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RESEARCH ARTICLE

Application of Dispersive liquid-liquid micro extraction combined with spectrophotometric technique for preconcentration and determination of Cadmium using new organic reagent

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ABSTRACT:

A new organic reagent namely 5-(4- isopropoxy-6-(methyl amino)-5- nitrosopyrimidine-2-yl) diazenyl) quinolin-8-ol (IMNDQ) was synthesized, characterized and employed for the estimation of Cadmium (II) afterwards preconcentration using Dispersive liquid- liquid microextraction (DLLME). In this precocentration method, chloroform and methnol were used as extraction and disperser solvents respectively and the ligand 5- (4- isopropoxy-6-(methyl amino)-5- nitrosopyrimidine-2-yl) diazenyl) quinolin-8-ol was used as a reagent for the extraction of Cd (II), Visible spectrophotometry was used for the estimation of the analyte after preconcentration. The influence of various factors on the extraction was investigated, for example disperser and extraction solvent type, pH and concentration of chelating agent. At optimum condition, the enrichment factors of (95) was gotten ,the calibration graph was linear in the range (20-100) ng .mL⁻¹ Cd⁺² with detection limit of (4.46) ng .mL⁻¹ and relative standard deviation (RSD) for seven duplicate measurements of 60 ng .mL⁻¹ of Cd⁺² was (1.12)%. The method was used to the estimation of Cd⁺² in some food samples.

KEYWORDS: Application, Dispersive liquid- liquid microextraction, Cadmium, preconcentration, new organic reagent.

INTRODUCTION:

Heavy metal present a serious threat to the environmental system due to toxicological effects on living organism. Cadmium is known as the sixth most poisonous substance which has no important function in human body and exposure to this heavy metal is known to cause cancer and targets the bodys gastrointestinal, cardiovascular, reproductive and respiratory systems¹⁻².

Cadmium enters in human body through food, air and water and because of its present at low concentrations in these matrices which fall below the detection limit of the conventional analytical techniques such as UV-VIS, FAAS and ICP-OES, thus the determination of cadmium in these matrices requires a sample pretreatment step before detection, the main target of this step is to both clear-out and enrich the cadmium³.

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Numerous preconcentration techniques to estimate Cadmium have been designed including separation methods for example solid phas extraction⁴⁻⁸, cloud point extraction⁹, coprecipitation¹⁰⁻¹³, flow-injection on –line sorbent extraction¹⁴, Liquid – Liquid extraction¹⁵⁻¹⁶ and dispersive Liquid – Liquid microextraction (DLLME).¹⁷

DLLME is an extraction technique centered on the use of triple solvent system in which miniaturized volume of solvents are used in procedures, Extraction solvent is used to extract the analytes from the sample and dispersion solvent is used to promoting the rapid transfer of analytes of interest from the samples¹⁸.

Diverse spectrophotometric methods have been united with DLLME for the estimation of Cadmium, , such as, atomic fluorescence¹⁹, inductively coupled plasma with optical emission (ICP-OES)^{20,21}, total reflection X-ray²², atomic absorption (AAS)^{23,24}, and UV-Visible^{25,26}, Between them, UV-Visible has been, definitely, the most broadly employed owing to its speed, easiness, flexibility, precision, accuracy, and cost-effectiveness. This method is usually employed in analytical chemistry for quantitative measurements of diverse analytes for example greatly conjugated organic reagents, and transition metal ions.

In the existing research, a new azo component namely 5-(4- isopropoxy-6-(methyl amino)-5- nitrosopyrimidine-2-yl) diazenyl) quinolin-8-ol was prepared, characterized, and exploited as a chelating reagent to consider (DLLME) method for preconcentration of ultra trace amounts of Cadmium ion using Chloroform (extractant solvent) and Methanol (disperser solvent) and their estimation by UV- Visible spectrophotometry. The established method was useful for the estimation of a trace amounts of cadmium (II) in food.

