Article

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Separation and Spectral Determination of Cd(II) as a Chelation Complexes in Aqueous Solution and Food Samples by Using 4-((4-hydroxyquinolin-3-yl) diazenyl) benzene sulfonamide and 3-((1H-indol-5-yl) diazenyl)quinolin-4-ol

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Abstract

This study reports on a cloud point extraction (CPE) method devised for the thorough separation, preconcentration, and spectrophotometric estimation of cadmium (Cd(II)) from solutions and food matrices using azo derivatives as complexing agents. The research problem under study concerns the sensitive and selective determination of Cd(II), a heavy metal recognized as toxic due to its profound environmental and health dangers. The specific aim was to optimize and check CPE method reproducibility for the more stable chelation complexes of cadmium (II) 4-((4-hydroxyquinolin-3-yl)diazenyl)benzenesulfonamide (HQDBS) and 3-((1H-indol-5-yl)diazenyl)quinolin-4-ol (IDQ). The optimization was performed by testing the following fundamental parameters: pH, type and volume of surfactant (Triton X-100), extraction temperature, and duration of heating. The maximum absorptions (λmax) of both examined complexes of cadmium with HQDBS and IDQ were found at 478 nm and 499 nm respectively. The spectroscopic methods and field emission scanning electron microscopy (FE-SEM) were applied to structural characterization of the extracted complexes. The developed method was applied to food samples and validated with Flame Atomic Absorption Spectroscopy (FAAS). It was showed that the methods gave highly sensitive and good selective responses which had a strong correlation with the FAAS results. F-test statistical calculations showed that the differences between techniques are insignificant, thus proving the reliability of CPE methodology expected for Cd(II) analytical chemistry. The CPE technique is recommended for determining the presence of Cd(II) in food and environmental samples since it is easy, economical, and less harmful to the environment.

Keywords: Cadmium (Cd(II)), Azo Derivatives, Cloud Point Extraction (CPE), Heavy Metal Analysis, Environmental Monitoring, Food Sample Analysis, Triton X-100, Preconcentration Technique.

Introduction

The assessment of occupational and environmental risks is closely linked to the monitoring of heavy metals in various matrices [1]. When working with environmental or biological samples, preconcentration or separation methods are usually necessary due to the low concentration of the relevant analytes [2]. One of the most toxic metals, cadmium (Cd), accumulates in humans primarily in the kidneys, liver, and lungs, from where it is excreted with a biological half life of 10–30 years [3]. Furthermore, an ongoing exposure to cadmium within biological systems triggers the calcium homeostasis that leads to cell injury and death. It is also a teratogenic and cancer-causing substance [4] that works by replacing zinc in its action as a cofactor for many enzymes. Cadmium (Cd) enters water naturally through the dissolution of rocks and soils, biological cycles, and atmospheric deposition. Human activities, especially industrial processes and waste disposal, also contribute significantly to cadmium contamination. This includes the production of nickel-cadmium (Ni-Cd) batteries, pigments, electronic devices, and the use of nickel as a catalyst in hydrogenation reactions[5]. Output The most used potable water in the US, which has been cleared by the USEPA, has a maximum contaminant level for CD at 10µg/L [6,7].

The determination of metals at trace levels using atomic absorption spectrometry offers significant sensitivity, good selectivity, high sample throughput, and relative simplicity[8]. For trace analysis, sufficient preconcentration and separation of the analyte from the sample matrix is often required to improve detection limits and reduce matrix and interferences effect. The task was done using coprecipitation and solid-liquid extraction technique, which are very time consuming and wasteful [9-11]. Besides, conventional liquid-liquid extraction uses solvents which are dangerous [12-14]. Nowadays, a notable alternative method to solvent separation and concentration is cloud point extraction (CPE) using a nonionic surfactant [15-18]. In aqueous samples, the nonionic surfactant creates micelles which, when heated to the cloud point temperature, changes to a turbid solution. When heated above the cloud point, the formed micellar system splits into a small volume and an aqueous phase rich in surfactants. CPE is advantageous for non-traditional or innovative approaches due to its effectiveness, low cost and low toxicity when compared to conventional extraction methods [19]. Azo compounds are among the most important colored organic substances, characterized by the presence of a (-N=N-) group in their structure. They are considered essential intermediates in the synthesis of various other organic compounds [20] and play a vital role in inorganic chemistry, serving as key ligands in the formation of many coordination complexes [21]. In analytical chemistry, azo compounds are notable for their vibrant colors and their resistance to water, diverse environmental conditions, and solvents, making them valuable reagents for metal detection [22].

Material and methods

Devises: For the spectrophotometric application and absorbance measurement, a double beam (UV-Vis) spectrophotometer Biochrom (Biochrom Libra) is used. The electrical balance was supported by the use assortment of Electrostatic Water Bath (G. Gerhardt) and A&D Company (Limited Dool CE HR200 Japan). A E163694 CE Germany laboratory pH meter with combination glass electrode was used to measure the pH of liquids

Solutions:

All chemicals used were of highest purity (BDH or Fluka) and used with out further purification. stock solution of 1mg/ml Cd(II) was prepared by dissolving 0.0210g of $Cd(NO_3)_2.4H_2O$ (Fluka) in 100mL purified water through volumetric flask. Organic reagents solution (1×10^{-3}M) **HQDBS and (IDQ)** were prepared by dissolving 0.008 and 0.0072gm respectively in 25mL distil water. Other employed solutions have been organized by dilution with purified water in a suitable volumetric flask, as well as all other solution need in this research prepared at the same procedure.

Cloud point extraction (CPE) procedure:

In a standard cloud point extraction (CPE) procedure, a 10 mL aqueous solution containing 100µg/mL of Cd(II) ion is prepared and 0.001M from organic reagents. A specific volume of the non-ionic surfactant TritonX-100 is added to this solution with optimal pH adjustment. The mixture is then heated in a water bath to reach the appropriate temperature and duration required for the formation of the cloud point layer (CPL). CPL was separated from the aqueous solution and dissolved in 5 mL ethanol. The absorbance of a chelation complexes formed by Cd(II) is determined by measuring at the respective wavelengths of maximum absorbance, which are λ_{max} = 478 nm for Cd(II) with **HQDBS** and λ_{max}= 499 nm for Cd(II) with **IDQ**. The concentrations of Cd(II) remaining in the aqueous phase were quantified spectrophotometrically.

