



Determination and Cloud Point Extraction of Copper (II) Ion by Using 1-[2-Cefixime Thiazolazo]- 2-Benzonaphthol

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Abstract

In this paper 1-[2-CefiximeThiazolazo]- 2-Benzonaphthol was first synthesized and characterized, as a organic reagent in the next step this reagent was used as a complexing agent in cloud point extraction for Cu(II). optimum conditions of this studing show $pH_{ex}=9$ by use $1 \times 10^{-4}M$ (1-[2-CefiximeThiazolazo)- 2-Benzonaphthol) and 0.6ml of 1% TritonX-100 and heating at $80^{\circ}C/353k$ for 10 min as well as this research involved thermodynamic study and other parameters effect on extraction efficiency such as determination of $Cu^{2+}(20\mu g)$ spectrophotometry.

Key Words: Thermodynamic, Parameters, Efficiency.

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Introduction

The cloud point extraction (CPE) of metals; was first reported by Watanabe and co-workers, who studied the pre-concentration of nickel (Ni) with a complexing agent 1-(2-thiazolylazo)-2-naphthol in Triton X-100 as a surfactant micellar solution. but this surfactant around $70^{\circ}C$ has a relatively high cloud point^[1-4]. By the concept of CPE, different metals can be extracted into micelles with a complexing agent in the presence of a surfactant. In this technic more than one separated phases must be created, this approach has been used for sample clean up and to concentrate the analyte, which can be achieved by several techniques, such as, atomic spectrometry, UV/Vis spectrophotometry or capillary electrophoresis ^[5-6]. The principle, and applications advantages of Cloud Point Extraction have been well-established in recent years. The use of pre-concentration steps based on CPE offers a conventional alternative to more traditional extraction systems and allows the design of extraction schemes that are, cheap, simple of high efficiency and of lower toxicity than traditional extractions that use different organic solvents^[7-9].

Copper is widely anthropogenic pollutant of environment and the determination of copper metal ion is a real problem. Copper is an important element for life in mammals and for plants, and it plays a vital role in lipid and carbohydrate metabolism. It has many biological effects as an essential element as well as a toxic effects^[10-11]. intake of 1.5-2 mg of copper is essential for adults at nearly 40 ng mL^{-1} is required for normal metabolism of many living organisms^[12]. Copper may be absorbed into the body by inhalation, ingestion and even through the skin. Short-term exposure to high levels of copper can cause convulsions, diarrhea, vomiting, Coma or even death. However, ongoing exposure to even small amounts of copper can be harmful, especially to infants and young children^[13-14]. The determination of copper is achieved by graphite and flame furnace atomic absorption spectrometry, as well as chemiluminescence, spectrophotometry and electro-thermal methods.

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However, due to presence of copper in low concentrations in different environmental samples and the matrix effects different pre-concentration and separation techniques such as precipitation, liquid-liquid extraction, solid phase extraction ion exchange, and membrane filtration improve the analytical detection limit^[15-20]. Cobalt, nickel and copper normally are at very low levels in the environment, therefore sensitive methods must be used to detect them in most environment and food samples. The determination of cobalt, nickel and copper in these matrices is usually carried out by flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) spectrophotometry inductively coupled optical emission spectrometry (ICP OES) chemiluminescence and electrochemical methods^[21-27].

Experimental

Instrument

For spectrophotometric studies used double-beam spectrophotometer: Biochrome(80-7000-11) Libra s60 cambridge CB4 0FJ (England). But for absorption measurements used single beam: optima, model: sp-300, serial No: 322951, Japan. And for the pH measurement used pH meter (HANNA Germany) as well as used shaker: Triup international copper.

LOT: 03320203, Ret: 03-7326T-09(Italy). And electrostatic water bath (WNB7-45) (England).FTIR-spectrophotometer was FTIR 8400S, Shimadzu corporation, serial No. A21274501282LP, (Japan).

