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Cloud point extraction spectrophotometric determination of nickel, copper, cobalt and chromium by 4- HBDA1, 5DPHP as reagent in wastewater of Iraq

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ABSTRACT

A simple, low cost and highly sensitive method based on cloud point extraction (CPE) used for separation/preconcentration of Nickel, Copper, Cobalt and Chromium has been described. After complexation with ligand 4- HBDA1, 5DPHP, the parameters which affecting of the separation phase and detection process, were optimized such as pH,4- HBDA1, 5DPHP, concentration of Triton X-100, incubation time and temperature. Calibration graph showed linear trend in rang of 5-50μgL^{-1},5-70μgL^{-1},5-80$\mu gL^{-1}$and 5-60μgL^{-1} for Ni(II), Cu(II), Co(II) and Cr(III) respectively, the recovery of analytes was in the range (98-99%, 97.5-99.8%, 96.5-99.7% and96-98%) detection limits was (2.805, 2.08, 0.456and 2.5μgL^{-1}) relative standard deviation (RSD) (1.6%,0.91%,1.8%,1.2%) respectively. The proposed method was applied successfully in wastewater samples.

KEYWORDS

Cloud point extraction;
4- HBDA1, 5DPHP;
Determination Ni(II), Cu(II) and Co(II) and Cr (III).

INTRODUCTION

Determination of trace metals such as Ni(II), Cu(II) and Co(II) and Cr(III) in environmental samples is a subject of considerable interest, because trace metals play important roles in biological processes both as essential components and as toxics[1]. Copper and cobalt are essential nutrients; nickel has no known beneficial health effects. However, these metals may be harmful if taken in excessive amounts[2]. The semetals normally occur at very low levels in the environment, so sensitive methods are needed to detect them in most environment and wastewater samples[3]. Many analytical techniques such as flame atomic absorption spectrometry (FAAS)[4]) inductively coupled plasma mass spectrometry (ICP-MS)[5], inductively coupled plasma optical emission spectrometry (ICP-OES)[6] and graphite furnace atomic absorption spectrometry (GFAAS)[7]. However, direct determination of metal ions at trace level by these analytical techniques does not present the sensitivity requirements, and, more importantly, it is affected by matrix interference. Thus, preliminary separation and preconcentration of trace element from the matrix are frequently necessary to improve the detection limit and the selectivity. Recently, cloud point extraction (CPE) has become an attractive area for the separation and preconcentration of trace metal ions[8,9]. The cloud point procedure (CPE) is based on the following phenomenon: an aqueous solution of some surfactant becomes turbid and separates into two isotropic phases if some condition such as temperature or pressure is changed or if an appropriate substance is added to the solution[10,11].

EXPERIMENTAL

Reagents

All the chemicals used were of analytical reagent grade and used without further purification; deionize water use to diluting the samples and reagents 4-aminoantipyrine (Qualilcems), salicylaldehyde (G.C.C), Triton X-100 (Merck), hydrochloric acid (BDH), Sodium hydroxide (BDH), Ethanol (G. C.C), Copper (II) (nitrate) $Cu(NO_3)_2.3H_2O$ (Fluka), Chromium (III) chloride Hexahdrate $CrCl_3.6H_2O$(B. D. H), Cobalt (II) Nitrate Hexahydrate $Co(NO_3)_2$. 6H2O (B.D.H) 1000µgL^{-1} Stock solution of Ni, Cu, Co and Cr was prepared by dissolving an appropriate amount $Ni(NO_3)_2$. $6H_2O$, $Cu(NO_3)_2.3H_2O$, $CrCl_3.6H_2O$ and $Co(NO_3)_2$. $6H_2O$ in deionize water and diluting to the mark0. 306 g in 100 ml volumetric flask. Working stock solution was prepared daily from the stock by appropriate dilution with water. 4-HBDA1,5DPHP stock solution was prepared by dissolving g in 10%(V/V) TritonX-100and diluting to the mark in 100 ml. Non-ionic surfactant, TritonX-100 10%(V/V) was prepared by dissolving 10g Triton X-100 in hot deionize water diluting to the mark in 100 ml volumetric flask,0.01M hydrochloric acid, 0.01M Sodium hydroxide use to adjust pH 2-14.

Instrumentation and apparatus

A thermo stated water bath model Unitemp, pH meter model BP 3001. Phase separation was achieved with centrifuge model REMI at 2500rpm in 10mL calibrated conical tube. UV-Visible Shimadzu model UV-160 A, FTIR Shimadzu, model IR-PRESTIGE 21, made in Japan, CHN Euro Vectro -3000A Element Analyzer at AL –Bayt University, Jordan.

General procedure for CPE

A typical cloud point experiment required the following steps: an aliquot of 10 ml of a solution containing a known amount Ni(II), Cu(II), Co(II) and Cr(III) metal ions, 10% (v/v) Triton x-100 and 4.5×10^{-4}4-HBDA1, 5DPHP ligand pH was adjusted by 0.01M HCl, 0.01M NaOH the mixture was shaken for 1 min and left to stand in a thermo-stated bath at 70^{0}C, for 20 min separation of the phases was achieved by centrifugation at 2500 rpm for 15 min, the remaining micellar phase was dissolved by methanol measurement of Ni(II), Cu(II), Co(II) and Cr(III) spectrophotometrically UV/VIS.

