Novel cyclic voltammetry behavior of 3-((benzothiazol-2-diazenylnaphthalene-2,7-diol and use it for spectrophotometric determination of copper (II)in honey sample

Fatma .A. Khazaal [a] ,* Hussein. J.Mohammed [b] and
.Muhammed .M.Radhi [c]
*Chemistry Department / Faculty of Science /Kufa University, Iraq P.O Box(21)
Email Hussein.alshujairi@uokufa.edu.iq

Abstract ;

The azo reagent 3-((benzothiazol-2-diazenylnaphthalene-2,7-diol] was synthesized and characterized by FT-IR ,^{1}H-NMR and ^{13}CNMR spectral techniques. The electrochemical behavior of the azo reagent and its complex with Cu (II) has been studied at glassy carbon disk GCE electrode in different supporting electrolyte at concentration (1M) and scan rate (100mv.s[-1]). Spectrophotometric determination of copper (II) is based on the formation of a 2:1 complex with above reagent. The complex has λmax at(588) nm and Ɛmax of($1.436 \times 10^{4)}$L.mol^{-1}.cm^{-1} .

 A linear correlation (0.1 – 3.0 µg. ml^{-1}) was found between absorbance at λmax and concentration . The effect of diverse ions on the determination of copper (II) to investigate the selectivity of the method were also studied . The stability constant of the product was (1.1×10^{8}) . The proposed method was successfully applied to the analysis of honey sample .

m Key Words: *Cyclic voltammetry,3(benzothiazol-2-diazenylnaphthalen-2,7diol],copper (II), spectroscopy*.

Introduction :

Azo compounds have been the most extensively used class of dyes owing to their versatile application in several fields, such as advanced application in organic synthesis, dyeing cloth fiber biomedical studies, azo dyes are also used in coloring agents in Pharmaceuticals and foods. Azo dyes have wide interest of applications in complexometric titration and in analytical chemistry . These compounds are also used in oils, plastics, waxes and polishes . In addition , azo compounds and their bio conjugates have attracted clinical interest related to photo therapy and photo diagnosis of tumors and their lesions [1-5] . The determination of metal ion at trace amount have been shown important in the fields of biological and environment studies literature date indication that azo compound have been broadly used in the spectrophtometric determination of metal ions [6-13]. Several instruments method are present in the literature used to determine copper ion, and these method inductively coupled plasma atomic emissions spectrometry [14,15], flame and electro thermal atomic absorption spectrometry [16,17], flow injection [18-19].According to the best of our knowledge , this reagent has not been reported in the literature as being used for any cation determination . In this study , we wish to report the electrochemical behavior of this reagent and as a selective reagent in spectrophotometric determination of micro amounts of copper (II).BTHN is a tridentate via azo group, hydroxyl group and nitrogen atom of thaizol group : it has the following structure:
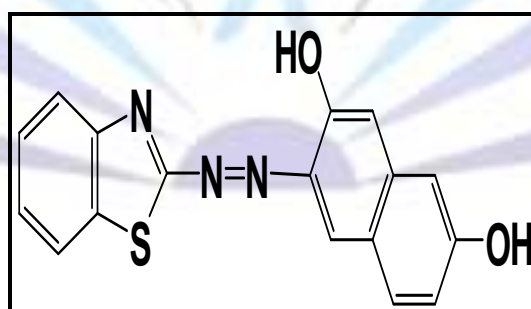

Structure of the (BTHN)

Experimental: All chemicals used in this work were of analytical grade.

 In this study the FT-IR spectra of azo compound was recorded on Schimadzu FT-IR spectrophotometer model in KBr wafer and the NMR spectra was obtained on BRUKER AV 400 AvanceIII 400MHz instrument using DMSO as solvent and reported relative to TMS as internal standard , CE440CHN/O/S Elemental Analyser was made by EAI while voltammetric experimentas were carried out using a computer – controlled electroanalysis system using an(EZ-State by NuVant) system .A three- electrod compination system was an Ag /AgCl reference electrode,a Pt wire auxiliary electrode and glassy carbone electrode as working electrode, the potential range selected was in the Range(1-1.25) mV. All measurements were carried out at room temperature.

4243 | P a g e
A u g u s t 2 0 1 6
c o u n c i l f o r I n n o v a t i v e R e s e a r c h
w w w . c i r w o r l d . c o m

I S S N 2 3 2 1 - 8 0 7 X
V o l u m e 1 2 N u m b e r 7
J o u r n a l o f A d v a n c e s i n C h e m i s t r y

Synthesis of thaizol derivative :

2- amino Benzothaizole(0.0066mole) 1.0000g was diazotized by dissolving it in (5ml) ethanol then (15ml) of HCl(4M) was added keeping the temperature at (0-5C⁰) then adding $NaNO_2$ solution gradually and left it about (15min) to cool well.The coupling material (2,7-dihydroxy naphthalen)(0.0066mole)(1.0650g) was dissolved in 15ml of NaOH(4M) and leave to cool well , then this solution was added to diazonium salt solution slowly drop by drop to maintain temperature (0-5C⁰)The mixture was allowed precipitate was filtered off and washed several times with (1:1) (alcohol:water) mixture then recrystallized from boiling ethanol and left to dry. Scheme (1).Dark Burgundy powder,m.p 230C⁰ Anal(calc) for $C_{17}H_{11}N_3O_2S$(%) : C (63.48 %),H(3.42 %), N (13.07%) ,S(9.97%). Found(%): C(63.39 %),H (3.38 %),N(12.89 %),S (9.82 %).
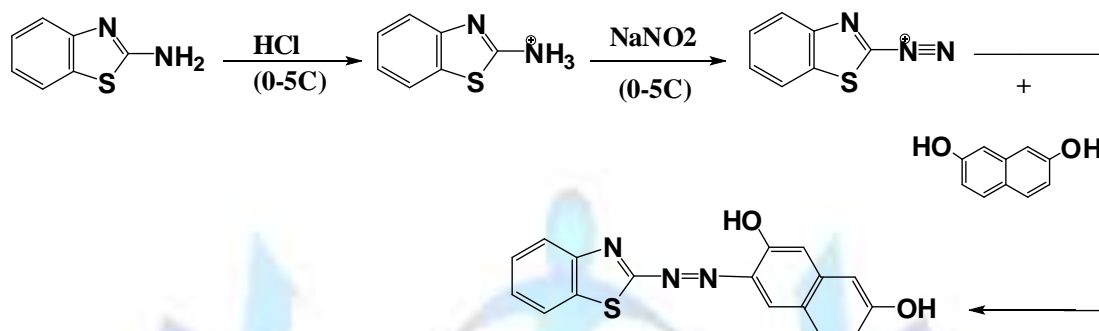
scheme (1).Synthesis of reagent (BTHN)

Reagents

Copper stock solution (100 µg.ml⁻¹) The solution was prepared by dissolving (0.00536 g) of copper chloride in (200 ml) of deionized water.

