

Radiation therapy's ripple effect: Cadmium levels in Halfaya oil field produced water and their impact on cancer risk

Anwer S. Salim, Mohammed Z. Thani, Abdull jabar KH. Atia

Department of Chemistry, College of Science, Al-Mustansiriyah University, Baghdad, Iraq

ABSTRACT

In this work, by converting 2-(4-aminophenyl) benzimidazole to diazonium salt and coupling it with 8-hydroxyquinoline in an alkaline medium, we were able to synthesize a new ligand, 2-(4 amino phenyl) benzimidazole azo derivative, which was used as the ligand to assess cadmium (II) in aqueous samples. The analysis of cadmium (II) in pure and aqueous components has been established and confirmed using micro-extraction techniques with UV-Vis measurement. In this work, the DLLME method was utilized for the separation, enrichment, and evaluation of cadmium (II) in pure form and aqueous samples by UV-Vis spectroscopy at 414 nm. Several experimental factors were achieved, including the type and volume of dispersive solvent, type and volume of extraction solvents, temperature, and time reaction, and centrifuging time. With a coefficient of determination (R^2) of 0.9966 for the spectroscopic technique and 0.9964 for the DLLME method, respectively, the procedures were linear in the range of 1.0 $\mu\text{g/mL}$ -50.0 $\mu\text{g/mL}$ and 1.0 $\mu\text{g/mL}$ -11.0 $\mu\text{g/mL}$ under ideal conditions. The Limit of Detection (LOD) was 0.71 $\mu\text{g/mL}$ and 0.16 $\mu\text{g/mL}$. The target analyte was recovered from aqueous samples using the spectroscopic approach between 96.6% and 99.6% and the DLLME method between 95.2% and 100.2%, respectively.

Keywords: microextraction, DLLME, cadmium (II), Spectroscopy, benzimidazole, cadmium

INTRODUCTION

The assessment of heavy metal ions in environmental samples has recently attracted a lot of attention [1-4]. There is growing concern regarding the identification and quantification of metals and metal ions, particularly transition metals, in both solid and solution samples due to increased environmental pollution worldwide [5]. Cadmium is one of the most environmentally harmful metals since it has a profoundly negative effect on human and animal health, plant metabolism, and soil biological activity. The World Health Organization (WHO) imposed the maximum acceptable dose at 3 $\mu\text{g mL}^{-1}$, while the US Environmental Protection Agency (EPA) imposed a limit of 5 $\mu\text{g mL}^{-1}$ [6, 7]. Several methods, including ICP-MS, ion chromatography, anodic stripping analysis, and electrothermal atomic absorption spectrometry, were used for assessing the presence of cadmium ions [8-11]. Among all of these sensitive techniques, spectrophotometry is an essential tool that is most frequently used in countries that are developing due to its low cost, ease of use, high accuracy and precision, and good selectivity when a selective chromogenic reagent for the analyte is specifically used [12-14]. However, as spectrophotometry's sensitivity is insufficient for water samples with low abundance levels of cadmium, there may be difficulties in the direct determination of cadmium by this method. As a result, before spectrophotometric detection of the analyte at an appropriate wavelength, an extraction and preconcentration step is frequently necessary [15, 16]. In this regard, it is important to note the recent development of faster, simpler, low-cost, and green analytical methods for metal enrichment in the context of so-called "green analytical chemistry" such as Liquid-Liquid Microextraction (LLM) [17, 18]. Dispersive Liquid-Liquid Microextraction (DLLME), one of the extraction techniques, is based on the cloudy solution formed when an adequate mixture of an extraction solvent and a disperser solvent is injected into an aqueous solution [19-22]. In this regard, the main purpose of the study is to assess the feasibility of combining DLLME preconcentration with spectrophotometry at 414 nm for the estimation of cadmium level in the produced water of the Halfaya oil field/ Maysan. In this method, a new azo compound was utilized as a complex reagent for the determination and extraction of trace cadmium using DLLME. Cadmium is considered one of the elements that have the ability to cause cancer, especially lung cancer, when large quantities are inhaled. Cadmium is considered one of the most abundant mineral elements due to its ability to accumulate within the tissues of living cells [23].

Address for correspondence:

Anwer S. Salim,

Department of Chemistry, College of Science, Al-Mustansiriyah University, Baghdad, Iraq

E-mail: anwaralasaki82@gmail.com

Word count: 3613 **Tables:** 06 **Figures:** 17 **References:** 27

Received: 03 May, 2024, Manuscript No. OAR-24-133943

Editor Assigned: 15 May, 2024, Pre-QC No. OAR-24-133943(PQ)

Reviewed: 20 May, 2024, QC No. OAR-24-133943(Q)

Revised: 25 May, 2024, Manuscript No. OAR-24-133943(R)

Published: 31 May, 2024, Invoice No. J-133943

MATERIALS AND METHODS

Instruments

An analytical grade single-beam UV-Visible spectrophotometer with a 1 cm quartz cell was used to measure absorbance at the selected wavelength of 414 nm. On an atomic absorption spectrophotometer (Shimadzu AA-670, Japan), cadmium was determined. Phase extraction was accelerated by using a centrifuge (Beckman type TJ-6, Germany).

