

Preconcentration of Cd(II), Co(II), Cu(II), and Pb(II) Utilizing Membrane Filtration Procedure and Their Flame Atomic Absorption Spectrometric Determination in Environmental Samples

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ABSTRACT: Before conducting flame atomic absorption spectrometric analyses, minute quantities of cadmium, cobalt, copper, and lead ions from environmental samples were concentrated and isolated utilizing an innovative and very sensitive enrichment membrane filtration method. A cellulose nitrate membrane filter was used to collect the analyte ions as (E)-4-(2-hydroxybenzylideneamino)-N-(pyrimidin-2-yl)benzenesulfonamide complexes. Nitric acid was then used to separate them. The concentration levels of cadmium, cobalt, copper, and lead ions in the final solutions were determined by flame atomic absorption spectrometry. A number of analytical factors were looked into because they affect the collection and identification of metal ions. These included pH, reagent amounts, sample volume, flow rates, matrix effects, and membrane filter type and size. The recovery values of the analyte ions, as determined through measurement, ranged from 95% to 102%. The accuracy of the proposed approach was evaluated by calculating the relative standard deviation (%), yielding a value of $\leq 4.0\%$. The method proposed exhibited detection limits ranging from 0.2 to 0.8 $\mu\text{g L}^{-1}$. The preconcentration factors for each analyte examined were 100. The examination of authorized reference sources verified the accuracy of the proposed methodology. The analyte ions in water and food samples have been successfully separated and preconcentrated, yielding good outcomes.

Keywords: Metals ions; Membrane filtration; Preconcentration; Environmental samples; Flame atomic absorption spectrometry.

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I. INTRODUCTION

Heavy metals are categorized as hazardous compounds due to their high toxicity to animals, humans, and plants, even at extremely low levels [1]. Therefore, accurately evaluating small amounts of heavy metals in environmental samples is a crucial goal for chemists who specialize in the field of environmental analytical chemistry [2–6]. Flame atomic absorption spectrometry (FAAS) [7, 8] and spectrophotometry [9] are two advanced analytical methods that must be used to accurately measure the small amounts of heavy metals present in environmental materials. Nevertheless, the hardest parts of these tests are finding the right amounts of metals that are below FAAS's detection limits and dealing with the problems that come up because of the samples' matrix. Hence, it is necessary to perform an initial separation or enrichment step before conducting the measurements in order to optimize sensitivity and enhance the precision of the estimation.

In recent times, the literature has recorded the rise of many analytical methods for isolating and intensifying trace quantities of heavy metals. The methods utilized are cloud point extraction [1, 3, 4, 6, 8, 10], solid-phase extraction [7, 11–14], co-precipitation [5, 15–18], and liquid-liquid microextraction [2, 19–21].

Adsorption is a highly effective and recommended method for eliminating heavy metals from wastewater. It is renowned for its advantageous velocity and simplicity of use [22].

Membrane filtration is a technique employed to intensify and segregate minute quantities of heavy metal ions in environmental samples. Cellulose nitrate and cellulose acetate are two types of membrane filters that are used in different situations to get small amounts of different chemicals, such as organic species [23], certain anions [24], and heavy metal ions [25–34]. Membrane filtering is an attractive preconcentration

technique because of its simplicity, speed, versatility, ability to reuse membranes, capability to produce a high preconcentration factor, and precision.

The present study employed an innovative, simple, and highly sensitive membrane filtration method to concentrate and separate small amounts of cadmium Cd(II), cobalt Co(II), copper Cu(II), and lead Pb(II) ions from water and food samples prior to their further analysis using FAAS. In our experiment, we employed (E)-4-(2-hydroxybenzylideneamino)-N-(pyrimidin-2-yl)benzenesulfonamide (HBAPBS) as a chelating agent. The process involved putting analyte ions on a cellulose nitrate membrane filter as HBAPBS complexes and then using nitric acid to wash them away. Flame Atomic Absorption Spectroscopy (FAAS) was employed to quantify the amounts of Cd(II), Co(II), Cu(II), and Pb(II) ions in the final solutions. A study was carried out to investigate the influence of various analytical parameters on the gathering and identification of the analyte ions under inquiry. The factors encompassed pH, amounts of reagents, volume of samples, type and size of membrane filters, flow rates, and matrix effects.

II. Materials and Methods

II.1. Apparatus

The Agilent 55B AA spectrometer, manufactured by Agilent Technologies Inc. in Santa Clara, USA, was used for the analysis. It was equipped with a 10 cm burner that operated with an air pressure of 350 KPa and a flow rate of 11-20 L/min, as well as an acetylene pressure of 75 KPa and a flow rate of 1.5-10 L/min. The spectrometer utilized hollow cathode lamps containing cadmium (228.8 nm), cobalt (240.7 nm), copper (324.8 nm), and lead (283.3 nm) to measure the analyte concentrations in both standard and sample solutions. The instrumental requirements were established in accordance with the manufacturer's specifications. The specimen was introduced into the FAAS nebulizer by a microinjection technique.

