

Cloud Point Extraction Method For Determination nickel In Different Water Samples Using An Imidazole Derivative

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Abstract

According to the cloud point extraction method (CPE), nickel ions were preconcentrated and separated in water samples by forming a complex with the organic reagent 2-[4-carboxymethylphenylazo]-4,5-diphenylimidazole (4-CMePADI). This method included adding ethanol at a volume of 5 mL to the cloud point layer before analysis and using a UV-Vis spectrophotometer. It had a wavelength for final absorbance under $\lambda_{\max}=540$ nm. Limited optimum conditions in this work, such as pH, nickel concentration, the volume of TritonX-100 (octylpoly ethylene glycol phenyl ether), heating time, temperature, and interference effects were reported. Stoichiometry for the formed complex, which investigation clarifies that the extracted species was under the status of 1:1 [reagent: nickel]. Also, this method applies to the quantitative determination of nickel (II) in different water samples. The limit of detection (LOD) of nickel ions is 3.0705 ppm, Limit of Quantity (LOQ) is 10.2535 ppm and Sensitivity (S) is 0.017 ppm.

Keywords: Cloud Point Extraction, Nickel, Separation, TritonX-100, Imidazole Derivative

Introduction

The determination of trace metals is a subject of considerable interest because these metals are essential components and toxins in biological processes [1]. There are reviews of studies that included cloud point extraction in analytical chemistry to separate and quantify many metal ions and various organic compounds [2-5]. This extraction method is considered one modern method and the best alternative technique for extraction, which uses surfaces extensively and mainly to extract the

organic and inorganic components in the separation process [6-9]. The Cloud point extraction method (CPE) was also used for separation and determination of Ni^{+2} using graphite atomic furnace absorption, 8-hydroxyquinoline as ligand, [40-57] Triton X-100, and then studied all study factors [10]. There were growing concerns about the selectivity and sensitivity behavior of azo compounds and their derivatives for complex formation with metals, which were given growing concern in studies [11,12]. The extraction of uranium and the effect of the alkyl group on the extraction uses the presence of azo compounds [13]. used Flame Atomic Absorption Spectrophotometric (FAAS) and CPE together to separate and determine trace Ag^{+1} using TX-114 and dimethyl dithiocarbamate (DDTC) as ligand. The results show the linearity of the calibration curve to work within the range of concentration between 1 and 500 ng/ml, and the limit of detection was 0.3ng/ml [14]. Depending on the use of the two methods together (graphite atomic flame absorption and cloud extraction method) [15-17] were isolated and determined ions (Cu, Ni, Pd, and Pb) in environmental samples of surface water [18]. Some researchers have been studying complexes of nickel (II) and other elements using Schiff base, and synthesized a new imidazole ligand, then studied its complexes with copper (II), cobalt (II), and nickel (II) [19]. The surfactants are amphiphilic organic compounds. They have both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, surfactant contains a water-insoluble component and a water-soluble component. The most common surfactant tail is a hydrocarbon chain that may be linear, branched, or aromatic [20-22]. Solvent extraction is used with cloud point extraction in several studies. It is distinguished by being sensitive to the separation and determination of nickel ions in the presence of cadmium, nickel, and lead, the cloud method using azo derivatives [23]. The cloud point extraction method [24] used 2-(2-benzothiazolyl azo)-5-(N, N-diethyl) amino phenol as a ligand and TX-114 as a surfactant [24]. Nickel ions are removed from different water samples by cloud point techniques and the atomic absorption spectrum of graphite, using TX-114 and 1-phenyl- 3-methyl-4-benzoyl-5-pyrazolone (PMBP) at optimum conditions [25]. The CPE method is followed by atomic absorption spectrometric to determine copper, nickel, and cobalt ions in different water, honey, and chocolate samples using (NTPHPI) as a complexing agent and TX-114 as a surfactant [26]. Using liquid ion-exchange joined with (CPE) to extract and separate Ni^{+2} from the presence of TritonX-100 as a surfactant [27]. used the CPE method and (CVAAS) for determination of total mercury (Hg) in different tissues of broiler chickens (breast, heart, leg, and liver). The limit of detection (LOD) of this method was 0.117 $\mu\text{g/kg}$ under optimal conditions [28]. The CPE method was applied to determine Bi (III) in human urine samples using Triton X-114 as a non-ionic surfactant. Also, the linearity was in the range of (4.60-120.0) ng ml^{-1} [29]. Lead (II) was determined by cloud point extraction in water and sediment samples with a limit of detection of 7.5 $\mu\text{g l}^{-1}$ and 0.33 $\mu\text{g g}^{-1}$, respectively [30]. CPE has become an attractive area for trace metal separation by coupling with different analytical methods [31-33].