Application of real samples

Analysis of wastewater of Rustimiyah city in Iraq and industrial sewage of Tannery Factories in Zafaraniyah for determining of analyte contents was performed as follows: About 1000 ml of sample filtering and add 3ml concentrated HNO_3 was added to eliminate and decompose organic matter. The wastewater samples were stored in polyethylene bottles. The aliquots of waste water was extracted and analyzed for the metals according of the proposed procedure of cloud point extraction.

RESULT AND DISCUSSION

Preparation of E-4-(3-hydroxybenylideneamino) 1, 5dimethyl-2-phenyl - 1Hpyrazol-3(2H)-one Ligand[12].

The ligand was prepared by condensation of 4-aminoantipyrine with salicylaldehyde in ethanol, 1.00 mmol of 4-aminoantipyrin was dissolved in 5ml of ethanol and 1.00 mmol of salicylaldehyde was dissolved in 5ml of ethanol added 4 drop acetic acid. The mixture was refluxed for 1hr at (100 ^{0}C) after cooling, a Yellow color precipitate was formed and filtered; recrystallized from hot ethanol the Schiff base ligand is soluble in organic solvents ethanol, DMF, DMSO. Melting point was measured for ligand (M.P.192-195 ^{0}C, yield percentage 84% and Mwt. 306.68 g moL^{-1}).

Characterization of Ligand

(a) Ultraviolet Spectrum of Ligand4-(HBDA1),5DPHPO and Complexes

The UV-Vis spectrum of the ligand dissolved in deionized water and 0.5ml Triton X-100(4.5×10^{-4} M) showed band peak at 488 nm caused by charge transfer between C=N and conjugated benzene ring it is also the cause of the wish yellow orange color of is, the band at 345nm, 272nm may be attributed to (n ’! π*) and (π ’! π*) electronic transition respectively[13]. Figure 1 showed the ultraviolet spectrum of ligand. The spectra of complexes are shown the complex with Ni (II) in surfactant-rich phase versus ligand blank prepared under similar conditions. It was appeared at pH 9, 50μgL^{-1} Ni (II), 1.0ml of 10 %(v/v) Triton X-100, maxima absorption of Ni-4-HBDA1, 5DPHPO at 412 nm, Cu- 4-(HBDA1), 5DPHPO. Maxima absorption at 410 nm was appeared at pH 9, 70 μgL^{-1},0.6 ml TritonX-100, Co-4-(HBDA1), 5DPHPO complex displays maxima absorption at 399 was appeared at pH 10, 80 μgL^{-1},1.4 ml Triton X-100 and Cr-4-(HBDA1), 5DPHPO complex, maxima absorption at 387nm was appeared at pH 10, 70 μgL^{-1}, 0.6 ml TritonX-100 while the 4- HBDA1, 5DPHPO ligand displays maxima absorption at 345nm shown in Figures (2),(3), (4) and (5).

The FTIR spectrum of ligand

FTIR spectrum of the ligand, Figure (6) exhibited a broad band at (3479cm^{-1}) assigned to ν (OH) stretching frequency. The broad bands at 1593cm^{-1}and1654cm^{-1} ascribed to ν (C=N) and ν (C=O) stretching vibration respectively[14].

C.H.N elemental analysis of 4-HBDA1,5DPHPO

(a) Effect of pH

The pH plays a unique role on metal-chelate formation and subsequent extraction, and is proved to be a main parameter for CPE[15], to find the best acidic function of the ion extraction process different

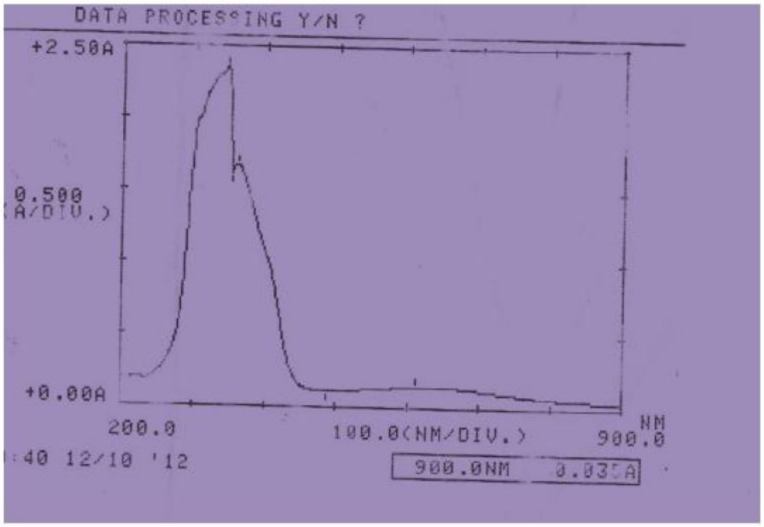

Figure 1 : Ultraviolet spectrum of 4-HBDA1,5DPHPO ligand 4.5×10^{-4}mol L^{-}

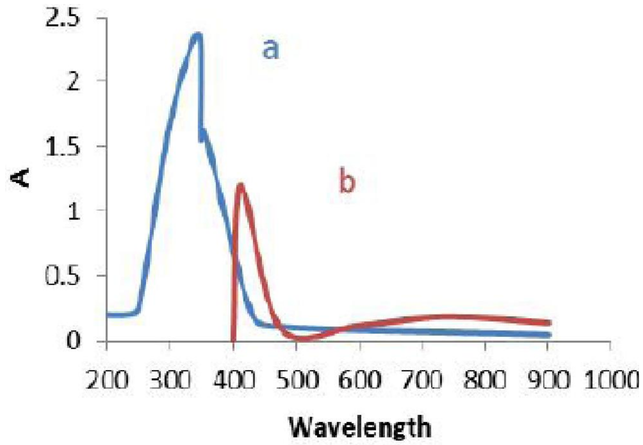

Figure 2 : Ultraviolet spectrum of Ni-4-HBDA1, 5DPHPO (b) Versus (a)