Materials

All chemical used as received without of more purification, stock solution of Cu^{2+} was prepared from CuCl_2 , ammonium chloride, copper chloride and sodium nitrate were purchased from Fluka, potassium nitrite, potassium persulphate, Triton X-100, ethanol, and hydrochloric acid were purchased from BDH, lithium chloride, sodium chloride, zinc chloride and dimethyl glyoxime were from Merk.

Procedure

1-Synthesis Organic Reagent: 1-[2-CefiximeThiazolazo)- 2-Benzonaphthol: 1-[2-CefiximeThiazolazo)- 2-Benzonaphthol was synthesized by dissolving of (0.01 mol, 3.9613g) of Doxycycline in (4ml, 12M HCl and 25ml distilled water). The mixture was cooled to (0 C) and then (1.4g) of sodium nitrate was dissolved in (10ml) distilled water at (0 C) and then diazonium solution was added to mixture of (1.0913g, 0.01mol 2-amino phenol) and (1.2g NaOH,150ml ethanol).

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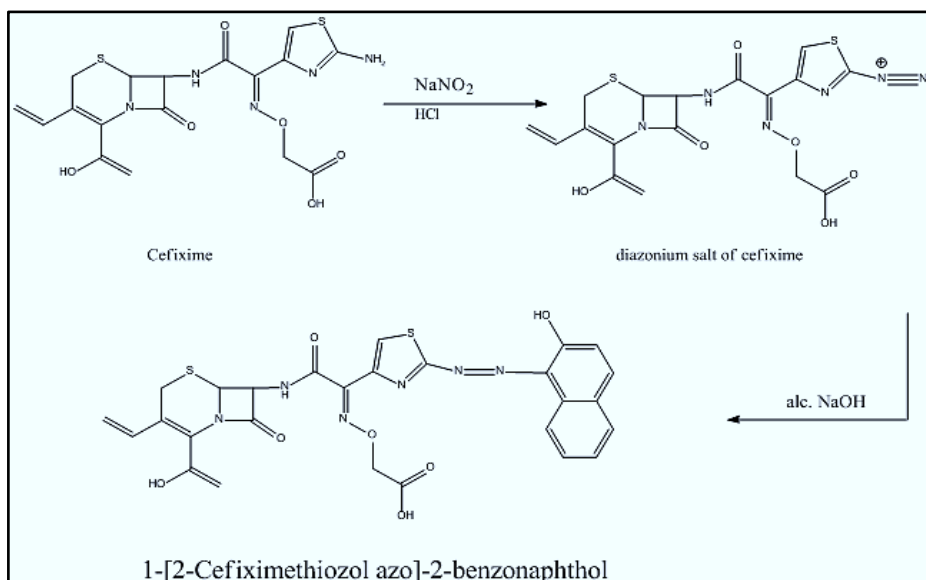


Figure 1. Synthesis Organic Reagent

2.Preparation of Solutions

1. Preparation of standard solution of 1 mg/ml of Cu^{+2} : Primary standard solution of Cu^{+2} 1mg/ml is prepared by dissolving of 0.2118g of

CuCl_2 in 100 ml of distilled water that containing 0.5 ml of HCl conc.

2. **Preparation of secondary solution of 100 µg/ml of Cu²⁺:** 10ml of primary solution of Cu (II) was poured in a 100ml volumetric flask.
3. **Preparation of standard solution of DMG:** 1g of DMG was dissolved in 100ml of ethanol in a 100ml volumetric flask.
4. **Preparation of standard solution of organic reagent 1-[2-CefiximeThiazolazo]- 2-Benzonaphthol:** 2*10⁻⁴M solution of organic reagent was prepared by dissolving of 0.121g of 1-[2-CefiximeThiazolazo]- 2-Benzonaphthol in

1 L of distilled water, then 1% of different volumes (0.2-0.7ml) of Tritonx100 was added to the reagent solution. Then different concentrations (1*10⁻⁵, 5*10⁻⁴, 1*10⁻⁴, 5*10⁻⁵) was prepared from standard solution.

