Extraction, Separation and Spectrophotometric Determination of Cadmium (II) Via Onium Method

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Abstract

By application new distinguished method for separation and spectrophotometric determination of micro amount of cadmium (II) in different samples which is called onium method. And for the majority of this work include the determination optimum conditions for application this method and the study overshadowed optimum values were illustrated the wave length of maximum absorbance for onium species was λ_{max}=260nm, and other optimum values were 0.5M HCl in the presence of 50µg/5mL of Cd^{2+} by using 1×10^{-4}M of 2,4-dimethyl-3-pentanone at shaking time 15min. in addition to other effective parameters such as temperature, electrolyte salts, interferences. So that prepared calibration curve for spectrophotometric determination of Cd(II) in different samples.

Key words: Onium method, Cadmium (II), Separation, Extraction, Spectrophotometric determination.

Introduction

Chromium (VI) as $Cr_2O_7^{=}$ and Mn(VII) as MnO_4^{-} extracted according to cloud point extraction method from HCl solutions by using Janus green B as complexing agent in the presence of non-ionic surfactant Triton X-100[1]. Cloud point extraction method applied for extraction Pt(II) as $PtCl_4^{=}$ after formed ion pair association complex with Janus green B and in the presence of Triton X-100[2]. Separation and determination of Cd(II) as $CdCl_4^{=}$ from HCl medium by using Crystal violet and non-ionic surfactant Triton X-100, the method applied for spectrophotometric determination of Cd(II) in different samples[3]. Zn(II) and Co(II) extracted according to onium system from HCl solution by used 2,4-dimethyl-3-pentanone, onium species have the structure $H(H_2O)(2,4\text{-}DMP)_3^{+};HZnCl_4^{-}$ and $H(H_2O)(2,4\text{-}DMP)_3^{+};HCoCl_4^{-}$ [4]. Methyl Stearate used as extractant to extract Zinc(II) as $ZnCl_4^{=}$ from HCl media, extracted

species has λ_{max}=275nm. The research involved limits all optimum conditions[5].Solvent extraction of Cd(II) from nitrate medium by using extractants were quaternary ammonium-based room temperature ionic liquid Aliquat 336 in either the chloride, thiocyanate and hydrogeno phosphate forms, diluted in the kerosene. In addition to study the effects of many parameters such as equilibration time, initial pH, Organic/Aqueous O/A molar ratio, extractant concentration and ionic strong on extraction of Cd(II)[6].

Experimental

Abiochromdouble beam UV-Vis. spectrophotometer, (Biochrom Libra S60) (Cambridge, UK).For shaking used HY-4 vibrator with AD Just about speed multiple (Italy).Electrostatic water bath (G, Gerhard, Germany).

All chemicals used as received from thecommercial company without any further purification. All aqueous solutions prepared with double distilled water. The Cd(II) standard solution (1mg/mL) prepared by dissolving (0.1631g) of $CdCl_2$ (Merck, 99.97%) in 100mL distilled water in volumetric flask. As well 2,4-dimethyl-3-pentanone (Fluka 99.99%) solution with 1×10^{-2} M concentration prepared by dissolving (0.0115g) in 10mL chloroform. All working solutions prepared by dilution appropriate volume.

General method

Aqueous solutions 5mL in volume contain 50µg of Cd(II) ion with optimum concentration of hydrochloric acid HCl afterward adding 5mL organic solution of organic reagent 2,4-DMP dissolved in chloroform at 1×10^{-4}M then shaking these two layers in electrostatic shaker for optimum shaking time at latter separate the organic phase from the aqueous phase and measuring the absorbance of organic phase at maximum absorbance wave length of extracted species λ_{max}, so that aqueous solution treated according to dithizone spectrophotometric method[7] to determine reminder quantity of metal ion in aqueous solution after return to calibration curve Figure 1, then subtract reminder quantity of metal ion from the original quantity in aqueous solution to determine the transfer quantity of metal ion to the organic phase to form onium extracted species, and from these two quantity calculate distribution ratio (D):