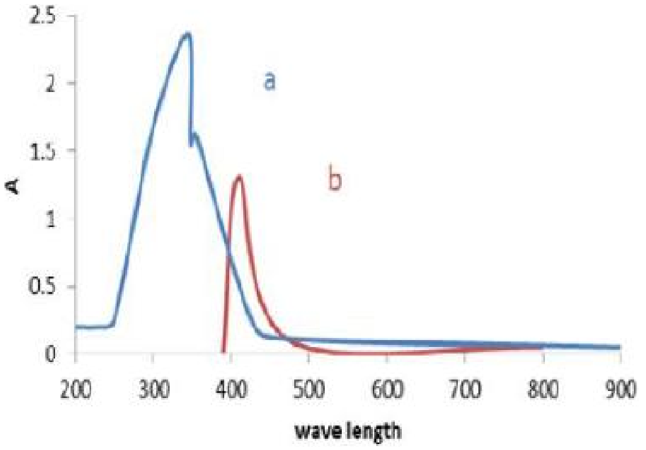

Figure 3 : Ultraviolet spectrum 5DPHPO (b) Versus ligand (a)

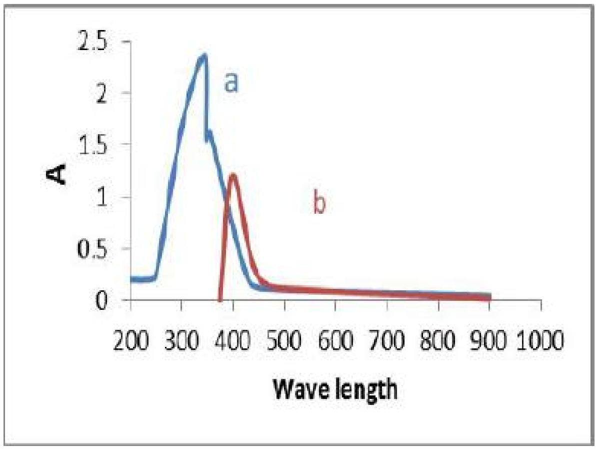

Figure 4 : Ultraviolet spectrum of (b) Co-4-HBDA1, 5DPHPO (a) versus

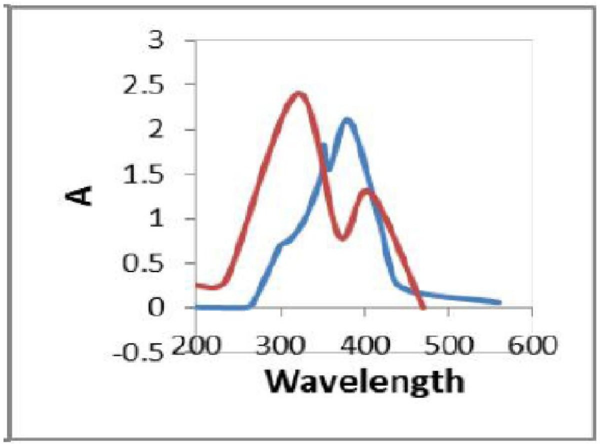

Figure 5 : Ultraviolet spectrum of Cr-4-HBDA1, 5DPHPO (b) versus (a)

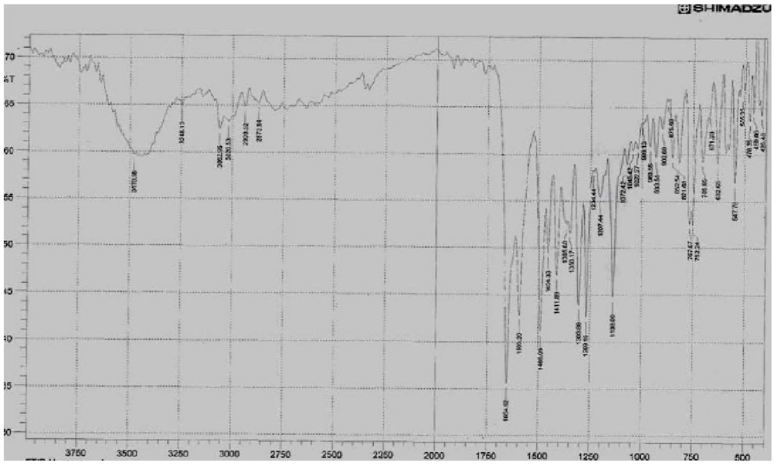

Figure 6 : FTIR spectrum of ligand 4- HBDA1,5DPHPO

value of pH 2-14. The results are shown in Figure (7), the best separation was achieved atpH = 9 for Ni(II), Cu(II), Co(II) and Cr(III). At lower pH, the ligand is prorogated and its ionic characteristics increase and led to decrease in its solubilization in the hydrophobic micellesat higher pH, the ligand is de-protonated and it behaves like a hydrophilic molecule easily soluble in the micelles[16].