The pH values of buffer solutions were determined using an AD1000 pH-meter (Adwa instruments Kft., Szeged, Hungary) equipped with a glass electrode. A centrifuge from Isolab, GmbH in Germany was employed to accelerate the separation of analytes from the sample solution. The Milli-Q purification apparatus, manufactured by Millipore in the United States, was utilized to acquire deionized/bidistilled water for the purpose of solution formulation. A Milestones Ethos D closed vessel microwave system, manufactured by Milestone Inc. in Italy, was utilized for the digestion of food samples. This system has a maximum pressure of 1450 psi and a maximum temperature of 300°C.

II.2. Reagents and solutions

The reagents and chemicals utilized were of superior quality and procured from reputable organizations such as Merck (Darmstadt, Germany) and Sigma Aldrich (St. Louis, USA). The experiment employed high-purity HNO₃ (65% by weight), HCl (37% by weight), and NH₃ (25% by volume). Stock solutions containing Cd(II), Co(II), Cu(II), and Pb(II) ions at a concentration of 1000 mg L⁻¹ were generated by dissolving high quality metal nitrate salts obtained from Merck (Darmstadt, Germany) in a 1.0 mol L⁻¹ solution of HNO₃. The diluted standard solutions were generated by systematically diluting the stock standard solutions with HNO₃ (1.0 mol L⁻¹) prior to their utilization.

Buffer systems have been designed to regulate the pH values of the solution with pH values ranging from 2.0 to 10 [35].

The validity of the proposed method was verified by analyzing certified reference materials (CRMs), such as spinach leaves (SRM 1570a), sandy soil standard (CRM-SA-C Sandy Soil C) from High-Purity Standard Inc., and fortified water TMDA-52.3 from the National Water Research Institute in Burlington, Canada.

Synthesis of (E)-4-(2-hydroxybenzylideneamino)-N-(pyrimidin-2-yl)benzene-sulfonamide (HBAPBS) Schiff base

The 15 ml ethanolic solution of salicylaldehyde (0.005 mol) was introduced to the 30 ml ethanolic solution of 4-amino-N-(pyrimidin-2-yl)benzenesulfonamide (0.005 mol) by shaking. The combination has undergone reflux in a water bath for a duration of three hours. The solution underwent evaporation using a rotary evaporator upon cooling to room temperature. The solid product obtained had a melting point range of 240-242 °C. It was dried in the presence of air, filtered, and then subjected to ethanolic recrystallization, resulting in a yield of 96.6% [36].

The following (%) information was obtained from the elemental analysis of the HBAPBS (C₁₇H₁₄N₄O₃S; M.Wt. 354.38); C:57.62; H:3.98; N:15.81 and found (%): C:57.60; H:3.99; N:15.84. Fig. 1 depicts the novel reagent's (HBAPBS) chemical structure.

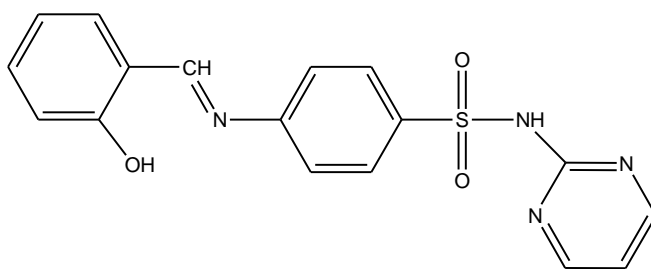


Figure 1. The chemical structure of (HPMAPBS).

A precise weight of HBAPBS was dissolved in ethanol in a 100-mL measuring flask to obtain a stock solution (0.2% w/v and 1.0×10^{-3} mol L⁻¹).

II.3. General procedure

A 40 mL portion of an aqueous solution containing Cd(II), Co(II), Cu(II), and Pb(II) ions in the range of 5.0–20 µg was added to a glass beaker. A 1.0 mL of a 0.2% (weight/volume) HBAPBS solution was added. The pH of the solution was modified to a pH range of 2.0–10 by adding buffer solutions. Subsequently, a metal-HBAPBS solution was obtained after a duration of 10 minutes by passing it through a cellulose nitrate membrane filter having a pore size of 0.45 µm and a diameter of 47 mm. The collection is expedited using suction filtering using an aspirator. Subsequently, the membrane was fully dissolved in 1.0 mL of concentrated HNO₃ at a temperature of 80 °C using a hot plate. The fluid was completely dried through evaporation. The remaining substance was mixed with (1.0 mol L⁻¹) HNO₃ to obtain a final volume of 4.0 mL. The concentration of the analytes in the final solution was measured using FAAS.