$$D = \frac{[Cd^{2+}]_o}{[Cd^{2+}]_{aq.}}$$

Results and Discussion

Spectrophotometric study for onium extracted species involved 5mL aqueous solution contain 50µg of Cd(II) ion and 0.5M hydrochloric acid HCl shaking with 5mL organic solution of organic reagent 2,4-DMP dissolved in chloroform with 1×10^{-4}M concentration for 10min. afterward separated organic phase from aqueous phase and taking the spectrum for organic phase against blank prepared at the same manner in absence metal ion Cd(II). The results were presented in **Figure 2** :

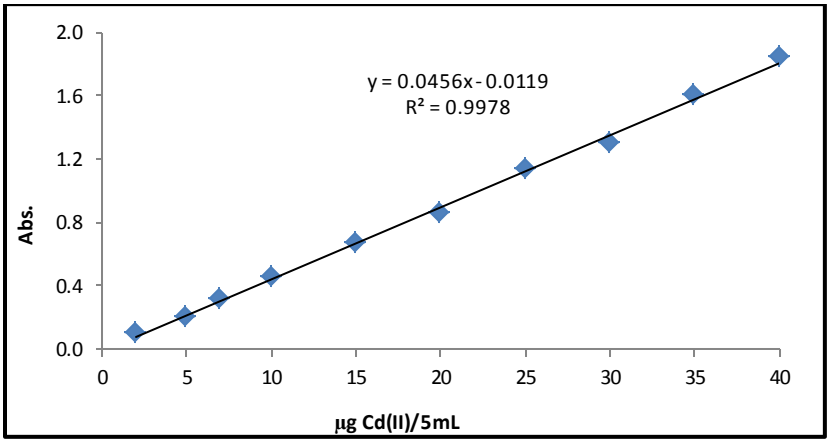

Figure 1 : Calibration Curve for determination Cd(II) ion in aqueous solutions

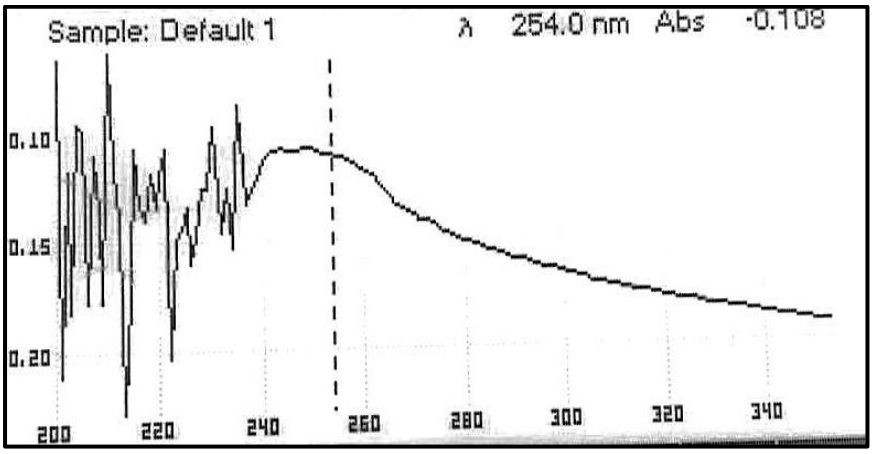

Figure 2 (a): Spectrum of extractant 2,4-DMP