(b) Effect of Triton X-100 amount

Type and concentration of surfactant are important factors, in cloud point extraction. Triton X-100 was chosen as a proper surfactant due to its physicochemical characteristics, commercial availability, relatively low price, low toxicity, it's high Density in the surfactant-rich phasethe TritonX-100volume range was examined 0.2-1.8 ml and the results are shown in Figure 8. As can be seen the absorbance increased with the increase Triton X-100, therefore chose 1.0, 1.0, 0.8 and 0.8 for Ni(II), Cu(II), Co(II) and Cr(III).

TABLE 1 : C.H.N elemental Analysis of 4-HBDA1, 5DPHPO

Percentage%				calculation
C	H	N	S	
70.35%	5.52 %	13.72%	0.000	Theoretical
71.55%	4.32%	13.02%	0.000	Practical

(c) Effect of 4-HBDA1,5DPHPO concentration

The effect of concentration of 4-HBDA1,5DPHPO on the CPE of Ni(II), Co(II), Cu(II) and Cr(III) was investigated in the concentration range of (5×10^{-5}-5 $\times10^{-4}$) Mol L^{-1}. Excellent absorbance found at 4.5×10^{-4}Mol L^{-1}. At lower than concentration of ligand, the insufficient amount of ligand causes incomplete complexation. A possible explanation for the decrease with higher concentrations may be attributed either to form

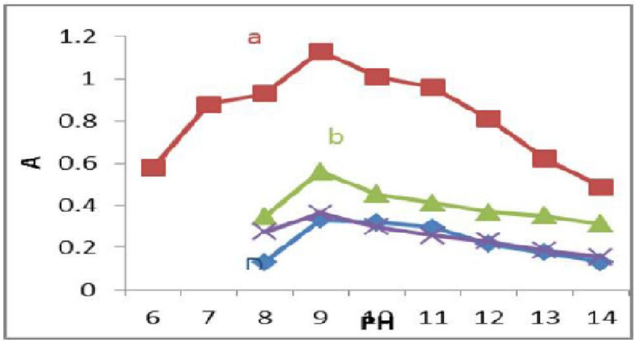

Figure 7 : Effect of pH conditionsof (a) Nickel, (b) copper (II), (c) cobalt, (d) chromium, Ni (II)=50µgL^{-1}, Cu(II)=70 µg L$^{–}$,^{1}Co(II)=80 µgL^{-1},Cr(III)==60 µgL^{-1},4-HBDA1,5DPHPO = 4.5×10^{-4}Mol L$^{–1}$, and 1.0, 1.0, 0.8, and 0..8ml 10% (V/V) (Triton X-100)

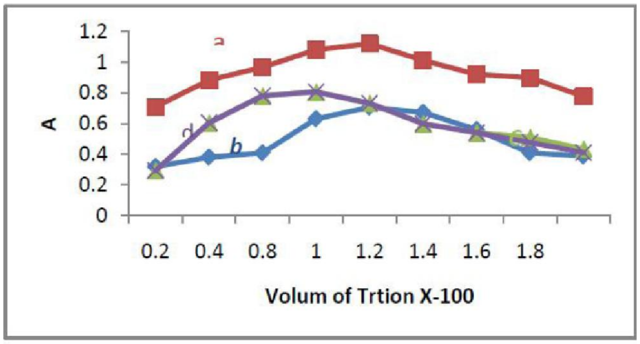

Figure 8 : Effectof Triton X-100 volume of (a) Nickel, (b) copper (II), (c) cobalt, (d) Ni (II)=50 µgL^{-1}, Cu (II)=70 µg L$^{–1}$, Co(II)=80 µgL^{-1}, Cr(III)= =60 µgL^{-1}, 4-HBDA1,5DPHPO = 4.5×10^{-4}Mol L$^{–1}$, and pH =9

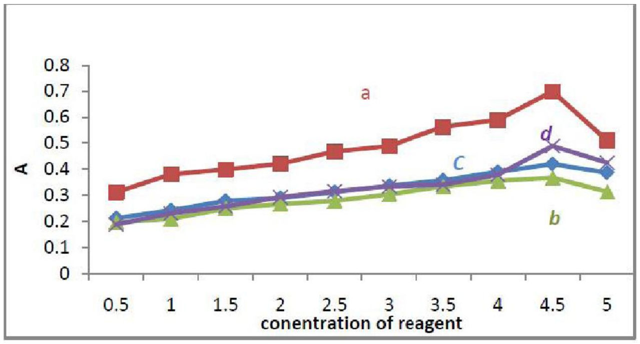

Figure 9 : Effect of concentration reagent (a) Nickel, (b) copper (II), (c) cobalt, (d)chromium Ni (II)=50 µgL^{-1}, Cu(II)=70 µg L$^{–1}$, Co(II)=80 µgL^{-1}, Cr(III)= =60 µgL^{-1}, pH =9

of charged complexes with excess ligand in the medium or remaining of excess of ligand in aqueous solution and competitive with surfactant-rich phase for formation of complex with metal ions in aqueous phase[2], the results are shown in Figure 9.