II.4. Application to real samples and CRMs

After adjusting the pH of the samples to 7.0, the membrane filtering method was used to successfully test the metal ions in tap, mineral, and sea water samples from Egypt and CRMs (fortified water TMDA-52.3). The technology of FAAS was employed to concentrate and detect the metal ions present according to the prescribed method. The preconcentration membrane filtration method was used on certified reference materials, such as spinach leaves (SRM 1570a) and CRM-SA-C Sandy Soil C Standard material (0.25 mg), as well as different food samples obtained from marketplaces in Egypt. The proposed method was employed to concentrate the analyte ions, and the results were determined by FAAS. [18]

III. RESULTS AND DISCUSSIONS

III.1. IR and ¹H-NMR spectra of HBAPBS

The IR spectra ν (cm⁻¹) of the HBAPBS Schiff base showed bands at 3160 (NH), 1618 (HC=N), 1337, 1148 (asym., S=O), 1269 (CN), 942 (S-N), 796 (C-S).

The ¹H-NMR (DMSO-d₆, δ , ppm) spectra of the HBAPBS Schiff base showed bands at 6.1 (s, 1H, Ar-H), 6.5 (s, 1H, Ar-H), 7.0 (m, 2H, Ar-H), 7.3–7.5 (m, 4H, Ar-H), 8.1 (s, 1H, Ar-H), 8.5 (d, 2H, pyrimidine), 8.9 (s, 1H, C=N, azomethine), 10.2 (s, 1H, NH, exchange with D₂O).

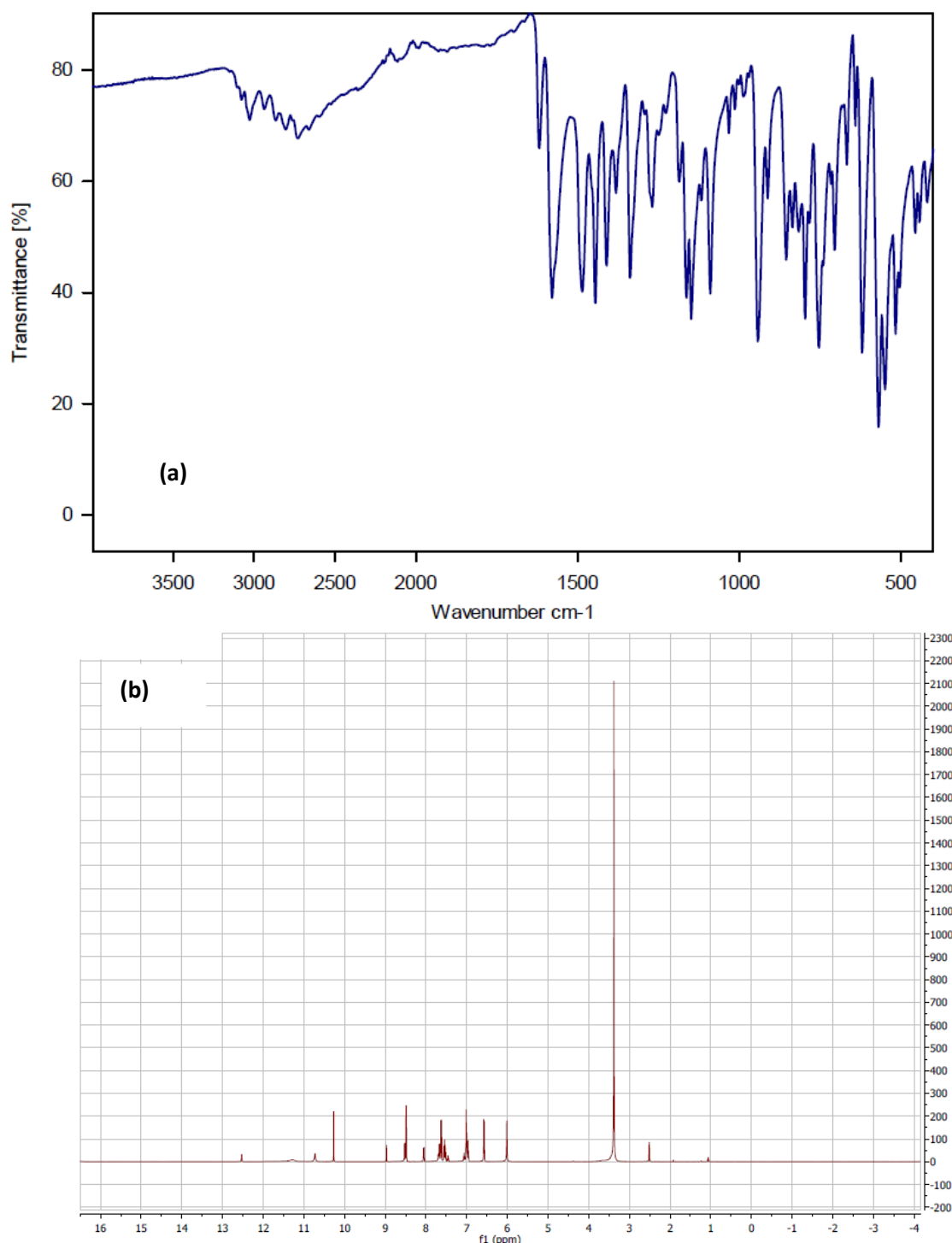


Figure 2: (a) FT-IR and (b) H-NMR spectra of HBAPBS.