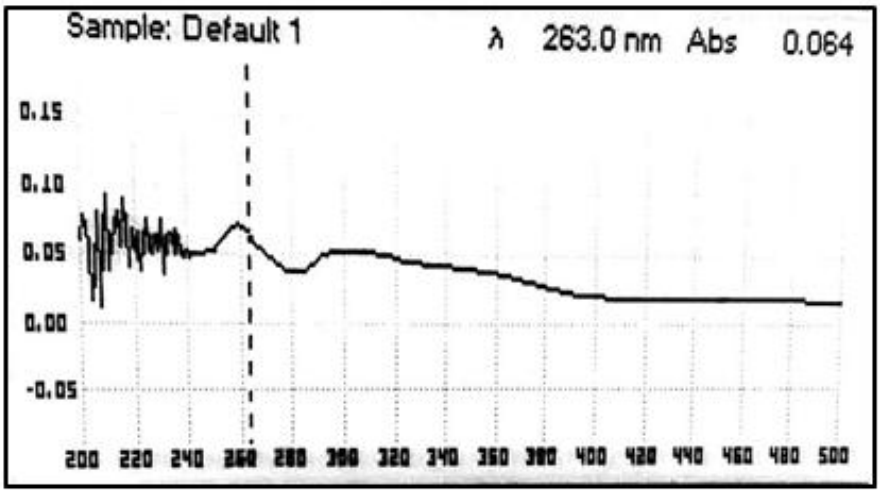

Figure 2 (b): Spectrum of onium species extracted

The spectrum appear maximum absorbance wave length was λ_{max}=260nm.

Effect of HCl Concentration

Aqueous solution 5mL in volume contain 50µg Cd^{2+} ion and different concentrations of hydrochloric acid HCl added to each solution 5mL organic solution of 1×10^{-4}M 2,4-DMP dissolved in chloroform and shaking to 10min., then treated the organic phase and aqueous phase after separated according to general method. The results were shown in **Figures 3,4**:

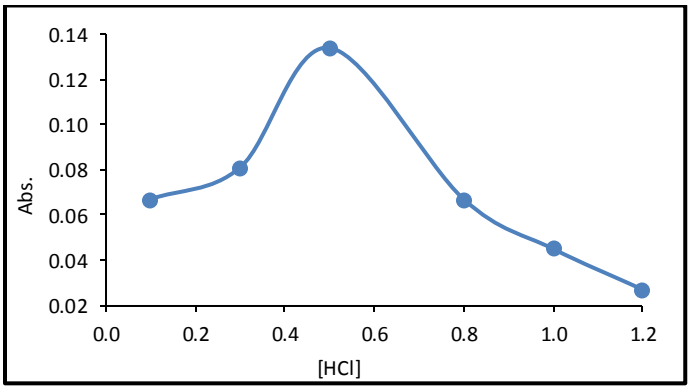

Figure 3: Effect of HCl concentration on formation and stability of onium species.

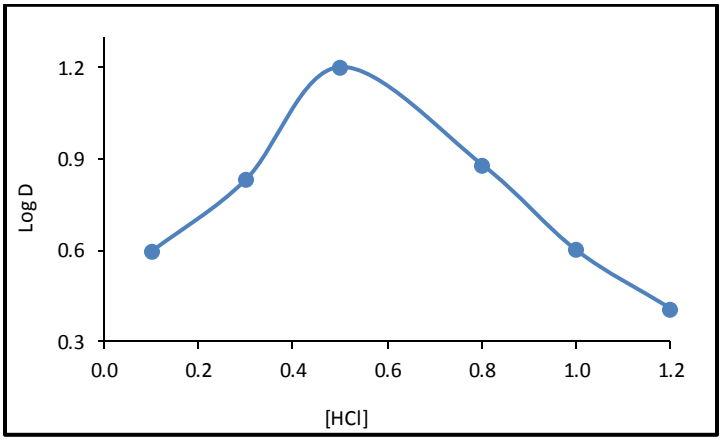

Figure 4 : Effect of HCl concentration on extraction efficiency and D value.