(d) Effect of Equilibrium Temperature and the Incubation Tim

It is desirable to have the shortest incubation time and the lowest possible equilibration temperature, which compromise completion of the reaction and efficient separation of the phasesthe effect of the equilibration temperature and time was studied with a range of 35–90°C and 5–35 min, The maximum absorption in (70, 80, 60, 70 ^{0}C) respectively, the decrease in absorbance at temperature higher than (70,80,60,70^{0}C) is probably due to decomposition of complex which reduces the extraction efficiency. The quantitative extraction found at (30, 15, 20, 20) minrespectively, the result are shown in Figure (10, 11).

Interferences study

The impact of cation and anion in the aqueous phase of its importance in the processes of extraction equilibrium the presence of cations in the aqueous phase may be compete with the cation under study in correlation

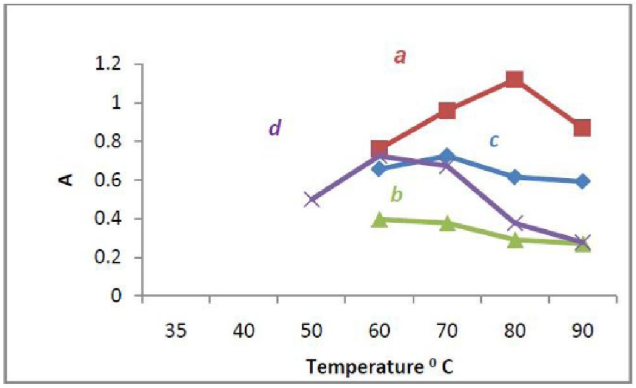

Figure 10 : Effect of temperature on cloud point (a) Nickel, (b) copper (II), (c) cobalt, (d) chromium Ni (II)=50 µgL^{-1}, Cu (II)=70 µg L$^{–1}$, Co(II)=80 µgL^{-1}, Cr(III)= =60 µgL^{-1}, 4-HBDA1,5DPHPO = 4.5×10^{-4}Mol L$^{–1}$, and pH =9

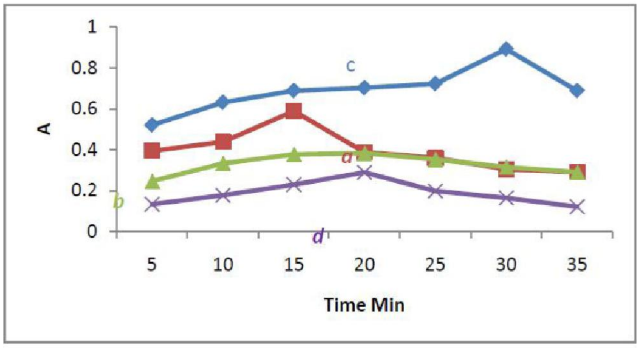

Figure 11 : Effect of time on cloud point (a) Nickel, (b) copper, (II) (c) cobalt, (d) chromium Ni (II)=50 µgL^{-1}, Cu (II)=70 µg L$^{–1}$, Co(II)=80 µgL^{-1}, Cr(III)= =60 µgL^{-1}, 4-HBDA1,5DPHPO = 4.5×10^{-4}Mol L$^{–1}$, and pH =9

TABLE 2

Interfering ion	Amount added µg L^{-1}	Percentage of Ni Interference (%)	Percentage of Cu Interference (%)	Percentage of Co Interference (%)	Percentage of Cr Interference (%)
K^{+}	200	+2.9	+2.26	+10	+0.52
Na^{+}	200	+1.6	+0.5	+6.1	+4.7
Ca^{+2}	200	+4.5	+6.3	+20	+8.7
Mg^{+2}	200	+15	+4.3	+28	+11.08
SCN^{-}	200	-0.6	-2.2	-8.0	-4.4
Br^{-}	200	-4.5	-1.0	-11.9	-7.3
So_4^{-2}	200	-3.3	-3.4	-3.6	-2.9
I^{-}	200	-9.35	-4.2	-13.9	-5.2

with organic reagent the anion may led to restrictmetal ion under study in the aqueous phase. The results are shown in TABLE 2.

Continuous variation method

A series of 1, 2, 3, 4, 5, 6, 7, 8, 9 ml of 4.5× 10^{-4} molL^{-1} Ni(II), Cu(II), Co(II), Cr(III) was pipetted in to each of 10 ml volumetric flask then 9,8,7,6,5,4,3,2,1 ml of 4.5× 10^{-4} molL^{-1} of 4-(HBDA1),5DPHPO the absorbance of the solutions were measured at λ_{max}=412, 410,399 and 387nm the stoichiometric ratio between the Ni, Cu, Co and Cr with 4-HBDA1,5DPHPO 1:2 the results are shown in Figures 12,13,14 and 15. The probable chemical structure show in Figure 16, 17, 18 and 1 9.