Reagents and solutions

Both the SDS and the cadmium nitrate that was bought from Fluka and Merck were of analytical grade. By dissolving 0.034 gm of Cd (NO₃)₂ · 4H₂O in the 100 mL of deionized water, a stock solution of 100 µg · mL⁻¹ Cd(II) was produced. By dissolving 0.01 g in 5 mL of ethanol and then adding deionized water to the mark (100 mL), a new azo compound in the concentration of 100 µg · mL⁻¹ was formed. Daily preparation of working solutions involved the proper dilution of the stock solutions.

Synthesis of (E)-5-((4-(1H-benzo[d]imidazol-2-yl) phenyl) diazenyl) quinoline-8-ol [5BIPQ] [24].

After adding conc. HCl (0.9 mL) and a solution of NaNO₂ (3.3 × 10⁻³ mol) in D.W (10 mL) to 2-(4-aminophenyl) benzimidazole (3 × 10⁻³ mol), the mixture was stirred frequently at 0–10°C for 12 minutes to yield a diazonium salt. 10% aq. NaOH (3 mL) was added to a solution of 8-hydroxy quinoline (3 × 10⁻³ mol) in water (15 mL), followed by the addition of the diazonium salt solution at 0–10°C. The resulting substance was filtered, lightly rinsed with water, and allowed to dry in the air to produce the orange compound.

Formula: C₂₂H₁₅N₅O; Mwt: 365.39 g/mol; Yield: 91%; m. p: 220°C–224°C; FTIR (cm⁻¹): OH (2450-3561), CH or (3058), NH (3227), C=N (1628), C=C (1563), N=N (1531); Mass spectra(m/z): 365, 337, 228, 209, 194, 181, 160, 145, 131, 117, 104, 91, 77, 63, 52 (Figure 1 and 2).

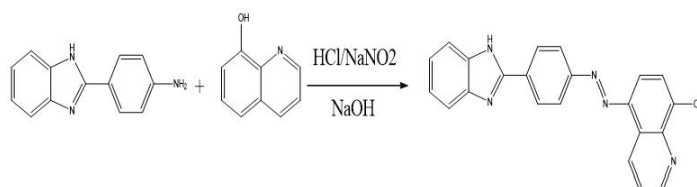


Fig. 1. Synthesis of 5BIPQ reagent

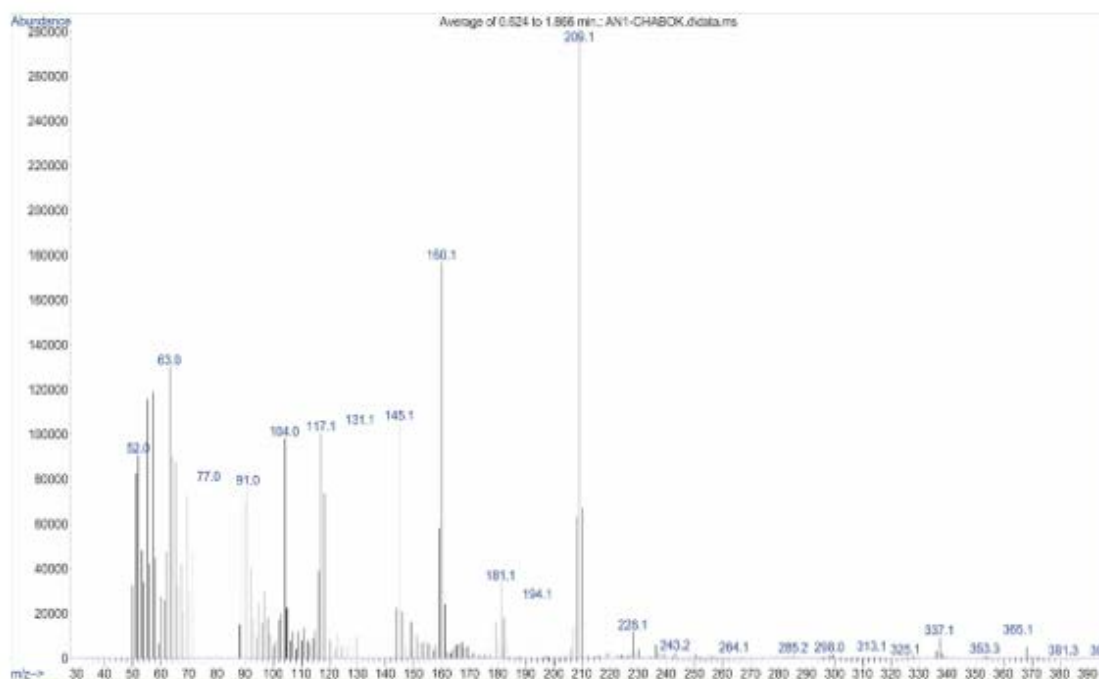


Fig. 2. Mass spectra of synthesized compound

General procedure of spectroscopy method

A 10 mL test tube having a series of standard solutions containing an aqueous solution containing 1.0 µg · mL⁻¹-50.0 µg · mL⁻¹ of cadmium (II) was mixed with 2 mL of the reagent 5BIPQ (100 µg · mL⁻¹), 3 mL of sodium hydroxide solution (0.1N), and 1 mL of SDS. The mixture was heated to 50°C for 10 min. after being diluted to the proper consistency with deionized water. At 414 nm, the absorbance was measured in comparison to a blank for the matching reagent. Using a calibration curve that was simultaneously established the cadmium content of an unknown sample

was assessed.