Results and Discussion

FTIR spectrum of 1-[2-CefiximeThiazolazo]- 2-Benzonaphthol: FTIR spectrum was achieved by shimadzu FTIR spectrophotometry (8400S series).

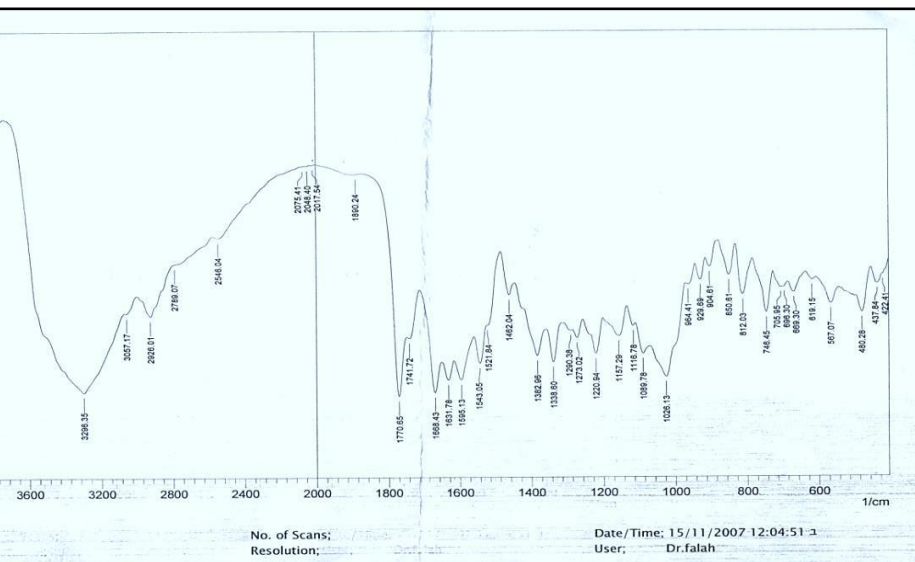


Figure 2. IR spectrum of Organic Reagent

Table1. FT.IR of Compounds

Wave number(cm ⁻¹)	IR Bands
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3296	O-H stretching (m, v)
3057	C-H aromatic (w, v)
2926	C-H aliphatic(w)
2546	S-C stretching (m, v)
1668, 1631	C=N (s, v)
1462,1543	N=N(m, v)
1595	C=C(m, v)
1770,1741	C-O(m, v)



1. Effect of PH

Several aqueous solution (10 ml volumetric flask) each one contain 100 µg Cu²⁺ at different pH values and contained 1×10⁻⁴M (1-[2-CefiximeThiazolazo)-2-Benzonaphthol), at T=80 °C, and 0.5 ml of 1% TritonX-100. when extraction process is complete CP layer was dissolved in 5ml of ethanol and measurements were at λ_{max}=394nm against blank prepared at the same manner without Cu²⁺ ion, so aqueous solution treated according to DMG spectrophotometric method and calculate distribution ratio at each pH as detailed in general method.

