1},υ(OH)= 1355,1295 Cm^{-1},υ(Cu O)= 629 Cm^{-1}

μ_{eff} 1.17 B.M

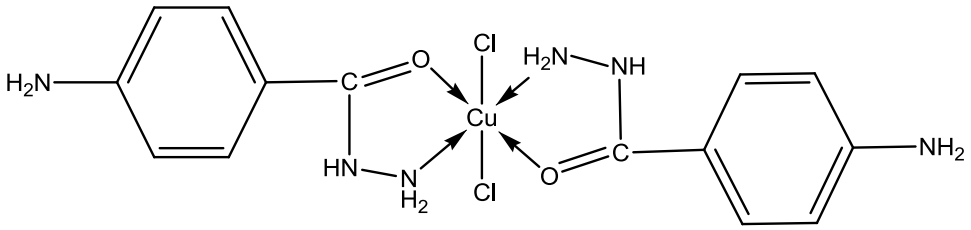
Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

UV-vis : 296 nm , 317 , 456 , 580 , 605 nm due to $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$ and d-d transitions .

ESR g_{11}= 2.14 g1 = 2.05 g_{iso} = 2.08

Octahedral structure with covalent bond character



.2H2O

Fig (8) the structure of and 3D of complex (7)

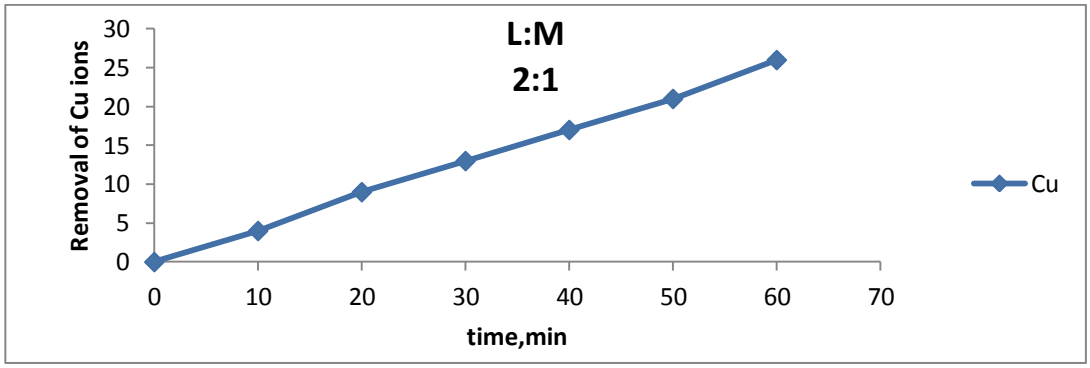


Chart (8) Removal Cu ions % complex (7) of Wast water

At 30 °C (2L : 1M)

15 min 5 %

30 min 10 %

45 min 14 %

60 min 19 %

Complex (8) (2L:5M) $Cu_3(Cl)_6$

Chemical Formula: $C_{14}H_{28}N_4O_9Cl_6Cu_3$, M.Wt : 801 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , Elemental Analysis, calc, C, 20.97, H, 3.5, N , 7.0, Cu ,23.71 , Found (%), C , 20.56, H , 3.22 , N , 6.82 , Cu , 23.45,

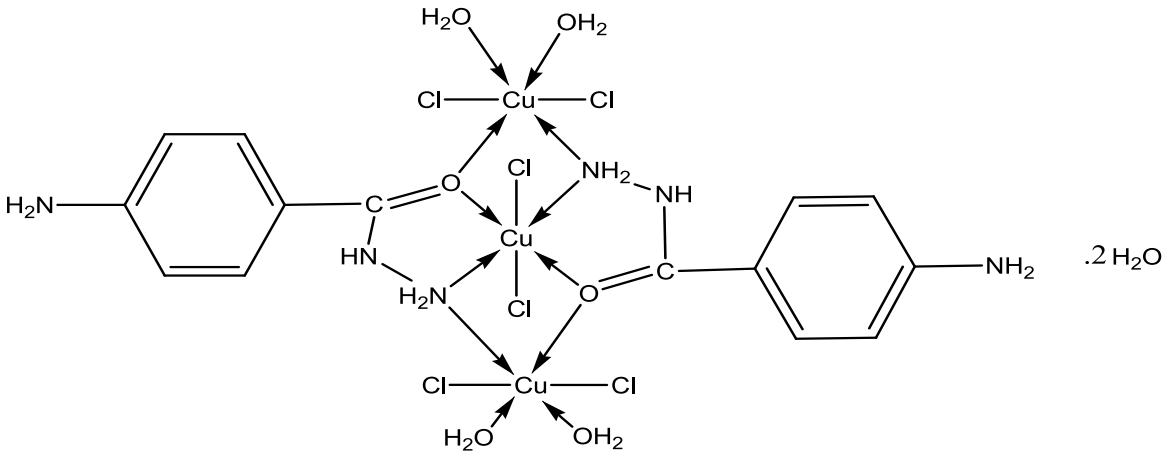


Fig (9) the structure of and 3D of complex (8)

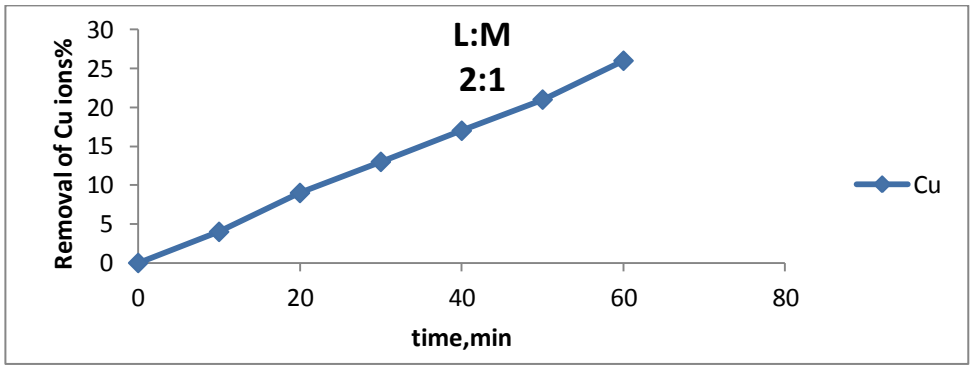


Chart (9) Removal Cu ions % complex (8) of Wast water

At 30 ºC (2L : 5M)

15 min 7.5 %

30 min 14 %

45 min 20.5 %

60 min 26 %

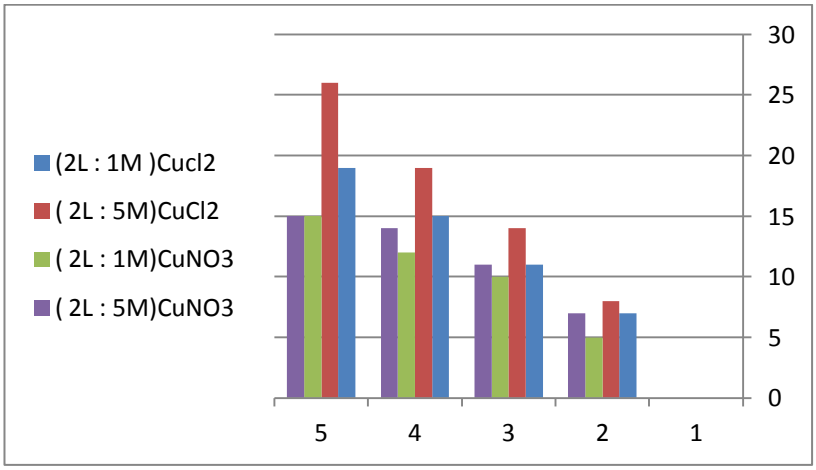
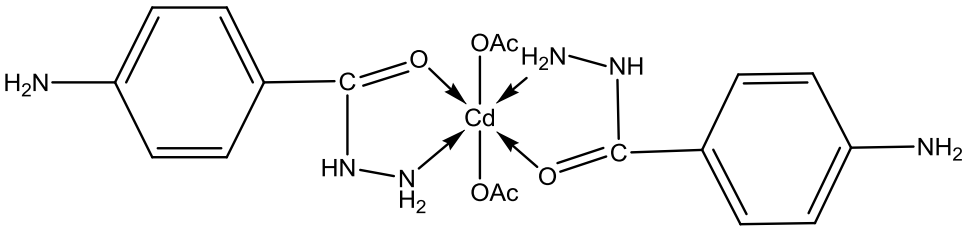


Chart (10) Removal Cu ions % complexes (5-8) of Wast water

Complex (9) (2L:1M) $Cd(OAc)_2$

Chemical Formula: $C_{18}H_{28}N_6O_{10}Cd$, M.Wt : 600 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , Elemental Analysis, calc, C, 36.0, H, 4.67 , N , 14.0, Cd,18.7 , Found (%), C , 35.826, H , 4.52 , N , 13.75 , Cd , 18.7



.2H2O

Fig (10) the structure of and 3D of complex (9)