III.2. Optimization of the analytical experimental conditions

III.2.1. Influence of pH

The pH scale of 2.0–10 was investigated by introducing buffer solutions and applying the previously reported membrane filtration process to these solutions. The findings derived from this investigation are displayed in Figure 3. For all subsequent investigations, a phosphate buffer solution with a pH of 7.0 was chosen as the most suitable pH.

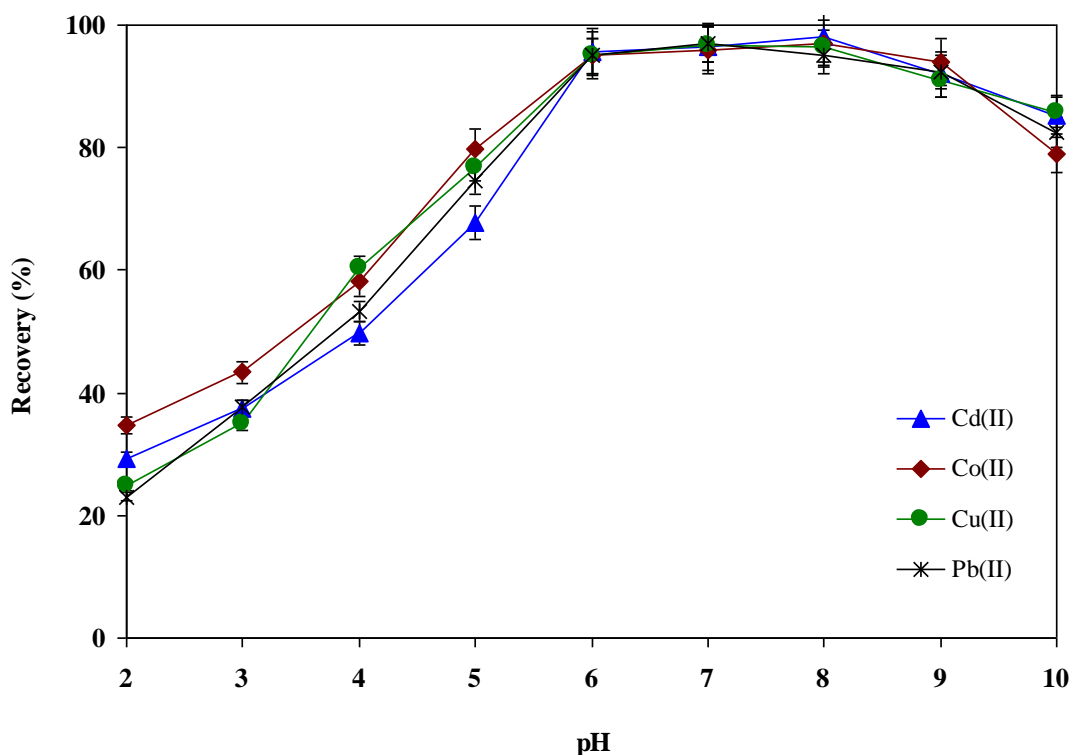


Figure 3. Effect of pH on the recoveries of analyte ions (Cd(II), Co(II), Cu(II), and Pb(II)), N=3.0.

III.2.2. Influence of HBAPBS amount

The impact of varying quantities of HBAPBS was investigated within the range of 0-8.0 mg of HBAPBS solution. However, by gradually increasing the quantity of HBAPBS solution (0.2%, w/v) up to 4.0 mg, there was a noticeable improvement in achieving complete recoveries, as shown in Figure 4. Hence, it is advisable to include 4.0 mg of HBAPBS for future investigations.

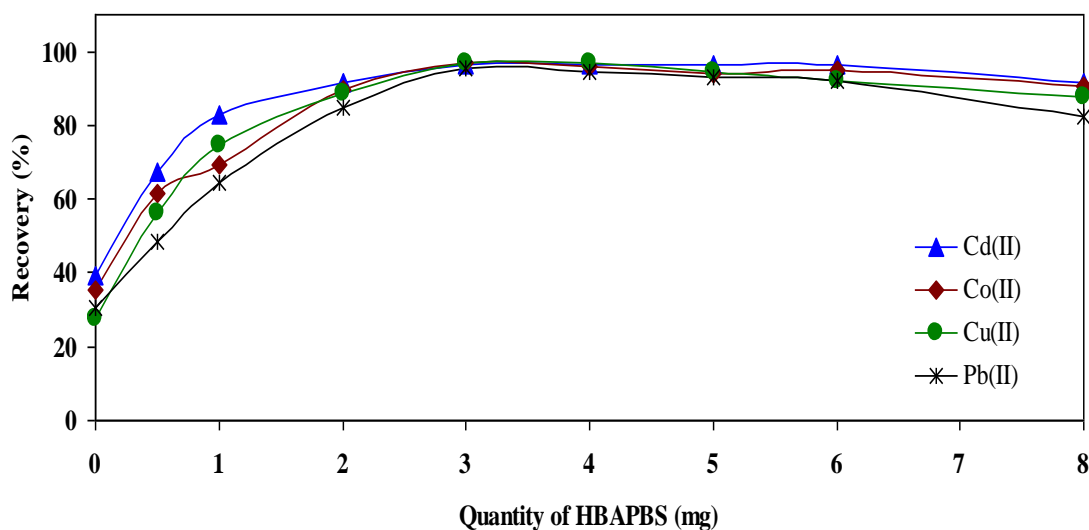


Figure 4. Effect of concentration of HBAPBS on the recoveries of analyte ions. (Cd(II), Co(II), Cu(II), and Pb(II)), N=3.0.