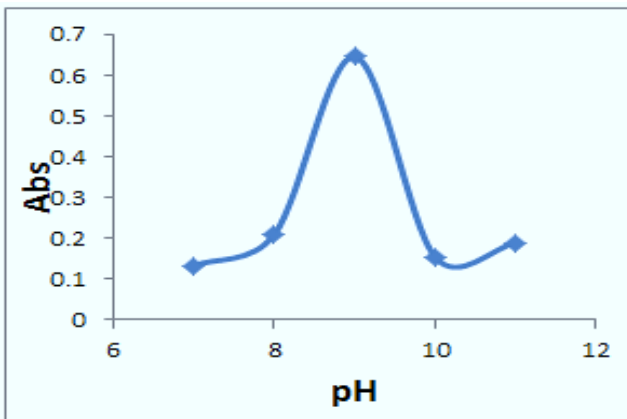


Figure3. Effect of pH on complex formation and extraction

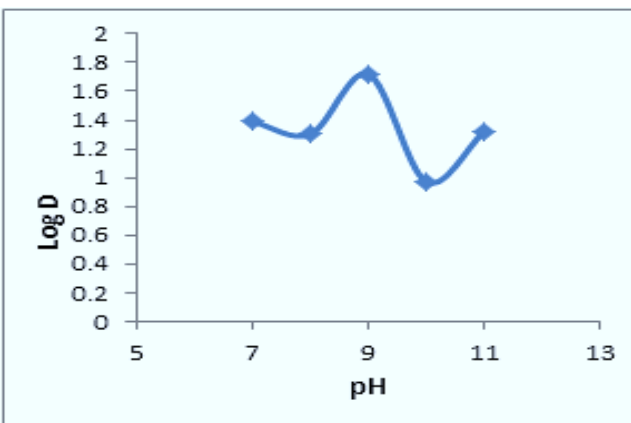


Figure4. D = F(pH)

The graphic results show that the optimum value of extraction efficiency and D value are at pH=9, other values of PH giving rise in minimizing of complexing agent with 1-[2-CefiximeThiazolazo)-2-Benzonaphthol.

2.2. Effect of 1% Tritonx-100 Volumes

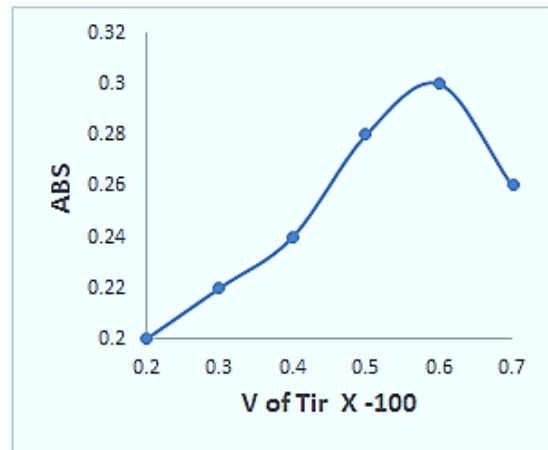


Figure 5. Effect of TritonX-100

Concentration on Complex Extraction

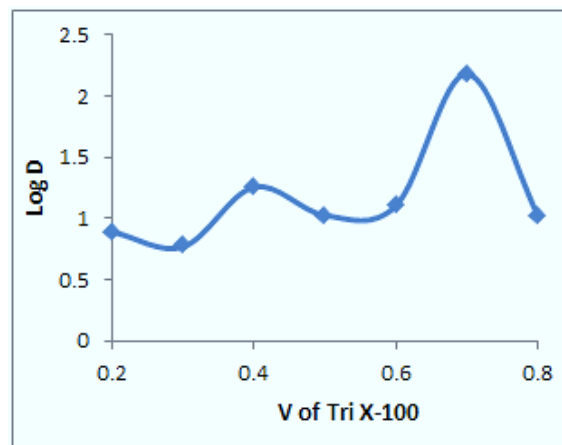


Figure6. Effect TritonX-100 concentration on Partition Complex to CPL As shown in the figures above, the optimum value of absorbance for 1% triton-100 is in volume (0.6ml) equilibrium state of extraction will be reached.