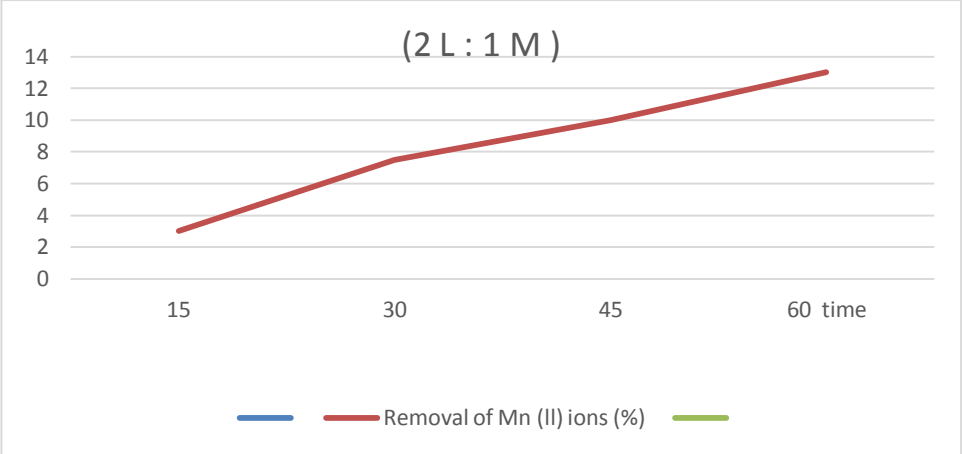


Chart (11) Removal Cd ions % complex (9) of Wast water

At 30 ºC (2L : 5M)

15 min 6 %

30 min 12 %

45 min 15 %

60 min 20 %

Complex (10) $Zn(OAc)_2$ (2L : 1M)

Chemical Formula : $C_{18}H_{28}N_4O_{10}Zn$, M.Wt : 553 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , 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 Spect :** $\upsilon(H_2O)$ = 3530 - 3320 Cm^{-1},3320-3155 Cm^{-1},υ(H-Bond)= 3604 - 3324 Cm^{-1},3310 - 2824 Cm-1,υ(OH) = 3470,3414 Cm^{-1},υ(C=O)= 1635,1615 Cm^{-1},υ(NH) = 3270 Cm-1,$\upsilon(NH_2)$ = 3376, 3350 Cm-1,υ(OAc) = 1515,1414 Cm-1,υ(OH)= 1354,1295 Cm^{-1},υ(Cu O)= 624 Cm^{-1}, υ(CuN)= 584 Cm^{-1}

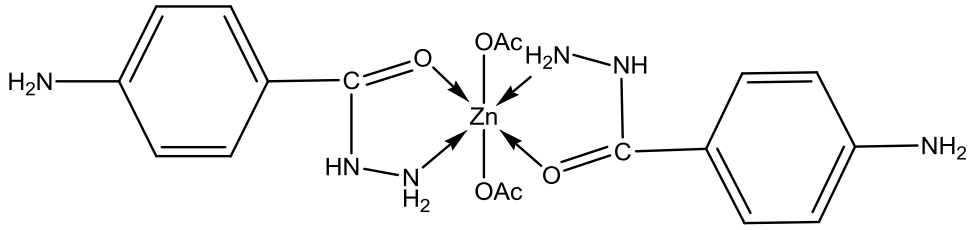
μ_{eff} Diamagnetic

Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

UV-vis : 299 nm , 318 , 424 , nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions .

Diamagnetic



.2H2O

Fig (11) the structure of and 3D of complex (10)

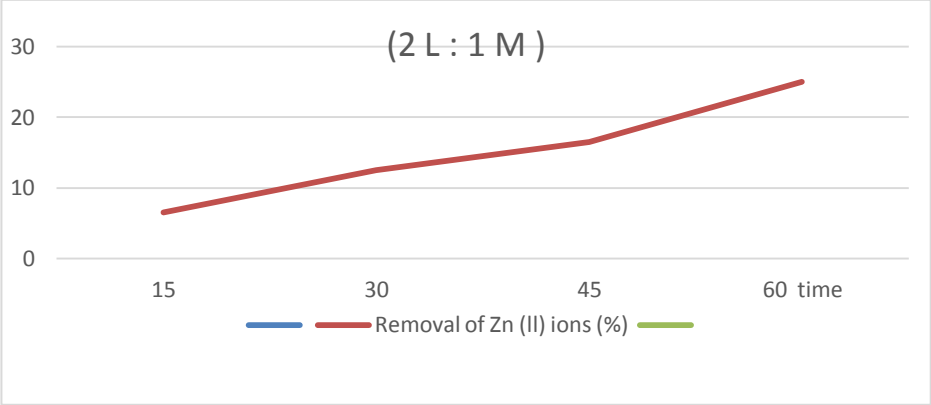


Chart (12) Removal Cu ions % complex (10) of Wast water

At 30 ºC (2L : 5M)	
15 min	4.5 %
30 min	7.5 %
45 min	12 %
60 min	15 %

$Cd(OAc)_2$ (2L : 5M) Complex (11)

Chemical Formula:$C_{26}H_{44}N_6O_{20}Cd_3$, M.Wt : 1096 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , Elemental Analysis, calc, C, 28.47, H, 4.01 , N , 7.66, Cd, 30.77 , Found (%), C , 28.0, H , 3.75 , N , 7.32 , Cd , 30.11

IR Spect : $\upsilon(H_2O)$ = 3533 - 3323 Cm^{-1},3320-3153 Cm^{-1},υ(H-Bond)= 3603 - 3323 Cm^{-1},3310 - 2828 Cm-1,υ(OH) = 3478,3418 Cm^{-1},υ(C=O)= 1638,1618 Cm^{-1},υ(NH) = 3270 Cm^{-1},$\upsilon(NH_2)$ = 3378, 3358 Cm^{-1},υ(OAc) = 1511,1410 Cm^{-1},υ(OH)= 1350,1298 Cm^{-1},υ(Cd O)= 620 Cm^{-1}, υ(CdO)= 588 Cm^{-1}

μ eff Diamagnetic

Mass spectrum :

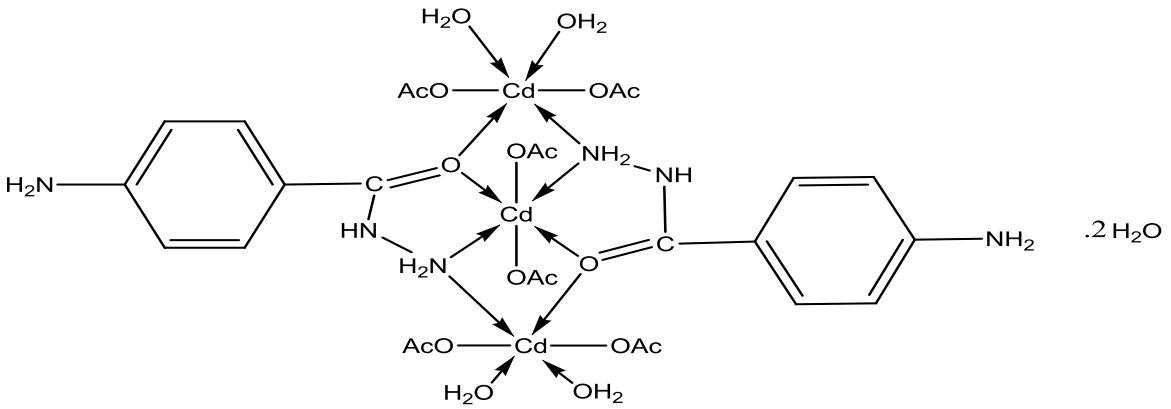
H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

UV-vis : 290 nm , 317 , 325 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions .

H-nmr (deuterated DMSO) : NH = 7.3 ppm , NH_2= 4.5 ppm , CH_2 group 2.70 -3.15 ppm , CH 2.2 ppm , OH 5.1 ppm

ESR giso = 2.03

Octahedral structure



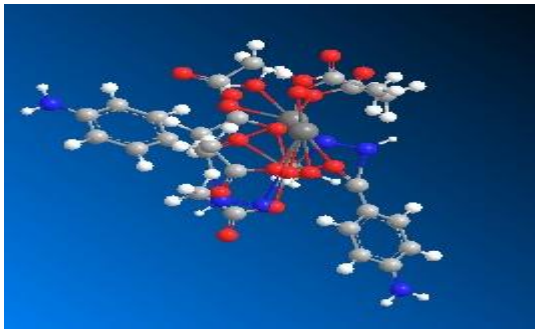


Fig (12) the structure of and 3D of complex (11)

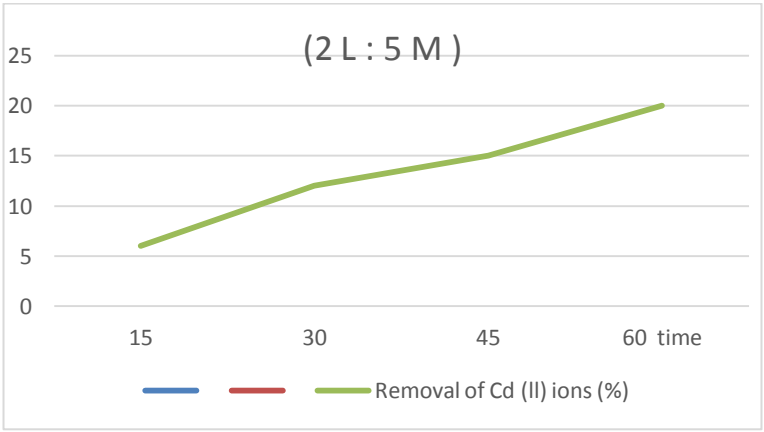


Chart (13) Removal Cd ions % complex (11) of Wast water

At 30 ºC (2L : 5M)

15 min 8.5 %

30 min 17.5 %

45 min 26 %

60 min 34 %

$Zn(OAc)_2$ (2L : 5M) Complex (12)