Results and Discussion:

Absorption spectra: Laboratory prepared azo derivatives HQDBS and IDQ were dissolved in ethanol at concentration 1×10^{-4}M give UV-Vis spectrum as in Figures (1,2):

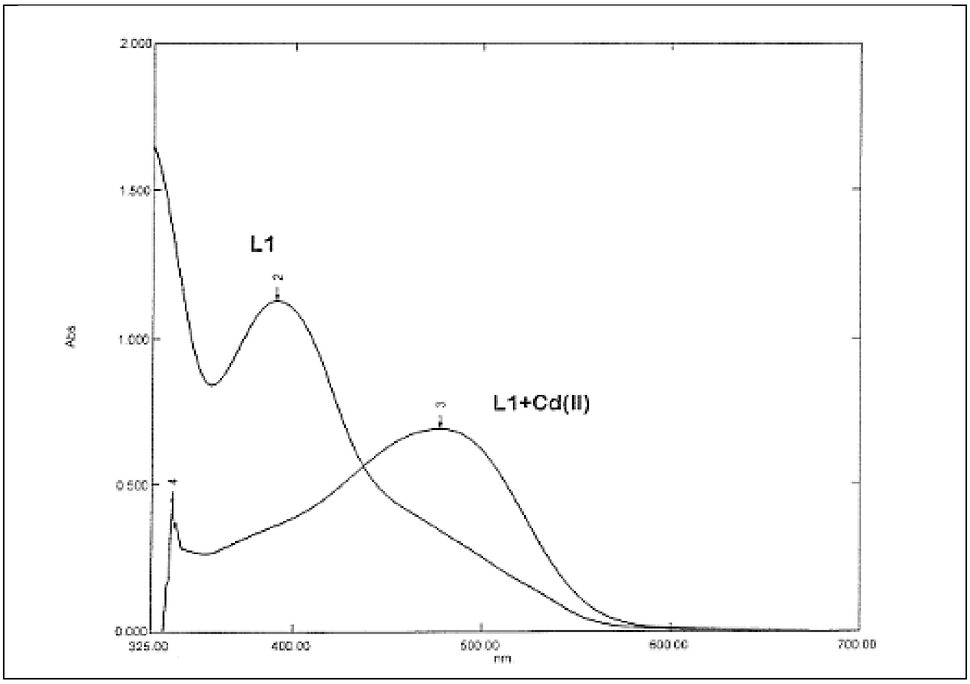


Fig.1. UV-Vis spectra for organic reagent (HQDBS) and Cd(ll)-HQDBS complex

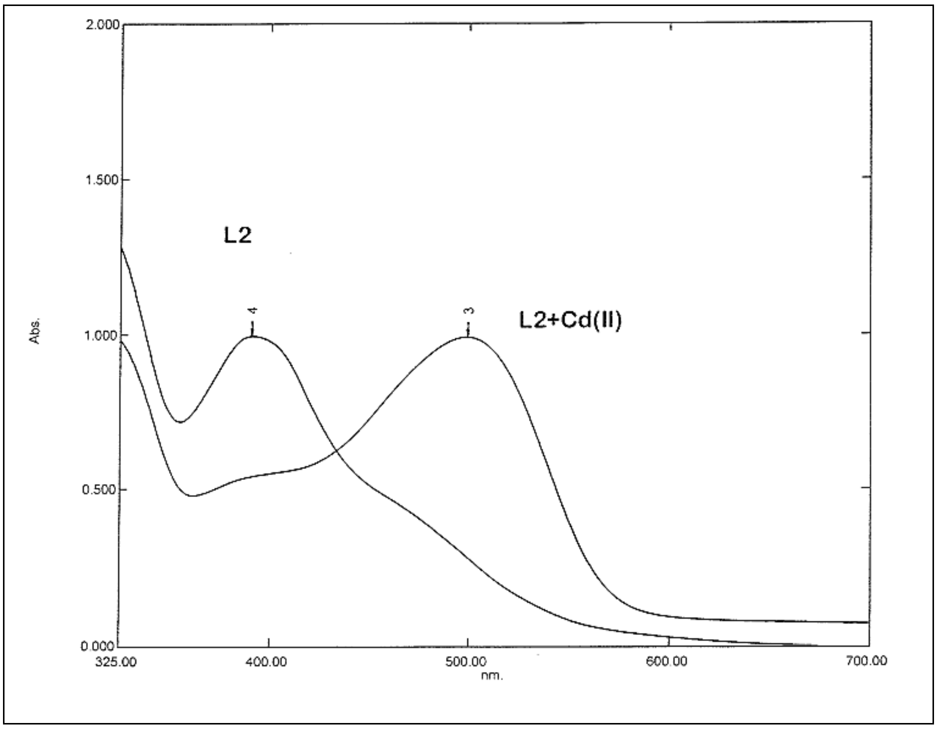
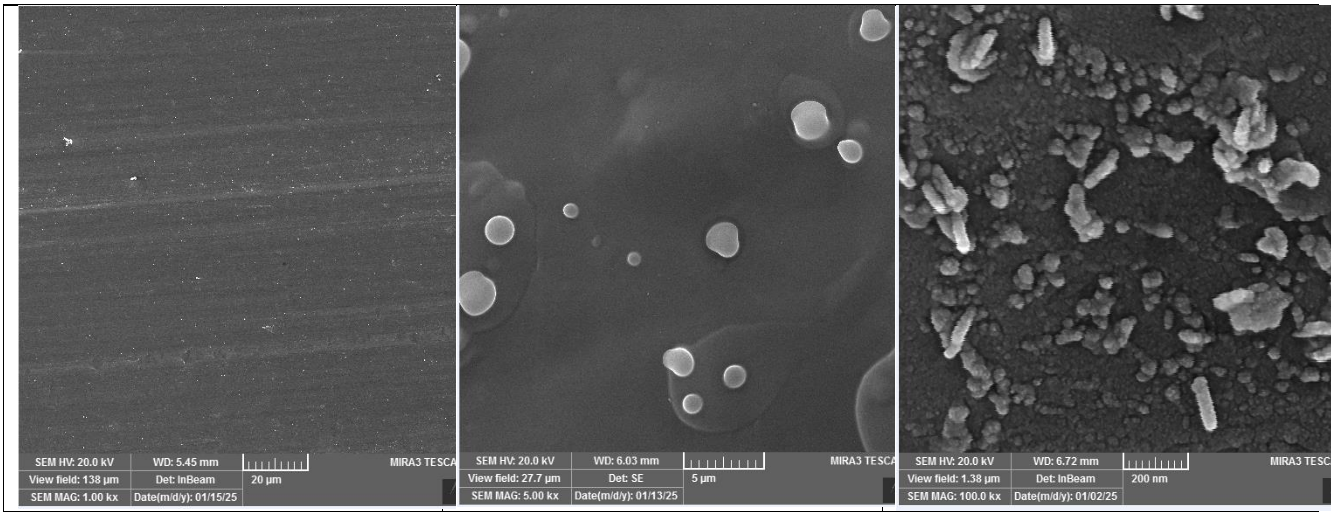