Calibration graph

Employing the optimum conditions described in the procedure of cloud point extraction, liner calibration graph of Nickel, copper, cobalt and chromium with agent 4-HBDA1, 5DPHPOwas obtained Figure 20, 21, 22 and 23 for each ions respectively. Beer law obeyed

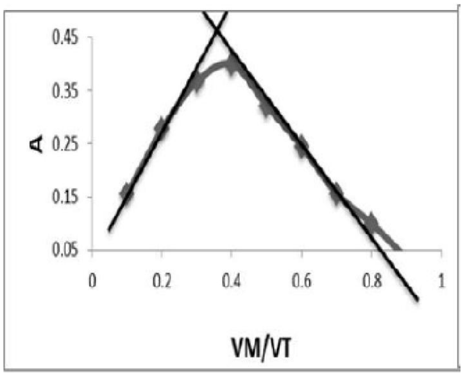

Figure 12 : Continuous variation method of plot complex between Ni(II) and 4-HBDA1

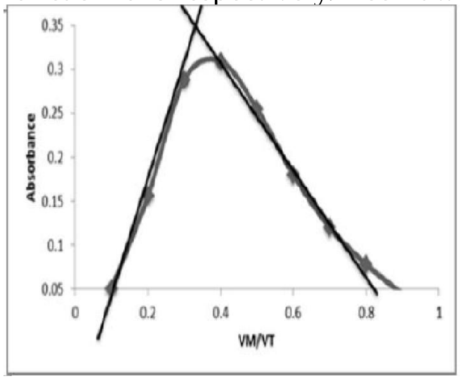

Figure 13 : Continuous variation method of 5 plot complex between Cu(II) and 4- HBDA1, 5

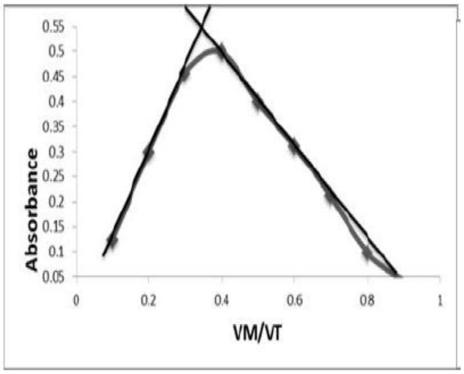

Figure 14 : Continuous variation method of plot complex between Co(II)

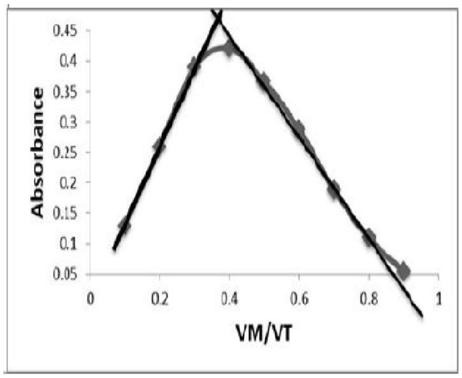

Figure 15 : Continuous variation method of 4- plot complex between Cr(III) and 4- HBDA1, 5 HBDA1, 5

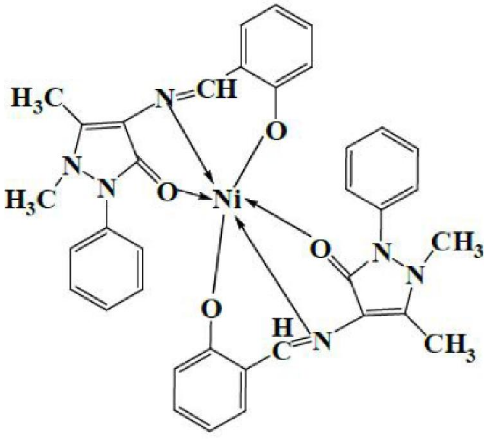

Figure16 : The probable chemical structure of (4-HBDA1, 5DPHPO) with Ni

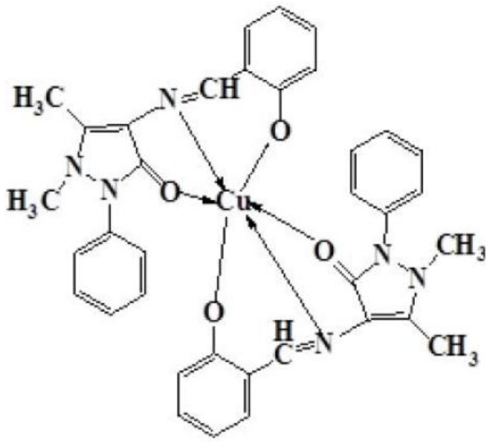

Figure 17 : The probable chemical structure of (4-HBDA1, 5DPHPO) withCu

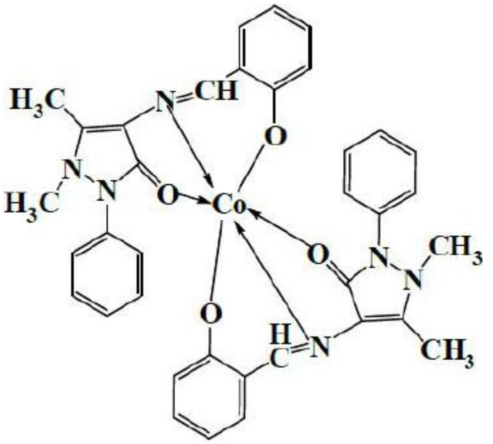

Figure 18 : The probable chemical structure of (4-HBDA1, 5DPHPO) with Costructure