carboxymethylphenylazo]-4,5-diphenylimidazole (4-CMePADI) is a suitable chelating agent used in this study. The cloud point method for determining a tiny amount of nickel (II) in water samples is selective, rapid, and chief among procedures. In addition to the favorable results that this method gave.

1.1-Experimental and Preparation of Standard Solutions

All materials in this work were used without any additional purification as received from the supplier company. Distilled water was employed for formulating the standard samples and reagents. TritonX-100 as a surfactant (purity about 99.6%) Sigma Ultra. HCL (Analar) Fluka. A stock solution of Ni⁺² ions (1 mg/ml) prepared by dissolving 0.2207 gm from NiCl₂.6H₂O (purity 99%) in distilled water containing 0.5ml from HCl and dilute the solution with distilled water in a suitable volumetric flask. Organic reagent 2- [4-carboxymethyl phenyl azo]-4,5-diphenyl imidazole as ligand.

Shimadzu double beam UV-Vis spectrophotometer UV-1700 (Japan) used for spectrophotometric studies. In each required experiment, pH meter WW, E163694 CE Germany, water bath Hamburg -90 to regulate cloud point temperature and electrical balance company limited, Dool, (±0.0001g), CE, HR200, Japan. Flame atomic absorption spectrophotometer, Shimadzu (AA-6800 pattern Kyoto, Japan) employed in this work.

1.2-General Procedure

A 10 ml of aqueous solution contains the finest quantity of nickel ion and 1×10⁻⁴ M of reagent (4-CMePADI) in the presence of a surfactant (TX-100) with optimum PH. This solution is heated in a water bath at a relevant temperature and time of heating to CPL realization. Then, they separated this layer and dissolved it in 5 ml of ethanol. The absorbance of the alcoholic solution measures against the prepared blank solution in the same manner but without adding nickel. At the maximum absorption wavelength of the extracted complex using a UV-Vis spectrophotometer at λ_{max} =540nm. As for the distribution ratio of the remaining nickel in the aqueous solution. It depends on the spectroscopic method of determination [34]. To determine the remaining amount of Ni (II) in the aqueous phase next to the extraction. Then subtraction from the original amount of 50 µg to calculate the transferred amount of Ni (II) into CPL as an ion pair complex using calibration.

Subsequently, compute the distribution ratio (D) in relation to equation (1).

$$D = \frac{[\text{Ni (II)}]_{\text{CPL}}}{[\text{Ni(II)}]_{\text{aq}}} - - - - - 1$$

Results and Discussion2-

2.1-Spectrophotometric study for complex (Ni-CMePADI)

The spectrophotometric study for the extracted complex shows a wavelength of maximum absorbance equal to 540 nm (Figure1).