Fig.2. UV-Vis spectra for organic reagent (IDQ) and Cd(ll)- IDQ complex .

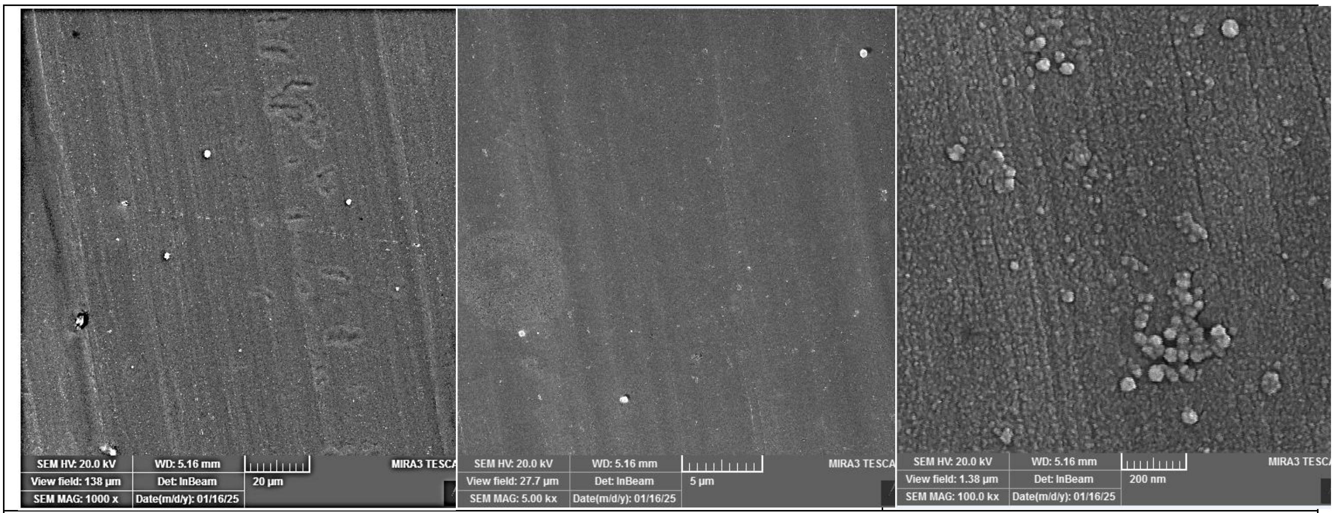
The results show that wavelength for the maximum absorbance of HQDBS and IDQ were at λmax=397nm,390nm respectively. To pinpoint the wavelength of maximum absorbance to chelation complexes of Cd^{+2} were extracted by applying a general method for CPE, 100µg of metal ion under study at fixed optimum pH and UV-Vis. Spectrum demonstrates λmax=478nm for Cd(ll)-HQDBS complex and λmax=499nm for Cd(ll)-IDQ complex.

Characterization of extracted complexes:

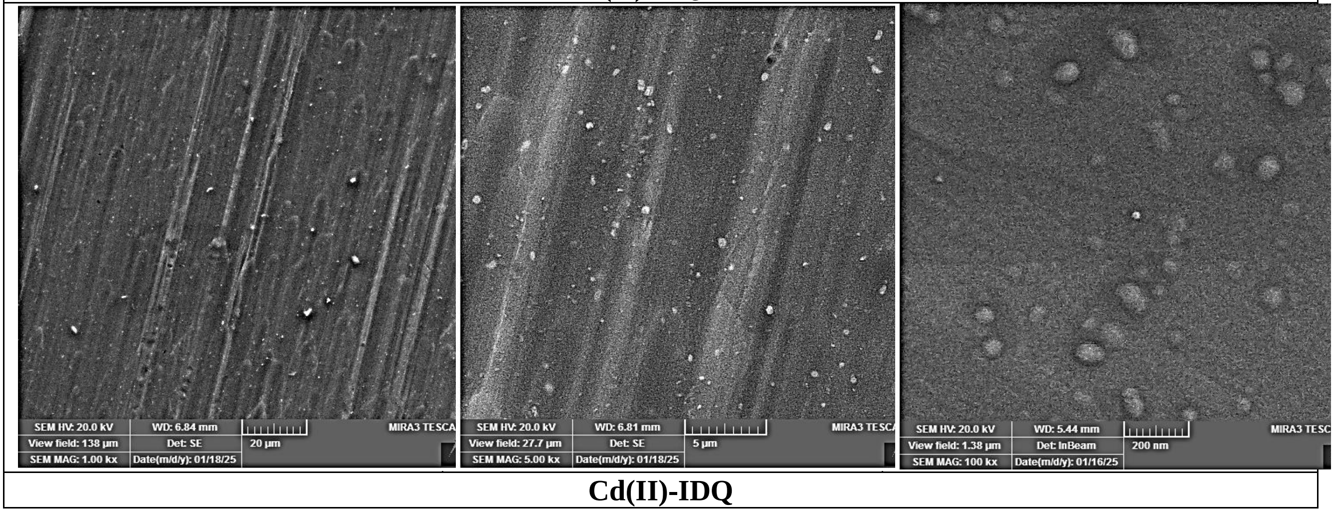
Field Emission Scanning Electron Microscopy (FE-SEM) The surface morphology of Cd(II) extracted complexes with HQDBS and IDQ, and the surfactant TritonX-100 was investigated.



