Extraction and spectrophotometric determination of Copper (II) and Silver (I) by using 2-[Benzothiazolyl azo]-4-benzyl phenol in sediments of Euphrate river, in Al-Najaf governorate.

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Abstract:-

Extraction methods for Cu^{+2} and Ag^+ shows optimum pH for extraction was $(pH_{ex}=7)$, for Cu^{+2} and $(pH_{ex}=8)$ for Ag^+ , as well as extraction procedure need shaking time (20minutes) for Cu^{+2} and (15minutes) for Ag^+ , in addition shows optimum concentration giving higher distribution ratio (D) was $(80\mu g) Cu^{+2} (2.52 \times 10^{-4} M)$ and $(60\mu g) Ag^+(1.1 \times 10^{-4} M)$, organic solvents effect on distribution ratio (D) for extraction shows there is not any linear relation between dielectric constant (ϵ) for organic solvents used and distribution ratio (D), but there is effect for organic solvent structure for both ion. Stoichiometry shows coordination complex extracted was (1:2) (Metal:Organic reagent) for Cu^{+2} , $[Cu^{2+}(BTABP^-)_2]$, but for Ag^+ was (1:1) (Metal:Organic reagent) [Ag^+(BTABP^-)], thermodynamic study shows the complexation reaction between metal ion and organic reagent was endothermic for Cu^{+2} and Ag^+ , as well as synergistic effect study. From other hand used this method and organic reagent BTABP for spectrophotometric determination of Cu^{+2} and Ag^+ in sediments of different locations of Euphrates river in Al-Najaf governorate.

1. Introduction:-

To be based on sensitivity and selectivity of azo compounds for complexation used these compounds to separation, extraction and spectrophotometric determination for transition elements. Prepared a new chelating resin by coupling Amberlite XAD-4 with 1-amino-2naphthole through an azo spacer. The resulting sorbent has been characterized by FT-IR, elemental analysis and thermo gravimetric analysis and studied for preconcentration of Cu (II) using FAAS for metal monitoring, and the optimum pH for sorption of the Cu²⁺ was 6.5[1]. Synthesized different imidazole derivatives and used these compounds as organic reagent and studied the complexation with Copper (II), Zinc (II) and Nickel (II) as well studied properties of these complexes[2]. The significant spectral overlap (Di)0.5 = 0.5667 which is about 75.3% overlapping of the UV/Vis. absorption spectra of Fe (II) and Cu(II) complexes necessitates chemometric assisted methods for analysis of these ions in the pharmaceutical mixture. These metal ions were analyzed simultaneously by UV/Vis. spectrophotometric method where 8hydroxyquinoline was used as a chromogenic reagent. The methods were applied for analyzing synthetic mixtures and commercial pharmaceutical preparation[3]. Synthesized chiral complexes of Zn(II) with imidazole derivatives and amino acid ester derivatives and studied characterization of these complexes[4]. Studied extraction of Zn(II), Cd(II), Hg(II) by use new imidazole derivatives as organic reagent 2-[4-chloro-2-methoxy phenyl azo]-4,5-diphenyl imidazole and definition all factors effect on the distribution ratio[5]. Synthesized new imidazole derivative and used as organic reagent as well as studied it's complexes with Cobalt (II), Nickel (II) and Copper (II) [6]. Determination of Cu(II) by using 2,3,4-trihydroxy acetophenone phenyl hydrazone (THAPPH) as a spectrophotometric method. The metal ion has formed 1:2 bluish green coloured complex with THAPPH in HCl-KCl buffer of pH 2.5. Beer's law was obeyed in the range 0.04-0.64 μ g/mLCu²⁺ at λ_{max} =385 nm. ϵ =1.0053×10⁵L.mol⁻¹cm⁻¹ and Sandell's sensitivity (0.0006265μ gcm⁻²). The interfering effect of various cations and anions was also studied. The reliability of the method was assured by analyzing the standard alloys, Brass, Bronze, and Phosphor-Bronze. This method was employed for the determination of Cu(II) in food and medicinal leafy samples and inter compared the experimental values using AAS[7]. Studied spectrophotometric method for determination of Cr(III) with 4-(2-thiazolyl azo)resorcinol, this study shows slowly formation of red complex at pH 5.7, accelerate the complex formation by irradiating the reacting mixture with microwave energy, the absorbance reached it's maximum with 5 min. of irradiation and remain stable[8]. The used solvent extraction method for extraction of Cu(II) and Ag(I) by 2-(α -Naphthylazo)-4,5-diphenyl imidazole, and studied optimum conditions for extraction as well as determined all factors effect on the extraction process and distribution ratio (D) [9]. Studied the extraction of Zn(II) in chloride medium with triphenyl phosphate in kerosene under different experimental conditions to understanding extraction mechanism[10].