2.3. Effect of Heating Time

Extraction 20µg of Cu(II) from 10ml aqueous solution at pH=9 and in presence 1×10⁻⁴M of 1-[2-CefiximeThiazolazo)- 2-Benzonaphthol and 0.6 ml 1% TritonX-100. Afterward heating the solutions for optimum temperature at (5-25min). then separated CPL from aqueous solution and dissolved CP layer at 5ml ethanol and determined the absorbance at 394nm against blank prepared at the same manner without Cu(II) so that aqueous solution treated as DMG method and calculated D-value according to the procedure detail in general method and gives following results shown in figures:



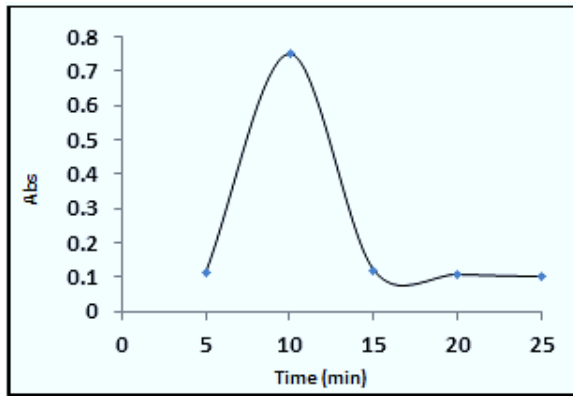


Figure7. Effect of heating time on complex formation and extraction

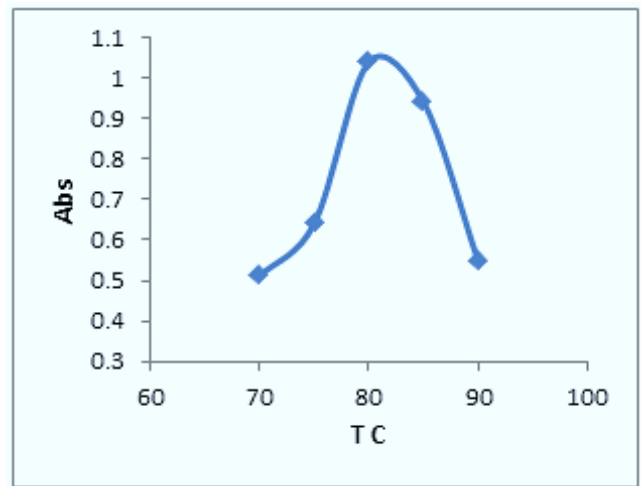


Figure9. Temperature effect on formation CPL and extraction

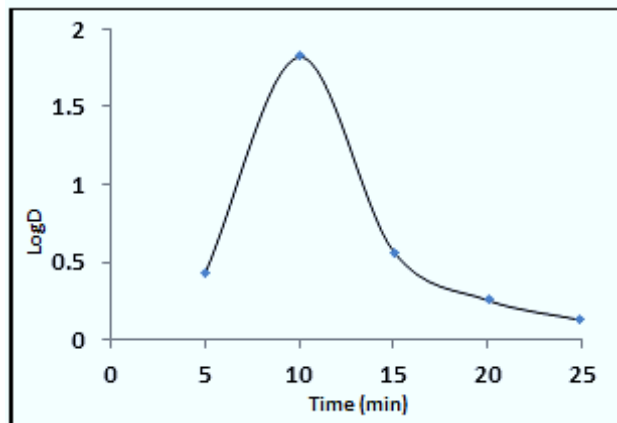


Figure8. Distribution ratio(D) changes as a function of heating time

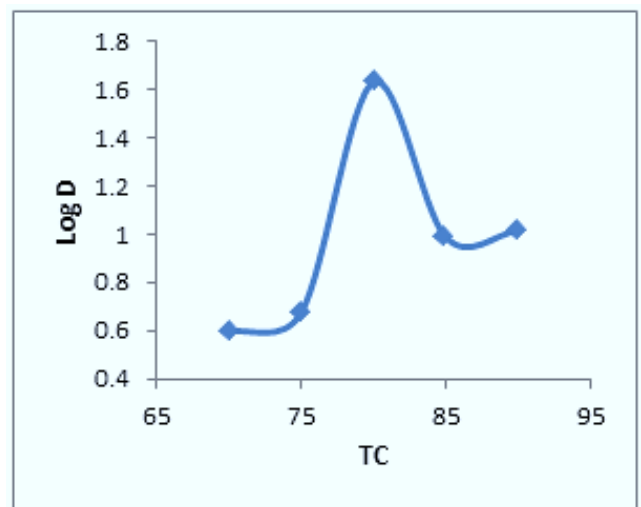


Figure10. Effect of temperature on extraction efficiency and D-value

Heating time appear from the results shown the effective for extraction according to cloud point extraction methodology from the results appear optimum heating time was 10 min, giving higher absorbance and D-value.