The results show 0.5M HCl was the optimum concentration of HCl in aqueous solution which is giving higher absorbance of organic phase and D value, because at this concentration reached to the favorite equilibrium to form onium species extracted, at this concentration of HCl obtained maximum concentration of hallow acidic species in aqueous phase and optimum thermodynamic and kinetic equilibrium $H(H_2O)_4^+;HCdCl_4^-$ this giving by best thermodynamic equilibrium the onium species extracted with higher concentration:

$$2H^+ + 4H_2O + 4Cl^- + Cd^{2+} \rightleftharpoons H(H_2O)_4^+;HCdCl_4^-$$

$$H(H_2O)_4^+;HCdCl_4^-{}_{aq.} + 2,4\text{-DMP} \rightleftharpoons H(H_2O)(2,4\text{-DMP})_3^+;HCdCl_4^-{}_{org.}$$

Any concentration of HCl less than optimum value giving decrease in the formation of onium species extracted and decline in extraction efficiency. So that any concentration of HCl more than optimum value effect to decrease extraction efficiency because effect of increase backward direction of formation hallow chloro acidic complex according to mass action law[8].

Effect of metal ion concentration

Extracted different concentrations of metal ion Cd(II) from 5mL aqueous solutions according to general method. The results were illustrated in **Figures 5,6** :

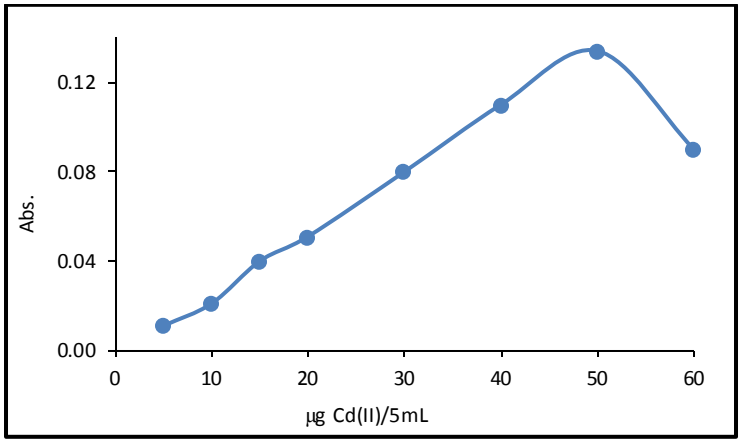

Figure 5 : Effect of metal ion concentration on formation and stability of onium species extracted.

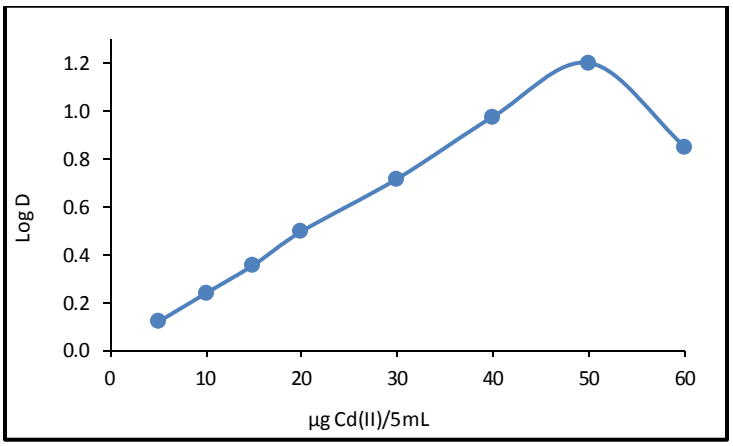

Figure 6 : Effect of metal ion concentration on extraction efficiency.

The results show 50µg Cd(II) in 5mL aqueous solution was the optimum concentration giving higher extraction efficiency because the concentration of metal ion is one of effective thermodynamic parameters and the increasing of metal ion Cd^{2+} in aqueous solution help to increase the rate of forward direction to form onium extracted species and the higher effect appear at 50µg which was gave maximum concentration of onium species as well as any concentration more than optimum effect to decrease the extraction efficiency by effect of increasing the rate of back ward direction of thermodynamic equilibrium which is much increase dissociation and decrease the concentration of onium species formation according to mass action law[9].