MATERIAL AND METHODS:

Chemicals and reagents:

The chemicals used in this research including, a 8-Hydroxyquinoline (Sigma Aldrich, Germany), Ethanol absolute (Scharlau, Spain), Sodium nitrite, sodium hydroxide (B.D.H, England), Hydrochloric acid (Him, India). Store solutions of Cd(II) ion (1000μ g.m L⁻¹) were ready by dissolving (2.686g)CdCl_{2.}2H₂O in deionized water. Working standard solutions of cadmium ion were freshly made by dilution the store standard solution.

Instrumentation:

Melting points were measured on a melting point apparatus (SMP3/Stuart, UK). NMR data were obtained on 400 MHz(1H) (13C) spectrometers (Bruker, Germany) with tetramethylsilane (TMS) as internal standard.

Either devices used in the spectral measurements are Infrared spectroscopy of type FT-IR spectrophotometer

(Shimadzu, Japan) where KBr tablet used as a reference for those measurements.

PG Instrument T80+ UV/Vis-Spectrometer (England) was employed for the scanning the absorption spectra of the complex created, and absorbance measurements were executed by spectrophotometer UV-7804C (China). The pH results were performed with a pH meter Philip PW model 9412.

Synthesis procedure of reagent namely 5-(4isopropoxy-6-(methyl amino)-5- nitrosopyrimidine-2-yl) diazenyl) quinolin-8-ol (IMNDQ)²⁷

dissolving 1g (0.0047 mol) of 6-isopropoxy-N-methyl-5-nitrosopyrimidine-2.4-diaminein in 40ml deionized water and 4ml hydrochloric acid concentration cooling and stirring with continuously at (0-6)°C and then adding Sodium nitrite solution prepared by dissolved 0.32g (0.0047mol) in 30ml deionized water by dropping to the solution of amine derivative and stirring at 0°C in ice bath for 30 minutes, then quit the solution to 20 minutes. The resulting solution of diazonium chloride was added drop by drop with constant stirring to solution 0.68g (0.0047 mol) of 8-Hydroxy quinolone dissolved in 50 ml ethanol and 20ml 5% NaOH then orange color observed, left the mixture to stable for one hour followed by addition amount of deionized water then adjusting the pH of solution to pH=6, leaving the solid precipitate for overnight then filtered and washed by deionized water.



Fig 1: Synthesis of azo reagent 5-((4-isopropoxy-6-(methylamino)-5-nitrosopyrimidin-2-yl)diazenyl)quinolin-8-ol (IMNDQ)

Dispersive liquid-liquid microextraction procedure:

The acidity of a (10ml) of the solution having Cd^{+2} in the rang (20-100)µg/L was adjusted to (pH=7) with 1.0 mol/ L acetate buffer and 1ml of reagent (IMNDQ) (1.0×10^{-1}) ³mol L-1)was placed in 10ml test tube with conical bottom . and (300)µL of methanol as(disperser solvent) having (200)µL of chloroform as (extraction solvent) was injected quickly in to the sample solution by a (1mL) syringe. A bleary solution (water, methanol and chloroform) was made in the tube, in this move Cd⁺² complex was extracted into very fine drops of chloroform in few seconds. The mix was thereafter centrifuged for 5 min at 3000rpm, next this process the dispersed fine drops of chloroform were precipitated at the bottom of the tube, then the sediment was diluted by 0.5ml of ethnol and the amount of Cd (II) ion was estimated at λ^{max} (652)nm.

Preparation of samples: Milk Powder Sample preparation²⁸

Milk Powder: 1.0g of milk powder (samples of Milk Powder were collected from the market (Dewanyia, Iraq). was weighed into a 50mL porcelain crucible, and then the powder was burnt at electric furnace., the crucible with the sample was heated up in the furnace with temperature of 500 ± 25 "°C for 4 h. After cooling the remainder was solved in 50mL 1%(v/v) HNO3. The pH of the sample solutions was checked by acetate-acetic acid buffer after the solutions volume was close 50 mL and then complete the solutions to 50mL.