3(benzothiazol-2-diazenyl naphthalen-2,7diol($1X10^{-3}M$): This solution was prepared by using (0.0321 g) of reagent in (100 ml) of eathanol.

Other ions (foreign) solution: All of ions were prepared by using a suitable amount of the compound in deionized water in a calibrated flask.

Results and Discussion:

Absorption Spectra:

The reagent (BTHN))nm possess a maximum absorption at 440 nm (Fig .1) reacts with ($CuCl_2.2H_2O$) at room temperature to give a (BTHN-Cu(II) colored complex at pH 7. . The absorption spectrum shows a maximum at 588 nm, whereas the reagent blank give no absorption at this wavelength (Figure. 2)
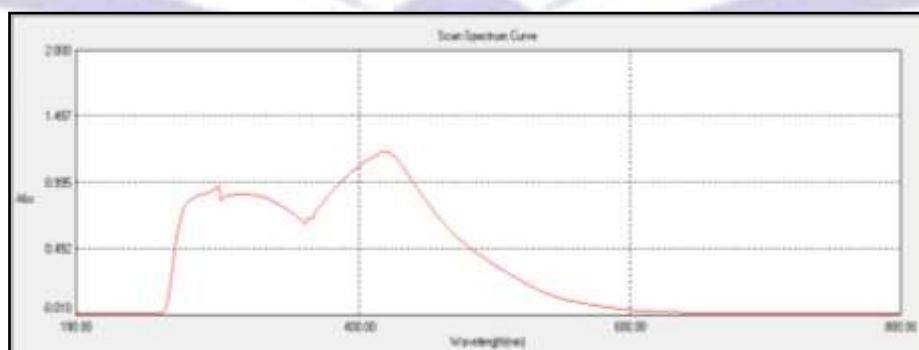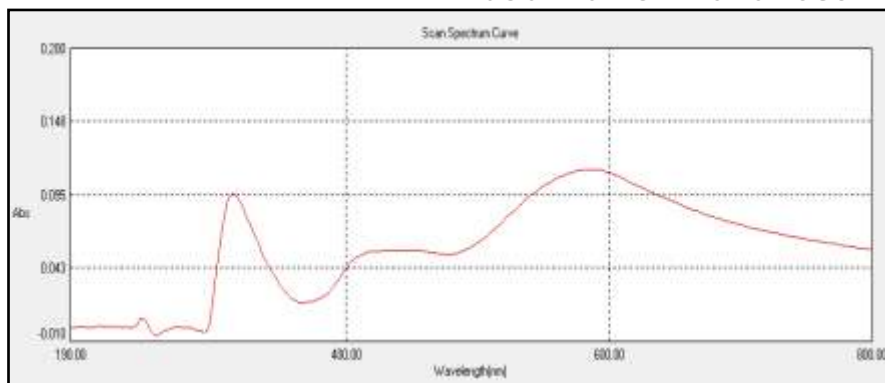

Fig (1)Absorption spectrum of reagent (BTHN)

4244 | P a g e
A u g u s t 2 0 1 6
c o u n c i l f o r I n n o v a t i v e R e s e a r c h
w w w . c i r w o r l d . c o m

Fig(2)Absorption spectrum of (BTHN-Cu(II))

The effect of various parameters on the absorption intensity of the formed products was

studied and the reactions condition were optimized. The reaction of(BTHN) with Cu(II) was studied at different pH by using HCl or NaOH(0.05N)in the range (2-10). It was found that the chelating complex was formed at pH 7. (Fig. 3) . It was found that absorbance rises with increasing reagent concentration and got its maximum value on using (1.5 ml of 1×10^{-3} M) in supsequent experiment.
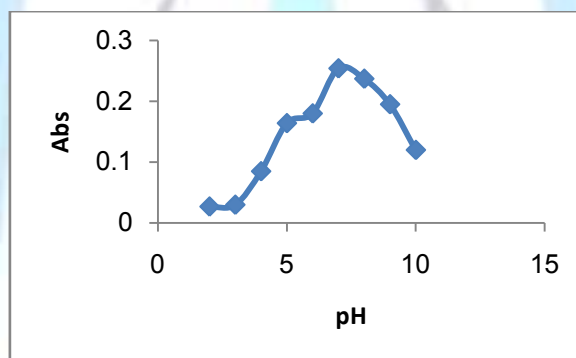

Fig (3) Effect of pH on the color intensity of (BTHN-Cu(II) complex

Quantification:

 In order to study the range in which the colored complex adhere to Beer's law the absorbance of the complex was measured at λmax for sequence of solutions containing increasing amounts of Cu(II) at optimum conditions. The validity of Beers law , molar absorptivity and Sandells sensitivity values were estimated and are given in Table .1 , showed that the method is sensitive . The proposed method showed a good linearity for the determination of Cu(II) with a good correlation coefficient (0.9588) . The relative standard devaiation %(RSD) for the analysis of six replicates of Cu(II)is equal to(0.464)showed that the method is precise and accurate, while detection limit is equal to (0.0139) . The stiochiometric ratio of (BTHN) and Cu(II) was studied applying the continuous variation(Job's) and mole ratio methods [20,21] using equimolar solutions of the new ligand and Cu(II) (1×10^{-4}).It was found that (BTHN) forms a dye coupled product with Cu(II) in the ratio 2:1 as in (Figure. 4).