Chemical Formula: $C_{26}H_{44}N_6O_{20}Zn_3$, M.Wt : 553 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1}, 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 Spect : $\upsilon(H_2O)$ = 3566 - 3326 Cm^{-1},3326-3156 Cm^{-1},υ(H-Bond)= 3606 - 3326Cm^{-1},3316 - 2820 Cm^{-1},υ(OH) = 3456,3426 Cm^{-1},υ(C=O)= 1636,1616 Cm^{-1},υ(NH) = 3276 Cm^{-1},$\upsilon(NH_2)$ = 3376, 3350 Cm^{-1},υ(OAc) = 1516,1416 Cm^{-1},υ(OH)= 1346,1296Cm^{-1},υ(Cu O)= 621 Cm^{-1}, υ(ZnN)= 585 Cm^{-1}

μ eff Diamagnetic

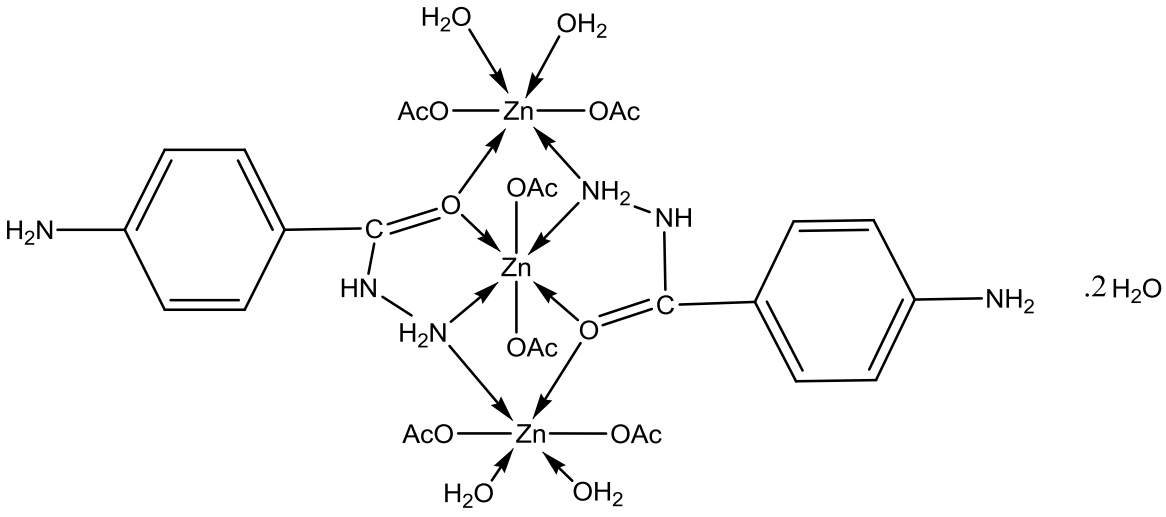
Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

UV-vis : 296 nm , 318 , 418 nm due to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions .

H-nmr (deuterated DMSO) : NH = 7.2 ppm , NH_2= 4.5 ppm , CH_2 group 2.70 -3.37 ppm , CH 2.0 ppm , OH 5.5 ppm

Diamagnetic



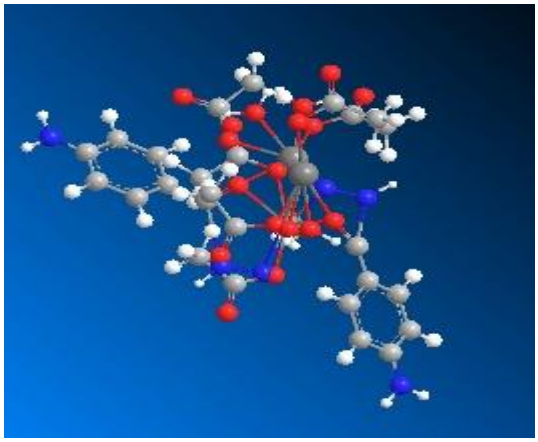


Fig (13) the structure of and 3D of complex (12)

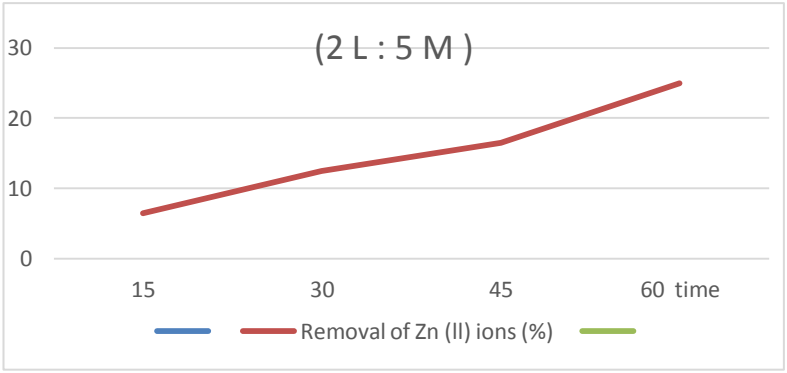
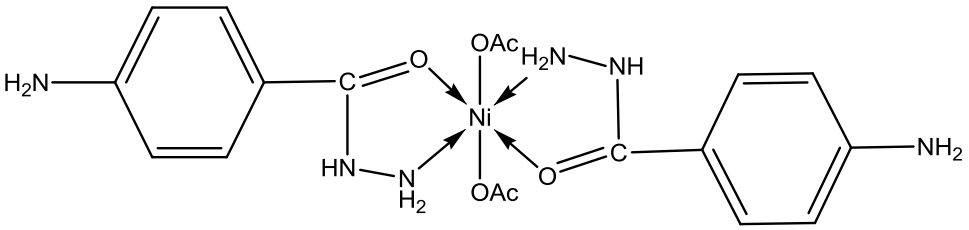


Chart (14) Removal Zn ions % complex (12) of Wast water

At 30 ºC (2L : 5M)	
15 min	6.5 %
30 min	12.5 %
45 min	16.5 %
60 min	25 %

$Ni(OAc)_2$ (2L:1M) Complex (13)

Chemical Formula: $C_{18}H_{28}N_6O_{10}Ni$, M.Wt : 547 , Color : Brown ,M.P : >300 C ,Cond : 9.45 $\Omega^{-1}mol^{-1}$ Cm^{-1} , Elemental Analysis, calc, C,39.49, H, 5.12 , N ,15.35, Ni,10.72 , Found (%), C , 39.23, H , 4.85 , N , 14.85 , Ni 10.58



.2H2O

Fig (14) the structure of and 3D of complex (13)

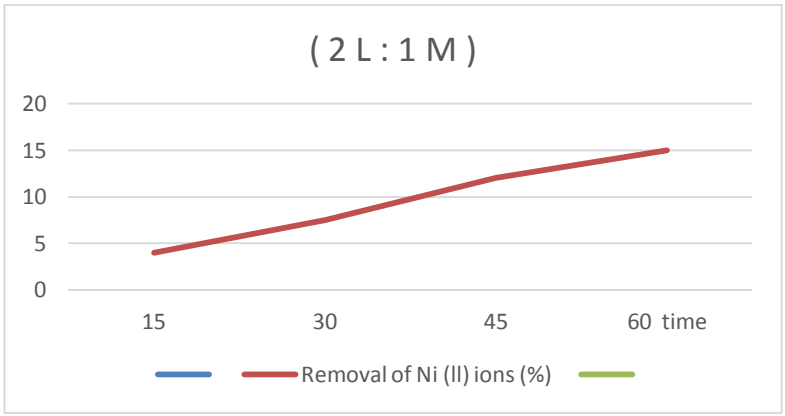


Chart (15) Removal Cu ions % complex (13) of Wast water

At 30 ºC (2L : 5M)

15 min 4 %

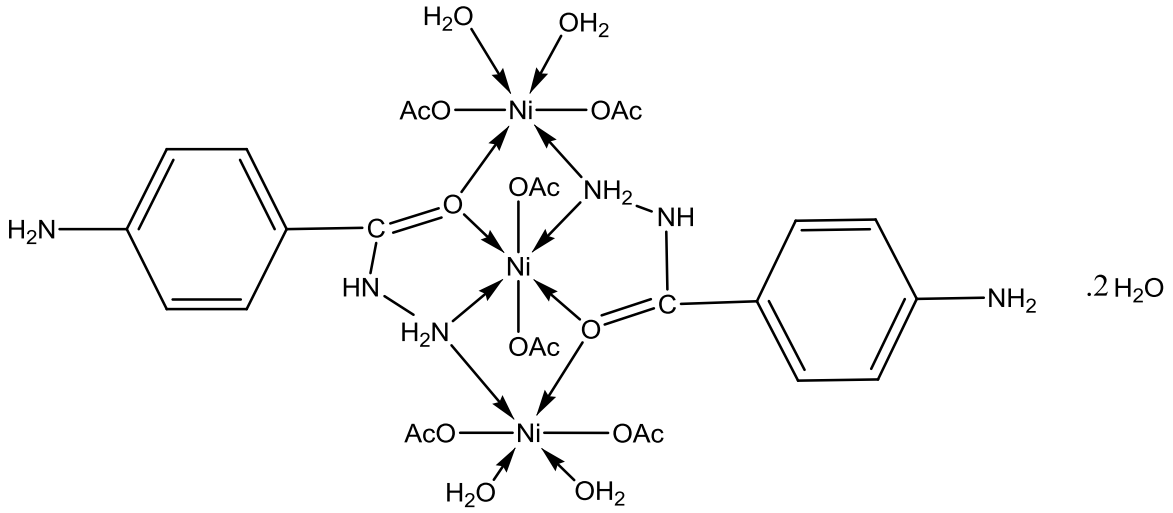
30 min 7.5 %

45 min 12 %

60 min 23 %

Complex (14) $Ni(OAc)_2$ (2L:5M)