Temperature Effect

Extracted 50µg of Cu(II) in 10 ml aqueous solution at pH=9 in presence 1×10⁻⁴M of organic reagent and 0.5ml from 1% TritonX-100 heated these solutions of different temperature for 15 min then determine the absorbance of ethanolic cloud point layer solution after separation at 394nm against blank prepared at the same manner as well treated aqueous phase according to DMG spectrophotometric method and calculated D-value at each temperature the results were as in Figures (9, 10).

Afterward calculated extraction constant (k_{ex})by application the relation below:

$$K_{ex} = \frac{[Cu(II)]_{aq} [1-[2-Cefixime Thiazol azo]-2-Benzonaphthol]_{org}}{D}$$

After determine (K_{ex})at each temperature plotted Log K_{ex} against 1/Tk. the results as in Figure 11:

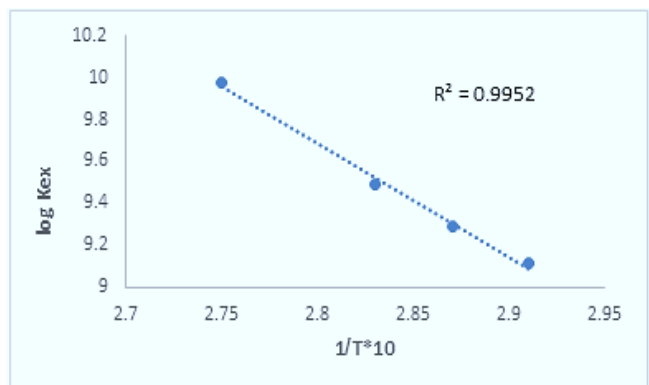


Figure 11.The relation between k_{ex} ,temperature

From the slope of straight line in Figure 15 determined in enthalpy of extraction by application the relation below:

$$\text{slope} = \frac{-\Delta H}{2.303R}$$

And free energy of extraction by relation below:

$$\Delta G_{ex} = -RT \ln K_{ex}$$

As well as entropy of extraction calculated by relation:

$$\Delta G_{ex} = \Delta H_{ex} - T \Delta S_{ex}$$

The results of thermodynamic data after application the relation above was:

$\Delta H_{ex} = 0.1126 \text{ KJ.mol}^{-1}$
$\Delta G_{ex} = -67.014 \text{ KJ.mol}^{-1}$
$\Delta S_{ex} = 165.16 \text{ J.mol}^{-1}.\text{k}^{-1}$

The small value of enthalpy of extraction reflect the near each ion together in ion association complex , as well as appear the extraction method was endothermic relation. As well as the large value of entropy demonstrate the extraction method was entropic in region.

Effect of Organic Reagent Concentration

Extracted 20µg Cu(II) and 0.5ml of 1% TritonX-100, after heated these solutions at 80 C temperature and 10 min and separated cloud point layer from aqueous solutions so determined absorbance of ethanolic CPL solution at 394 nm and calculated distribution ratio (D).The results were as in Figures (12,13).