2. Experimental:-

All materials and solvents provide with commercial sources and used as received, in addition to used distilled water to prepare all working solutions, but organic reagent 2-[Benzothiazolyl azo]-4-benzyl phenol synthesized as in the work [11], for spectrophotometric and absorbance measurements used single beam schimadzu (UV-100-02) spectrophotometer and (UV-1700) double beam spectrophotometer, Japan, for all pH measurements used (HANNA pH-meter). General procedures for spectrophotometric determination of Cu⁺² and Ag⁺ in aqueous solutions used methods detailled in [12], from absorbance values at λ_{max} =500nm for Cu⁺² complex with dithiazone and λ_{max} =620nm for Ag⁺ complex with dithiazone and calibration carve Figure (1) can be determine remaining quantity of each ion in aqueous phase, depend on subtraction remainder quantity of metal ion in aqueous phase from real quantity to determine transferred quantity to organic phase of metals ion recently calculate distribution ratio (D).



Figure (1): Calibration curve for Cu⁺² and Ag⁺ in dithiazone



Figure(2):UV-Vis. Spectrum of organic reagent BTABP and its complexes with Cu²⁺& Ag⁺



3. Results and discussion:-

3.1. Effect of pH:-

5mL aqueous solution contain (40µg) Cu^{+2} (1.26×10⁻⁴M) or (20µg) Ag^+ (3.68×10⁻⁵ M) at different acidity function (pH=4-12), added(5mL) of organic reagent (BTABP) dissolved in chloroform at (1×10⁻⁴M), after shaking two layers for 10 minutes separate these two layers and determine the remaining quantity of each ion in aqueous solution calculate distribution ratio (D) according to procedure detailed in [12]. Recently plot log D versus pH provide the Figure (6).



Figure (6): pH Effect on distribution ratio (D) for extraction Cu⁺² and Ag⁺

The results in Figure (6) shows optimum pH_{ex} was (7) for Cu^{+2} ions and (8) for Ag^+ ions which is demonstrate condition for more stable ion pair complex extracted.

3.2. Effect of Metal Ion Concentration:-

5mL of aqueous solution contain (5-80 μ g) for Cu⁺² (1.57×10⁻⁵ -2.5×10⁻⁴ M) at (pH=7) but for Ag⁺ (9.2×10⁻⁶ - 1.47×10⁻⁴M) at (pH=8) after added (5mL) of organic reagent (BTABP) dissolved in chloroform at (1×10⁻⁴M), and shaking for 10 minutes separate organic phase from aqueous phase and determine remainder quantity of each ion in aqueous phase spectrophotometricaly according to methods in [12]. Latter calculate distribution ratio (D) for each concentration and plot log D versus μ g Mⁿ⁺ provide Figure (7).



Figure (7): Effect of metal ion concentration on distribution ratio (D)

The results in Figure (7) shows thermodynamic equilibria for complex formation between metal ion and organic reagent (BTABP) was increasing thermodynamically with increasing of

metal ion concentration to reach optimum concentration of metal ion concentration which is giving higher stability of complex formation at $(80\mu g)(2.5 \times 10^{-4} M)$ for Cu⁺² ions and $(60\mu g)(1.1 \times 10^{-4} M)$ for Ag⁺ ions.

 $Cu^{2+}_{aq.} + BTABP_{org.} = [Cu^{2+}(BTABP)^{-}_{n}]_{org.}$ $Ag^{+}_{aq.} + BTABP_{org.} = [Ag^{+}(BTABP)^{-}_{n}]_{org.}$

3.3. Effect of Shaking Time:-

For (5mL) of aqueous solutions contain ($80\mu g$) ($2.5 \times 10^{-4} M$) of Cu⁺² ions at (pH=7) or ($60 \mu g$) ($1.1 \times 10^{-4} M$) of Ag⁺ ions at (pH=8) added (5mL) of ($1 \times 10^{-4} M$) organic reagent (BTABP) dissolved in chloroform, and shaking for different time (5-25min.), latter separate organic phase from aqueous phase and determine remainder quantity of metal ions in aqueous phase and distribution ratio (D), at each shaking time according to spectrophotometric determination methods [12], graph log D against shaking time provide Figure (8).