Table (1) characteristics data of Cu(II)-BTHN complex

parameter	Values of method
Beers law limits (µg.ml^{-1})	(0.1-3.0)
Molar absorptivity (L.mol^{-1}.cm^{-1})	1.436*104
LOD(µg/ml)	0.0139
R.S.D %	0.464%
Correlation coefficient	0.9588
Sandell's sensitivity µg .cm^{-2}	0.0044
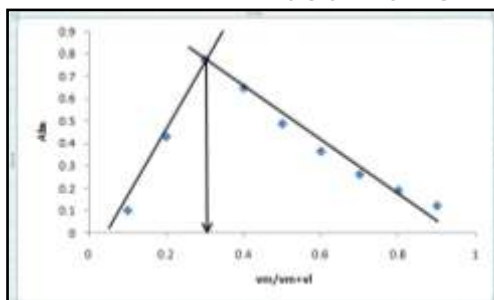
Fig(4)continuous variation plot of the Cu-BTHN

F TI.R Analysis:

The FT-IR spectra of the free ligand have abroad band about(3421-3176)cm^{-1}which could be attributed to(-OH)stretching vibration ,the shape and intensity of band were changed that led to expect coordination wasaccurein complex(Cu-BTHN), likewise the stretching frequency of (N=N) at (1561)cm^{-1} was shifted to a lower frequency (1531) cm^{-1} in complexes. The bands at frequency (1651-1593)of(C=N)also was changed as well as the band at(1305-1201) which corresponding with (C-N=N-C) and (C=N-N=C) were shifted towards lower frequency[22-24]. The FT-IR spectra of copper complex also shows additional bands in (495)cm^{-1} which is due to the formation of (M-O*)* and (449) cm^{-1} for (M-N). (Fig. 5.6)
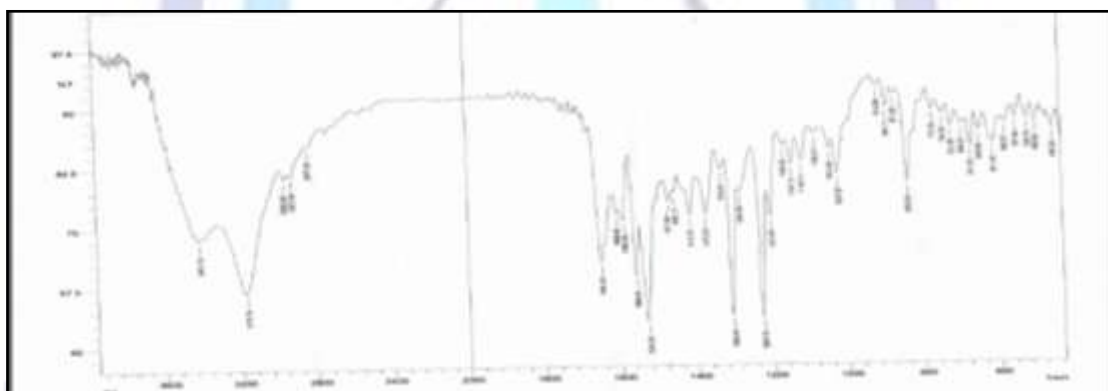

Fig (5) TheFT- IR Spectrum of the dye (BTHN)
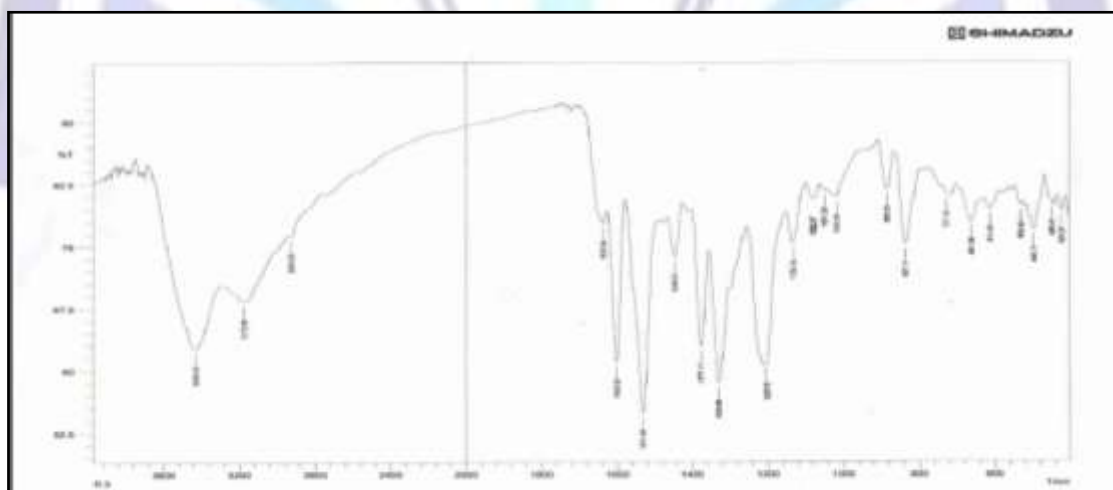
Fig(6)The FT-IR Spectrum of (Cu-BTHN)complex

[1] H-NMR data of BTHN and it complex with Copper(II) :

The [1] H-NMR and[13] C-NMR spectra of the prepared azocompound was made ligand in DMSO solution with tetra methylsaline as an internal standard indications the following signals as in Table. 2 and Table .3.(Fig.7-10)

4246 | Page
August 2016
council for Innovative Research
www.cirworld.com

I S S N 2 3 2 1 - 8 0 7 X
V o l u m e 1 2 N u m b e r 7
J o u r n a l o f A d v a n c e s i n C h e m i s t r y

Table(2) [1] H-NMR data of BTHN and it complex with Copper(II)

compound	C-OHAr	CH-	Ar-H naphthalene	CH benzothaizol	CH3 of DMSO
BTHN	10.3 8.48	-----	6.93-6.184	7.84	2.5
Cu-BTHN	10.2	3.387	7.120-6.8	7.32-7.75	2.5