General procedure of DLLME

A 10 mL test tube containing 1.0 µg · mL⁻¹-11.0 µg · mL⁻¹ of Cadmium standard solution, the 2 mL 5BIPQ (100 µg · mL⁻¹), 0.5 mL KOH solution (0.1 N), and 0.5 mL SDS were added. With D.W., the volume was completed to 10 mL. After being shaken for 8 minutes, the mixture was heated at 50°C for 10 minutes. 800 µL dichloromethane as an extraction solvent and 800 µL ethanol as a dispersive solvent were rapidly injected into the mixture with a

micro syringe to produce a cloudy solution. The mixture was centrifuged at 5000 rpm for 10 minutes. The cadmium complex was obtained using a micro syringe, and the absorbance at 414 nm was measured in comparison to a blank.

RESULTS AND DISCUSSION

In this study, we synthesized a new azo compound of 2-(4-amino-

phenyl) benzimidazole with 8-hydroxyquinoline in the presence of concentrated HCl and NaNO₂, and this compound was used as a ligand for the determination of cadmium ions in the aqueous solution. The fundamental research seems to be the complex reaction of 5BIPQ with cadmium ions, which produces the orange color at λ_{max} 414 nm. Figure 3 illustrates the complex's absorption spectra in comparison to a reference solution.

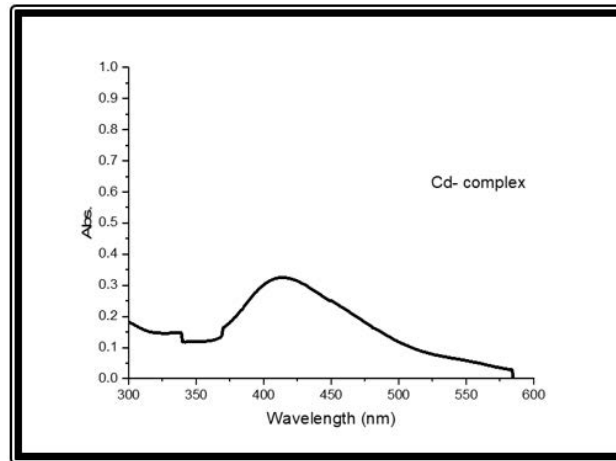


Fig. 3. Absorption spectrum of cadmium complex

Optimization of the system

The results of the investigation into the effects of different bases, including NaOH, KOH, NH₃, and Na₂CO₃, on the formation of the cadmium complex can be seen in figure 4. The impact of base

volume on the developed at a constant concentration of cadmium complex solution was investigated in the range (0.25 mL-3.0 mL). 3.0 mL of KOH was the ideal volume, as seen in figure 5.

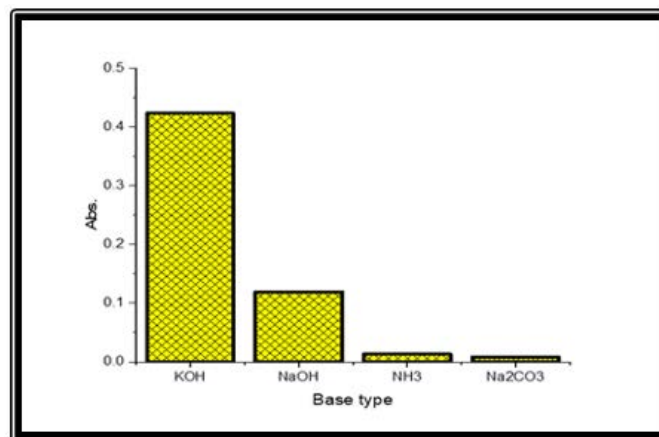


Fig. 4. Effect of the base type

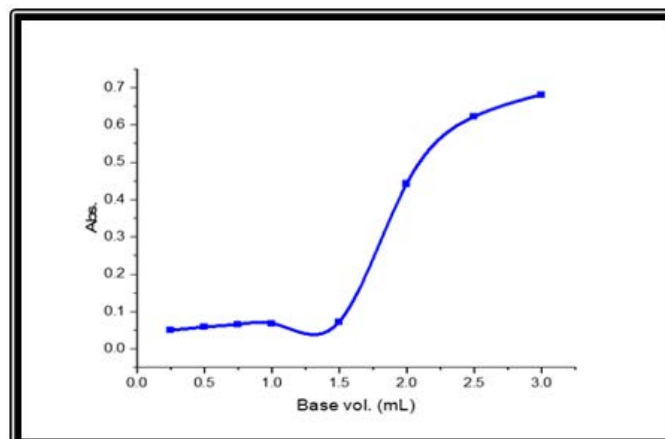


Fig. 5. Effect of the base volume

SDS, CTAB, and Tween-20 were used to test absorbance, and the findings showed that SDS was the most effective, as shown in figure 6. Since the volume of the reagent (5BIPQ) will influence the maximum absorbance, several amounts of the 5BIPQ solution in

the range of 0.25 mL-3.0 mL were added. The best absorbance signal was produced by 2.0 mL of 5BIPQ solution, as shown in figure 7, and this was used to carry out the further steps.