III.2.3. Influence of membrane filter type and size

The impact of the membrane filter's type and size on the recovery values of Cd(II), Co(II), Cu(II), and Pb(II) ions was also investigated under the ideal analytical conditions. The analyte ions achieved complete recovery under ideal conditions for cellulose nitrate (47 mm, 0.45 μm) (95-99 %) and cellulose acetate (47 mm, 0.45 μm) (95-97 %) membrane filters. When employing cellulose ester (47 mm, 0.45 μm) and polysulfone

(PES) membrane filters for preconcentration/separation experiments, the recovery values for all analytes did not reach quantifiable levels within the range of 70-90% on the membrane filter. Subsequently, a cellulose nitrate membrane filter measuring 0.45 μm in size and 47 mm in diameter was consistently employed in all subsequent experiments.

Various mineral acids, such as H_2SO_4 , HCl and HNO_3 , have been employed to dissolve the cellulose membrane filters (Table 1). 1.0 mL of concentrated HNO_3 was used to quantitatively recover Cd(II) , Co(II) , Cu(II) , and Pb(II) ions, with a recovery rate of at least 95%. This fact is also consistent with our previous findings about cellulose nitrate membranes.

Table 1. The effects of various acids on the recoveries of analyte ions (N=3.0).

Eluent type	Recovery (%) \pm SD ^a			
	Cd(II)	Co(II)	Cu(II)	Pb(II)
Concentrated HNO_3	96 \pm 3	97 \pm 2	98 \pm 4	95 \pm 2
Concentrated HCl	78 \pm 4	81 \pm 3	80 \pm 2	77 \pm 3
Concentrated H_2SO_4	71 \pm 5	79 \pm 4	75 \pm 3	72 \pm 2

^a Mean \pm standard deviation.

III.2.4. Influence of sample volume

The impact of sample volume on the retention of the analytes was assessed by altering the sample volume within the range of 25-600 mL. The findings indicated that the metal recoveries were complete up to a volume of 400 mL for Cd(II) , Co(II) , Cu(II) , and Pb(II) (Figure 5). The preconcentration factor was calculated by dividing the greatest sample volume for the analyte ions by the final volume (4.0 mL). Consequently, a preconcentration factor of 100 was attained.

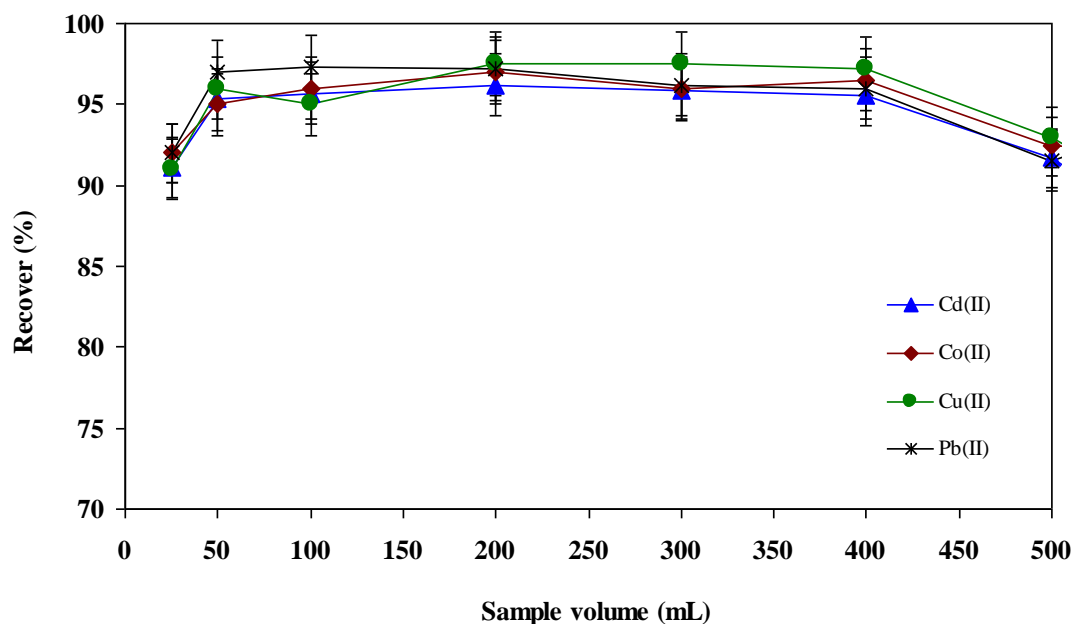


Figure 5. Effect of sample volume on the recoveries of analyte ions (Cd(II) , Co(II) , Cu(II) , and Pb(II)), N=3.0.