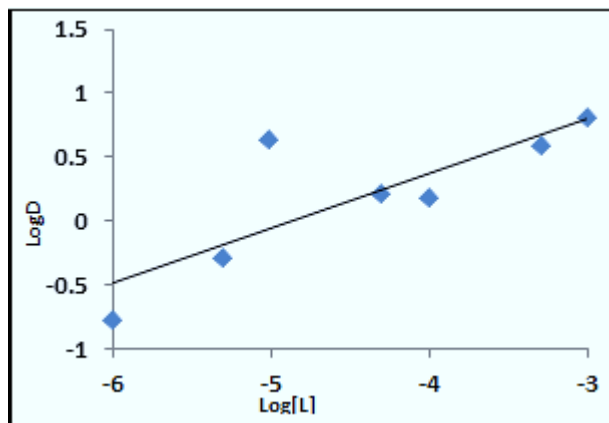


Figure13. Effect of complexing agent concentration on extraction efficiency

Effect of Cu²⁺ Concentration

Extraction of Cu²⁺from 10ml aqueous solutions contain different quantity of Cu(II) ion at optimum pH according to procedure detailed in general method .The results was as in Figures (14,15).

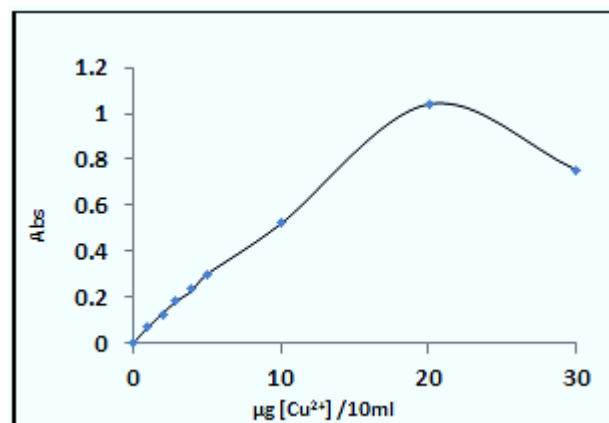


Figure 14. Complex formation and extraction as function of metal ion concentration

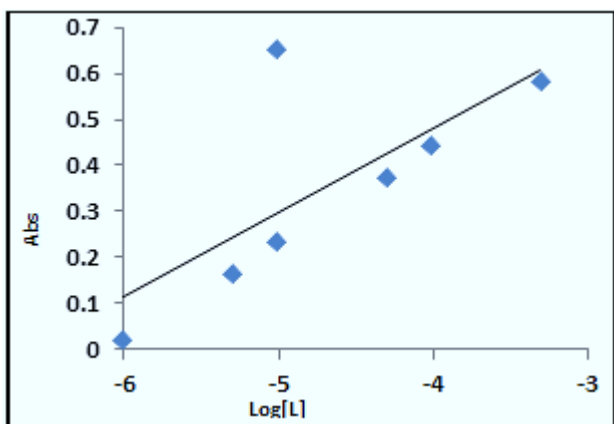


Figure12. Effect of complexing agent concentration on complex formation

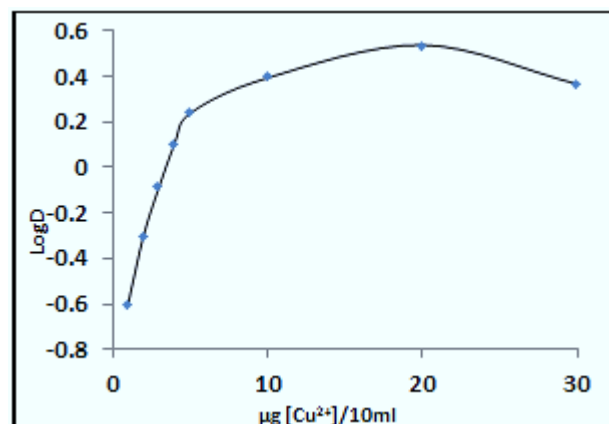
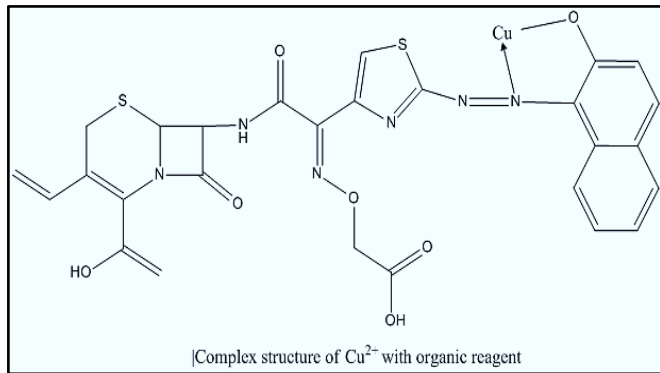