Chemical Formula: $C_{26}H_{44}N_6O_{20}Ni_3$, M.Wt : 937 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} $mol^{-1}Cm^{-1}$, Elemental Analysis, calc, C,39.49, H, 5.12 , N ,15.35, Ni,10.72 , Found (%), C , 39.23, H , 4.85 , N , 14.85 , Ni 10.58



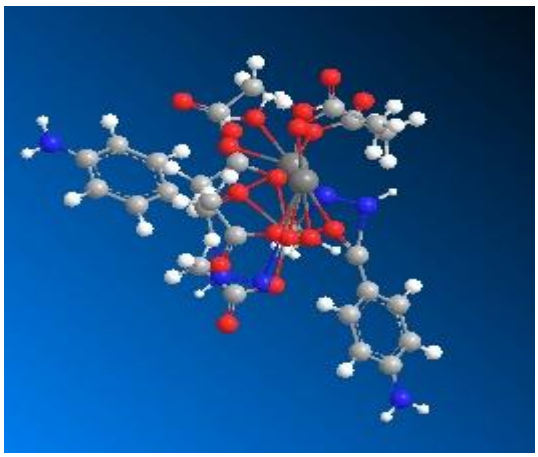


Fig (15) the structure of and 3D of complex (14)

Complex (15) Mn(OAc)2 (2L:1M)

Chemical Formula : $C_{18}H_{28}N_6O_{10}Mn$, M.Wt : 543 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , Elemental Analysis, calc, C,39.78, H, 5.16 , N ,15.47, Mn ,10.13 , Found (%), C , 39.56, H , 5.0 , N ,15.16 , Mn9.98 **IR Spect :** υ(H_2O) = 3530 - 3320 Cm^{-1},3320-3150 Cm^{-1},υ(H-Bond)= 3600 - 3320 Cm^{-1},3310 - 2820 Cm-1,υ(OH) = 3470,3410 Cm^{-1},υ(C=O)= 1635,1615 Cm^{-1},υ(NH) = 3270 Cm^{-1},υ(NH_2) = 3376, 3350 Cm^{-1},υ(OAc) = 1511,1410 Cm^{-1},υ(OH)= 1355,1295 Cm^{-1},υ(Mn O)= 625 Cm^{-1}, υ(MnN)=579 Cm^{-1}

μ eff 6.1 B.M

3600

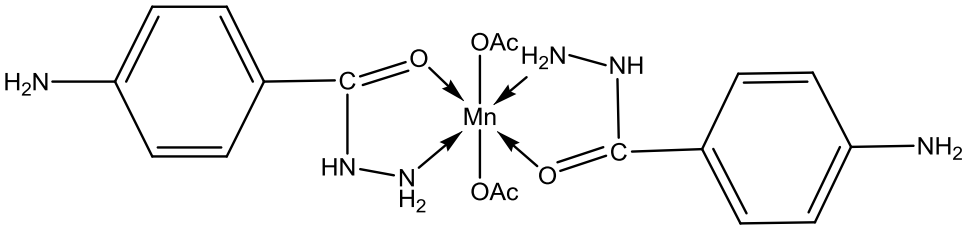
Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

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

ESR g_{iso} = 2.05

Octahedral structure with covalent bond character



.2H2O

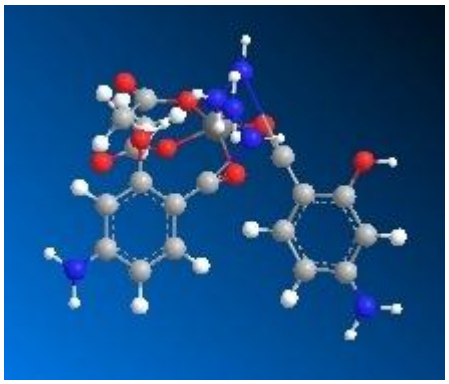


Fig (16) the structure of and 3D of complex (15)

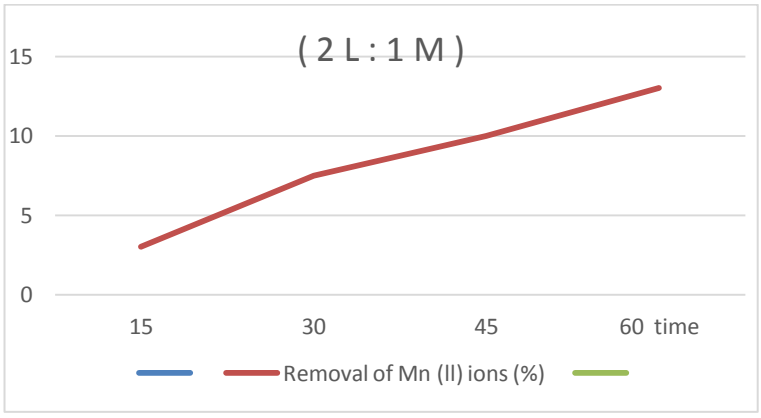


Chart (16) Removal Mn ions % complex (15) of Wast water

At 30 ºC (2L : 5M)

15 min 3 %

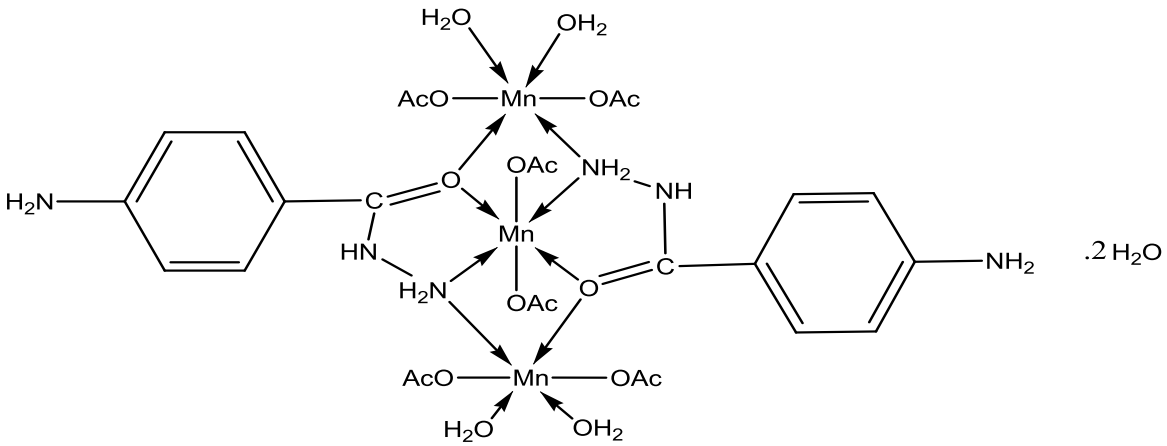
30 min 7.5 %

45 min 10 %

60 min 13 %

Complex (16) $Mn(OAc)_2$ (2L:5M)

Chemical Formula: $C_{26}H_{44}N_6O_{20}Mn_3$, M.Wt : 925 , Color : Browen , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , Elemental Analysis, calc, C,33.73 H, 4.76 , N ,9.1, Mn ,17.84 , Found (%), C , 33.61, H , 4.45 , N , 8.87 , Mn 17.68



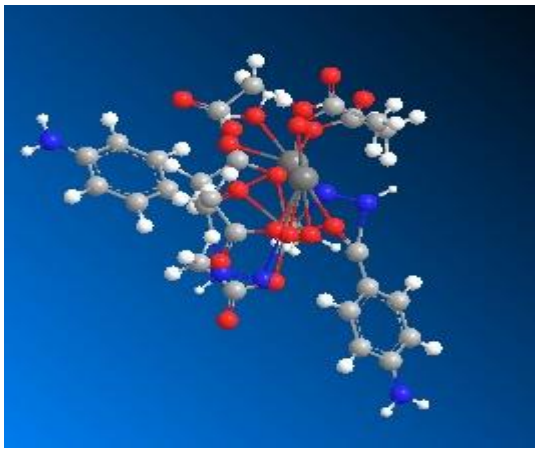


Fig (17) the structure of and 3D of complex (16)

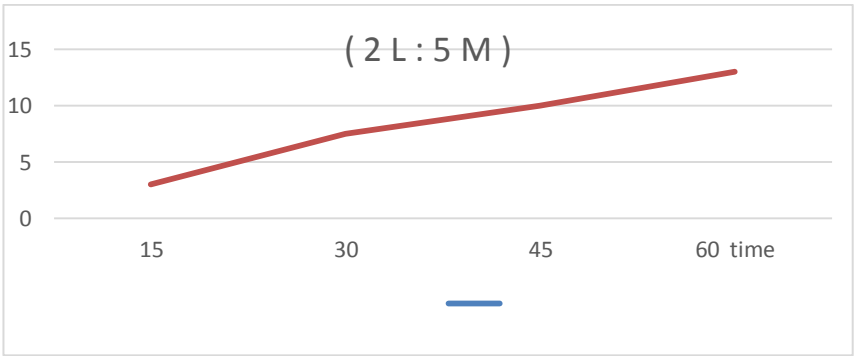


Chart (17) Removal Mn ions % complex (16) of Wast water

At 30 ºC (2L : 5M)

15 min 8.5 %

30 min 17.5 %

45 min 26 %

60 min 34 %

Complex (17) $Fe(SO_4)_2$ (2L:1M)