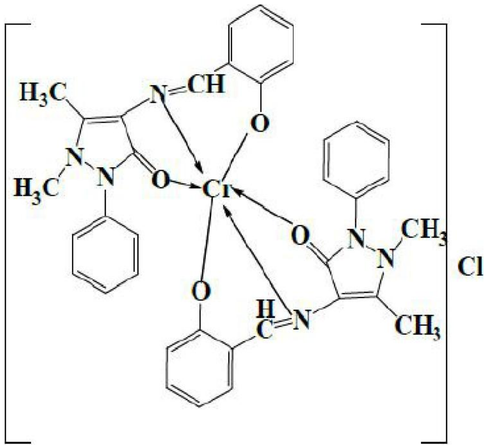

Figure 19 : The probable chemical of (4-HBDA1, 5DPHPO) withCr

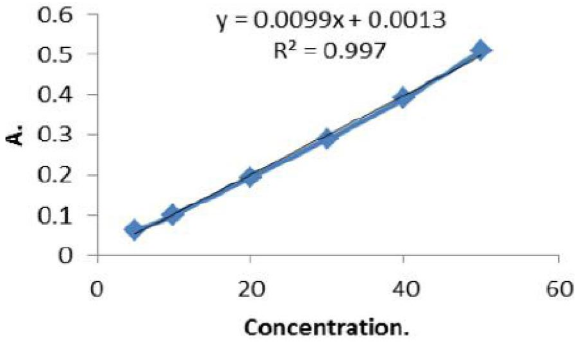

Figure 20 : Calibration graph for Ni(II)

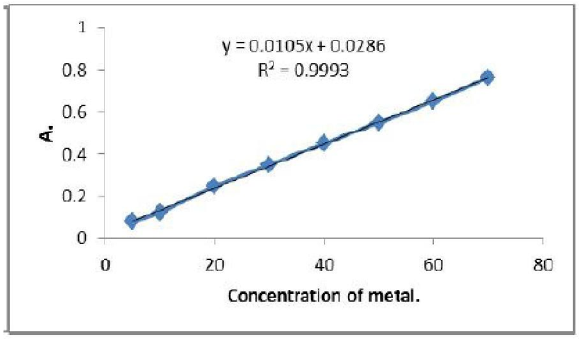

Figure 21 : Calibration graph for Cu(II)

over the concentration range of 5-50 μgL^{-1},5-70 μgL^{-1}, 5-80 μgL^{-1} and 5-60 μgL^{-1}with correlation coefficient Ni(II) and Cu(II), Co(II) and Cr(III) equal to 0.9997,0.993,. All other analytical characteristics data are summarized in TABLE 3.

Accuracy and precision

The accuracy and precision of proposed methods were determined at two concentration level of, Ni(II), Cu(II), Co(II), and Cr(III) by analyzing five replicate sample of each concentration. The relative standard deviation for results did not exceed 1.6, 0.91, 1.2 and 1.8 TABLE 4 show high reproducibility of results and precision of the methods.

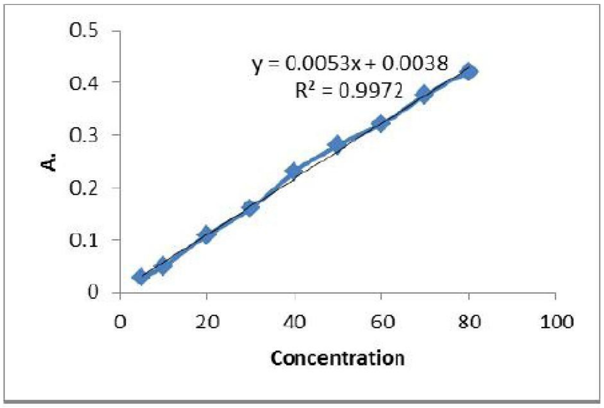

Figure 22 : Calibration graph for Co(II)

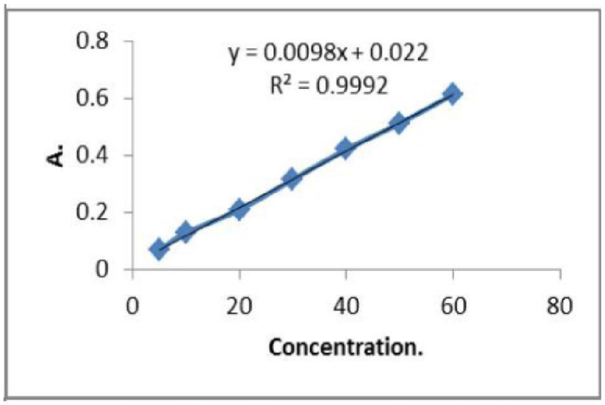

Figure 23 : Calibration graph for Cr(III)

TABLE 3 : Analytical characteristics data of the proposed method

Parameter	Ni(II)	Cu(II)	Co(II)	Cr(III)
λ_{max} nm	410	412	399	387
R^2	0.997	0.9993	0.9972	0.9992
RSD (%)	1.6	0.91	1.2	1.8
Linear range μgL^{-1}	5-50	5-70	5-80	5-60
Limit of detection LOD ($3S_b$/m) μgL^{-1}	2.805	2.08	0.45	2.5
Limit of quantitative LOQ ($10S_b$/m)	9.351	6.96	1.523	8.5
Recovery	98-99%	97.5-99.8%	96.5-99.7%	96-98%
Molar absorptivity	2958.332	2958.332	1698.36305	2722.537334
Slope	0.0099	0.0105	0.0053	0.0098
Intercept (a)	0.0013	0.0286	0.038	0.022