White sugar sample preparation²⁹:

1.0g from each sample was exactly weighed and transmitted to a 25ml Teflon microwave acid-digestion vessel. A 4.5ml of concentrated nitric acid and a 6.0ml of 30% H₂O₂ were added. The vessels were firmly closed and then placed in the microwave oven. The

system was worked at whole power for 3.0min. The digest was vaporized to dryness. The remainder was solved with 10ml of 5% nitric acid and was then filtered.

Infrared spectra:

The infrared spectrum data of the reagent (IMNDQ) appeared band at (3286) cm⁻¹ for (O-H), 3039 cm⁻¹ for (Ar-H), 869cm⁻¹ for (C-H) for (CH₃),1589cm⁻¹ for nitroso group (N=O),1658cm⁻¹ for (C=N) of aromatic ring,1404 cm⁻¹ for (N=N) and 1520cm⁻¹ due to aromatic(C=C) and 1296 cm⁻¹ for (C-O) bond.

H¹ NMR Spectra:

The ¹HNMR (DMSO) spectrum data of the reagent (IMNDQ) show δ :6.9-8.2 (m, 5H, Ar-H), 1.2 (m, 6H, CH₃), 3.3 (s, 1H, NH), 10(s, 1H, OH), 2.8 (s, 3H, CH₃), 4.5 (m, 1H, CH-O).



Fig 2: A:H NMR Spectra of ligand (IMNDQ) B: ¹³C NMR Spectra of ligand (IMNDQ

C¹³-NMR Spectra:

The C¹³-NMR (DMSO) spectrum data of the reagent (IMNDQ) showed signals δ at: 21.6 for (C1), 26.4 for (C3),75(C2),112.6(C9),123(C12),124.7(C7),126(C8),13 0.4(C14),137(C13)atoms,138.3(C4),140(C11),152(C10), 156(C5),161.3(C15),185.9(C6).

Absorption spectra:

The electronic spectra of (IMNDQ) $_2$ Cd complex was registered versus a reagent blank prepared with the same conditions. The spectrum of Cd(II) complex display the maximum absorption at 652 nm with molar absorptivities of 6.5×10^5 L mol⁻¹cm⁻¹. While, the reagent (IMNDQ) gave the maximum absorption at 514 nm as described in Figure (3 a).





Fig3: A: Absorption spectra of (IMNDQ) Reagent = 1×10^{-3} M , (IMNDQ)₂Cd complex, Cd(II) =60 ng mL⁻¹, (IMNDQ) =0.4 mL of 1×10^{-3} M, Buffer pH = 7, B: The probable chemical structure of the cadmium (II) complex

The chelating agent (IMNDQ) reacts with Cd(II) ion at pH 7 forming a green complex, and the absorbance reached its maximum within 5 min and stayed constant, for at least one day. The stoichiometry of (IMNDQ)₂Cd complex was studied, in the recognized experimental conditions, by mole ratio and Job's methods. The gained results showed that the composing of complexes was (1: 2). In addition this complexes was described by spectroscopic techniques and the proposed related chemical structure is shown in figure (3b)

Optimization of DLLME method:

The effect of special factors which impact the DLLME procedure for Cd^{+2} complex such as type of the disperser and extraction solvents, pH and the concentration of reagent were examined using one variable-at-a-time (OVAT) strategy in checking of the best possible conditions, to increase the sensitivity and detection limit of Cd^{+2} complex in the selected matrices. Each

experiment of the following variables were followed the general DLLME procedure.

Effect of type of the extraction and disperser solvents:

In the DLLME extraction solvent should be low solubility in water ,higher density than water, and an extraction capability of the interested compound , To study this effect four different solvents such as ethanol, chloroform, methanol, and carbon tetra chloride were tested and according to the absorbance signals at (652) nm, the most suitable solvent was chloroform (Fig 4a). also the disperser solvent should be mixable with both water and extraction solvent. Therefore ethanol, acetone, methanol and acetonitrile were examined as disperser solvent. Under the similar conditions, and according to the absorbance signals at (652) nm, the most suitable solvent was methanol. (Fig 4b).