Chemical Formula: $C_{14}H_{23}N_4O_{11}SFe$, M.Wt : 510 , Color : Brown , M.P : >300 C ,Cond : 9.45 $\Omega^{-1}mol^{-1}$ Cm^{-1} , 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 Spect : $\upsilon(H_2O)$ = 3531 - 3311 Cm^{-1},3321-3151 Cm^{-1},υ(H-Bond)= 3601 - 3321 Cm^{-1},3311 - 2821 Cm^{-1},υ(OH) = 3471,3411 Cm^{-1},υ(C=O)= 1631,1611 Cm^{-1},υ(NH) = 3271 Cm^{-1},$\upsilon(NH_2)$ = 3371, 3351 Cm^{-1},υ(OAc) = 1511,1411 Cm^{-1},υ(OH)= 1351,1291 Cm^{-1},υ(Cu O)= 621 Cm^{-1}

SO4=1271,1181,1021,681 Cm^{-1}

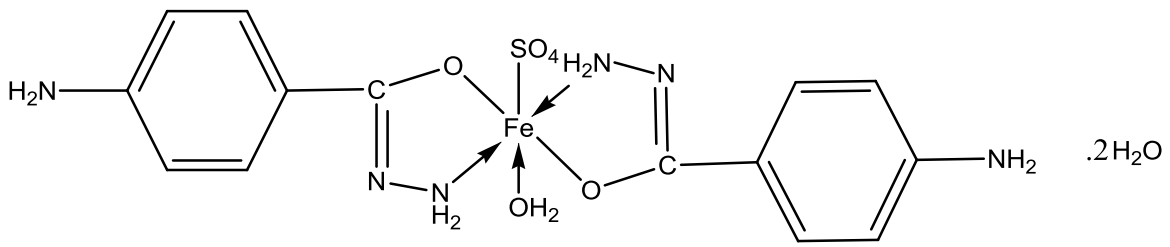
μ_{eff} 5.81 B.M

Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

UV-vis : 291 nm , 311 , 441 , 571 , nm due to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and Charge transfer transitions .

Octahedral structure with covalent bond character



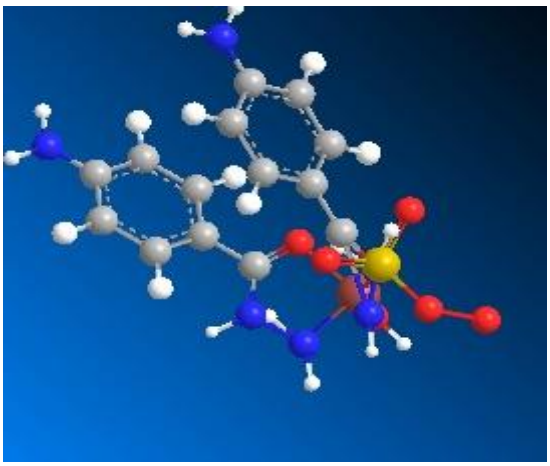


Fig (18) the structure of and 3D of complex (17)

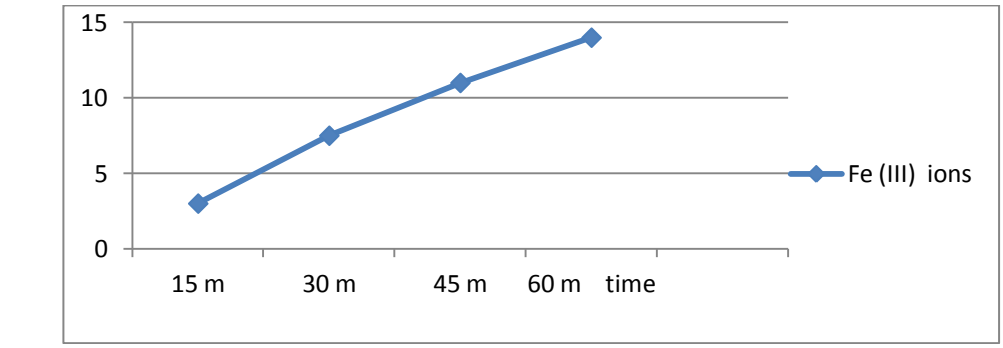
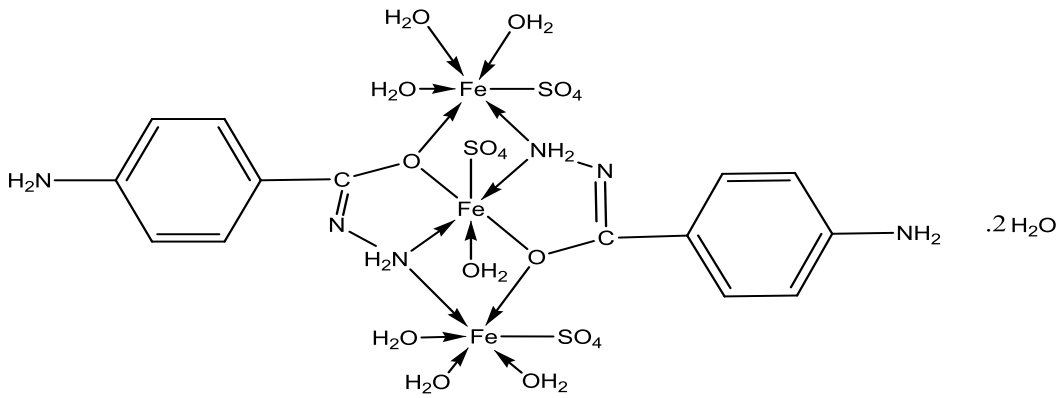


Chart (19) Removal Fe ions % complex (17) of Wast water

At 30 °C (2L : 5M)	
15 min	3 %
30 min	7.5 %
45 min	11 %
60 min	14 %

Complex (18) Fe SO_4 (2L:5M)

Chemical Formula: $C_{14}H_{27}N_4O_{23}S_2Fe_3$, M.Wt : 850 , Coulor : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , 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



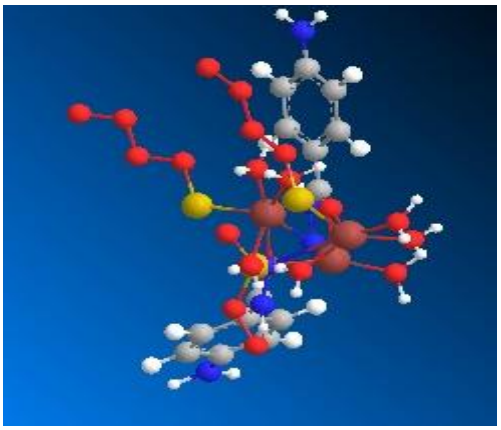


Fig (17) the structure of and 3D of complex (18)

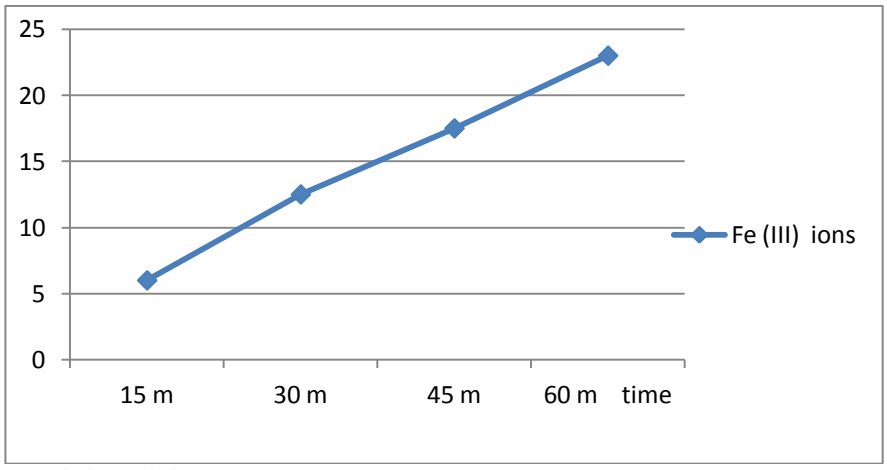


Chart (20) Removal Fe ions % complex (18) of Wast water

At 30 ºC (2L : 5M)

15 min 6 %

30 min 12.5 %

45 min 17.5 %

60 min 23 %

Complex (19) $CrSO_4$ (2L:1M)

Chemical Formula : $C_{14}H_{23}N_4O_{11}SCr$, M.Wt : 507 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , Elemental Analysis, calc, C, 33.14, H, 4.53 , N ,11.04, Cr 10.25 , Found (%), C , 32.86, H , 4.22 , N , 10.75 , Cr 9.82

IR Spect : $\upsilon(H_2O)$ = 3532 - 3322 Cm^{-1},3322-3152 Cm^{-1},υ(H-Bond)= 3602 - 3322 Cm^{-1},3312 - 2822 Cm^{-1},υ(OH) = 3472,3412 Cm^{-1},υ(C=O)= 1632,1612 Cm^{-1},υ(NH) = 3272 Cm^{-1},$\upsilon(NH_2)$ = 3372, 3352Cm-1,υ(OAc) = 1512,1412 Cm^{-1},υ(OH)= 1352,1292Cm^{-1},υ(Cu O)= 622 Cm^{-1}, υ(SO4)= 1272,1182,1032,672 Cm^{-1}

μ eff 3.62 B.M

Mass spectrum :

H_2N_2,M/Z= 32 amu ,$C_3H_{10}N_2$,m/z=74 amu , $H_6N_2O_4$, m/z=98amu , $C_5H_{11}N_2O_2$,m/z=131 amu , $C_7H_{13}N_2O_2$,m/z=189 amu , $C_{10}H_{22}N_4O_4$, m/z=262 amu