TABLE 4 : Accuracy and precision of proposed methods

Amount of Ni (II) μg L^{-1}		RSD%*	Recovery%
Present	**Found**		
70	69.16	1.6	98.8
30	29.33	1.7	97.7
Amount of Cu(II) μg L^{-1}		**RSD%***	**Recovery%**
Present	**Found**		
70	69.98	0.93	99.9%
30	29.23	0.9	97.4%
Amount of Co(II) μg L^{-1}		**RSD%***	**Recovery%**
Present	**Found**		
70	69.60	1.3	99%
30	29.74	1.1	99%
Amount of Cr(III) μg L^{-1}		**RSD%***	**Recovery%**
Present	**Found**		
70	69.03	1.7	98.6%
30	29.13	1.88	97%

*** Average seven determination**

Analytical application

The suggested methods was applied to the quantitative determination ofNi(II), Cu(II), Co(II) and Cr(III) in wastewater of Rustimiyah city in Iraq and industrial sewage of Tannery Factories in Zafaraniyah, it was gave a good accuracy and precision as shown in TABLE 5 the proposed method was compared successfully with other literature methods as shown in TABLE 6.

CONCLUSION

The determination of Ni(II), Cu(II), Co(II) and Cr(III) in wastewater samples was successfully performed by using cloud point extraction by applying4-HBDA1, 5DPHPOas extracting reagent.4-HBDA1, 5DPHPOis a stable and selective complexing reagent.

TABLE 6 : Application of proposed method for determination

	Real sample	Taken	Found	RSD%*	RSD% average	Recovery%	Recovery% average
Ni	Waste water (input) of Rustimiyah city	5o	49.57	0.3	0.35	99	99%
		30	29.76	0.4		99	
	Waste water (output) of Rustimiyah city	50	49.86	0.2	0.3	99.7	99%
		30	29.68	0.4		98.8	
	Waste water ofTannery Factories	50	50.75	0.25	0.9	101	101.5%
		30	30.78	1.3		102	
Cu	Waste water (input) of Rustimiyah city	50	49.76	0.2	0.3	99.5	99.5%
		30	29.88	0.38		99.6	
	Waste water (output) of Rustimiyah city	50	49.55	0.2	0.35	99%	
		30	29.75	0.5		99%	99.5%
	Waste water of Tannery Factories	50	49.95	0.22	0.33	99.9%	
		30	29.66	0.44		98.8%	99.8%
Co	Waste water (input) of Rustimiyah city	50	49.63	0.55	0.47	99%	
		30	29.75	0.4		99%	99%
	Waste water (output) of Rustimiyah city	50	49.79	1.2	0.95	99.5	99.3%
		30	29.55	0.7		99.2	
	Waste water of Tannery Factories	50	49.96	0.8	0.57	99.9	98.9
		30	29.45	0.35		98	
Cr	Wastewater (input) of Rustimiyah city	50	49.95	0.67	0.77	99.9	99.7%
		30	29.86	0.88		99.5	
	Wastewater (output) ofRustimiyah city	50	49.57	0.45	0.67	99	99.3%
	Wastewater of Tannery Factories.	50	51.00	1.2	0.9	102	102.6

TABLE 7 : Comparison of the proposed method with reported methods for the preconcentration and CPE of Nickel, Copper, Cobalt and Chromium

IONS	Chelating agent	Surfactant	Technique	Linear range	RSD%	The detection limits	Ref
Cu (II) Co (II)	PAN	TritonX-114	capillary electrophoresis	3-100μg l^{-1}	1.8% 0.74%	0.26 μg/l 0.12	17
Ni (II)	DMG	TritonX-114	UISV/V	10-150 ng mL^{-1}	1.04	4 ng mL^{-1}	18
Cr(III)	BCB	TritonX-114	AAS	-	-	0.42	19
Co (II)	4-(2-pyridylazo)-resorcinol	TritonX-114	ICP-OES.	10-500	5.57	1.2	20
Cr(III)	Dithizone	TritonX-114	ICP-OES	_	_	1.2	21
Cr(III)	DDTC	TritonX-114	HPLC	50- 1000μg l^{-1}	0.6%	3.4μgL^{-1}	22
Cu(II)	BIYPYBI	TritonX-114	FAAS	15-200ng mL^{-1}	4.1	1.4	23
Co(II)	(APDC)	TritonX-114	TS-FF-AAS	2.1–100μgL^{-1}	5.8%	2.1μg l^{-1}	24
Ni Cu Co Cr	4- HBDA1, 5DPHPO	Triton X-100	UV/VIS	5-50 5-70- 5-80 5-60	1.6 0.91 1.2 1.8	2.805 2.08 0.45 2.5	My propos method

BIYPYBI:-6-1H-benzo[d]imidazol-2-yl) pyridin-2-yl)-1H-benzo[d]Imidazole], APDC: ammonium pyrrolidinedithiocarbamate, DMG: dimethylglyoxime, PAN: 1-(2-pyridylazo)-2-naphthol

Cloud point extractionis simple, rapid, safe, easy to use and inexpensive when comparison with solvent extraction methods. The method gives low limit of detection and good R.S.D. values.

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