Figure (8): Effect of shaking time on distribution ratio (D)

The results in Figure (8) shows optimum shaking time was (20min.) for Cu^{+2} ions and (15min.) for Ag^+ ions which is necessary to reach the favorite equilibrium for the more stable complex extracted throw the reaction between metal ions and organic reagent (BTABP), shaking less than optimum time for each ion not allow to reach equilibrium state, but shaking at time longer than optimum time effect to increase dissociation equilibria.

3.4. Effect of Organic Solvents:-

For (5mL) of aqueous solutions contain (80µg) Cu^{+2} (2.5×10⁻⁴ M) at (pH=7) or (60 µg) Ag⁺ (1.1×10⁻⁴M) at (pH=8) added (5mL) of organic reagent solution (BTABP) dissolved in different organic solvents differ in dielectric constant (ϵ) at (1×10⁻⁴M). After shaking for (20min.) with Cu⁺² ions or (15min.) with Ag⁺ ions and separate the two layers and determine the distribution ratio (D) with each organic solvent provided the result at Table (1) which is shows there is not any linear relation between dielectric constant (ϵ) for organic solvents and distribution ratio (D), but there is effect for organic solvent structure on distribution ratio (D), giving higher value with Dichloromethane for Cu⁺² ions and Benzene for Ag⁺ ions.

Organia galvanta		D		
Organic solvents	ε	Cu ⁺²	Ag^+	
Dichloromethane	9.08	8.7	17.46	
Chloroform	5.708	7.69	16.14	
Bromo benzene	5.4	7.5	19	
Benzene	2.804	7	23	
Toluene	2.438	6.69	12.3	
Carbon tetrachloride	2.38	8.09	14	

Table (1): Effect organic solvents on distribution ratio (D)

3.5-Stoichiometry:

3.5.1. Slope Analysis Method:-

Extraction (80µg) Cu^{+2} (2.5×10⁻⁴M) at (pH=7) or (60µg) Ag⁺ (1.1×10⁻⁴M) at (pH=8) in (5mL) aqueous solutions by (5mL) organic reagent solution (BTABP) dissolved in chloroform at different concentration (1×10⁻²-1×10⁻⁵M). After determine distribution ratio (D) at each concentration of organic reagent solution according to spectrophotometric determination method [12], latter graph log D versus log [BTABP] provide straight line with slope (1.76) for Cu^{+2} ions shows the more probable structure of complex extracted was (1:2)(metal : organic reagent)[Cu^{2+} (BTABP⁻)₂], but the slope of straight line for Ag⁺ ions was (0.37), demonstrate the structure of complex extracted was (1:1) (metal :organic reagent) [Ag⁺(BTABP⁻)].



Figure (9): Slope analysis method

3.5.2. Mole Ratio Method:-

For (5mL) of aqueous solutions contain (80µg) Cu^{+2} (2.5×10⁻⁴ M) at (pH=7) or (60 µg) Ag⁺ (1.1×10⁻⁴M) at (pH=8) added (5mL) organic reagent solution (BTABP) dissolved in chloroform at different concentration (1×10⁻⁵M-1×10⁻²M), after shaking the two layers for optimum shaking time for each metal ion and separate these two layers, determine absorbance of organic phase at λ_{max} =500nm for Cu⁺² complex or at λ_{max} =620nm for Ag⁺ complex, latter graph absorbance (A) values versus C_L/C_M where C_L different concentration of organic reagent solution and C_M the constant concentration of metal ion provide Figures (10,11).