TritonX-100



Cd(II)-HQDBS



Cd(II)-IDQ

SEM imaging of Triton X-100 in Cloud Point Extraction (CPE) usually focuses on capturing the morphology of the surfactant-rich phase, micelles, or any extracted nanoparticles. However, since Triton X-100 is a nonionic surfactant and forms a liquid phase, direct imaging of its pure form can be challenging. The images show embedded Cd(II) ions complexes with HQDBS and IDQ in the surfactant matrix [23,24].

Effect of PH

Te removal of the metal ions using the CPE technique involves extraction of a metal chelate complex containing the requisite amount of hydrophobicity to be extracted from the surfactant enriched medium. The metal ion chelate's formation and later extraction is, ceteris paribus, greatly pH dependent, and so, pH emerge as one of the key parameters for CPE. The pH impact on absorbance and D values of Cd(II)-HQDBS and Cd(II)-IDQ complexes at 478 nm and 499 nm respectively are shown in Figures 3 and 4. The best extraction results were received when the pH was around 8-9. Thus, for further studies, the pH value in the range of 8 – 9 was preferred

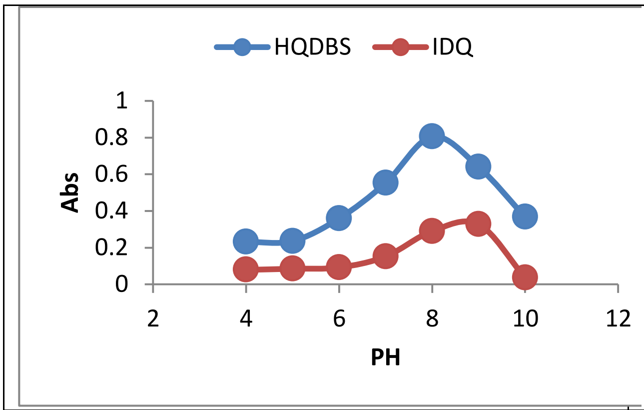


Fig. 3. Effect of pH on absorbance values

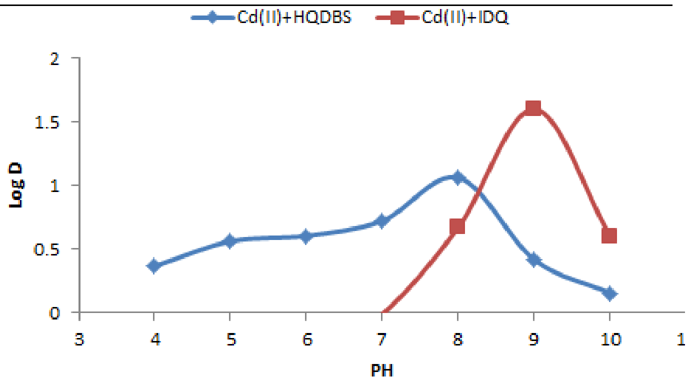


Fig. 4. Consequence of pH on extraction efficiency and D

3.3. Surfactant Volume Effect

To examine the influence of volume of Triton X-100 surfactact on extraction of organic substances, two sets of 10 mL aqueous solutions containing 100 µg of Cd(II) and 1×10^{-4} M organic reagents (HQDBS, IDQ) were prepared at pH 8 and 9, with gradually increasing amounts of Triton X-100 surfactant added. The results are presented in Figures 5 and 6. The results show that 0.5 mL of TritonX-100 is preferred for both organic reagents as it is the volume that enables the extraction efficiency to full with the CPL determined by the critical micelle concentration (CMC) needed to form most efficient interface for extraction with out any further increase in volume of surfactant. Any other volume not conforming to this optimal value will not lead to CMC state hence resulting in poor extraction efficiency[25].

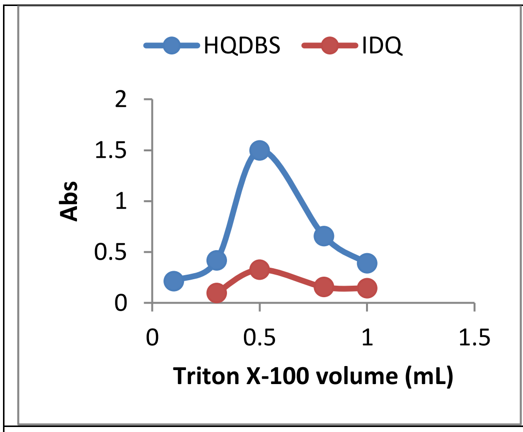


Fig. 5. Effect of Surfactant volume on Excellent CPL Formation.

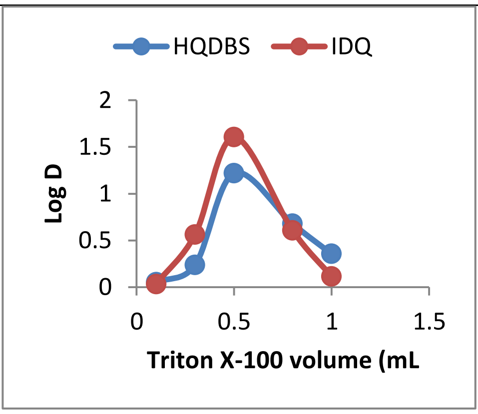


Fig.6. Effect of Surfactant volume on Extraction Efficiency.

3.4. Temperature and Heating Time Effect:

Cadmium (II) was removed from solution while following the overall procedure within a set period of time and at increasing temperatures until CPL formation was achieved. At each temperature point now CPL could be isolated from the aqueous layer and the experiment was finished giving the results shown in figures 7, 8, 9 and 10. According to the results, the highest rates of extraction of both the

HQDBS and IDQ were observed at approximately 80-90 degrees Celsius. This temperature defines the region of the maximum thermodynamic equilibrium for CPL production and extraction [26].