Fig. 4: A :Effect of type of the extraction solvent on the formation of Cd (II) complex by DLLME [Conditions: 60 ng mL⁻¹ Cd(II) (IMNDQ)=, 0.4 mL of 1x 10⁻³M (b) :Effect of type of the disperser solvent on the formation of Cd (II) complex by DLLME [Conditions: 60 ng mL⁻¹ Cd(II) , 0.4 mL of 1x 10⁻³M (IMNDQ)

Effect of pH:

The pH is a very important factor for the complexation of the ligand with the metal ions and their subsequent extraction by DLLME methodology. Thus the impact of pH was studied by acting a number of DLLME experiments and changing the pH of sample solution over a varied range (2 -9) using diverse pH acetate buffer solutions. The results are shown in Figure(5a). As can be noticed from **Fig(5a).** that the absorbance first increased with increasing pH and attained a maximum at pH 7.0. Afterwards, the absorbance regularly decreased because of partial dissociation of the complexes at greater pH, which may result in deficient extraction of complexes. So, pH 7.0 was chosen as the best pH' for complete formation of Cd (II) complex.



Fig.5: A: Effect of pH on the formation of Cd (II) complex by DLLME [Conditions: 60 ng mL⁻¹ Cd(II), 0.3 mL of 1x 10^{-3} M (IMNDQ), b: Effect of concentration of reagent (IMNDQ) on the DLLME of Cd (II) [Conditions: 60 ng mL-1 Cd(II), X mL of 1x 10-3M reagent, pH =7

Effect of 5-(4- isopropoxy-6-(methyl amino)-5nitrosopyrimidine-2-yl) diazenyl) quinolin-8-ol (IMNDQ) concentration:

DLLME effectiveness The depends on the hydrophobicity of the ligand and the complex formed. So, in order to evaluate the role of chelating agent in DLLME of Cd(II), similar DLLME experiments were performed by adding varying volume from 0.1 to 0.7mL of 1 x 10^{-3} mol L⁻¹ from this reagent to a suitable concentration, 60µg .L⁻¹ of Cd(II) at pH 7. Figure (5b) displays that, at low(IMNDQ) concentration, the analytical responses of the analyte is low because the quantity of ligand required for complexation of all the quantity of the analytes is insufficient. Then, the analytical responses significantly increases by increasing (IMNDQ) concentration till maximum absorbance was attained at 0.4 mL (IMNDQ). The absorbance of the analytes remains constant upon the use of higher concentrations of the chelating agent. Consequently, 0.4 mL of 1 x 10⁻³ mol L⁻¹ of (IMNDQ) was chosen as optimum for Cd(II) ion.

Calibration graphs:

In the enhanced conditions determined by DLLME method, a group of standard Cd(II) solutions ranging from 20-100 ng mL⁻¹, was taken and undergone to the general DLLME so as to check the linearity of the method. The statistical valuation for the calibration

graphs has displayed that a strong connection among signal and Cd(II) concentration may occur (r = 0.9998). The statistical analytical results for the calibration data for Cd(II) is summed up in Table 1.

Table 1	 Method 	validation a	of the	determination	Cd(II) complex
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Cd(II)	Parameter
y = 0.009+ 0.0031 x	Regression equation
0.9998	Correlation coefficient(r)
0.00463	Std. dev. of regression line (sy/x)
20-100	Concentration range (ng mL-1)
4.46	Limit of Detection (ng mL-1)
14.88	Limit of Quantitation (ng mL-1)
3.2x10-4	Sandell's sensitivity (µg cm-2)
6.5×105	Molar absorptivity (L.mol-1.cm-1)
1:2	Composition of complex (M:L)*
1.12 %	RSD% (n=7)
95	Enrichment factor (EF)**

**EF is calculated as the ratio of slope of calibration curves obtained with and without DLLME

The suggested method has attained enriching factor of 95 fold and this allowed to get on the detection limit of 4.46 μ g.L⁻¹ for Cd(II) in aqueous solution. It can be concluded that the new organic ligand in this work aside from DLLME -Spectrophotometry gave acceptable analytical figures of merit for Cd(II) which were much better than with those gotten by selected prior studies (Table 2). But, they were in harmony with most studies that used analytical methods in incorporation with DLLME.