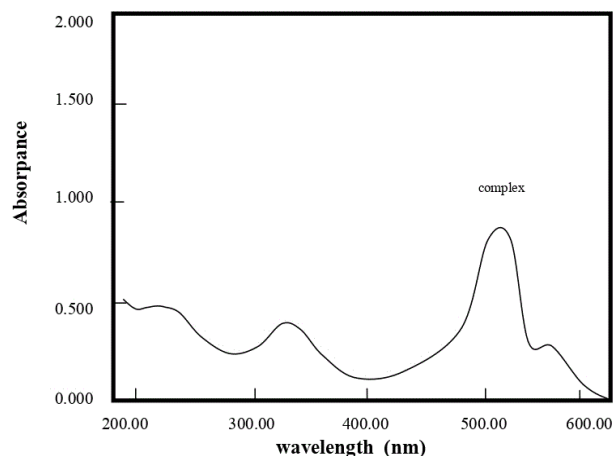


Fig.(1):UV-VIS absorption spectrum of the extracted complex with Ni²⁺

Effect of pH2.2-

The pH is the most important parameter affecting the extraction. It is necessary to choose the optimum pH at first [35]. The 10 ml of aqueous solution contains 50 µg of nickel ion, a suitable volume of TX-100, 1×10^{-4} M of reagent (4-CMePADI), and a pH range of 4-12. Then, these heated solutions were in the water bath at an 80°C temperature for a suitable time until cloud point layer formation. separated this layer from the aqueous solution and dissolved it in ethanol. The absorbance of the alcoholic solution is measured at $\lambda_{\text{max}}=540$ nm against a blank that was prepared similarly without adding Ni (II). The aqueous solutions are treated according to the spectrophotometric method [34]. The results are shown as in figure (2).

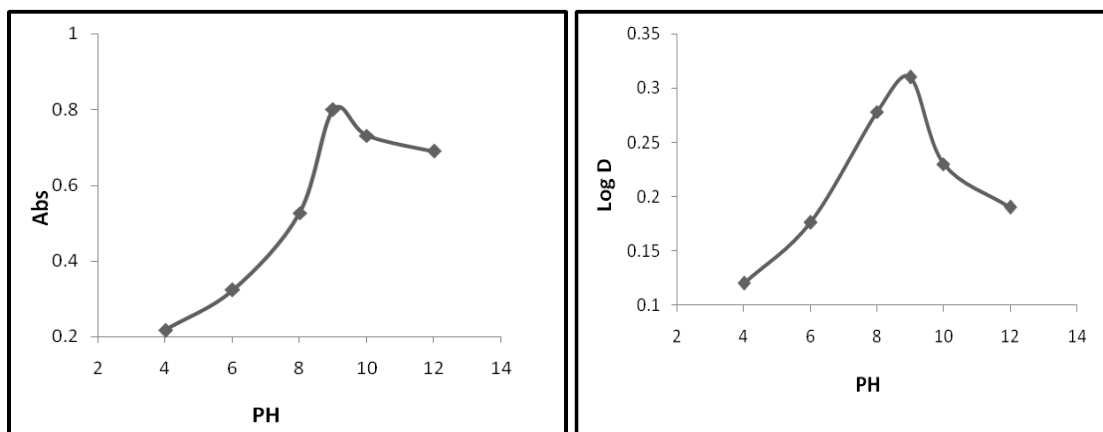


Fig. (2a) Effect pH On Formed Micelles

Fig. (2b) Effect pH On D Values

Appear from the figures that the optimum pH was 9. At this value of the acidic function, extraction efficiency is the best possible because at which reached favorable thermodynamic equilibrium for extraction and giving higher values of absorbance and D-values. If the medium is less than 9 will cause a decrease in extraction efficiency and is not allowable to reach thermodynamic equilibria. Also, the value above 9 reducing the extraction efficiency and increasing the back reaction of dissociation equilibrium.

2.3-Effect Nickel Ions Concentration

One of the influence factors on the extraction efficiency, the formation of micelles, and the stability of the formed complex is the concentration of the metal ion. The solutions contain nickel concentrations within a range from 5 μg to 80 μg were prepared with optimal working conditions. The figures (3a and 3b) showed the results.