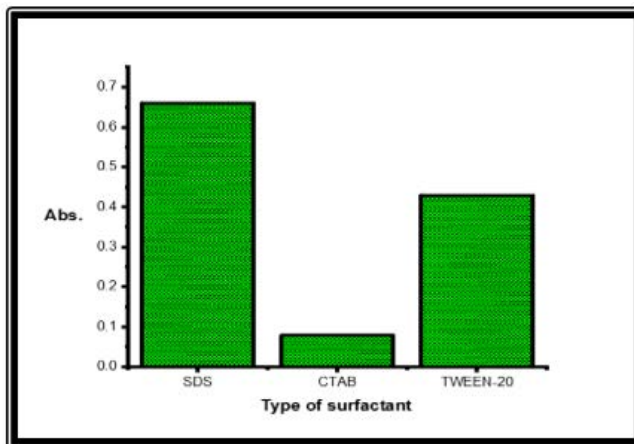


Fig. 6. Effect of surfactant

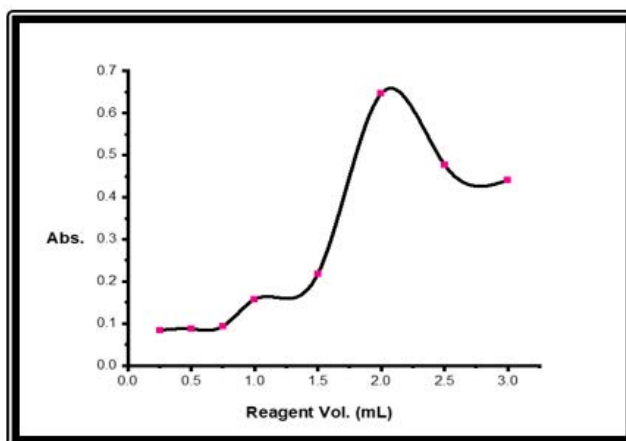


Fig. 7. Effect of reagent volume

In the temperature range of 40°C to 70°C, the influence of reaction temperature was examined. The best absorbance was determined at 50°C so that temperature was chosen for further procedures. The effect of reaction time on complex formation was examined between 10 minutes and 30 minutes, maintaining a reaction temperature of 50°C. It was discovered that 10 minutes was all that was needed to produce a formation complex. The next experiences, shown in figure 8 and 9, used a reaction time of 10

minutes. An attempt was made to ascertain the complex's makeup as the Cd(II) ion formed the colored complex with the 5BIPQ reagent. Job's method [25-26], which is related to data presented in figure 10, was used to make these determinations to find the complex's stoichiometry. Figures 10 and 11 show that Cd(II) combines with the 5BIPQ reagent to create a stable 1:2 (metal: ligand) yellow-colored complex.