III.3. Influence of matrix ions

The presence of matrix ions can significantly impact the viability of the suggested approach, posing a major challenge in the determination of trace metals. In order to assess the impact of coexisting ions on the retrieval of metal ions in the membrane system, different quantities of foreign ions were introduced into solutions containing constant levels of the analyte ions, and the prescribed method was thereafter carried out. The metal ions were successfully recovered with a quantitative yield of at least 95%, as shown in Table 2. The tolerance limit was established as the ion concentration that exhibits a relative inaccuracy below $\pm 5\%$ in relation to the membrane filtration and characterization of the analyzed elements. The findings should be relevant to actual samples, encompassing a range of salts with significant concentrations.

Table 2. The effect of matrix ions on the recovery of the analyte ions (N=3.0).

Ions	Added as	Concentration (mg L ⁻¹)	Recovery (%) ^a			
			Cd(II)	Co(II)	Cu(II)	Pb(II)
Na ⁺	NaCl	4,000	96 ± 3	98 ± 3	97 ± 3	97 ± 3
K ⁺	KCl	4,000	95 ± 2	96 ± 2	98 ± 2	98 ± 3
Ca ²⁺	CaCl ₂	2,000	97 ± 3	95 ± 2	96 ± 3	95 ± 2
Mg ²⁺	MgCl ₂	2,000	98 ± 2	97 ± 4	97 ± 3	96 ± 3
Cl ⁻	NaCl	6,000	96 ± 2	96 ± 3	96 ± 1	97 ± 4
PO ₄ ³⁻	Na ₃ PO ₄	2,000	99 ± 3	97 ± 1	95 ± 3	98 ± 2
CO ₃ ²⁻	Na ₂ CO ₃	5,000	97 ± 4	96 ± 2	96 ± 3	96 ± 3
SO ₄ ²⁻	Na ₂ SO ₄	3,000	95 ± 2	97 ± 2	96 ± 2	97 ± 2
NO ₃ ⁻	Na ₃ NO ₃	6,000	97 ± 3	96 ± 1	97 ± 3	96 ± 3
Al ³⁺ , Cr ³⁺ , Mo ⁶⁺ , Fe ³⁺ , Hg ²⁺ , Bi ³⁺ ,	Nitrate salts	50	98 ± 3	97 ± 2	96 ± 2	99 ± 3
Mixed ^a			96 ± 2	97 ± 4	98 ± 3	95 ± 2

^a Mean ± standard deviation.

III.4. Method validation and applications

The reproducibility and precision of the suggested method were assessed by measuring the recovery and calculating the relative standard deviations (RSDs%) from ten replicate studies of the model solutions. The relative standard deviations (RSDs) for the examined metal ions were determined to be less than or equal to 4.0%. The limit of detection (LOD) is defined as 3 times the standard deviation of the reagent blank signals (s) divided by the slope of the calibration curve (b), with N being the number of samples. The LOD (limit of detection) values for Cd(II), Co(II), Cu(II), and Pb(II) were determined to be 0.2, 0.3, 0.6, and 0.8 µg L⁻¹, respectively.

In order to assess the precision of the current method, we conducted an addition/recovery test using varying quantities of the metal ions under investigation. These ions were intentionally introduced into diverse water samples, including tap water, mineral water, and seawater. The outcomes are presented in Table 3. The recovery values for the analytes were within an acceptable range of 95-99%, indicating adequate performance. The dietary samples (cabbage, spinach, black tea) were also subjected to the membrane filtration technique. The outcomes are presented in Table 4. The findings obtained demonstrated the successful use of the suggested method for concentrating, separating, and determining analyte ions in actual water and food samples. The validation of the membrane filtering process was confirmed through the examination of three approved reference materials, namely SRM 1570a spinach leaves, CRM-Sandy Soil C, and fortified water TMDA-52.3. The outcomes are presented in Table 5. The quantitative recovery results exhibited a high level of concordance with the certified values.

Table 3. Spiked recoveries of analyte ions from water samples using the proposed method (N=3.0).