The results in Figures above shows the more probable structure of complex extracted was (1:2) (Metal: organic reagent) for Cu⁺² ions [Cu²⁺(BTABP⁻)₂] and (1:1) (Metal: organic reagent) for Ag⁺ ions [Ag⁺(BTABP⁻)] as in slope analysis method. **3.5.3. Continuous Variation Method:-**

Prepared aqueous solution for each metal cations Cu^{+2} and Ag^+ at concentration of $(1 \times 10^{-4} \text{ M})$ and organic solution of organic reagent (BTABP) dissolved in chloroform at $(1 \times 10^{-4} \text{ M})$ concentration also after that mixing different volume of these two solution to total volume (5mL) at optimum pH for each cations after shaking for optimum shaking time for each metal ion separate organic phase and determine it's absorbance at λ_{max} =500nm for Cu^{+2} complex and λ_{max} =620nm for Ag^+ complex, the graph of absorbance versus (V_M/V_T) for organic solutions provide Figures (12,13).



Figure (12): Continuous variation for Cu⁺²



Figure (13): Continuous variation for Ag⁺

The results emphasize the structure of complex extracted was (1:2) (Metal: organic reagent) for Cu^{+2} [$Cu^{2+}(BTABP)_2$] and (1:1) (Metal: organic reagent) for Ag^+ [$Ag^+(BTABP)$].

3.5.4. Slope ratio Method:-

The first experiment include prepare aqueous solutions for each ion Cu^{+2} or Ag^+ at rang $(1 \times 10^{-6} - 1 \times 10^{-3} \text{ M})$ at optimum pH for each ion, adding to each solution $(1 \times 10^{-4} \text{ M})$ for organic reagent BTABP after shaking for (20min.) with Cu^{+2} ions and for (15min.) with Ag^+ ions afterward separate the two phase and measure the absorbance of organic phase at higher absorbance wave length λ_{max} =500nm for Cu^{+2} and λ_{max} =620nm for Ag^+ .

The second experiment include prepared aqueous solution contain metal ions Cu^{+2} or Ag^+ at $(1 \times 10^{-4}M)$ at pH= 7 for Cu^{+2} ions and pH=8 for Ag^+ ions extracted each ion with solutions of organic reagent BTABP at concentration $(1 \times 10^{-6} - 1 \times 10^{-3} \text{ M})$ with shaking time (20min.) with Cu^{+2} ions and for (15min.) with Ag^+ ions at later separate aqueous phase from organic phase and measured absorbance of organic phase at λ_{max} =500nm for Cu^{+2} and λ_{max} =620nm for Ag^+ .

For the first experiment plot absorbance versus molar concentration of metal ions Fig.(14,15) and calculate the slope of straight line, and for the second experiment plot absorbance versus molar concentration of organic reagent in figures(14,15) and calculate the slope of straight line and with division slope of second experiment on slope of first experiment get value for complex structure.



The results emphasize the structure of complex extracted was (1:2) (Metal: organic reagent) for $Cu^{+2} [Cu^{2+}(BTABP)_2]$ and (1:1) (Metal: organic reagent) for $Ag^+ [Ag^+(BTABP)]$.



Figure(16):Structure of Cu²⁺ complex with organic reagent BTABP



Figure(17):Structure of Ag⁺ complex with organic reagent BTABP

3.6. Temperature Effect:-

Extracted metal cation from (5mL) aqueous solutions contain (80µg) Cu^{+2} (2.5×10⁻⁴M) at (pH =7) or (60µg) Ag⁺ (1.1×10⁻⁴M) at (pH =8) by (5mL) of (1×10⁻⁴M) organic reagent solution (BTABP) dissolved in chloroform at different temperature (5°C-60°C), latter determine distribution ratio (D) at each temperature according to spectrophotometric method [12], after that calculate extraction constant K_{ex} by the relation below:

$$K_{ex} = \frac{D}{[M^{n+}]_{aq.} [BTABP]_{org.}}$$

Latter plot $\log K_{ex}$ versus 1/TK and from the slope of the straight line determine thermodynamic data according to:

Slope = $\frac{-\Delta H_{ex}}{2.303R}$ ΔG_{ex} =-RTln (K_{ex}) ΔG_{ex} = ΔH_{ex} -T ΔS_{ex}

T °C	1/T K	D		K _{ex} ×10 ⁸		∆H _{ex} KJ mole ⁻¹		∆G _{ex} KJmole ⁻¹		ΔS_{ex} J mole $^{-1}K^{-1}$	
	×10	Cu ²⁺	Ag^+	Cu ²⁺	Ag^+	Cu ²⁺	Ag^+	Cu ²⁺	Ag^+	Cu ²⁺	Ag^+
5	3.6	3.25	2.16	1.29	1.96			-50.95	-53.30	153.00	160.00
10	3.5	3.30	2.24	1.31	2.04						
15	3.47	3.39	2.53	1.35	2.30	0.00197	0.00197 0.00783				
20	3.4	3.45	2.75	1.37	2.50						
30	3.3	3.52	3.29	1.39	2.99						
40	3.2	3.56	3.44	1.41	3.13						
50	3.1	3.65	3.60	1.45	3.27						
60	3.0	3.76	4.20	1.49	3.50						