Effect of 2,4-DMP Concentration

Extracted 50µg Cd^{2+} from 5mL aqueous solution in presence 0.5M HCl by different concentrations of 2,4-Dimethyl-pentan-3-one dissolved in chloroform according to general method. The results were shown in **Figures 7,8** :

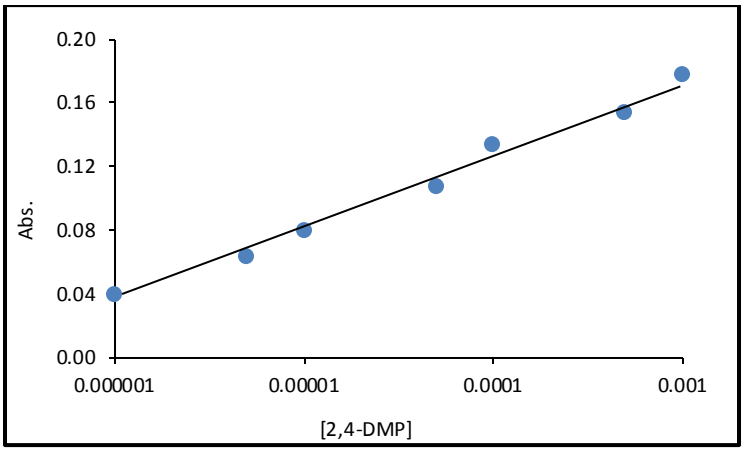

Figure 7 : Effect of organic reagent concentration on formation and stability of extracted species.

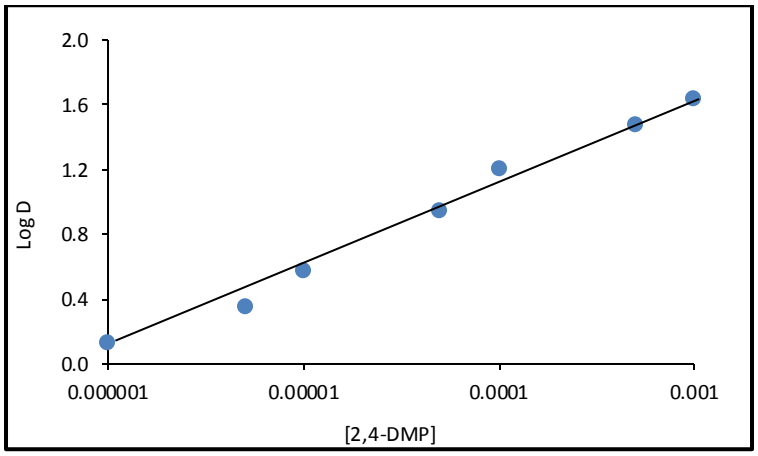

Figure 8 : Effect of organic reagent concentration on extraction efficiency.

The results appear linear relation between absorbance so that D values with rising concentration of organic reagent 2,4-DMP, and these results proof the organic reagentconcentration behave as thermodynamic parameter controlled the thermodynamic equilibrium of formation and extraction ion pair association complexes. So appear increasing concentration of 2,4-DMP effect to increase the rate of forward direction in equilibrium that is mean increasing the ion pair complex concentration and the extraction efficiency.

Effect of Shaking Time

50µg Cd^{2+} ion in 5mL aqueous solution was extracted according to general procedure at optimum conditions and in different shaking time the results were demonstrated in **Figures 9,10** :