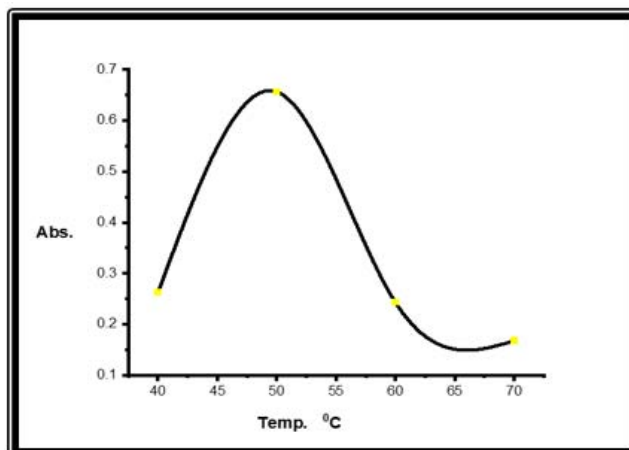


Fig. 8. Effect of reaction temperature

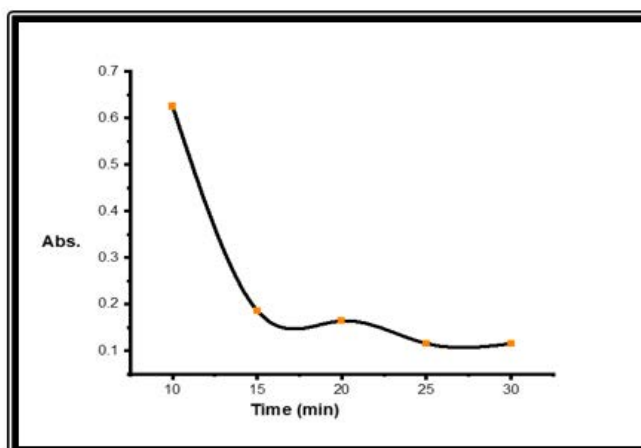


Fig. 9. Effect of reaction time

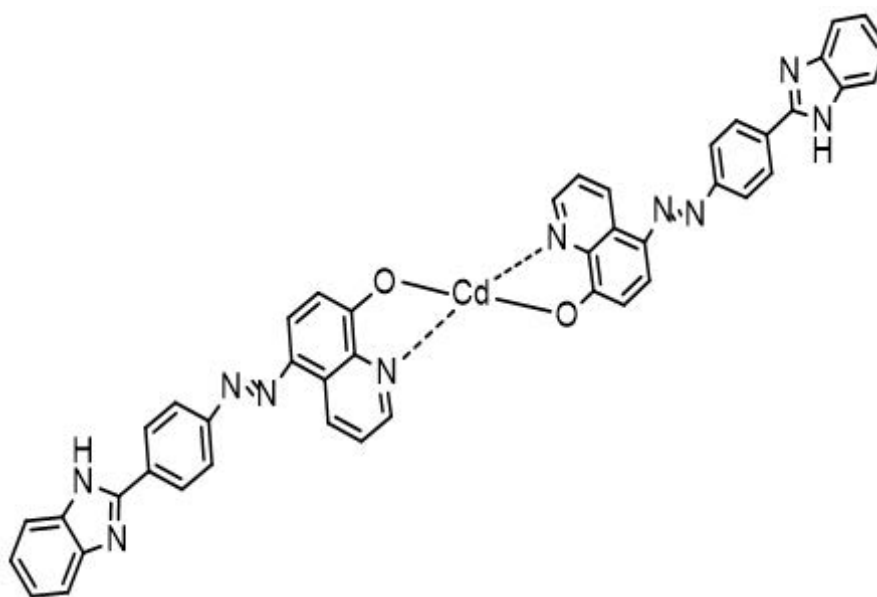


Fig. 10. Proposed structure for Cd (II)- 5BIPQ complex

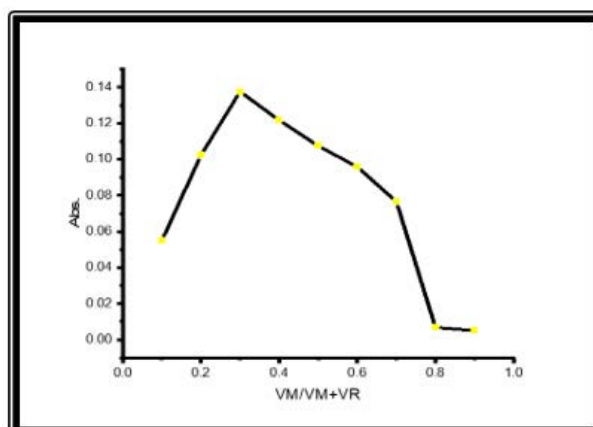


Fig. 11. Job's method (Cd (II)- 5BIPQ Complex)

When the Cd(II)-5BIPQ complex was determined at the lower EDTA was used as a masking agent to get removal of Cr(II) and concentration level listed in the table .1, the cations Cr (II) and Ni Ni(II) interference [27]. (II) significantly interfered. Before adding further 5BIPQ, 1mL of

Cation	Reco. %
Pb ⁺²	92.7
Cu ⁺²	96.8
Ni ⁺²	70.3
Cr ⁺²	73.7
Al ⁺³	101.7
Mn ⁺²	98.9

Analytical performance

Under the optima circumstances described above, a linear calibration curve was obtained from 1.0 µg. mL⁻¹–50.0 µg. mL⁻¹ for Cd, with regression coefficients (R²) always better than 0.9966 (Figure 12). The limit of quantification (LOQ=10 Sb/m) and detection (LOD =3.3 Sb/m) was 2.17 µg. mL⁻¹ (limit of quantification) and 0.71 µg. mL⁻¹ (detection limit) for Cd. The method

was determined utilizing relative standard deviation (RSD%) at 3 concentrations of 10.0 mL⁻¹, 20.0 µg. mL⁻¹ and 30.0 µg. mL⁻¹ (Figure 13). The RSD% was found less than 1.1%, 1.3%, and 4.5% for Cd. The accuracy based on recovery was calculated as the ratio of the ions' final concentration to their beginning concentration in the sample solution. It ranged from 96.6% to 99.6% recovery.

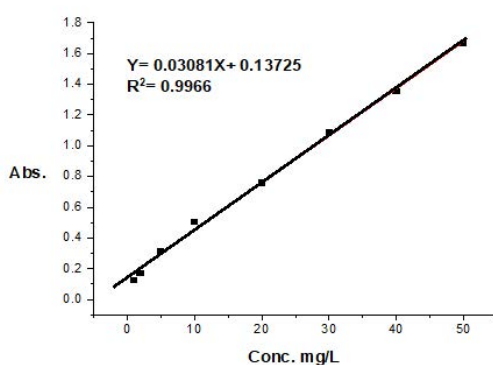


Fig. 12. Calibration curve of Cd- complex

Optimization of DLLME

In the so-called dispersive liquid-liquid microextraction, many parameters significantly affect the system's performance and the analyte species it traps. It is known that the DLLME of metal ions depends on a variety of variables, including the type and volume of the extraction solvent, the type and volume of the disperser solvent, and the number and time of rotation. To create ideal circumstances, we examined the DLLME process. In systems based on DLLME, the extraction solvent plays a major and important role.

The solvent should have specific characteristics that are necessary for the successful extraction of analytes, including lower density than water, low solubility in aqueous solution, and high analyte extraction efficiency. These qualities led to the choice of dichloromethane as the solvent extraction (Table 2). In the figure 13, a series of volumes of extraction solvent (300 µL-900 µL) was studied. It is found that the 800 µL gave better absorbance and was used in the subsequent steps.