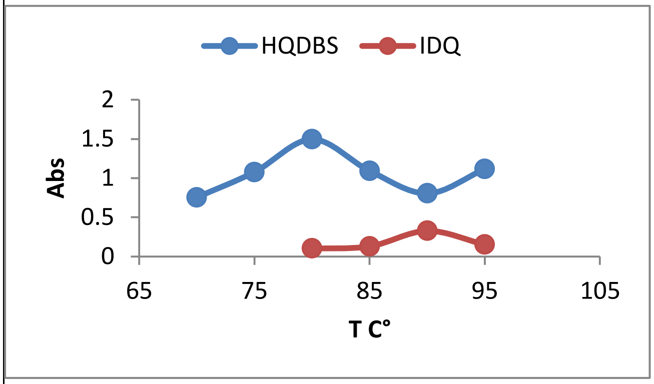


Fig.7. Effect of Temperature on Formation and Quality CPL

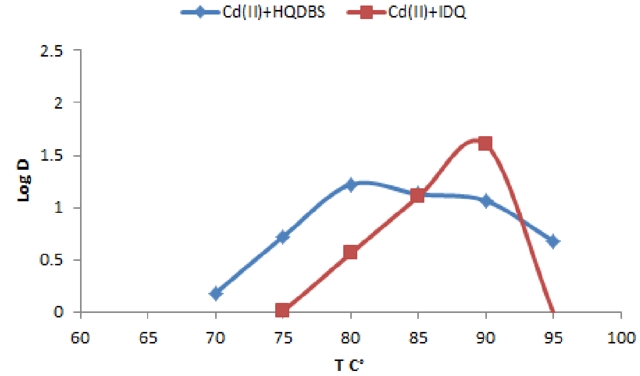


Fig.8. Effect of Temperature on Extraction Efficiency

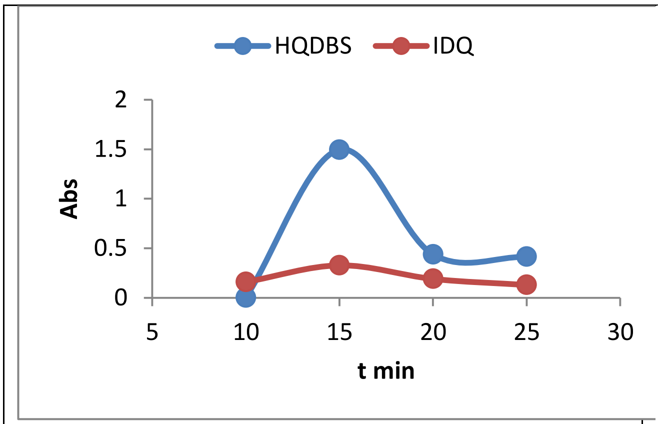


Fig. 9. Effect of Heating Time on Formation and Stability of CPL

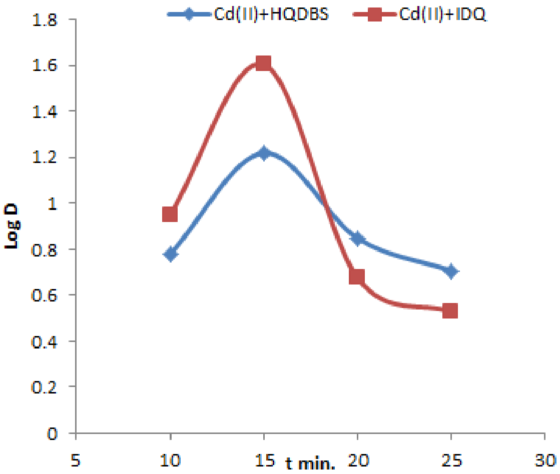


Fig. 10. Heating Time as a function of D

Cadmium (II) was obtained through ideal temperature-controlled CPL formation over the specified time period. At every temperature, CPL was removed from the aqueous layer, completing the process which produced the results in Figures 7, 8, 9, and 10. From the data, the optimal temperature for the extraction efficiency of both HQDBS and IDQ was 80-90 °C.

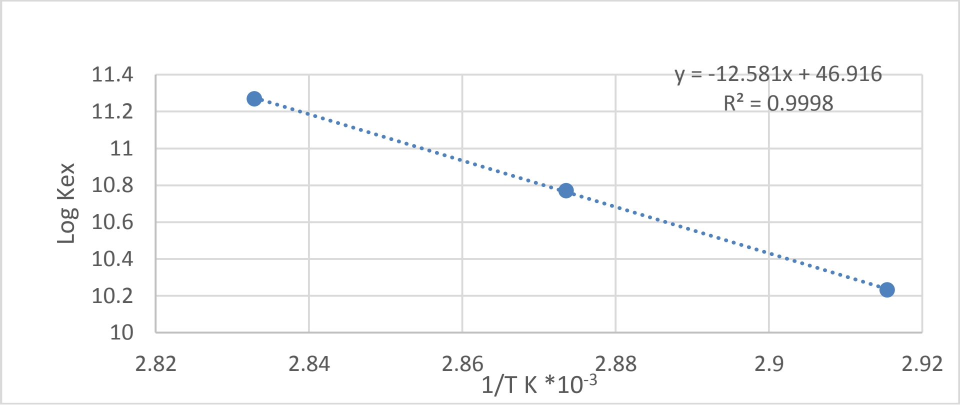


Fig.11. Effect of Temperature on Extraction Content K_{ex} for Cd(ll)-HQDBS complex