Figure 15.Extraction efficiency and D-value change as function of metal ion concentration



With optimum value 20µg/10ml giving favorable thermodynamic equilibrium to produced higher concentration of complex extracted. Any concentration less optimum not enough to reach equilibrium as well as concentration more than optimum effect to increase rate backward reaction and dissociation according to Lech atelier principle and mass action law.



Interferences Effect

Extracted 20µg Cu²⁺in 10ml aqueous solution at pH=9 at optimum conditions and in presence 0.1M from different metal cations, according to general procedure and determine absorbance and D-values,The result were as in Table (2).

Table 2. Interferences effect

Cations	CPLAbsorbance	D
Mn ²⁺	0.106	0.229
Ag ⁺	0.124	0.264
Pb ²⁺	0.740	1.845
Ni ²⁺	0.141	0.238

The results show large interferences of these ion in the extraction of Cu²⁺, that is mean these metal cations participate Cu²⁺in complex formation with organic reagent, this behavior effect to decrease concentration of complex Cu²⁺formed and extracted appear as decrease in absorbance and D-values.

Electrolyte Effect

Extracted 20µg Ni²⁺ion in 10mL aqueous solution at pH=9 according to CPE methodology at optimum condition and as procedure detailed in general method in presence 0.1M of different electrolyte salts, after determine absorbance and D value the results were as in Table(3):

Table 3. Electrolyte effect

Electrolytes	CPLAbsorbance	D
K ₂ S ₂ O ₃	0.202	0.372
Na NO ₃	0.128	0.406
MgCl ₂	0.120	0.338
NaCl	0.138	0.404

The results show in presence electrolyte in aqueous solution effect to enhancement extraction efficiency because the electrolytes cause to increase dehydration to the micelles aggregation to increase CPL with higher density and smaller volume as well as these electrolyte effect to destroyed the hydration shell of metal cation Cu²⁺ and remove the water molecules nearly to functional group of organic reagent (1-[2-CefiximeThiazolazo)- 2-Benzonaphthol) this behavior effect to increase the chances of interaction between ligand and metal cation and increase it's stability and the results appear Na⁺ giving higher absorbance and D-value because having smallest ion radio and with drawing more of water molecule.

Spectrophotometric Determination

For determination Cu²⁺spectrophotometrically in different samples prepared calibration curve by application cloud point extraction method at optimum conditions to extraction Cu²⁺ion from 10ml aqueous solution contain different quantity (ppm) of Cu²⁺ ion, the results were as in Figure (16).

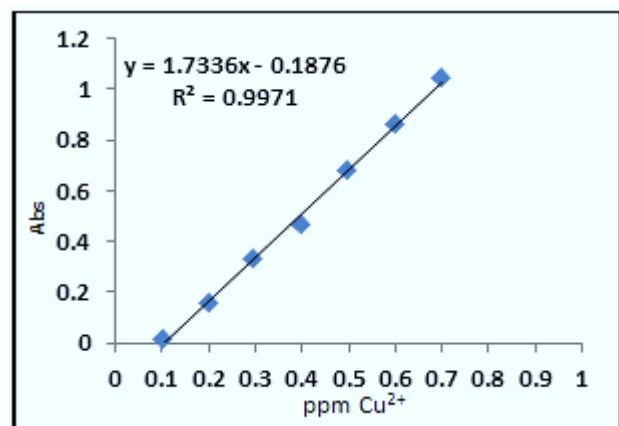


Figure 16.Calibration curve for spectrophotometric Determination of Ni²⁺

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