Table (3) [13] C-NMR data of BTHN and Cu-BTHN complex

compound	C-N benzothaizol	C-OH naphthalene	C-H benzothaizol	C-H napthalene	C-N naphthalene
BTHN and Cu-BTHN	160	156.3	136.76-122.34	122.34-115.7	107.7
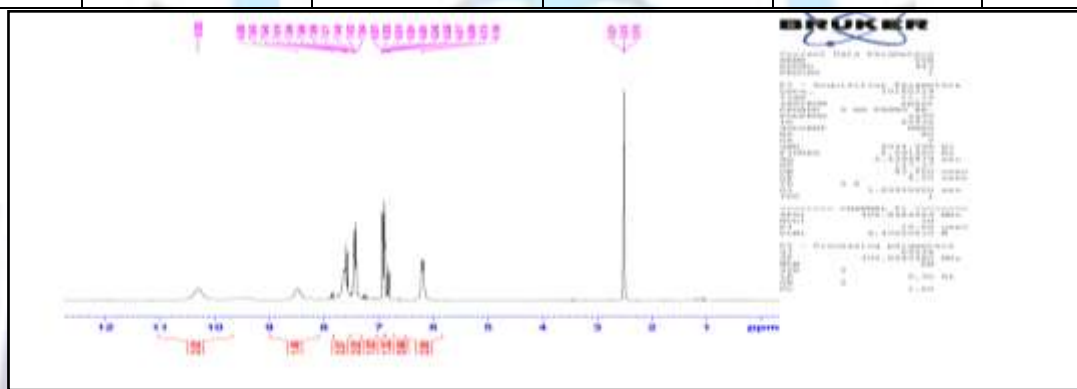
Fig (7):The ^{1}H NMRspectrum of azo compound (BTHN)
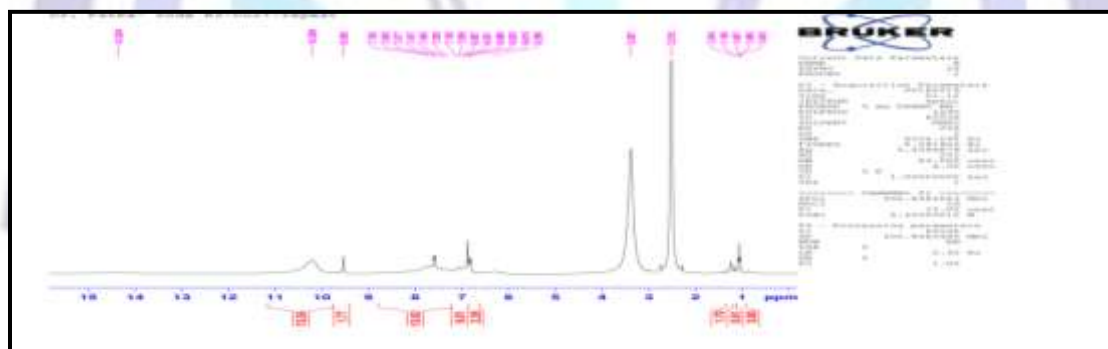
Fig (8): The ^{1}H NMRspectrum of(Cu-BTHN)complex

4247 | P a g e
A u g u s t 2 0 1 6
c o u n c i l f o r I n n o v a t i v e R e s e a r c h
w w w . c i r w o r l d . c o m

I S S N 2 3 2 1 - 8 0 7 X
V o l u m e 1 2 N u m b e r 7
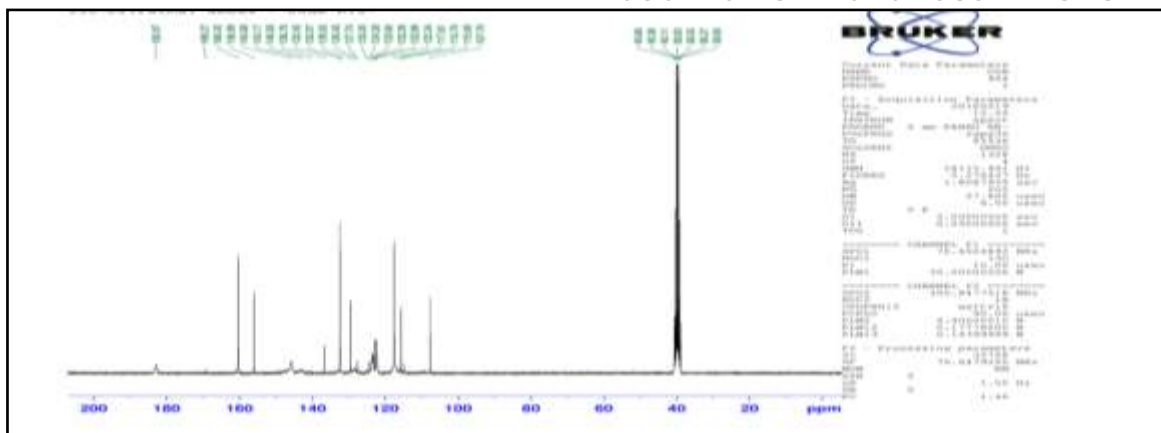J o u r n a l o f A d v a n c e s i n C h e m i s t r y

Fig (9): The ^{13}C NMR spectrum of compound (BTHN)
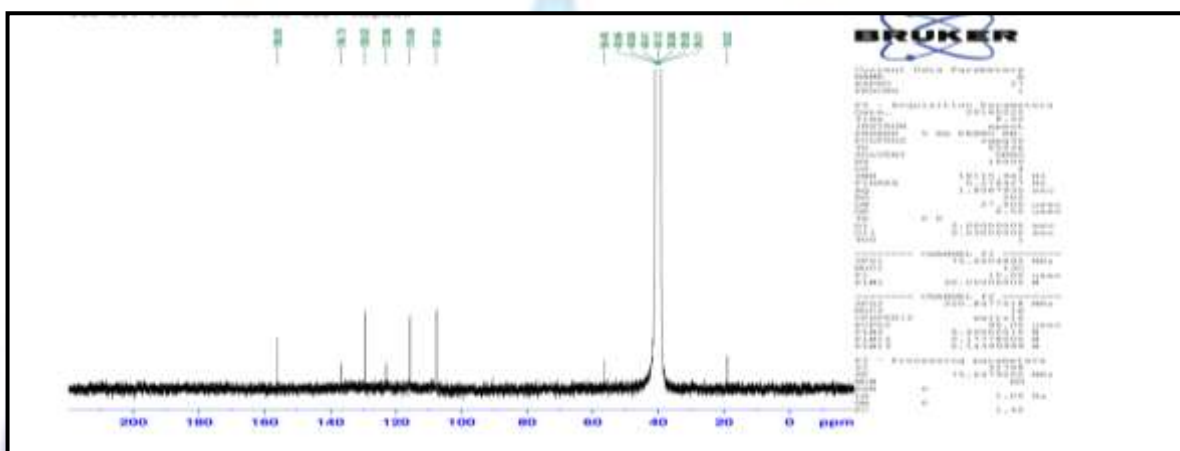
Figure (10):The ^{13}C NMR spectrum of complexCu-(BTHN)

According to the results of the FT-IR,^{1}H-NMR, ^{13} C-NMR, stoichiometric and elemental analysis the structure of complex can be suggested as the following:
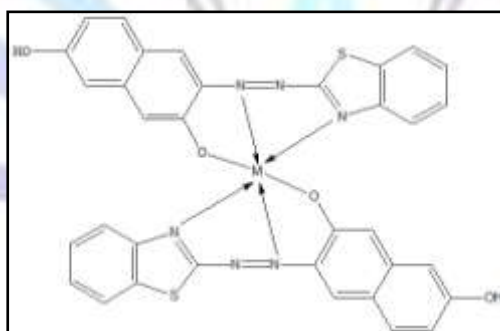
Structure of (BTHN)