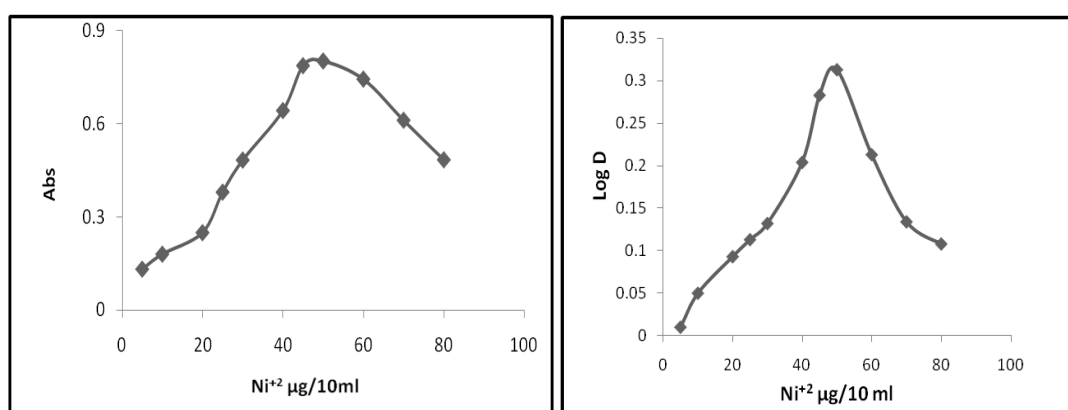


Fig. (3a) Effect of Ni^{+2} Concentration on CPE Fig(3b) Effect of Ni^{+2} Concentration on D values

It is clear from the results that the highest sensitivity for extraction is when the nickel concentration is 50 μg . When a nickel quantity is less than 50 μg , the reaction does not reach thermodynamic

equilibrium. Also, the large concentrations of nickel ions lead to the opposite effect as it causes the dissociation of the complex. And an increase in the ionic form according to mass action law and LeChatlier principle.

2.4-Temperature Effect

The determined temperature for CPL formation includes the experiment using a temperature range of 65°C to 100°C. The work is complete as the general procedure. And the results show optimum temperature for extraction was 80 °C, then, calculated constant of extraction K_{ex} depended on the relation (2). After that plotting $\log K_{ex}$ against $1/T_K$ give a straight line as shown in figure (4).

$$K_{ex} = \frac{D}{[Ni^{2+}]_{aq} \cdot [ligand]_{org}} \quad \text{--- 2}$$

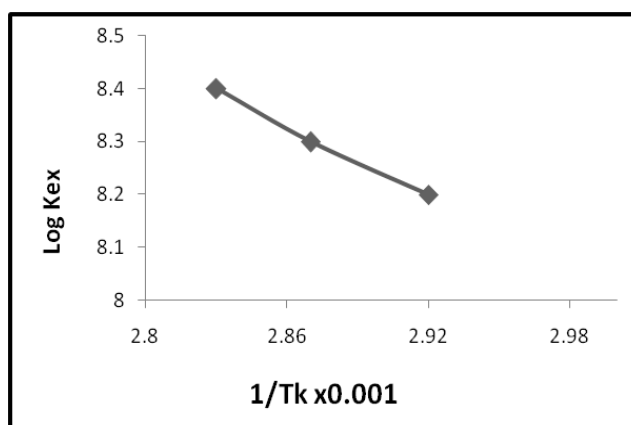


Fig. (4) Temperature Effect On K_{ex}

From the slope of this straight line in figure (4) enthalpy of extraction calculate to be

$$\text{slope} = \frac{-\Delta H_{ex}}{2.303R} \quad \text{--- 3}$$

Also, free energy for extraction and entropy values calculated using the relations below (4,5):

$$\Delta G_{ex} = -RT \ln K_{ex} \quad \text{--- 4}$$

$$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex} \quad \text{--- 5}$$

The results show thermodynamic data as in table (1).

Table (1): Thermodynamic Data of CPE Method

ΔH_{ex}	ΔG_{ex}	ΔS_{ex}
0.056 KJ.mole ⁻¹	-56.75 KJ.mole ⁻¹	160.92 J.mole ⁻¹ K ⁻¹

2.5- Heating Time Effect

Heating time is one of the most factors affecting extraction and CPL formation, this experiment was carried out in time range (5-40 min) complete the procedure at the optimum conditions of 50 µg of Ni(II), 1×10^{-4} M of reagent, and a suitable volume of surfactant, the results were as shown in figure (5)