Element	Added (µg L ⁻¹)	Tap water		Mineral water		Sea water	
		Found ^a (µg L ⁻¹)	Recovery (%)	Found ^a (µg L ⁻¹)	Recovery (%)	Found ^a (µg L ⁻¹)	Recovery (%)
Cd(II)	0	< LOD ^b	-	< LOD	-	8.2 ± 0.1	-
	10	9.7 ± 0.4	97.0	9.8 ± 0.2	98.0	17.4 ± 0.5	95.50
	20	19.5 ± 0.5	97.5	19.8 ± 0.6	99.0	27.4 ± 0.8	97.0
Co(II)	0	< LOD ^b	-	< LOD	-	7.0 ± 0.3	-
	10	9.5 ± 0.2	95.0	9.7 ± 0.3	97.0	16.3 ± 0.4	96.0
	20	19.70 ± 0.7	98.5	19.5 ± 0.6	97.5	27.5 ± 0.7	98.0
Cu(II)	0	5.0 ± 0.1	-	< LOD	-	9.0 ± 0.2	-
	10	14.3 ± 0.5	95.0	9.5 ± 0.2	95.0	18.2 ± 0.5	96.0
	20	24.0 ± 0.7	96.0	19.2 ± 0.8	96.0	28.4 ± 0.7	98.0
Pb(II)	0	< LOD	-	< LOD	-	4.0 ± 0.1	-
	10	9.6 ± 0.2	96.0	9.8 ± 0.4	98.0	13.9 ± 0.3	99.0
	20	19.4 ± 0.8	97.0	19.8 ± 0.5	99.0	22.8 ± 0.7	95.0

^a Mean ± standard deviation.^b LOD: limit of detection.

Table 4. The addition-recovery results for the analyte ions in food samples using the proposed method (N=3.0).

Analyte	Added ($\mu\text{g L}^{-1}$)	Cabbage		Spinach		Black tea	
		Found ^a ($\mu\text{g g}^{-1}$)	Recovery (%) ^b	Found ($\mu\text{g g}^{-1}$)	Recovery (%)	Found ($\mu\text{g g}^{-1}$)	Recovery (%)
Cd(II)	0	< LOD	-	< LOD	-	2.0 \pm 0.1	-
	10	9.75 \pm 0.2	97.5	9.60 \pm 0.5	96.0	11.80 \pm 0.4	98.0
	20	19.00 \pm 0.5	95.0	19.30 \pm 0.7	96.5	21.30 \pm 0.8	97.0
Co(II)	0	2.40 \pm 0.1	-	4.0 \pm 0.2	-	4.0 \pm 0.3	-
	10	11.90 \pm 0.3	96.0	13.85 \pm 0.4	99.0	13.30 \pm 0.5	95.0
	20	22.60 \pm 0.8	101.0	23.0 \pm 0.9	96.0	23.50 \pm 0.8	98.0
Cu(II)	0	2.0 \pm 0.2	-	4.0 \pm 0.2	-	3.0 \pm 0.3	-
	10	11.40 \pm 0.4	95.0	14.15 \pm 0.3	101.0	12.60 \pm 0.4	97.0
	20	21.6 \pm 0.7	98.0	23.30 \pm 0.6	97.0	22.50 \pm 0.8	98.0
Pb(II)	0	< LOD	-	< LOD	-	< LOD	-
	10	9.8 \pm 0.4	98.0	9.90 \pm 0.5	99.0	9.70 \pm 0.3	97.0
	20	19.2 \pm 0.9	96.0	20.0 \pm 1.0	100.0	19.0 \pm 0.6	95.0

^a Mean \pm standard deviation.^b Recovery% = [Observed value of analyte ion / Expected value of analyte ion] \times 100^c LOD: limit of detection.**Table 5.** The analysis results of certified reference materials after application of the proposed procedure (N=3.0).

Analyte	SRM 1570A spinach leaves			CRM-SA-C Sandy Soil C			TMDA-52.3 fortified water		
	Certified value ($\mu\text{g g}^{-1}$)	Found ^a ($\mu\text{g g}^{-1}$)	Recovery, %	Certified value ($\mu\text{g g}^{-1}$)	Found ^a ($\mu\text{g g}^{-1}$)	Recovery, %	Certified value ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Recovery, %
Cd(II)	2.89 \pm 0.07	2.83 \pm 0.10	97.80	109.0 \pm 8.0	108.0 \pm 9.0	99.0	90.6 \pm 3.89	86.60 \pm 3.30	95.60
Co(II)	0.39 \pm 0.05	0.38 \pm 0.07	97.50	12.40 \pm 0.6	12.40 \pm 0.50	100.0	134 \pm 4.0	130.0 \pm 3.80	97.0
Cu(II)	12.20 \pm 0.60	12.0 \pm 0.50	98.30	63.60 \pm 4.0	61.10 \pm 3.70	96.0	193 \pm 10.2	185.0 \pm 11.0	96.0
Pb(II)	< LOD	< LOD	-	120.0 \pm 8.0	115.0 \pm 7.0	95.80	358 \pm 16.1	347.0 \pm 14.0	97.0

^a Mean \pm standard deviation.^b LOD: limit of detection.

III.5. Analysis of the proposed method in comparison to existing methods

The suggested methodology in Table 6 is being compared to the existing published approaches [25–34] for trace metal ions. The discovered parameters were similar to those previously documented. In comparison to existing methodologies, the recommended method exhibits a much lower level of dispersion (LOD) or relative standard deviation (RSD) and a considerably higher performance factor (PF).