Interferences

The effect of different ions in the determination of copper (II)was studied . Cu(II) can be determined in presence of 10 or more fold excess of cation and the interference via the various ions were removed by using suitable masking agent Table(4)

Table(4):Interferenc of ions and removed them by masking agent

No	Foreign ions	Conc. ppm	Error%	Masking agent	Error%
1	Co^{+2}	10	48.08	Thiourea(1ml)	0.52
2	Cd^{+2}	10	1.21	----	----
3	Sr^{+2}	10	-3.11	----	----
4	Ni^{+2}	10	-35.88	Formaldehyde(0.5ml)	0.36
5	Sn^{+2}	10	2.7	----	----
6	Cs^{+2}	10	1.52	----	----
7	Zn^{+2}	10	0.8	----	----
8	Pb^{+2}	10	-2.39	----	----
9	Mn^{+2}	10	12	Formaldehyde(1ml)	0.28
10	Hg^{+2}	10	-1.913	----	----
11	Ag^{+1}	10	2.8	----	----
12	Fe^{+3}	10	51.3	Na_2HPO_4(1ml)	0.45

Determination of Copper(II) in honeysample

0.1g of honey digested in microwave with 5ml of concentrated HNO_3 and 3ml of 30% H_2O_2. The result of digested solution was diluted to 100ml with deionized water ,from this solution transfer 2ml in centerfuge tube for 10 min and analysis with UV-Vis proposed method and atomic absorption [25] . The results are shown in Table 5, indicate that satisfactory precision and accuracy could be attained with proposed method

Table(5):Cu(II) levels in Honey Sample

Tabe of Honey	Amount found by our spectrophotometric method($\mu g.ml^{-1}$)	Amount found by Atomic Absorbtion($\mu g.ml^{-1}$)
Granja San Francisco	0.33	0.29

Electrochemical behavior of azo dye(BTHN)and redox mechanisum in aqueous solution:

The cyclic voltammogrames of investigated azo dyes shown one to three irreversible cathodic peaks [26 ,27] .The number of peaks depends on pH and nature of compounds. The peaks observed are due to the reduction of azo –N=N- center . The reduction mechanism includes the formation of hydrazo derivatives followed by the cleavage of the –N=N- bond and the final formation of amines [28,29] according to the following

$$-N=N- +2H^+ +2e^- \text{ -----------} -NH=NH- \text{ --------(1)}$$

$$-NH=NH- +2H^+ +2e^- \text{ -----------}2(-NH_2-) \text{ ---------(2)}$$

Different supporting electrolyte was be used with the reagent(BTHN) at GCE with scan rate (0.1Vs^{-1}) for all cyclic voltammograms .All voltammograms are shows reduction peak of azo group (-N=N-) at potential ranged (-500mv –750mv). The choice of the better supporting electrolyte depends on the higher current for oxidation peak and clarity of peak (Fig.12-14) Table .6 .
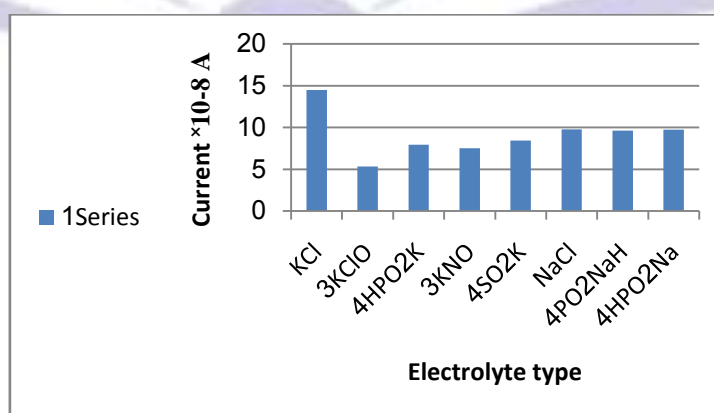
For reagent(BTHN) was proposed that the best supporting electrolyte is (KCl) (Fig. 11,12),current was highest between other electrolytes , cyclic voltammogram shows irreversible electrochemical system in which the electron transfer rates are significantly less than the rate of mass transport and the reduction in two steps , the first reduction attributed to azo group giving a hydrazo derivative , second reduction peak to breaks N-N linkage to form two primary amine molecules (scheme . 2). All current peak ratio shows irreversibility of electrochemical system at different electrolyte due to the Ipc/Ipa≠1 Table .7, the deviation from number one due to the chemical reaction that arises subsequent transmission electron ,such interactions can be complex , involving dissociation and isomerization [30].

Table(6) Current –Potential data of(BTHN) in several supporting electrolyte Solution (1M) with scan rate (0.1Vs^{-1})

R3	Supporting Electrolyte	Ia$_1$ μA	Ea$_1$ mv	Ia$_2$ μA	-Ea$_2$ mv	Ia$_3$ μA	-Ea$_3$ mv	-Ic$_1$ μA	-Ec$_1$ mv	Ic$_2$ μA	-Ec$_2$ mv	Ic$_3$ μA	Ec$_3$ mv
1	KCl	14.5	461	5.38	246	---	---	22.6	510	27.3	701		
2	KClO3	5.31	-250	11.8-	679	---	---	23.0	497	---	---		
3	K2HPO4	7.95	266	3.64	113	---	---	21.4	701	---	---		
4	KNO3	7.50	66.5	3.41	276	---	---	6.59	159	24.1	688		
5	K2SO4	8.41	465	5.45	220	-6.59	677	5.68	192	23.9	599		
6	NaCl	9.76	497	6.19	132	3.88	335	5.77	146	21.3	580		
7	NaH2PO4	9.62	699	6.15	89.6	---	---	5.19	163	23.5	675		
8	Na2HPO4	9.72	78.9	---	---	---	---	23.1	596	---	---		
9	TBABr	No res.											
10	B.R	No res.											