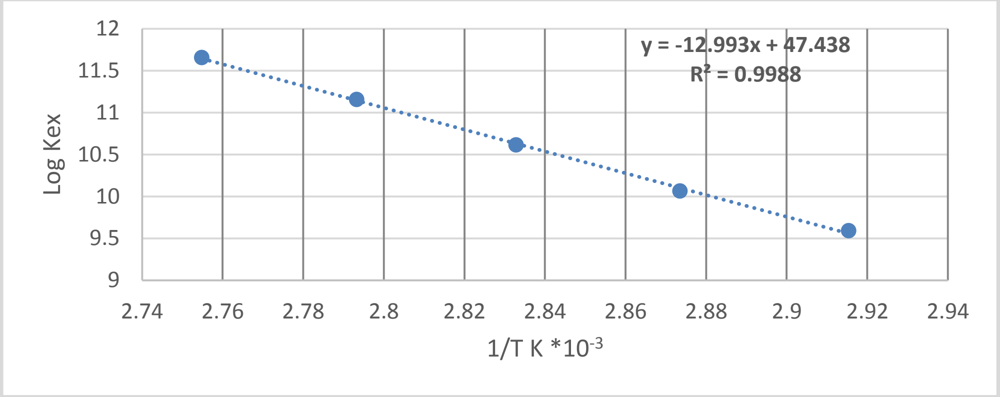


Fig.12. Effect of Temperature on Extraction Content K_{ex} for Cd(ll)-IDQ complex

Table 1: Thermodynamic Data for Cloud Point Extraction Method

Complex	ΔH_{ex} K.J.mole^{-1}	ΔG_{ex} K.J.mole^{-1}	ΔS_{ex} J.mole^{-1}K^{-1}
Cd(ll)-HQDBS	240.895	-81.444	913.142
Cd(ll)-IDQ	248.778	-83.853	916.339

Selection of Diluents for the Surfactant Rich Phase:

To study the influence of various organic solvents 2-propanol, methanol, chloroform, acetone, ethanol on the absorption of the extracted complexes Cd(ll)-HQDBS and Cd(ll)-IDQ in the micelle containing surfactant, the complexes were thoroughly examined along with the surfactant-rich phase obtained after cloud point preconcentration. The results were summarized in Table 2

Table.2. the effect of different organic solvents on the absorption behavior of Cd(ll)-HQDBS and Cd(ll)-IDQ complexes

Organic solvent	Cd(II)-HQDBS		Cd(II)-IDQ		Dielectric constant
	λ_{max}	Absorbance	λ_{max}	Absorbance	
Methanol	471nm	0.594	403nm	0.710	32.6
Ethanol	478nm	0.751	499nm	0.991	24.6
Acetone	468nm	0.690	454nm	0.640	21.01
2-propanol	438nm	0.512	407nm	0.805	19.92
Chloroform	400nm	0.489	391nm	0.573	4.81

All tested solvents shown satisfactory solubility for the Cd(ll)-HQDBS and Cd(ll)-IDQ complexes in the miceller phase; however, ethanol was favored over the other solvents due to its ability to furnish the highest analytical signals. Ethanol showed the maximum absorbance of the chelation complexes allowing dissociation of the ethanol but dissolving them in other solvents. Thus, ethanol was used as the ideal solvent for reducing viscosity and allowing the sample to be easily transferred into a quartz cell.

Selection of the Surfactant:

The choice of surfactant is very important in the cloud point extraction process. The research was conducted as per standard protocols with different surfactants like Tween-80, Tween-40, Tween-20, Cetyltrimethylammonium bromide (CtMABr), and Sodium Decyl Sulfate (SDS). The surfactant-rich phase has not been formed. Others did not show so low value of distribution ratio compared to Triton X–100.

Composition of the Extracted Complex:

Two spectroscopic methods - slope analysis and mole ratio Method – were used to determine the probable structure of the extracted chelation complexes. This was based on a general procedure.

1-Slope analysis method:-This method involved using different concentrations of each (HQDBS) and (IDQ) with fixed concentrations of Cd(II). The results are shown in Figures 13 and 14.

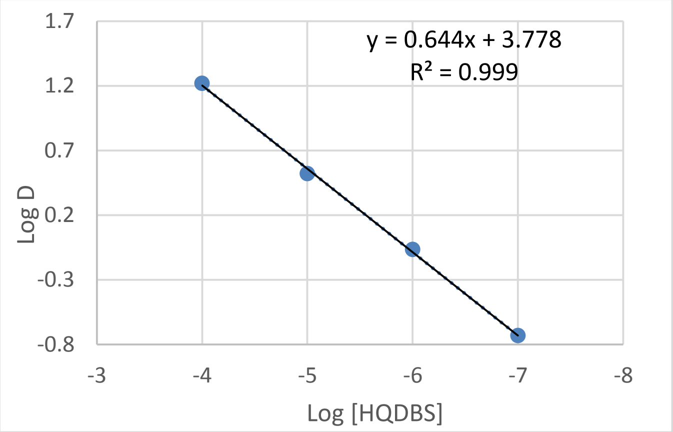


Fig.13. Slope analysis method for (HQDBS)

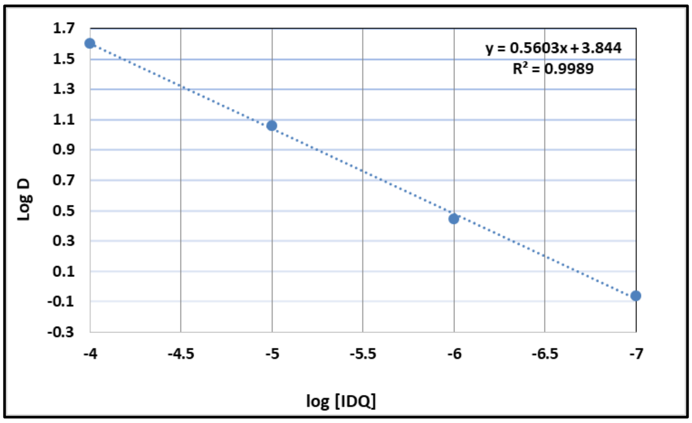


Fig.14. Slope analysis method for (IDQ)

2- Mole Ratio Method:-

In this method, different quantities of reagents solutions with the same concentration of both Cd(II) ion and reagent were mixed and absorption measurement were taken. The result were represented in Figures 15, 16..