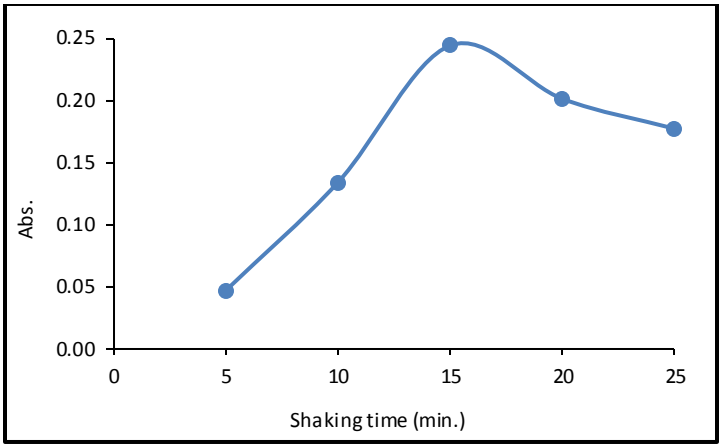

Figure 9 : Effect of shaking time on ion pair association complex formation

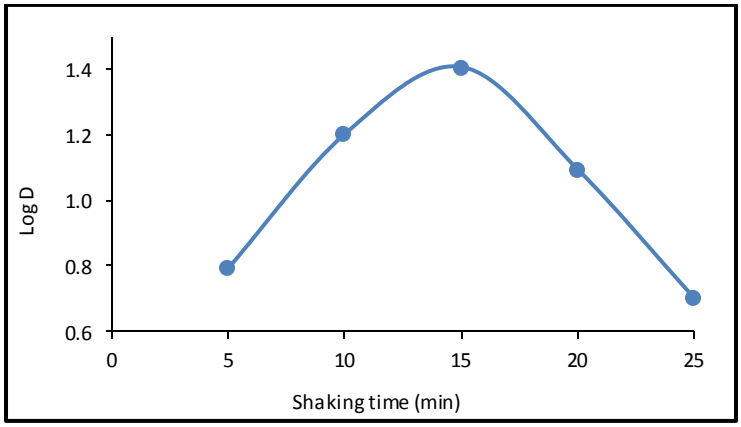

Figure 10 : Effect of shaking time on extraction efficiency and D value

The results show 15min. was the optimum shaking time to reach higher extraction efficiency whereas shaking time represent the kinetic side of extraction method at this time reaching maximum ion pair association complex formation and extraction, any time less than optimum not allow to reach the favorable equilibrium, so that any shaking time more than optimum shaking time effect to decrease extraction efficiency because increase backward

direction of equilibrium that is mean increase the rate of dissociation and decreasing in ion pair complex extracted.

Effect of Temperature

Extracted 50µg Cd^{2+} ion from 5mL aqueous solution at optimum according to general method after shaking for 15min. in water bath shaker at different temperature. The results were presented in **Figures 11,12** :