Type of extraction solvent	Abs.
CHCl ₃	0.2701
CH ₂ Cl ₂	0.4002
CCl ₄	0.1987

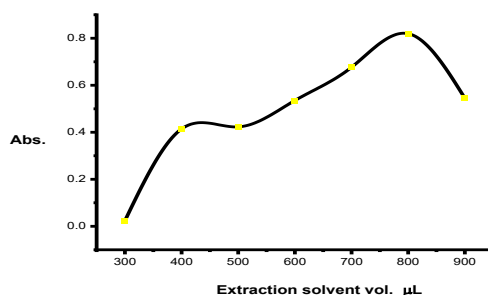


Fig. 13. Effect of volume of extraction solvent

Both an extraction solvent and an aqueous solution, as well as the disperser solvent, should be miscible. As a result, acetone, acetonitrile, methanol, and ethanol were among the main solvents used as disperser solvents. Ethanol was chosen for additional studies because it is a good disperser solvent, as shown by the data in table 3. Ethanol was soluble in dichloromethane and was miscible with water. According to the obtained data, ethanol enabled more disperse dichloromethane as tiny particles in an aqueous phase and forms a cloudy solution and therefore had greater extraction ef-

iciency. For the purpose of evaluating the disperser volume on analyte extraction, ethanol volumes of 500 μL to 1500 μL were utilized in the experiments, and the resulting signals were displayed in figure 14. In lower volumes, the cloudy state in the solution is not produced completely and thus analytes are not extracted well. On the other hand, in volumes greater than 800 μL the interested analytes are dissolved in the aqueous phase, and thus the extraction efficiencies decrease. Hence, 800 μL of ethanol was considered the perfect value solvent of the disperser.

Tab. 3. Effect of disperser solvent type

Type of disperser solvent	Abs.
Ethanol	0.4002
Methanol	0.3597
Acetonitrile	----
Acetone	0.1696

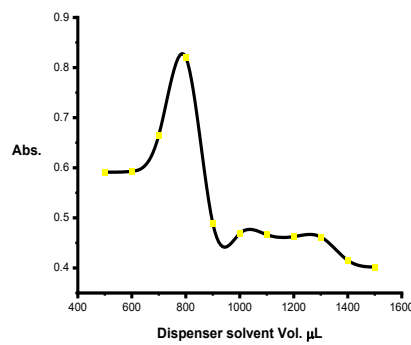


Fig. 14. Effect of volume of disperser solvent

It is essential to consider how number and time rotation affect Cd^{2+} complex extraction in the centrifuge. The highest absorbance is achieved at 5000 rpm for 10 minutes, as illustrated in figures 15 and 16.

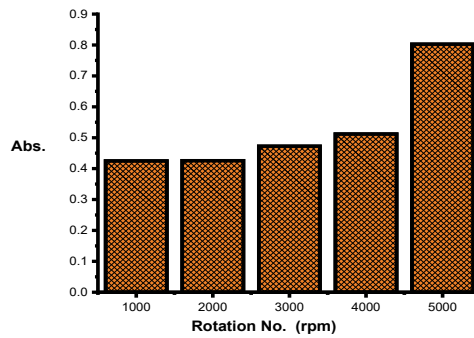


Fig. 15. Effect of rotation number

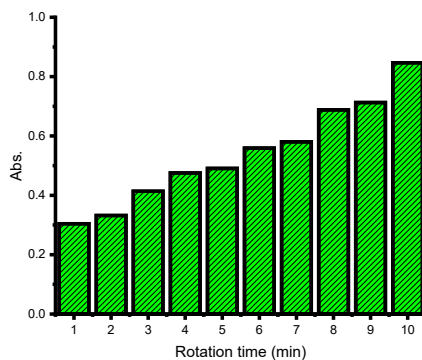


Fig. 16. Effect of the rotation time

The effect of 20-fold molar excess of many species of various cations was tested in the determination of Cadmium (II) with 5BIPQ ligand. The results are in a table 4 showed that these cations did not interfere in the determination of Cadmium (II) with 5BIPQ.

Tab. 4. Effect of interference on the Cd-complex formation	Cation	Reco. %
	Pb ⁺²	97.3
	Cu ⁺²	92.5
	Ni ⁺²	91.7
	Cr ⁺²	96.3
	Al ⁺³	89.4
	Mn ⁺²	93.2

Analytical performance

A linear calibration curve from 1.0 µg mL⁻¹ to 11.0 µg mL⁻¹ for Cd was achieved under the optimal conditions mentioned above, with regression coefficients (R²) always better than 0.9964, Figure 17 For Cd, the Limits of Quantification (LOQ) and detection (LOD) were 0.48 µg mL⁻¹ and 0.16 µg mL⁻¹ (LOQ=10 Sb/m and LOD=3.3 Sb/m), respectively. Relative standard deviation

(RSD%) was used to calculate the DLLME technique at three different doses of 3.0 µg mL⁻¹, 5.0 µg mL⁻¹, and 7.0 µg mL⁻¹ (Table 5). For Cd, the RSD% was discovered to be less than 1.3%, 2.4%, and 4.1%. The accuracy based on recovery was calculated as the ratio of the ions' final concentration to their beginning concentration in the sample solution. There was a 95.2% to 100% recovery.