Enhancement in current of peak follows the following sequence:

KCl > NaCL > Na$_2$HPO$_4$ > NaH$_2$ PO$_4$ > K$_2$SO$_4$ K$_2$HPO$_4$> KNO$_3$>KClO$_3$

Fig(11) Effects of supporting electrolyte on the anodic peak current of reagent (BTHN)

4250 | P a g e
August 2016
council for Innovative Research
www.cirworld.com

I S S N   2 3 2 1 - 8 0 7 X
V o l u m e   1 2   N u m b e r 7
J o u r n a l   o f   A d v a n c e s   i n   C h e m i s t r y

Table (7)Current –Potential data for(BTHN)) at different supporting electrolyte (1M) and scan rate (0.1 Vs-1)

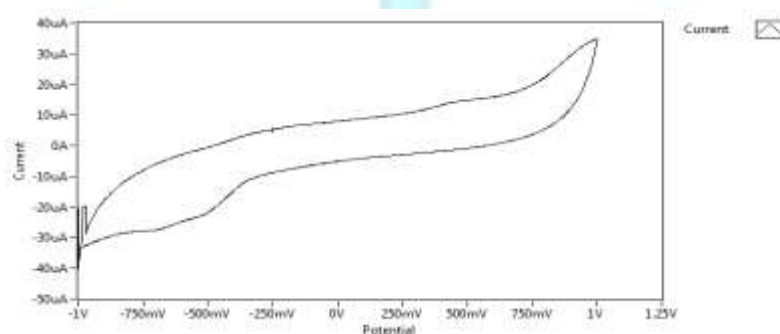|	Supporting electrolyte	Ea_1 mV	$-Ec_1$ mV	Ia_1 µA	$-Ic_1$ µA	ΔE_1 mV	$E_{1/2}$	Ia_1/Ic_1
1	KCl	461	14.5	510	22.6	49	-24.5	0.641
2	$KClO_3$	-250	497	5.31	23.0	248	373.5	0.230
3	KNO_3	66.5	159	7.50	6.59	225.5	-46.25	1.138
4	K_2HPO_4	266	701	7.95	21.4	435	-217.5	0.371
5	NaCl	497	146	9.76	5.77	643	175.5	1.691
6	Na_2HPO_4	78.9	596	596	23.1	674.9	-258.55	0.420
7	NaH_2PO_4	699	163	9.62	5.19	862	268	1.85

Fig (12) Cyclic voltammogramof (BTHN) in supporting electrolyte 1M of KCl at scan rate 0.1Vs⁻¹
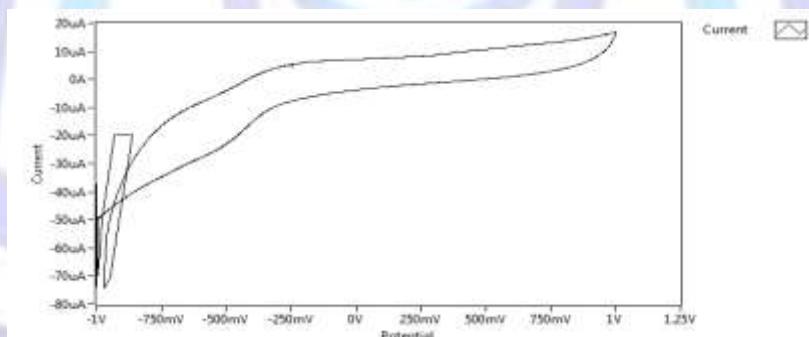
Fig (13) Cyclic voltammogram of(BTHN)in supporting electrolyte 1M of $KClO_3$ at scan rate 0.1Vs⁻¹

I S S N 2 3 2 1 - 8 0 7 X
V o l u m e 1 2 N u m b e r 7
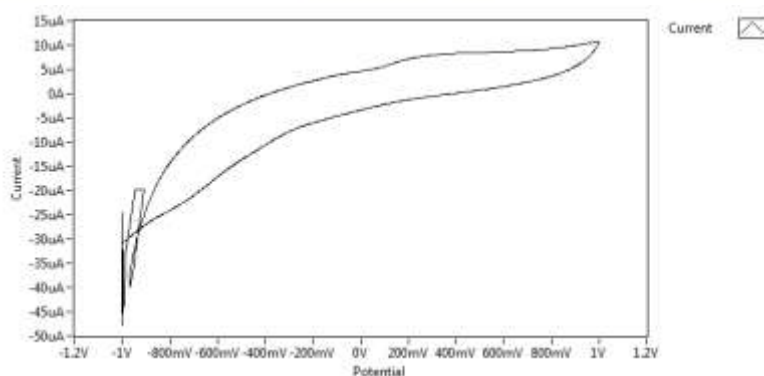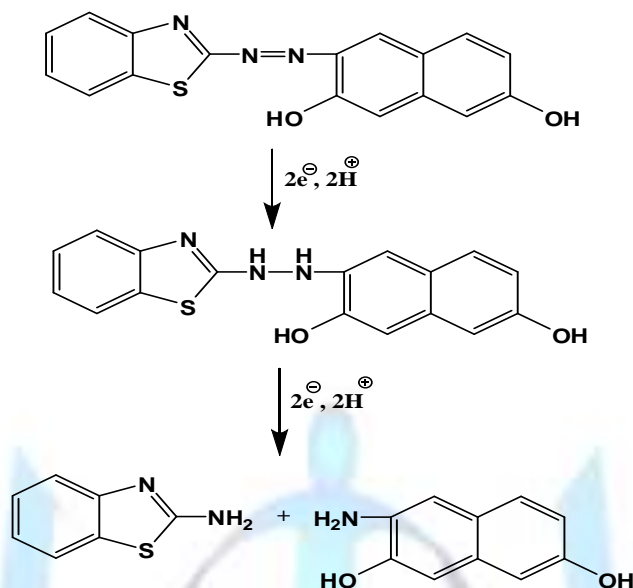J o u r n a l o f A d v a n c e s i n C h e m i s t r y

Fig (14) Cyclic voltammogram of (BTHN) in supporting electrolyte 1M of K$_2$HPO$_4$ at scan rate 0.1 V s-1


Scheme(2) Proposed mechanism of voltammetric reduction of reagent(BTHN)