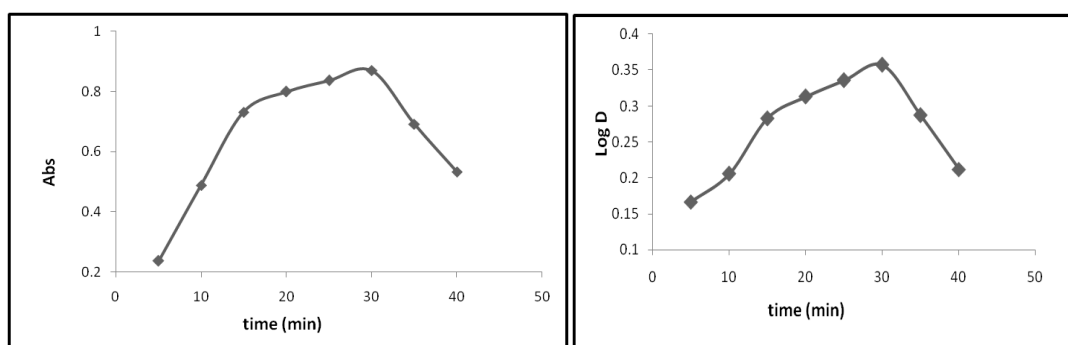


Fig.(5a) Heating Time Effect on CPE Fig. (5b) Heating Time Effect on D Values

The figures demonstrate that the favorite heating time for extraction and cloud point formation was 30 minutes. At this value, the CPL formation is completing and giving the best thermodynamic equilibrium for extraction. But if the heating time is less than 30 min, it will increase the diffusion of micelles in aqueous solutions and decrease the density of CPL. Also, the efficiency of extraction reduces when heating time is more than 30 minutes.

2.6-Triton X-100 Volume Effect

To determine the optimal volume of the surfactant, which gives the best results for the cloud point layer, were taken different volumes of Triton X-100 within a range from (0.1 ml to 2 ml) with other optimum conditions, heated these solutions at 80°C⁰ in the water bath for 30 min, complete this work according to general procedure, the results obtained shown the figures (6a and 6b).

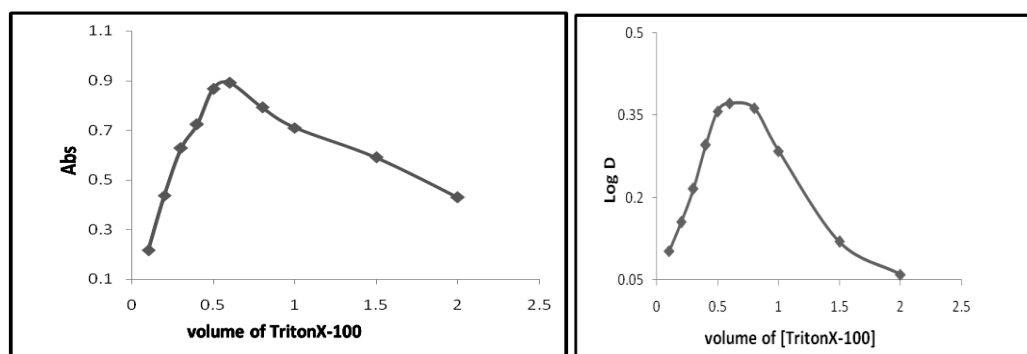


Fig.(6a) TX-100 Volume Effect on CPE Fig.(6b) TX-100 Volume Effect on D values

The previous figures show that the optimum volume of the surfactant was 0.6 mL. This volume of surfactant produced a critical micelles concentration to create a CPL with higher density and smaller volume for CPL volumes. Hence, the maximum extraction efficiency. When the value is more than the optimum value causes a decrease in the extraction efficiency and increases the diffusion of micelles. On the other hand, any volume less than 0.6 mL decreases (D and absorbance) values.