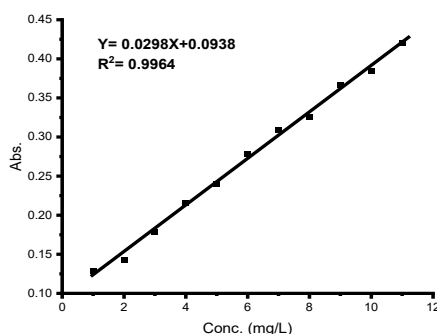


Fig. 17. Calibration curve Cd-complex in the DLLME

Validation of the method

It was looked into if the two methods for analyzing cadmium ions in their pure form and in their aqueous samples were valid. Table 5 below contains the findings for pure ions. Analyzing three replicas of the cadmium ion allowed researchers to check the procedures'

accuracy and precision. The best precision and reproducibility of the procedures are indicated by the low relative standard deviations (RSD%) figures. The table 5 contains the findings of the examination of cadmium ions. The RSD% data were low, and the results were repeatable (Table 6).

Tab. 5. Analytical and statistical parameters of Spectroscopy and DLLME method	Parameter	Before extraction	DLLME
	λ max (nm)	414	
	color	Yellow	
	linearity range mg/L	1.0 mg/L-50.0 mg/L	1.0 mg/L-11.0 mg/L
	Molar absorptivity (L.mol ⁻¹ cm ⁻¹), ε	3.46 × 10 ³	3.34 × 10 ³
	Sandell's sensitivity µg/cm ²	0.032 µg/cm ²	0.033 µg/cm ²
	Correlation coefficient (R ²)	0.9966	0.9964
	Regression equation	Y=0.03081 X+0.13725	Y=0.0298 X+0.0938
	Slope(b)	0.03081	0.0298
	Intercept(a)	0.13725	0.0938
	Enrichment factor (EF)	-----	20.2
	Preconcentration factor (PF)	-----	12.5

Limit of detection mg /L LOD	0.71	0.16
Limit of quantification mg/L LOQ	2.17	0.48
*C.L. for the X1 mg/L at 95%	9.66 ± 0.65	2.98 ± 0.06
*C.L. for the X2 mg/L at 95%	19.70 ± 0.39	5.01 ± 0.18
*C.L. for the X3 mg/L at 95%	29.88 ± 0.51	6.67 ± 0.41
T-test _{cal.} (T-test _{able.}) [26]	0.54(3.18)	0.54(3.18)
F-test _{cal.} (F-test _{able.}) [26]	1.62(9.55)	1.62(9.55)

*Spectroscopy method (X1=10, X2=20, X3=30), DLLME (X1=3, X2=5, X3=7)

Tab. 6. Application of the suggested methods (Spectroscopy, DLLME and AAS) for the evaluation of cadmium ions

Station	Conc. of Cadmium $\mu\text{g}/\text{mL}^{-1}$			RSD (%) n=3
	Add ($\mu\text{g}/\text{mL}$)	Spectrophotometric method	AAS	
Station 1	----	0.81	0.87	0.81
	2	2.93		0.99
	3	3.85		0.72
	----	0.55		3.28
Station 2	2	2.61	0.64	2.77
	3	3.59		1.93
	----	0.85		0.24
Station 3	2	2.81	0.92	0.83
	3	3.96		1.44
		DLLME method	AAS	
	----	0.78	0.87	1.7
2	2.82	1.1		
3	3.98	2.3		
----	0.64	0.67		
Station 2	2	2.61	0.64	1.2
	3	3.59		2.4
	----	0.95		3.06
Station 3	2	2.88	0.92	3.33
	3	3.91		2.71

CONCLUSION

Within 10 minutes, Cd (II) can be micro extracted instantly using the 5BIPQ reagent as an auxiliary ligand. As a result, the developed improved analytical method is simple, quick, sensitive, and synergistic for spectrophotometric determination of Cd (II). A sensitive analytical chromogenic reagent with very low reagent

concentration in a single step can be used to estimate trace concentrations of Cd (II). With a putative stoichiometry of extracted species 1:2 (M:L), the cadmium-5BIPQ complex remained stable for more than 10 hours. An accurate determination of the presence of cadmium in the generated water from Halfaya oil field samples was made.