## Redox behavior of(Cu-BTHN) complex

Cyclic voltammograms of copper complex was recorded in different supporting electrolyte ,the results are summarized in Table.8 (Fig . 15-18), NaH$_2$PO$_4$ 1M as supporting electrolyte was proposed the best electrolyte depending on the clarity of redox peaks (Fig . 23) .It clearly reveals that the redox process of the copper (II) complex at the scane rate (0.1Vs^{-1}) involves one reduction cathodic peak (Epc=-48.6 mv) . In the anodic side the direct oxidation of complex is observed with a strong peak at(Epa= 90.2 mv) .It is observed that ∆Ep values was found equal to (***138.***8 mv) and the ratio of anodic to cathodic peak currents(Ipa/Ipc≠1) corresponds to more than one electron transfer process. The difference in the value of (Epc-Epa is ∆Ep) which is smaller than the value required for a reversible process (59 mv) indicating that , reduction of copper complex at silver electrode is irreversible Table .9 [31,332].
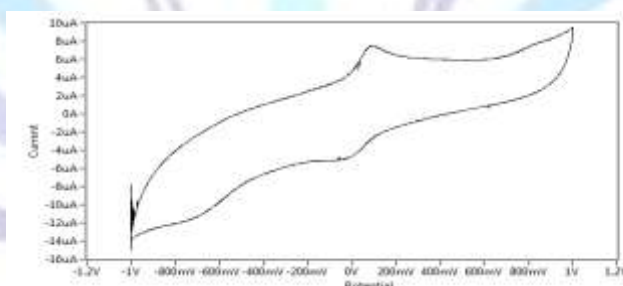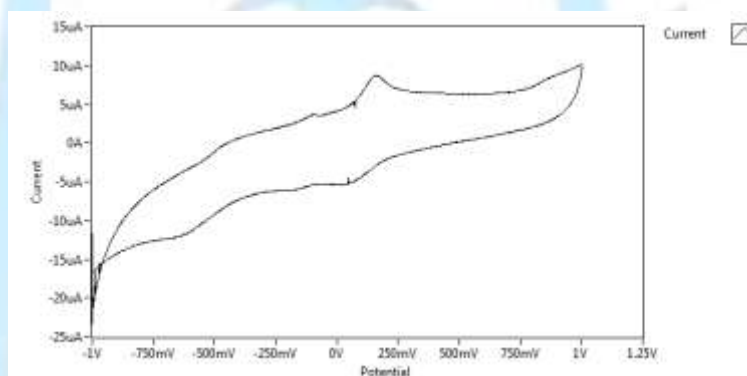

Fig(15)cyclic voltammograms for(Cu-BTHN)complex in(NaH$_2$PO$_4$) (1M) at scan rate 0.1Vs-^{1}
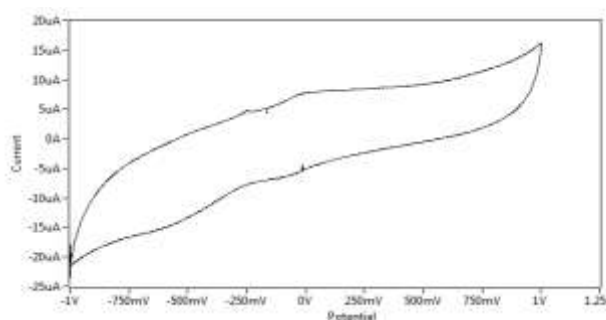
Fig(16)cyclic voltammograms for(Cu-BTHN)complex in(KNO$_3$) (1M) at scan rate 0.1Vs^{-1}
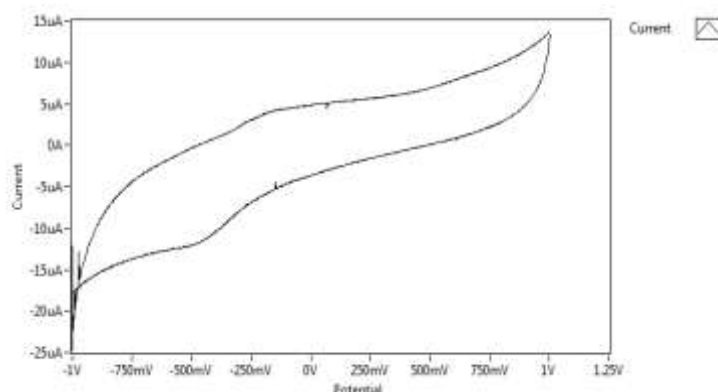
Fig(17)cyclic voltammograms for(Cu-BTHN)complex in(NaCl) (1M) at scan rate 0.1Vs^{-1}

Fig(18)cyclic voltammograms for(Cu-BTHN)complex in(K$_2$HPO$_4$) (1M) at scan rate 0.1Vs^{-1}

Table (8)Current –Potential data for(Cu-BTHN))complex at different supporting electrolyte (1M) at scan rate (0.1 Vs^{-1})

	Supporting Electrolyte	Ia$_1$ μA	Ea$_1$ mv	Ia$_2$ μA	.Ea$_2$ mv	Ia$_3$ μA	.Ea$_3$ mv	-Ic$_1$ μA	.Ec$_1$ mv	Ic$_2$ μA	.Ec$_2$ mv	Ic$_3$ μA	Ec$_3$ mv
1	KCl	9.41	626	4.37	181	--	--	5.14	129	12.0	471	--	--
2	KClO$_3$	12.2	645	6.29	+92.1	1.89	289	29.4	535	--	--	--	--
3	K$_2$HPO$_4$	7.31	166	3.81	80.9	385 nA	432	4.58	53.5	6.50	211	13.0	632
4	KNO$_3$	7.88	31.8	4.74	250	--	--	6.12	59.2	14.3	549	--	--
5	K$_2$SO$_4$	8.08	539	5.87	150	--	--	5.14	133	14.7	514	--	--
6	NaCl	4.51	132	--	--	--	--	11.3	460	--	--	--	--
7	NaH$_2$PO$_4$	7.55	90.2	--	--	--	--	5.0	48.6	11.4	701	--	--

I S S N 2 3 2 1 - 8 0 7 X
V o l u m e 1 2 N u m b e r 7
J o u r n a l o f A d v a n c e s i n C h e m i s t r y

Table (9) Current –Potential data for(Cu-BTHN)) at (NaH$_2$PO$_4$)(1M) as supporting electrolyte at scan rate (0.1 Vs^{-1})

| compound	Ea$_1$ mV	Ec$_1$ mV	Ia$_1$ µA	-Ic$_1$ µA	∆Ep	(Ipa/Ipc)	E$_{1/2}$ mV
Cu-BTHN	90.2	48.6	7.55	5.0	138.8	1.5	20.8

Conclusion:

This work azo employing 3-((benzothiazol-2-diazenylnaphthalene-2,7-diol(BTHN) was successfully applied for the estimation of copper(II) ion .Due to of the sensitivity ,rapidly and selectivity of the method , its application canbe estimation of this ion in biological sample.