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

Octahedral structure

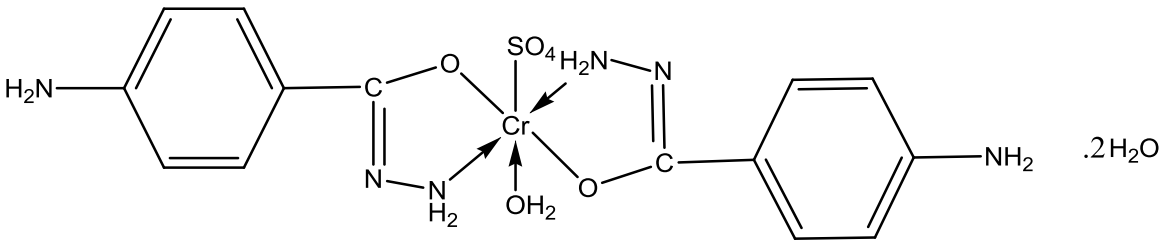


Fig (20) the structure of and 3D of complex (19)

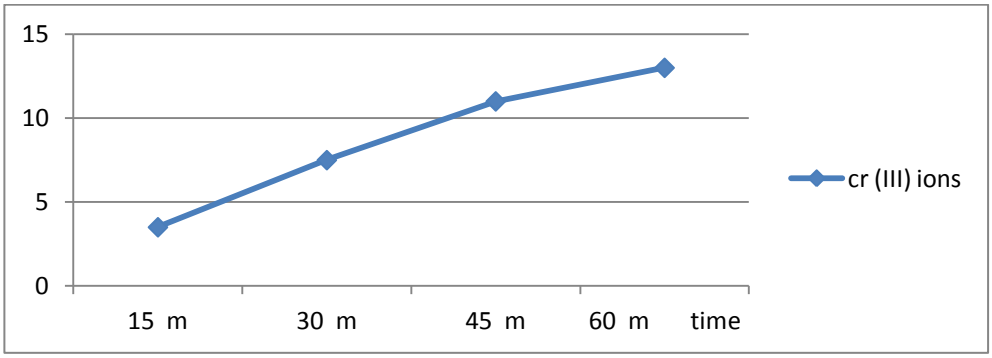


Chart (21) Removal Cr ions % complex (19) of Wast water

At 30 ºC (2L : 5M)

15 min 3.5 %

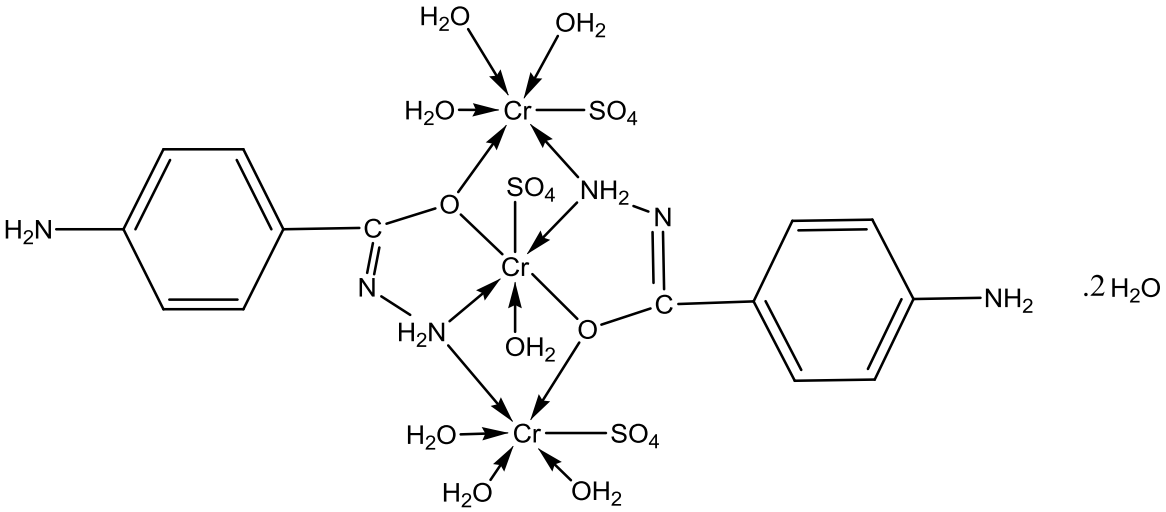
30 min 7.5 %

45 min 11 %

60 min 13 %

Complex (20) $CrSO_4$ (2L:5M)

Chemical Formula: $C_{14}H_{27}N_4O_{23}SCr_3$, M.Wt : 841 , Color : Brown , M.P : >300 C ,Cond : 9.45 Ω^{-1} mol^{-1} Cm^{-1} , 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



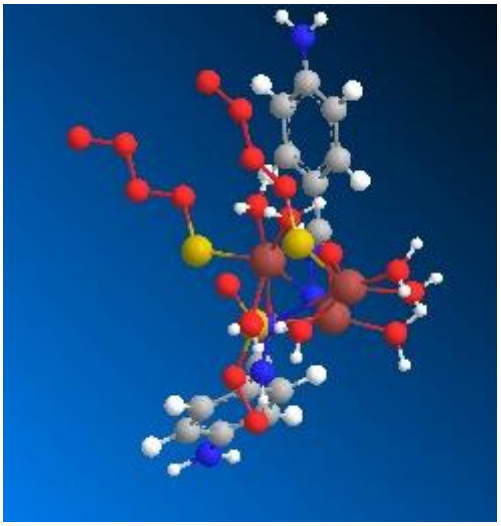


Fig (21) the structure of and 3D of complex (20)

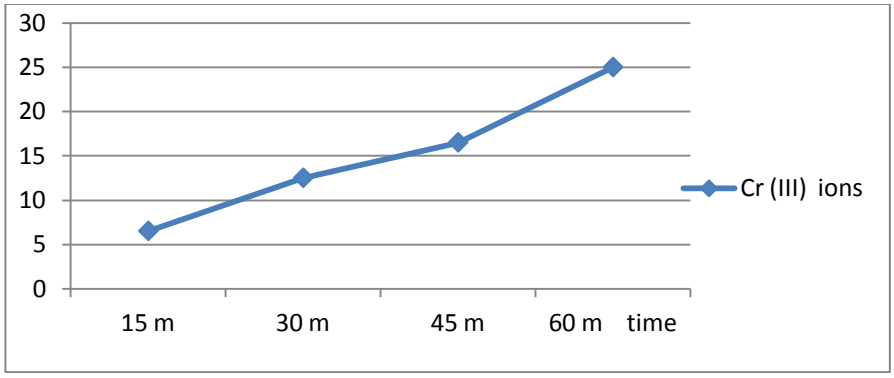


Chart (22) Removal Cr ions % complex (20) of Wast water

At 30 ℃ (2L : 5M)

15 min 6.5 %

30 min 12.5 %

45 min 16.5 %

60 min 19 %

2.RESULTSAND DISCUSSION:-

2.1. 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 M : 1 L) molar ratio, we found that, the removal efficiency after 30 min and after 60 min were recorded 65% while at(2 M :1 L) molar ratio, we found that, the removal efficiency of metal ions elevated after 30 min and after 60 min were recorded as follows , at (2 M :1 L) molar ratio, we found that the removal efficiency of metal ions after 30 min (at 25ºC) was52% and after 60 min was 100% .

2.2. Preparation of metal ligand in laboratory:

Municipal waste water from El Wadi El Gadid wastewater treatment contains notorious metal ions such as Cu (II), Zn (II), Fe (III), Ni (II) and Cr (III). In order to know the capacity of the Ligand to remove these ions, metal complex of these ions have been prepared in the laboratory as followed (0.5g,0.003 mol) of the ligand dissolved in 30 ml ethanol solution and then (1M:1L) equimolar amounts of the following metal salts were added: (0.83g, 0.003 mol) $Cu(NO_3)_2.6H_2O$ complex bald (2), (0.53g, 0.003mol)) $ZnCl_2.3H_2O$ complex (3), (1.37 g, 0.003mol) $Fe_2(SO_4)_3.5H_2O$ complex (4), (1.03g, 0.003mol) $Pb(NO_3)_2.2H_2O$ complex (5) and (1.1g, 0.003mol) $Cu(NO_3)_2.6H_2O$ complex (6). Refluxed with continuous stirring for 1-2 hrs, then left to cool at (R.T)room temperature, filtered off, washed the precipitate formed with ethanol and dried in desiccators in the presence of CaCl2.Repeated the above experiments using [2 L: 1M] and [5 L:1M] ratios.

3. Effect of the ligand on turbidity with different conditions on waste water .

3.1.Turbidity with time at 25 °C.