 Table 2: Comparison of the suggested Method of DLLME with the selected prior methods

Preconcentration technique	LOD	Linear range	Sample	Ref
DLLME-GFAAS	0.6ng / L	2-20ng / L	water	30
DLLME-ICP-MS	0.53µg / L	1-1000µg / L	water	31
DLLMG-FAAS	0.4µg / L	5-100µg / L	Water and food	32
NB-DLLME UV-Vis	6.3µg / L	50-900	Tap water	33
DLLME-FAAS	0.03µg / L	-	Saline	34
DLLME-UV-Vis	0.016ng / L	-	Water and food	35
DLLME-UV-Vis	μg /L 4.46	20-100	Food	This work

Effect of interference:

The influences of some metal ions on the preconcentration and estimation of 60 μ g. L⁻¹ Cd (II) solutions were tested subsequent the general DLLME method. It is approved that an unrelated ion considered to interfere acutely when it provides a relative error percent of further than ± 5%. The results indicated that a some of metal ions like, Na (I),Ca (II),)and, K (I), have no significant influences on the cadmium ion responses, whereas the another metal ions like, Ni(II), Zn(II), Co(II) Mn (II), Cr (III),A g (I) and Fe (III) have exceeded the allowable limits of interferences for Cd(II) as shown in Table 3.

Most of these interferences can be simply overcome by masking with suitable reagents

Table 3. Effect of divers ions on the absorption signal of Cd(II) (60 ng mL⁻¹, Abs= 0.698 by DLLME-spectrophotometry

Interfering	Interferent /	Α	ΔΑ	Erel
ion	Cd(II)			(%)
\mathbf{K}^+	1000	0.695	-0.003	-0.43
Na ⁺	1000	0.696	-0.002	-0.28
Mg^{+2}	1000	0.695	-0.003	-0.43
Ca ⁺²	1000	0.699	0.001	0.14
Ni ⁺²	250	0.658	-0.04	-6.07
Zn^{+2}	250	0.662	-0.036	-5.43
Co ⁺²	250	0.653	-0.045	-6.89
Mn ⁺²	250	0.659	-0.039	-5.91
Cr ⁺³	250	0.652	-0.046	-7.05
Ag ⁺¹	250	0.655	-0.043	-6.56
Fe ⁺³	250	0.650	-0.048	-7.38

Determination of Cadmium ion in food samples:

So as to confirm the validity of the suggested DLLME procedure, the mode has been utilized to the estimation of the traces of Cd(II) in milk powder and white sugar samples. The results and the recoveries for the samples

were presented in Table 4 and Table 5. It can be observed that the recovery for the samples is between 91% and 98% for milk sample and between 92% and 95%. for white sugar samples.

able 4. Determination of Cu (11) in Mink powder samples				
Milk powder	Added	Found	Recovery	
Sample	(µg.g ⁻¹)	(µg.g ⁻¹)	%	
1	0	2.9±0.2	-	
	5	7.8±0.3	98	
	10	12.5±0.6	96	
2	0	3.2±0.3	-	
	5	7.9±0.5	94	
	10	12.3 ± 0.1	91	
3	0	1.7±0.4	-	
	5	6.4±0.1	94	
	10	11.3±0.1	96	

Table 4: Determination of Cd (II) in Milk powder samples

Table5: Determination of Cd (II) in White sugar powder

White sugar Sample	Added (µg.g ⁻¹)	Found (µg.g ⁻¹)	Recovery %
1	0	1.3±0.4	-
	5	5.9±0.1	92
	10	10.8±0.2	95
2	0	3.2±0.5	-
	5	7.9±0.2	94
	10	12.4±0.3	92

CONCLUSION:

In this part of work, a new DLLME coupled with spectrophotometric method using synthesized ligand was established for the determination of Cd(II) in some food samples. The combined advantages of the DLLME methodology was rapid, easy, safe and inexpensive). The method gives good RSD values and a very low limit of detection. The results of this study clearly show the versatility and potential of this method, which could be applied to monitoring Cd spectrophotometrically in various food samples.

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