REFERENCES

1. Kalthor EG, Behbahani M, Savabi A. Spectrophotometric determination of selected heavy metals in real samples at trace levels by combination of solidified floating organic drop micro-extraction and net analyte signal-based method. *Appl Chem*. 2019;14:55-66.
2. Nabid MR, Preparation and application of poly (2-amino thiophenol)/MW-CNTs nanocomposite for adsorption and separation of cadmium and lead ions via solid phase extraction. *J Hazard Mater*. 2012;203:93-100.
3. Bagheri A, Simultaneous separation and determination of trace amounts of Cd (II) and Cu (II) in environmental samples using novel diphenylcarbazide modified nanoporous silica. *Talanta*. 2012;89:455-461.
4. Kakavandi MG, Behbahani M, Omid F, Hesam G. Application of ultrasonic assisted-dispersive solid phase extraction based on ion-imprinted polymer nanoparticles for preconcentration and trace determination of lead ions in food and water samples. *Food Anal Methods*. 2017;10:2454-2466.
5. Echioda S, Oguniye AO, Salisu S, Abdulrasheed AA, Chindo IY, et al. UV-Vis spectrophotometric determination of selected heavy metals (Pb, Cr, Cd and As) in environmental, water and biological samples with synthesized glutaraldehyde phenyl hydrazone as the chromogenic reagent. *Eur J Adv Chem Res*. 2021;2:1-5.
6. World Health Organization. Boron in drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality. World Health Organization; 2009.
7. Bakhshpour M, Denizli A. Highly sensitive detection of Cd (II) ions using ion-imprinted surface plasmon resonance sensors. *Microchem J*. 2020;159:105572.
8. Rose M, Knaggs M, Owen L, Baxter M. A review of analytical methods for lead, cadmium, mercury, arsenic and tin determination used in proficiency testing. *J Anal At Spectrom*. 2001;16:1101-1106.
9. Muraviev D. Application of extraction and ion exchange chromatographic techniques for the separation of metal ion mixtures: problems and perspectives. *Solvent Extr Ion Exch*. 2000;18:753-778.
10. Osipova EA, Sladkov VE, Kamenev AI, Shkinev VM, Geckeler KE. Determination of Ag (I), Hg (II), Cu (II), Pb (II), Cd (II) by stripping voltammetry in aqueous solutions using complexing polymers in conjunction with membrane filtration. *Anal Chim Acta*. 2000;404:231-240.
11. Sato H, Ueda J. Electrothermal atomic absorption spectrometric determination of cadmium after coprecipitation with nickel diethyldithiocarbamate. *Anal Sci*. 2000;16:299-301.
12. Gurkan R, Altunay N. Determination of trace cd in alcoholic and nonalcoholic beverages by coupling cloud point extraction with spectrophotometry. *Polish J Food Nutr Sci*. 2013;63. 253-260.
13. de A. Bezerra M, Arruda MAZ, Ferreira SLC. Cloud point extraction as a procedure of separation and pre-concentration for metal determination using spectroanalytical techniques: a review. *Appl Spectrosc Rev*. 2005;40:269-299.
14. Ojeda CB, Rojas FS. Separation and preconcentration by a cloud point extraction procedure for determination of metals: an overview. *Anal Bioanal Chem*. 2009;394:759-782.
15. Schiavo D, Neira JY, Nóbrega JA. Direct determination of Cd, Cu and Pb in wines and grape juices by thermospray flame furnace atomic absorption spectrometry. *Talanta*. 2008;76:1113-1118.
16. Pyrzynska K, Kilian K. On-line sorption-based systems for determination of cadmium with atomic spectrometry detectors. *Water Res*. 2007;41:2839-2851.
17. Dadfarnia S, Shabani AMH. Recent development in liquid phase microextraction for determination of trace level concentration of metals—A review. *Anal Chim Acta*. 2010;658:107-119.
18. Marguí E, Queralt I, Hidalgo M. Determination of cadmium at ultratrace levels in environmental water samples by means of total reflection X-ray spectrometry after dispersive liquid-liquid microextraction. *J Anal At Spectrom*. 2013;28:266-273.
19. Kareem NK, Thani MZ, Al-Rawi KF. New approach for determination of Phenylephrine HCl in Pure and Pharmaceutical Formulation using various Microextraction Methods. *Res J Pharm Technol*. 2022;15:1648-1652.
20. Kareem NK, Al-Rawi KF. New microextraction methods for the evaluation of bromhexine HCl in pure and pharmacological formulations. *Egypt J Chem*. 2022;65:1-2.
21. Kraševac I, Prosen H. Development of a dispersive liquid-liquid microextraction followed by LC-MS/MS for determination of benzotriazoles in environmental waters. *Acta Chim Slov*. 2019;66:247-254.
22. Quigley A, Cummins W, Connolly D. Dispersive liquid-liquid microextraction in the analysis of milk and dairy products: A review. *J Chem*. 2016.
23. Al-Chaarani N, El-Nakat JH, Obeid PJ, Aoud S. Measurement of levels of heavy metals contamination in vegetable growth and sold in selected areas in Lebanon. *Jordan J Chem*. 2009;4:303-315.
24. Thani MZ, Dadoosh SA, Fahad AS, Abdullah AM, Fahad YS. Synthesis of New Azo Compound and its Application for Spectrophotometric Determination of Sulfamethoxazole and Extraction using Cloud Point Extraction. 2022;12:1311-1318.
25. Parikh KS, Patel RM, Patel KN. New spectrophotometric method for determination of cadmium. *E-Journal Chem*. 2009;6:496-500.
26. Laskar MA, Siddiqui S, Islam A. Reflection of the Physiochemical Characteristics of 1-(2-pyridylazo)-2-naphthol on the Pre-concentration of Trace Heavy Metals. *Crit Rev Anal Chem*. 2016;46:413-423.
27. Kumar BN, Kumar SH, Redhi GG. Spectrophotometric determination of cadmium (II) in water and soil Samples using Schiff's bases. *Asian J Chem*. 2016.