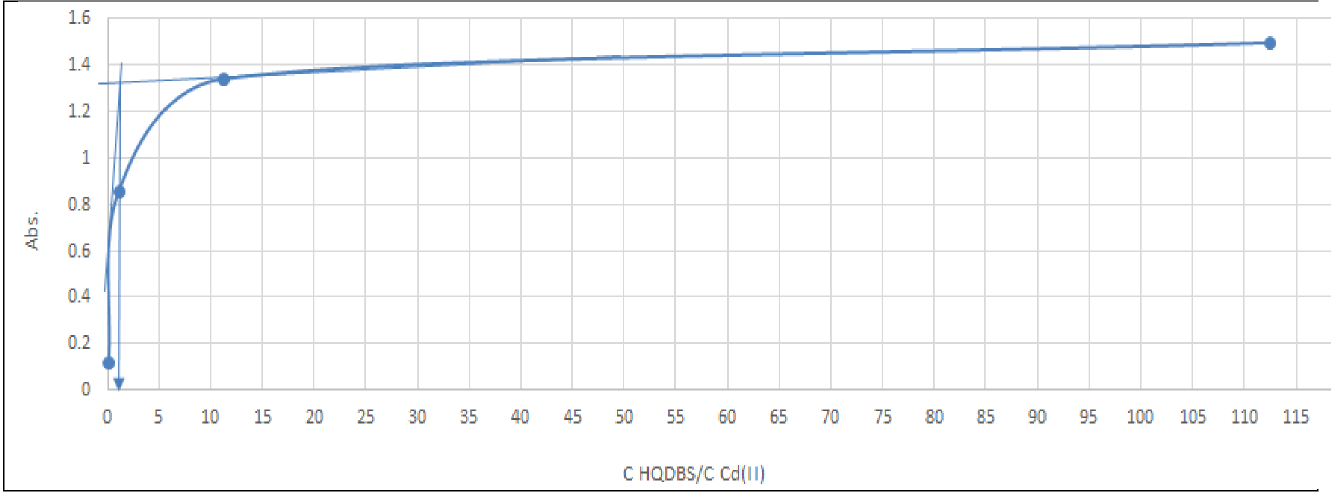


Fig.15. Mole ratio of Cd(II)-HQDBS complex.

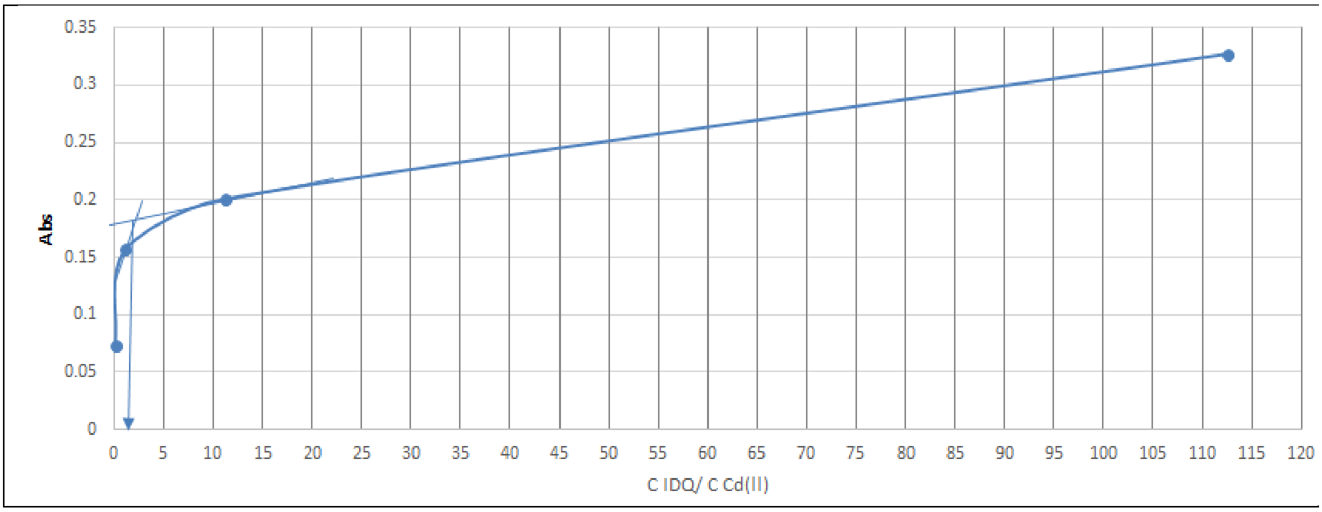
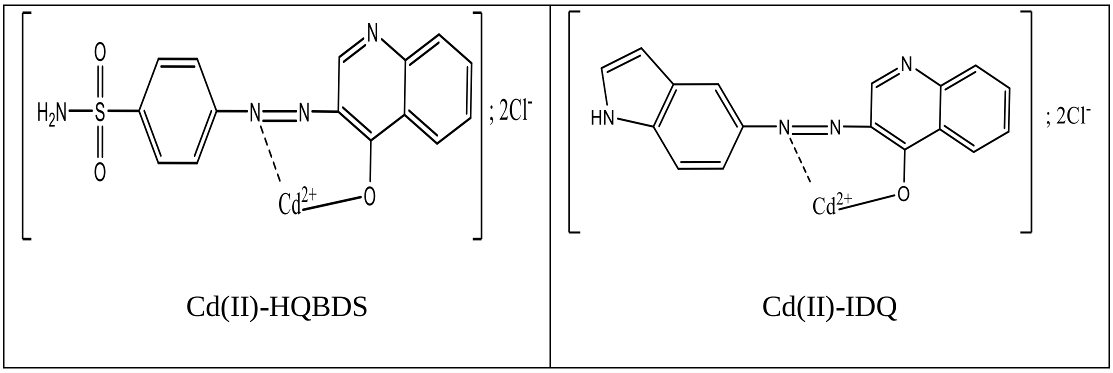


Fig.16. Mole ratio of Cd(II)-IDQ complex.