III.6. Comparison between the proposed method and the reported methods

Table 6 presents a summary of the analytical properties of various analytical procedures, as well as the suggested membrane filtration approach, for the extraction and quantification of Cd(II), Co(II), Cu(II), and Pb(II) in different genuine samples. The majority of the analytical properties of the suggested approach were favorable and on par with those of the other documented approaches. The method has excellent repeatability, with a smaller relative standard deviation (RSD) compared to some alternative methods. Additional benefits of this method, in comparison to alternative approaches, are a low limit of detection (LOD) and a low limit of quantification (LOQ).

Table 6. Comparison of the proposed method with some reported methods.

Analytes	Membrane filter	Chelating agent	Detection system	PF ^a	DL ($\mu\text{g L}^{-1}$) ^a	Samples	Reference
Cr(III), Co(II), Cu(II), Fe(III), Pb(II)	Cellulose nitrate	Calmagite	FAAS	150 Cr(III), 50 Co(II), 250 Cu(II), 250 Fe(III), 150 Pb(II)	2.5 Cr(III), 0.76 Co(II), 0.06 Cu(II), 0.33Fe(III), 1.18 Pb(II)	Water samples	[25]
Cd(II), Co(II), Cu(II), Fe(III)	Cellulose nitrate	8-hydroxyquinoline (8-HQ) (oxine)	FAAS	50 Cd(II), 125 Co(II), 125 Cu(II), 125 Fe(III)	0.5 Cd(II), 3.1 Co(II), 3.9 Cu(II), 9.8 Fe(III)	Natural waters, some ammonium salts, and black tea samples	[26]
Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II)	Cellulose acetate	Cochenille red	FAAS	40 Cd(II), 40 Co(II), 30 Cu(II), 50 Fe(III), 40 Ni(II), 40 Pb(II)	1.5 Cd(II), 2.6 Co(II), 1.9 Cu(II), 3.1 Fe(III), 2.4 Ni(II), 3.6 Pb(II)	Water, hair, urine, and fish samples	[27]
Cd(II), Co(II), Cu(II), Ni(II), Pb(II)	Cellulose nitrate	Ammonium pyrrolydine dithiocarbamate (APDC)	FAAS	150 Cd(II), 125 Co(II), 150 Cu(II), 175 Ni(II), 150 Pb(II)	1.1 Cd(II), 10 Co(II), 33 Cu(II), 55 Ni(II), 31 Pb(II)	Natural waters, table salts, tea and urine samples	[28]
Cd(II), Cr(III), Cu(II), Ni(II), Pb(II),	Cellulose nitrate	ND ^b	FAAS	60	0.9 Cd(II), 0.3 Cr(III), 3.1 Cu(II), 7.8 Ni(II), 0.02 Pb(II)	Environmental samples	[29]
Cd(II), Cu(II), Pb(II)	Mixed cellulose ester membrane	ND	FAAS	100	0.2 Cd(II), 2 Cu(II), 3 Pb(II)	River water, urine and sediment samples	[30]
Co(II), Fe(III), Pb(II)	Cellulose nitrate	1-(2-pyridylazo) 2-naphthol (PAN)	FAAS	75	3.6 Cu(II), 9.5 Fe(III), 10.3 Pb(II)	Natural water samples	[31]
Cu(II), Pb(II)	Cellulose acetate	PAN	FAAS	60 Cu(II), 20 Pb(II)	1.2 Cu(II), 3.5 Pb(II)	Water and geological samples	[32]
Cd(II), Co(II), Cr(II), Cu(II), Pb(II)	Cellulose nitrate	Carmine	FAAS	50	0.08 Cd(II), 0.32 Co(II), 0.76 Cr(II), 0.40 Cu(II), 0.93 Pb(II)	Environmental samples	[33]
Cd(II), Co(II), Cu(II), Ni(II), Pb(II)	Cellulose nitrate	Quinalizarin	FAAS	100 Cd(II), 100 Co(II), 100 Cu(II), 100 Ni(II), 125 Pb(II)	0.1 Cd(II), 0.3 Co(II), 0.5 Cu(II), 0.5 Ni(II), 0.7 Pb(II)	Environmental samples	[34]
Cd(II), Co(II), Cu(II), Pb(II)	Cellulose nitrate	CHPMAPBS	FAAS	100	0.2 Cd(II), 0.3 Co(II), 0.6 Cu(II), 0.8 Pb(II)	Environmental samples	The proposed method

^a PF: preconcentration factor; DL: detection limit. ^b ND: not detected

IV. Conclusion

An innovative membrane filtration method was developed using a novel chelating agent (HBAPBS) to effectively separate and quantify heavy metal ions (Cd(II), Co(II), Cu(II), and Pb(II)) in different environmental samples. This approach is characterized by its simplicity, efficiency, and speed, while also achieving outstanding recoveries, a low limit of detection (LOD), and high reliability and accuracy. The matrix was unaffected by any foreign ions. The correctness and precision of the suggested approach were confirmed through an investigation of the approved reference materials.

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