The cyclic voltammetric system of (BTHN) led to the formation of same hydrazine derivative which remains at the electrode surface according to equations :
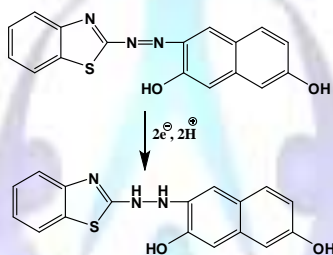
The cyclic voltammetric system of complex (Cu-BTHN)) led to the formation of two reagent molecule and copper (II) ion according to equation below :
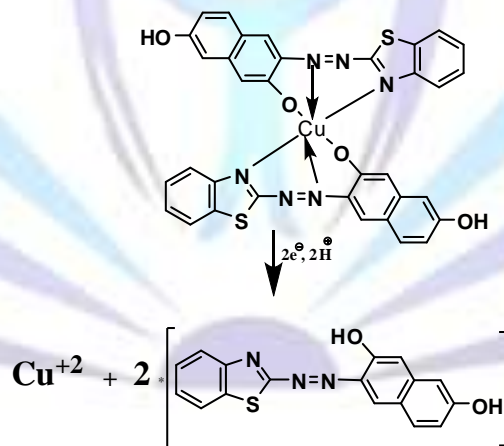
Acknowledgment

References

1. 1-D.AJohnson,T.M.Florence,Anal.Chim.Acta,53,73,1971.
2. 2-A.S.Amin,A.S.AL-Attas,J.SaudiChem.Soc.,16,451, 1971.
3. 3-N.Menek,O.Cakir,H.Kocaokutgen,Mikrochim.Acta, 122,203,1996.
4. 4-N.Menek,Ph.D Thesis,, Ondokuz Mayis University,Samsun,Turkey(1994).
5. 5-T.Hihara,Y.Okada and Z.Morita.Dyes and pigments,73,141,2007.
6. 6- H. J Mohammed, A. Y .Muhi and H. al- meisslemaw E-Journal of Chemistry, 8(S1), S425-S433,2011.

4254 | P a g e
A u g u s t 2 0 1 6
c o u n c i l f o r I n n o v a t i v e R e s e a r c h
w w w . c i r w o r l d . c o m

7. 7- H. Khazal and H..J. Mohammed Inter. J. of Civil & Env Engin IJCEE-IJENS Vol: 14 No: 04,1,2014
8. 8-H.J.Mohammed , M. A.Awad , Sh.H.Mallah , Inter. J. of Basic & Appl Sci IJBAS-IJENS Vol:15 No:02 ,25 ,2015
9. 9- M.A. Awad and H.J.Mohammed,Chem. Sci. Transactions, 3(3) pp, 2014.
10. 10- N. k. Saeed&H.J.Mohammed, Inter. J. of Civil & Env. Eng. IJCEE-IJENS Vol: 14 No: 04 ,8 ,2014.
11. 11-W. Mohammed & H.J. Mohammed Inter. J. of Civil & Env. Eng. IJCEE-IJENS Vol:13 No:06 ,37, 2013
12. 12- A.A.Sayhood and H. J. Mohammed, Int. J. Chem. Sci.: 13(3), 1123-113, 2015.
13. 13- A.A.Sayhood and H. J. Mohammed, Der Pharma Chemica,Der Pharma Chemica, 7(8), 50-58, 2015.
14. 14-L.Zhang,Z.Li,X.Du,R.Li and X.Chang,Spectrochimica Acta partA: Molecular and Biomolecular
15. Spectroscopy, 86,443-448,2012
16. 15-H.Xie,X.D.Nie and Y.G.Tang;Chin.Chem.Lett,17(8),1077-1080,2006.
17. 16-M.Ghaedi,A.Shokrollahi and F.Ahmadi;J.Haz.Mater.,142,272-278,2007
18. 17-S.F.A.Ali,N.Imtiaz,S.U.Mehdi and M.Asif;InternationalConference on Chemical Engineering and
    Pharmaceutical Sciences,(13-15),140-142.2012
19. 18- A. V .Pereira, , & O.Fatibello-Filho, ;. Anal. Chim. Acta, 366(1), 55-62. (1998).
20. *19*-S.Lunvongsa,T.T suboi and S.Motomizu;Anal.Sci.,22,169-172,2006.
21. *20-*   G. W. Ewing, Instrumental Methods of Chemical Analysis, Mcgraw-Hill College, USA, 5th ed., 1985.
22. *21-*   W. C. Vosburgh and G. R. Cooper, J. Am. Chem. Soc., 63, 437–442,1941.
23. 22-B.R.Hsieh,D.Desilets,and P.M.Kazmaier, ,'Dyes and Pigments,.14,no.3,.165-189,1990.
24. 23-A.V.Zemskov,G.N.Rodionova,Y.G.Tuchin,and V.V.Karpov,"IR soectra and structure of some azo dyes-p-
    azobenzene derivatives-in various aggregate states,"Zhurnal Prikladnoi Spektroskopii,.49,no.4,.581-586,1988
25. 24-K.Ueno,"Polyazobenzenes.III.Infrared absorption spectra of some polyazobenzenes," J.Am. Chem.
    Soc,.79,no.12,.3205-3208,1957.
26. 25- Tuzen M, Soylak M , and Elci.L,Anal chim Acta , ,584,101-108,2005.
27. *26*-L.Dubenska,H.Levytska, and N.Poperechna,"Polarographic investigation of reduction process of some azo dyes and
    their complexes with rare –earths" ,Talanta , .54,no 2..221-231,2001.
28. 27- G.W.Latimer, "Polargraphic behavior of metal chelates of o,òdihydroxyazo dyes ," Talanta , .15,no.1,.1-14,1968
29. *28*- D.K.Gosser Jr., Cyclic Voltammetry : Simulation and Analysis of reaction Mechanisms ,VCH Publishers ,New York
    ,NY,USA,1993
30. 29-C.H.Bamford"Electrode kinetic princiles and methodology" .23, .17-21,1986.
31. *30*-A.J.Bard and L.R.Faulkner,Electrochemical Methodes ,Fundamentals and Application,Wiley,NewYork.Ny,USA,2nd
    edition,2001.
32. *31*-R.N.Patel,n.Singh, D.K.Patel,and V.L.N.Gundla,"Synthesis,characterization and superoxide dismutase studies of
    square pyramidal copper (II) complexes with bi and tri dentate polyamine ligands,"Indian Journal of chemistry
    A.46,no.3,422-427,2007

32- G.D.Levitskaya,N.P.Poperechnaya , and L.O.Dubenskaya, Polarographic behavior of eriochrome red B and   .33
its complexes with rare –earth ions,"Journal if Analytical Chemistry , .56,no 6,552-556,2001

4255 | P a g e
A u g u s t   2 0 1 6   c o u n c i l   f o r   I n n o v a t i v e   R e s e a r c h
                                                w w w . c i r w o r l d . c o m