The result showed turbidity decrease when time Increase at temperature 25 **ºC** After 10 min turbidity is 3.52 NTU while After 50 min Turbidity is 0.74

Turbidity	Time (min)
3.52 NTU	10
2.9 NTU	20
2.22 NTU	30
1.52 NTU	40
0.74 NTU	50

Table (1)Turbidity with time At **Volume** = 15 ml wastewater ,**Temperature**=25 **ºC , , Wt of ligand (1)** = 0.5gm

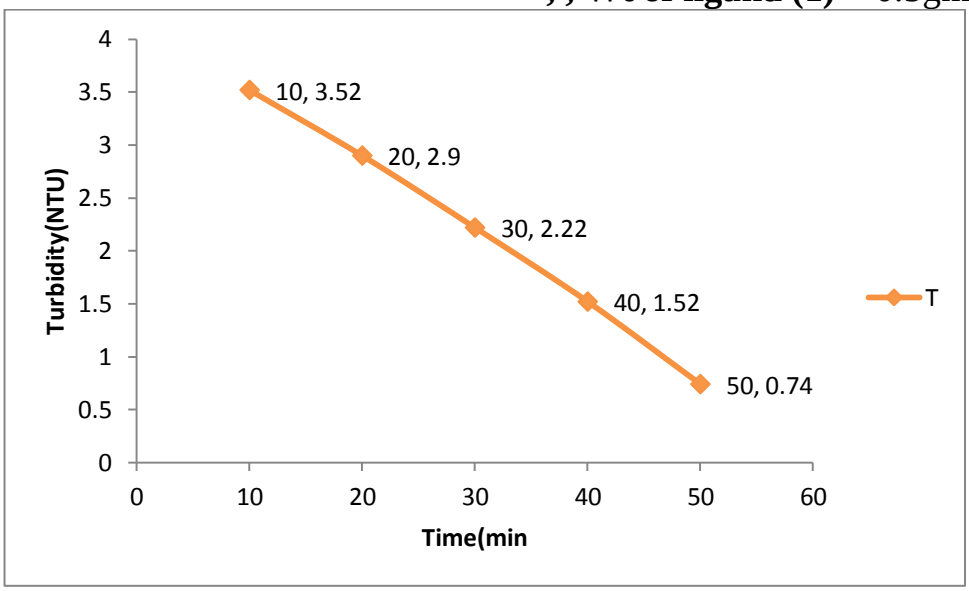


Chart (23) This figure showed relationship between turbidity and time .

3.2.Turbidity with time at 35 c.

The result showed turbidity decrease when time Increase at temperature 35 **ºC** After 10 min ,turbidity is 4.21 NTU while After 50 min Turbidity is 0.28

[2]

Turbidity	Time (min)
4.21 NTU	10
3.52 NTU	20
2.11 NTU	30
1.12 NTU	40
0.28 NTU	50

Table (2)Turbidity with time At **Volume**= 15 ml wastewater ,**Temperature**=35 **ºC , Wt of ligand (1)** = 0.5gm

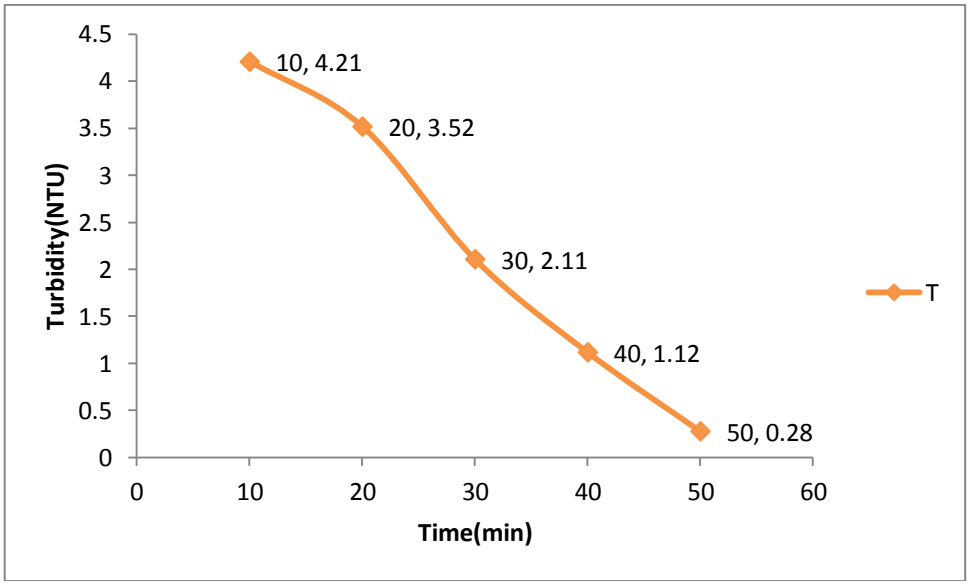


Chart (24) This figure showed relationship between turbidity and time at 35c

3.3.Turbidity with volume at 25 ºC.

The result show the turbidity decrease when Volume Increase at temperature 25 **ºC** At volume 15 ml turbidity is 0.52 NTU while At 35 ml Turbidity is 1.10

Turbidity	Volume (mL)
0.52 NTU	15
0.63 NTU	20
0.98 NTU	25
0.99 NTU	30
1.10 NTU	35

Table (3)Turbidity with time At **Time** = 30 Minutes, **Temperature**=25 **ºC ,Wt of ligand (1)** = 0.5gm

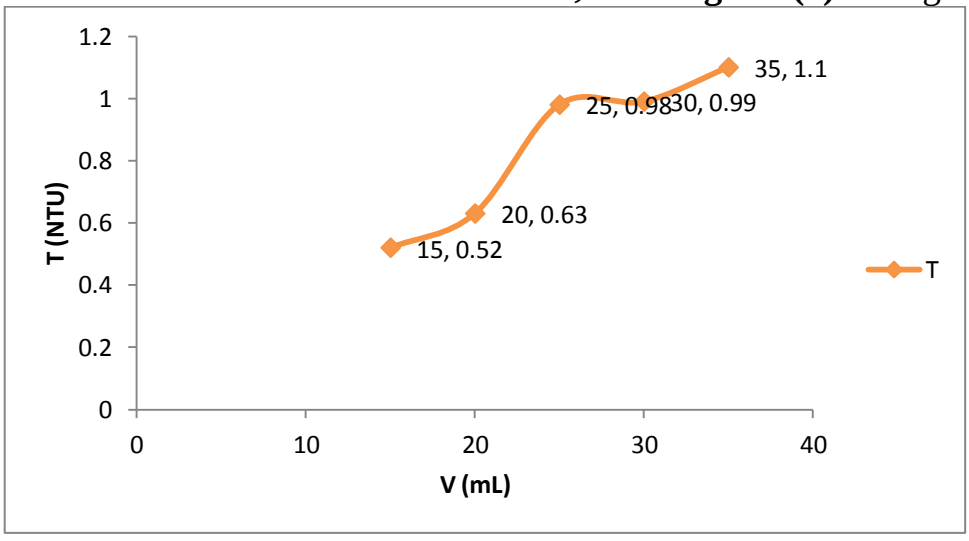


Chart (25) This figure showed relationship between turbidity and volume at 35 **ºC**

3.4.Turbidity with different weight of ligand .

The result show the turbidity decrease when weight of ligand increase at temperature 25 **ºC** at time 30 min at weight 0.2 gm Turbidity is 5.11 NTU while weight 1 gm Turbidity is 0.98 NTU

Turbidity	Wt of lig (1) gm
5.11 NTU	0.2
4.21 NTU	0.4
3.25 NTU	0.6
1.11 NTU	0.8
0.98 NTU	1

Table (4)Turbidity with time At **Time**= 30 Minutes, **Temperature**=25 **ºC** **Volume** = 15ml

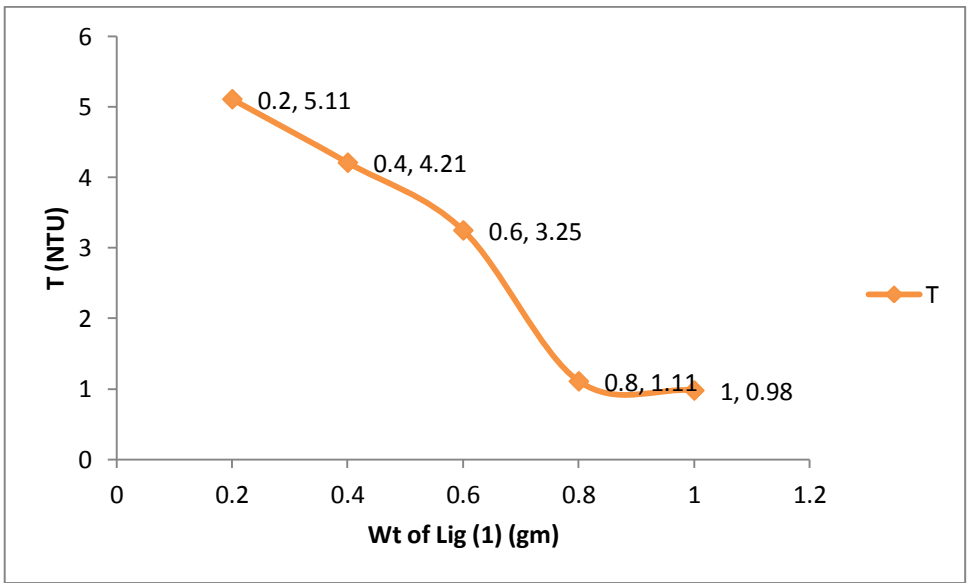


Chart (26) This figure showed relationship between turbidity and different weight of ligand at 35 **ºC**

<u>Post-treatment at RHT 1hrs and 3hrs in absence of the ligand:</u>

Table (5):- Performance results in treating 5Lsemisolid at a total HRT of 1hrs(at dose 1.0 gL^{-1} from the ligand).