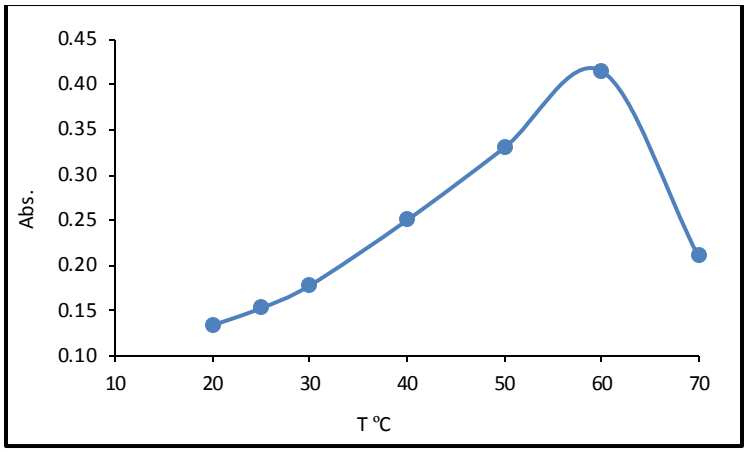

Figure 11 : Effect of temperature on ion pair formation and stability

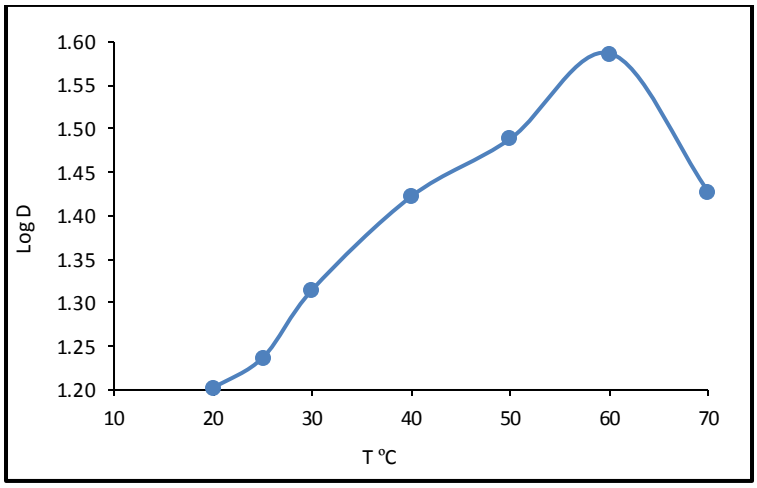

Figure 12 : Effect of temperature on extraction efficiency

After calculated extraction constant at different temperature according to relation below, the results were as in Figure 13:

$$K_{ex} = \frac{D}{[Cd^{2+}][2,4-DMP]}$$

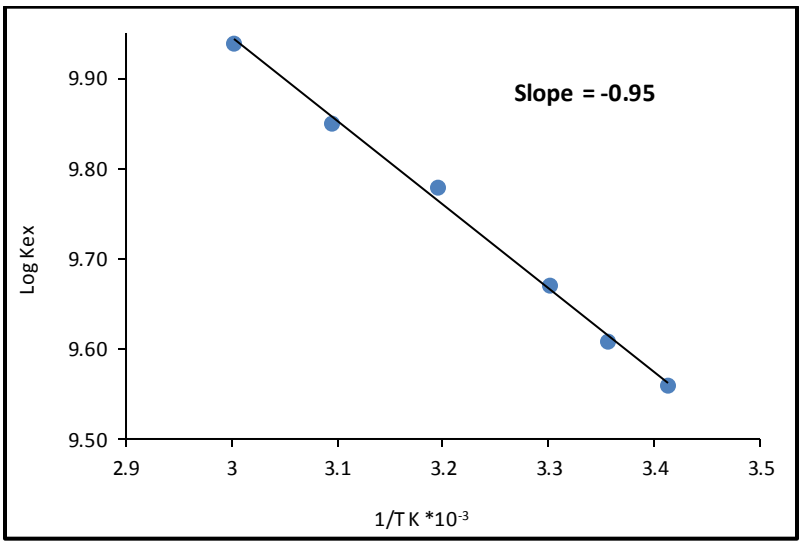

Figure 13 : Effect of temperature on extraction constant

From the slope of straight line and relations below calculated thermodynamic data demonstrated in **Table 1**:

$$slope = \frac{-\Delta H_{ex}}{2.303R}$$

$\Delta G_{ex} = - R T \ln K_{ex}$

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

Table 1: Thermodynamic data for extraction Cd^{2+} ion as onium species

ΔH_{ex} kJ/mol	ΔG_{ex} kJ/mol	ΔS_{ex} J/mol.K
0.0182	-63.387	190.29

Effect of Electrolytes

50µg Cd^{2+} ion in 5mL aqueous solution was extracted according to onium method in the presence 0.01M of some electrolytes in aqueous solutions and follow the procedure detailed in general method. The results were shown in **Table 2** :

Table 2 : Effect of electrolytes on extraction efficiency of Cd^{2+} as onium species

Electrolyte	*Abs. at λ_{max}=260nm*	*D*
LiCl	0.467	30.93
NaCl	0.382	25.21
KCl	0.361	20.22
NH_4Cl	0.285	17.78
$MgCl_2$	0.404	27.65
$CaCl_2$	0.346	22.67
$AlCl_3$	0.365	21.54

The results appear the presence of electrolyte in aqueous phase effect to increase extraction efficiency because the electrolyte causing decrease in polarity and dielectric constant of aqueous phase as well as destroy the hydration shell of metal ion Cd^{2+} and this effect change and ionic radius with higher charge density giving higher effect.