The mole ratio values were 1.0, 1.2 for Cd(ll)-HQBDS and Cd(ll)-IDQ respectively which demonstrate more probable structure of chelate extracted complexes into CPL were 1:1, as in below scheme:



Cd(II)-HQBDS

Cd(II)-IDQ

Scheme 1. Structure of extracted complexes of Cd(II) ion with HQBDS and IDQ

Applications

To test how effective the proposed methodology is, it is applied to measure the concentration of Cd(II) in some samples. The food sample solutions were prepared by adding around 5g of the dried sample into a 250 mL conical flask. Subsequently, 10 mL of concentrated HNO_3 was introduced to the flask. The contents of the flask were carefully heated on an electric hot plate until the volume reduced to about 2-3 mL. Once cooled, the following was added: 10 mL of concentrated HNO_3, 5 mL of concentrated H_2SO_4, 4 mL of 30% H_2O_2 and heated to boiling until the volume reached 2-3 mL. At that point, 10mL of distilled water was added and heated until the organic matter was completely oxidized which was indicated by the appearance of colorless steam. After cooling, the solution was transferred into a 100 mL volumetric flask and water added until the mark was filled [27,28]. From the prepared sample solution, a volume of 5 mL was aliquoted and brought to a total volume of 10 mL for analysis. After the CPE treatment, under the specified optimal conditions from preceeding experiments, a 0.1M $KNaC_4H_4O_6 \cdot 4H_2O$ solution was added as a masking agent and the procedure was followed until the CPL was formed. This layer was separated from the solution and dissolved in 3 mL of ethanol. The solution was then assessed for absorbance at the λmax for HQDBS and IDQ of 478 nm and 499 nm respectively while using a blank solution prepared without the addition of Cd(II) ions. This method was used to determine the concentration of Cd(II) in six food samples from a local market. The outcomes of the two techniques—the suggested CPE and flame atomic absorption spectroscopy (FAAS)—are displayed in Table 4. This technique may be appropriate for determining the Cd(II) levels in a variety of samples, as evidenced by the high agreement between the procedure and direct analysis by FAAS [29-31].

1- **Calibration curve of Cd(II):** by application general procedure at different concentration from Cd(II) at optimal conditions, the calibration curves for Cd(II) as in Figure 17, the parameters of calibration curve illustrated in table 3

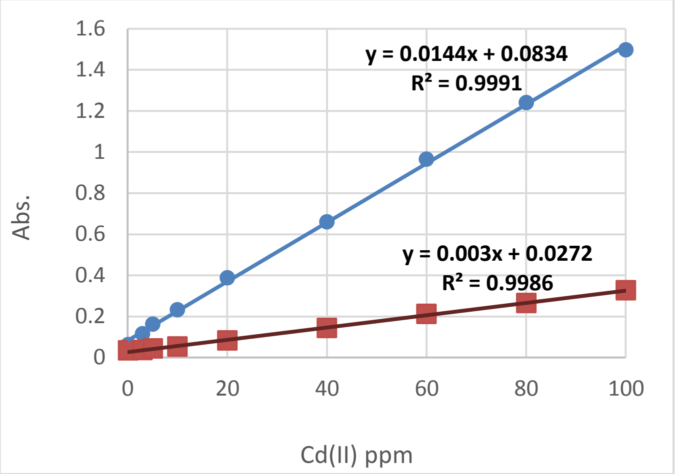


Fig.17.: Calibration curves of Cd(II) using HQDBS and IDQ

Table (3): Parameters for the determination of Cd(II) using HQDBS and IDQ

Parameter	*HQDBS*	*IDQ*
λ_{max} (nm)	**478**	**499**
Bear's law obey (ppm)	**0.1-100**	**0.1-100**
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	**16.179×10^3**	**33.672×10^3**
Limit of Detection(μgmL^{-1})	**0.156**	**0.139**
Limit of Quantity (μgmL^{-1})	**0.473**	**0.422**

Table 4. Determination of Cd(II) using the CPE method and comparison with FAAS, and comparison the results of two methods statistically using F-test method.

No	**Sample Name**	**Cd(II) amount**			**CPE**	**FAAS**
		CPE	**FAAS**	Mean	0.4975	0.498333
1.	Flaxseeds	0.475	0.470	Variance	0.00201	0.001968
2.	Sunflower seeds	0.472	0.473	Observations	6	6
3.	Perch	0.442	0.441	df	5	5
4.	Sea Fish	0.563	0.563	F		1.021563
5.	Canned Sardine	0.533	0.531	P(F<=f) one-tail		0.490946
6.	Chard Plant	0.505	0.507	F Critical one-tail		5.050329

All statistical results performed by the F-test for comparison of variance between the CPE and FAAS methods for samples under study. Have revealed that all p values [P(Fcal.<Fcrt.)two tailed] based on the 5% critical values of 5.05 (F critical) were more than the F calculated values indicating acceptance of null hypothesis (Ho), this means that no significant difference between CPE method and FAAS method.

Conclusions:

This research outlined the development and optimization of a cloud point extraction (CPE) method for the separation, preconcentration, and spectrophotometric quantification of cadmium(II) in water samples and food products using azo type derivatives HQDBS and IDQ as complexing agents. The results proved passable CPE has reasonable efficiency, in terms of cost, time, and environmental factors, for analyzing cadmium with the sensitivity and selectivity indicators being high. Key parameters such as pH, surfactant volume, extraction temperature, and heating time were evaluated in order to maximize extraction efficiency, which led to the optimization of the method. The extracted complexes of cadmium with ligands of HQDBS and IDQ were spectrophotometrically analyzed for their absorption signals at 478 nm and 499 nm, respectively. Structural characterization of the chelation complexes was confirmed by various spectroscopic techniques and FE-SEM imaging. The method was verified based on a statistical study with Flame Atomic Absorption Spectroscopy (FAAS) and found remarkable correspondents which confirm the proposed method's reliability in real sample analysis. In addition, statistical tests made through the F-test showed no significant difference between the methods, confirming the reliability of the developed method in terms of accuracy and reproducibility. With the proven capability of the method using food samples, the method has high potential for monitoring the presence of heavy metals in various environmental and biological samples. All in all, CPE offers an efficient, fast and eco-friendly substitute to conventional extraction processes, which makes it useful for heavy metal analysis in different disciplines such as environmental monitoring and checking food safety.

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