2.8-Stoichiometry

To know the most probable structure of the complex according to this method used two spectrophotometric methods for this purpose as follows:

A-Slope Ratio Method

The range of ligand and metal ions concentration use to apply the slope ratio method is (1×10^{-6} M to 5×10^{-4} M). The obtained results are in figures (7,8). the results show that the expected composition of the nickel complex with the reagent is in a ratio of 1:1 [Ni^{+2} : Ligand]

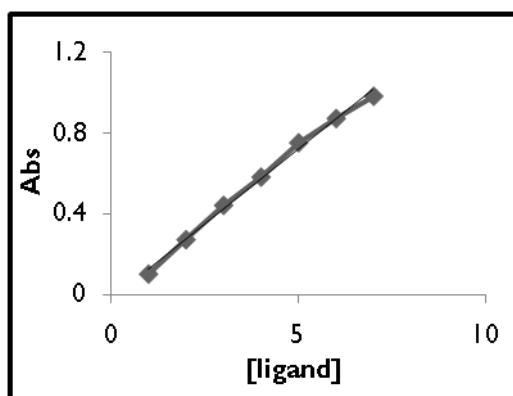


Fig. (7) Slope Ratio Method with Change [L]

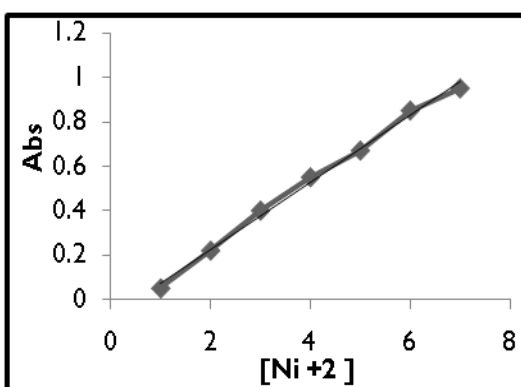


Fig. (8) Slope Ratio Method with change [Ni+2]

B-Mole Ratio Method

Working according to this method included the extraction of the nickel ion using different concentrations of the reagent with a range (1×10^{-6} M to 5×10^{-4} M), the results in figure (9) in which it appears that the complex composition is 1:1. All the methods used show that there is one molecule of the reagent binding with the nickel ion in the extracted complex in figure (10).

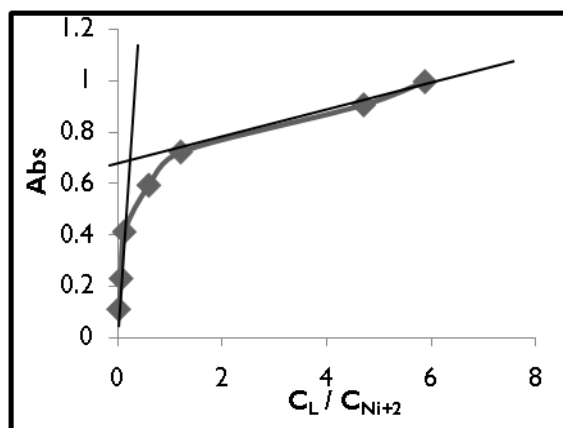


Fig.(9) Mole Ratio Method

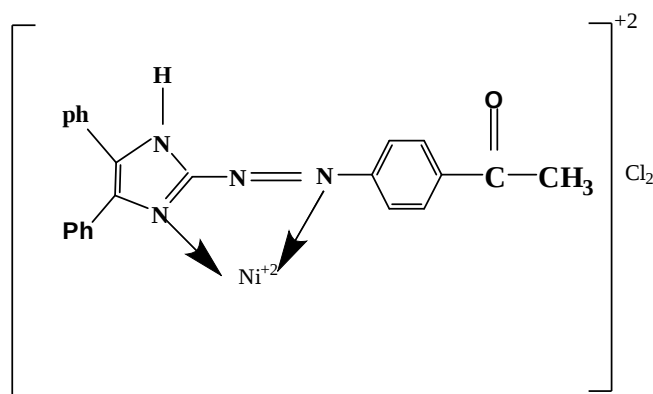


Fig.(10) The Structure of Extracted Complex Using CPE Method

2.9-Interference Ions Effect

The presence of cations and anions in the aqueous solution affected the extraction process and efficiency. This work extracted Ni^{+2} from a 10 ml solution with optimum PH and other factors in the general procedure. Additional 0.1 M different anions and cations. Table (2) shows the results of the interference effect.