CO	TS	TD	p	BO	Te	E.X.
153	105	350	8.2	95	29	Ra
6	3	34	7.9	4	25	Ru
(95.7%	(96.7%	(90.2%	(3.7%	(95.2%		

Parameter		**Un**	**Ra**	**Ru**	**Efficienc**
Heavy meta remova	Cu(I	mgL	4.2	0.6	86%
	Cr(I	mgL	5.2	0.3	92%
	Fe(I	mgL	4.9	1.1	75%
	Ni(I	mgL	2.2	0.4	79%
	Zn(I	mgL	1.7	0.3	81%
Fecal Colifor		unit/l00m	5.4x10	3 x10	99.9%

At, **Volume** = 5L Semisolid sludge ,**(RT) Retention Time** = 1 hours

Wt of Lig(1)=1.0gm

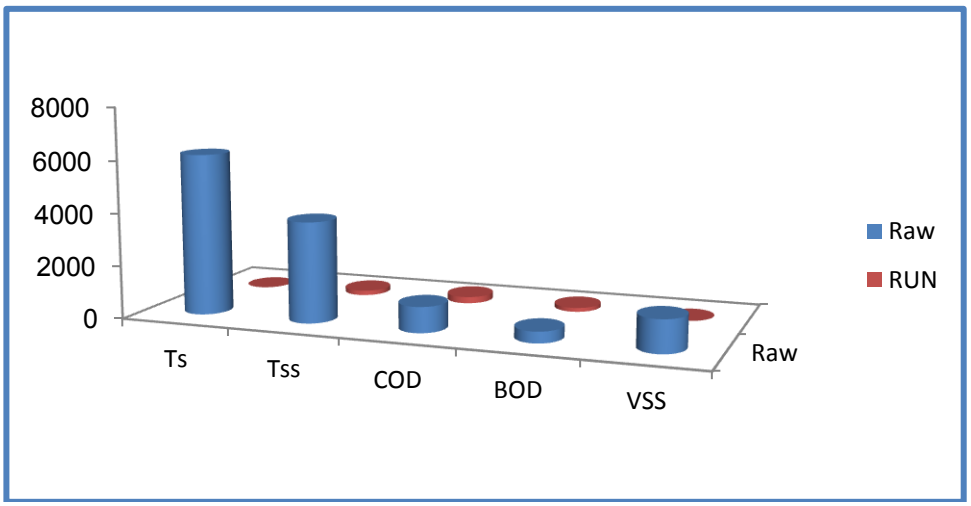


Chart (27): Performance results at a total HRT of 1 hrs.(at dose 1.0 gL^{-1}).

Heavy metals removal efficiency:

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 $3.4x10^6$ to $3.4x10^3$ (99.9%).

Table (6): Performance results in treating 5L semisolid at a total HRT of 3hrs(at dose 1.0 gL^{-1} from the ligand).

CO	TS	TD	p	BO	Te	E.X.
153	105	350	8.2	95	29 °	Ra
5	2	25	7.2	3	28 °	Ru
(96 %	**(97.5%**	**(92.7%**	**(12.02%**	**(95.8%**	**(3.5%**	

	Parameter	**Un**	**Ra**	**Ru**	**Efficienc**
Heavy meta remova	Cu(I	mgL	4.2	0.6	85
	Cr(I	mgL	5.2	0.2	94
	Fe(I	mgL	4.9	0.1	76
	Ni(I	mgL	2.2	0.4	81
	Zn(I	mgL	1.7	0.2	88
Fecal Colifor		unit/l00n	5.4x1(	3 x1(	99.9

At, **Volume** = 5L Semisolid sludge, **(RT) Retention Time** = 3 hours

Wt of Lig(1)=1.0 gm

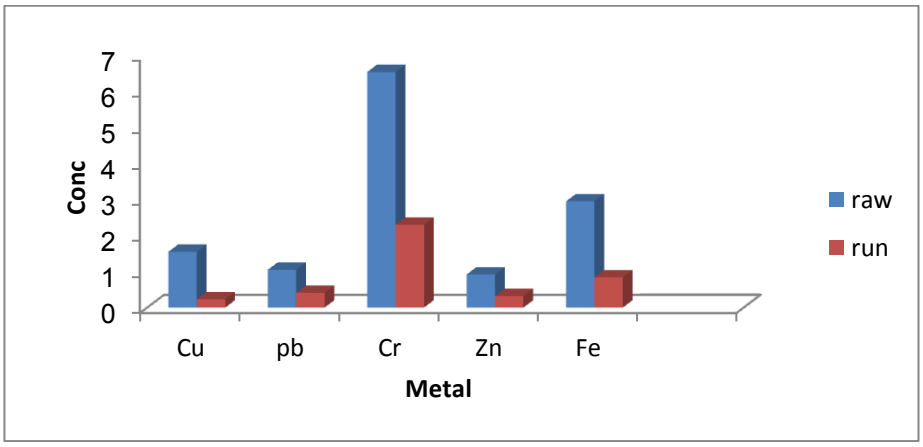


chart (28) Variation in heavy metals concentrations along raw and treated wastewater.

Heavy metals removal efficiency:

The results showed that concentration of heavy metal decreases as HRT 3hrs at dose 1.0 $mg.L^{-1}$ The Cu amount decrease from 4.23 to 0.60 mgL^{-1} (85.0%).The Cr amount decrease from 5.22 to 0.27 mgL^{-1} (94.0%). the Fe amount decrease from 4.98 to 0.14 mgL^{-1} (76.0%).

Ni amount decrease from 2.20 to 0.40 mgL^{-1} (81.0%).The Zn amount decrease from 1.77 to 0.20 mgL^{-1} (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 3.4x106 to 3.4x103 (99.9%).

Post-treatment at RHT 3hrs in presence of the organic ligand(at dose 3.0 gL^{-1} from the ligand):

Table (7): Performance results of treating municipal wastewater at a total HRT of 3hrs(at dose 3.0 gL^{-1} from the ligand).

CO	TS	TD	p	BO	Te	E.X.
153	105	350	8.2	95	25 º	Ra
5	2	9	7.8	3	25 º	Ru
(96.0%	**(97.5%**	**(92.6%**	**(12.01%**	**(95.7%**	**(3.4%**	

	Parameter	**Un**	**Ra**	**Ru**	**Efficienc**
Heavy meta	Cu(I	mgL	4.2	0.3	91
remova	Cr(I	mgL	5.2	0.1	96
	Fe(I	mgL	4.9	0.4	96
	Ni(I	mgL	2.2	0.2	91
	Zn(I	mgL	1.8	0.0	97
Fecal Colifor		unit/l00n	5.4x1(	3 x1(	99.9

At, **Volume** = 5L Semisolid sludge, **(RT) Retention Time** = 3 hours

Wt of Lig(1)= 3 gm

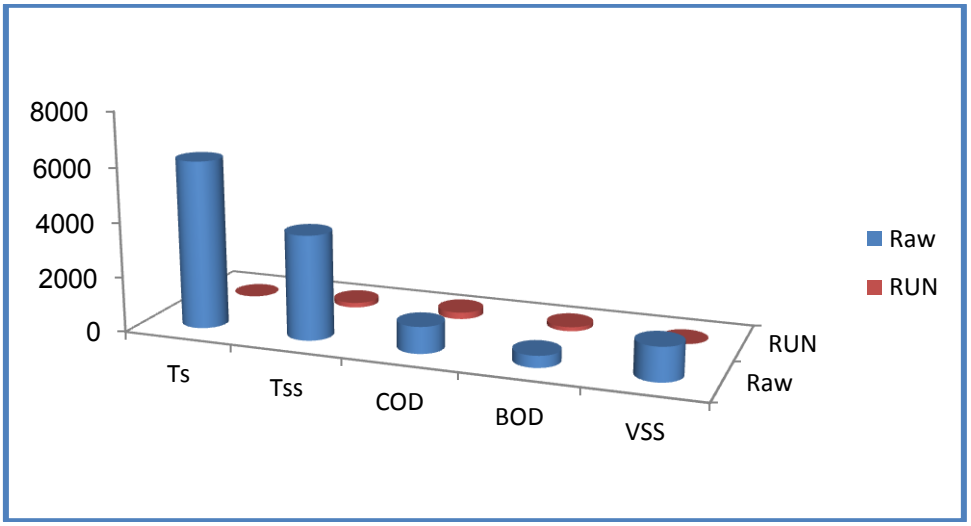


Chart (29): Performance results at a total HRT of 3 hrs.(at dose 3.0 gL^{-1}).

Heavy metals removal efficiency:

The results show that concentration of heavy metal decreases as HRT 3hrs at dose 1.0 mg.L-1 The Cu amount decrease from 4.25 to 0.30 mgL-1 (91.0%).The Cr amount decrease from 5.24 to 0.11 mgL-1 (96.0%). The Fe amount decrease from 5.01 to 0.44 mgL-1 (96.0%).The Ni amount decrease from 2.23 to 0.20 mgL-1 (91.0%).The Zn amount decrease from 1.87 to 0.03 mgL-1 (97.0%)

Conclusion:

The removal efficiency of heavy metals Cu (II), Ni(II) , Zn (II),Cr (III) and Fe(III) were increased by increasing the concentration of ligand and the temperature of medium. The concentration of ligand was increased by passing time reach at 60 min and the temperature reached to 50ºC caused increasing in removal efficiency until reached to 100% in Cu(II) , Ni(II),Zn(II),Cr (III) and Fe (III).

We observed that, when these metals treated with ligand, their amount were decreased as they captured firstly in surface of ligand and then digestion and biodegradation process occurred in the land and the available data indicated good performance of ligand regarded to heavy metals removal efficiency. The result also, showed that, residual values of fecal coliform when treated by ligand with different concentration the amount of heavy metals decrease to 99.9%.

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Conflicts of Interest

The authors declare no conflict of interest.

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