Effect of Interferences

50µg Cd^{2+} was extracted from 5mL aqueous solutions according to onium technique in the presence 0.01M of some interferences metal cation by following general procedure the results were demonstrated in **Table 3** :

Table 3 : Interferences effect on extraction activity of Cd^{2+} ion

Interferences	*Abs. at λ_{max}=260nm*	*D*
Co^{2+}	0.06	6.81
Ni^{2+}	0.091	10.25
Hg^{2+}	0.081	9.67
Fe^{3+}	0.182	17.31

The results show there is an interference for all metal cations presence in the aqueous phase with the metal cation under study and this interference differ with each metal cation, that is mean all these metal cations participate Cd^{2+} ion to forming onium species with 2,4-DMP by different activity belong to behavior effect to consumption some of hydrochloric acid and organic reagent 2,4-DMP and decrease down the optimum concentration necessary to extraction $Cd^{2+}$and then effect to decline extraction efficiency[11].

Effect of Organic Solvent

According to general method 50µg Cd^{2+} in 5mL aqueous phase was extracted by using different solvents for 2,4-DMP the results were demonstrated in **Table 4** :

Table 4 : Organic solvent effect on extraction efficiency of Cd^{2+}ion

Organic solvent	ε_r	*Abs. at λ_{max}=260nm*	*D*
Nitro benzene	35.74	0.256	26.73
Amyl alcohol	15.8	0.445	33.46
1,2-DCM	10.65	0.421	30.12
DCM	9.08	9,383	28.44

Chloroform	4.806	0.244	25.15
Benzene	2.804	0.343	27.15
Toluene	2.438	0.388	29.21

The results appear there is not any linear relation between dielectric constant (ε_r) of organic solvents and absorbance and D values that is mean there not any effect for polarity of organic solvents on extraction efficiency which is mean participate of organic solvent in the formation of extracted species.

Spectrophotometric Determination

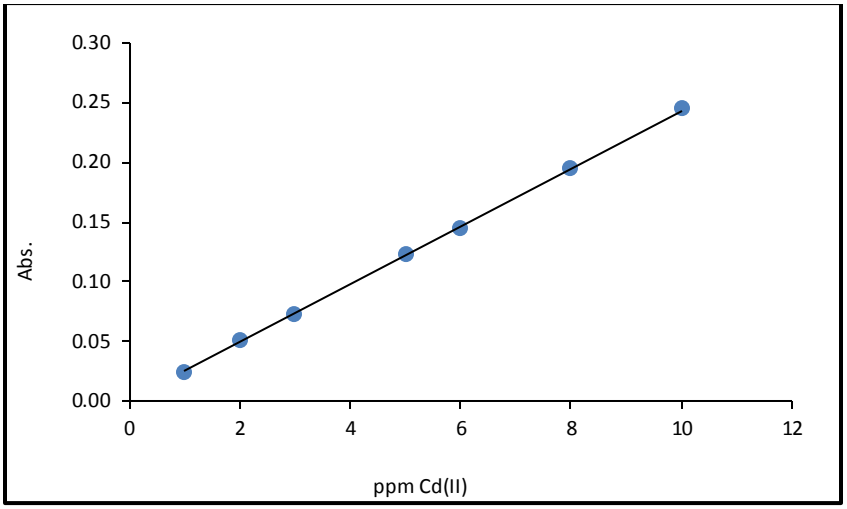

Figure 14 : Calibration curve for spectrophotometric determination of Cd(II) by onium method.

Table 5 : Application

No.	Sample name	ppm of Cd(II)
1	*Onion*	1.58
2	*Celery*	1.76
3	*Tomato*	1.27
4	*Pomegranate*	0.82
5	*Old holy city*	5.15
6	*Sediment of Euphrates river(Kufa)*	4.83
7	*Sediment of drainage*	5.50
8	*Soil of sand quarry*	8.80
9	*Al-Milad Neighborhood*	8.82

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