Table (2): Effect of Interference Ionson D Values

Cation	D
Na^{+}	31.22
Fe^{+3}	1.48
Mg^{+2}	52.10
Sn^{+2}	0.32

NH₄⁺	23.27
K⁺	28.6
Ca⁺²	41.26
Anion	D
CH₃COO⁻	0.784
SO₄⁻²	2.187
SCN⁻	4.268
C₂O₄⁻²	1.480
CrO₄⁻²	0.697
ClO₃⁻	1.745

The results interpret, the presence of cations is increasing the extraction efficiency. So the distribution ratio through dehydration increase by using different inorganic salts. But the anions have the opposite effect of good extraction because they attack nickel ions and formed a complex that cannot extract. As well as cause reduction in the distribution ratio values except for SCN⁻ ion.

2.10-Spectrophotometric Determination

The dependence on the calibration curve shows in figure (11). For the determination of nickel ions in different water samples, work was under optimum conditions.

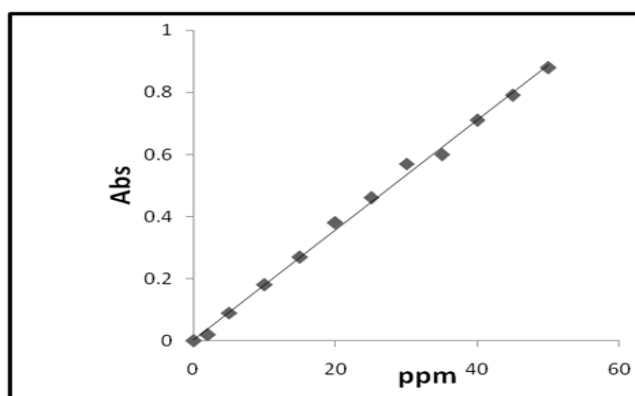


Fig.(11): Calibration Curve of the Applied Method to Determine Ni(II) in Water Samples.

3- Analytical Parameters for The Applied Method

Method appear from calibration curve given in table (3)

Table (3): Analytical Parameters of CPE Method

Parameters	Ni (II)
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$\lambda_{\max}$	540 nm
Correlation Coefficient (R)	0.9984
Limit of Detection (LOD)	3.0705ppm
Sensitivity (S)	0.017ppm
Limit of Quantity (LOQ)	10.2535ppm
Intercept	0.004

4- Applications

Table (4):Determination Micro Amount Ni⁺²In Different Water Samples

Sample	[(4-CMePADI)] method ppm	RSD %	FAAS method ppm
Shatt Al-Mhinawia	0.137	0.4	0.135
Najaf River	0.062	0.3	0.061
Shatt al-Shamiya	1.20	0.7	1.19
Mabzil al-Shamiya	0.12	0.2	0.12
Mabzil al-Hafaar	0.18	0.4	0.17

5- Comparison with other studies to determine Nickel ions using CPE method

Table (5) Comparison Between Data in This Work and Other CPE MethodsUsing to Determine Ni (II) In Different Samples

Method	Surfactant	Ligand	Detection limit	Sample volume	samples	Ref
CPE/FAAS	TX-114	5-Br-PADAP	1.7ng·ml ⁻¹	50ml	water	36
CPE/UV-VIS	TX-100	4-HBDA1,5DP HP	2.805 µg l ⁻¹	10ml	waste water	37
CPE/UV-VIS	TX-114	Dithiocarbamate	91.4 µg l ⁻¹	10ml	water	38
CPE/UV-	TX-114	HPAB	-	10 ml	Differen	39

VIS					t samples	
CPE/UV- VIS	TX-100	4-CMePADI	3.0705ppm	10 ml	water	This work

Abbreviations: 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP),

E-4-(3-hydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one [4-HBDA1,5DPHP], 2-(4-hydroxyphenylazo)-4-benzonaphthol (HPAB).

Conclusion

The Cloud point extraction method is one of the indirect extraction and separation methods. It has different advantages, like using a minimal amount of surfactant, low cost, and makes it attached to green chemistry methods with lower toxicity than those using organic solvents. This work extracted Ni^{+2} with (4-CMePADI) by using TX-100 surfactant. It has investigated selectivity, simplicity, and ecological safety. It is possible to use this method for preconcentration and separation of nickel ions present in different samples.

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