Table (2): Effect of temperature on distribution ratio (D)

The results shows the reaction between organic reagent BTABP and cations Cu^{+2} and Ag^+ was endothermic reaction as in bellow figures as well as high entropy values mean the complexation reaction was entropic in region.



3.7. Synergism Effect:

Extracted (80µg) Cu^{+2} (2.518×10⁻⁴M) at (pH =7) or (60µg) Ag⁺ (1.104×10⁻⁴M) at (pH =8) in (5mL) aqueous solutions by (5mL) organic solutions for organic reagent (BTABP) dissolved in chloroform at (1×10⁻⁴M) concentration contain different concentration of tributylphosphate (TBP) (1×10⁻⁵-5×10⁻⁷M) after shaking for optimum shaking time for each metal ion and calculate distribution ratio (D) in each concentration of TBP according to previous method detailled, graph log D versus log [TBP] provide Figures (20,21).







The results from the slope values demonstrate there is one molecule of TBP participate in the complex structure extracted [Cu²⁺(BTABP)₂(TBP)] and [Ag⁺(BTABP)(TBP)], from other hand the participation of TBP get enhancement in distribution ratio (D) which is replace molecule of water coordinate to the coordination shell of metal ion to increase transfer complex to the organic phase and increase distribution ratio (D).

3.8. Spectrophotometric determination of Copper (II) & Silver(I):

3.8.1. Calibration Curve for spectrophotometric determination:

Under the optimum conditions described in the recommended procedure, the calibration curves were constructed with ten standard solutions containing 1-30µg/5mL of copper (II) or Silver(I), the formula for the best line of calibration, y=0.002x+0.001 for Cu²⁺ ions, and v =0.0053x - 0.0093the for Ag⁺ ions, the correlation coefficient was obtained with the method of least squares, $R^2 = 0.995$ for Cu^{2+} ions, $R^2 = 0.9901$ for Ag^+ ions.



3.8.2. Spectrophotometric determination of Copper (II) & Silver(I) by BTABP The sediments contains copper at the range 16-110ppm and silver at the range 0.6-10ppm this sediments according to WHO measurements^[13]. different return to nature of Spectrophotometric determination of Cu²⁺ ions and Ag⁺ ions in sediments of different location of Euphrates river in al-Najaf governorate and the results demonstrate at in Table (3).

Sample	Sample Name	Ag	AAS*	Cu	AAS*
110.		phu	ppm	ppm	ppm
1	Waste water Al-Qadisia area	0.74	0.74	2.7	2.80
2	Al-Qadisia river	0.52	0.53	0.15	0.15
3	Al-Kufa river	0.98	0.99	0.12	0.13
4	Waste water Al-Najaf Sea area	0.98	0.98	2.57	2.56
5	Spring water Al-Najaf Sea area	0.41	0.42	0.16	0.15
6	Al-Mishkhab river	0.63	0.63	0.14	0.13
7	Waste water Al-Kufa area	0.33	0.33	2.2	2.21
8	Al- Kufa waste water	0.10	0.11	1.5	1.5
9	Al-Mishkhab Wast water	0.34	0.34	0.49	0.5
10	Al-Abasia river	0.54	0.54	1.9	1.9
	Average	0.557	0.561	1.193	1.203
PL**		0.6-10		16-110	

Table (3): The quantity of Copper(II) in sediments samples

*AAS: quantity of ions determined by atomic absorption spectroscopy. **PL: Permissible limits according to World health organization WHO (mg/L)



Figure(24): The quantity of Copper(II) in sediments samples



Figure(25):The quantity of Silver(I) in sediments samples

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الاستخلاص والتقدير الطيفي للنحاس (II) والفضة (I) من المحاليل المائية بواسطة 2-[بنزوثيازوليل آزو] -4-بنزيل فنيل في ترسبات قاع نهر الفرات لمحافظة النجف

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الخلاصة: -