Comparative study for the separation, preconcentration, and determination of copper and cadmium in real samples by using two different ligands

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Abstract: Two new solid phase extraction methods have been developed for simultaneous separation and preconcentration of Cu(II) and Cd(II) in some food and environmental samples before their determination by flame atomic absorption spectrometry (FAAS). One of these methods is based on the absorption of the Cu(II) and Cd(II) complexes with [3-(cyanomethyl)-5-(4-methylphenyl)-4H-1,2,4-triazol-4-yl]carbamate (L1) and the other is based on the absorption of the Cu(II) and Cd(II) complexes with 4-(4-methylphenyl)-5-{[pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]methyl}-4H-1,2,4-triazole-3-thiol (L2) on Amberlite XAD-1180 resin. The metal complexes are retained on resin at pH 6.0 and eluted with 1.0 mol L^{-1} HCl in acetone in both methods. After the optimum conditions were determined, the methods were applied to seawater, stream water, rice, lentil, tea, tobacco, bulgur, chickpea, wheat, red pepper, black pepper, peppermint, and dried eggplant samples in order to determine the levels of copper and cadmium.

Key words: Preconcentration, solid phase extraction, heavy metal, flame atomic absorption spectrometry

1. Introduction

Environmental pollution via heavy metals is a global problem.[1] The main sources of heavy metals are industrial wastewater, exhausted gas from industry and traffic, and urbanization. Accumulation of heavy metals in plants, animals, and human results in various diseases and disorders.[2−5] For instance, accumulation of Cd in the liver and kidneys seriously damages the urinary system. Furthermore, Cd causes lung and prostate cancer by disruption of the deoxyribonucleic acid (DNA) repair system, leading to tumor formation.[6] Cu has important roles in carbohydrate and lipid metabolisms, energy generation, and incorporation of Fe into hemoglobin. However, deficiency or elevated levels of copper causes heart failure, nausea, anemia, vomiting, decrease of growth, hypertension, impaired reproductive performance, gastrointestinal bleeding, and dermatitis.[7−9] Therefore, determination of these elements in food and environmental samples is vital due to their effects on humans.

Some analytical methods such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF-AAS), inductive coupled plasma optical emission spectrometry (ICP-OES), and inductive coupled plasma mass spectroscopy (ICP-MS) are used for fast and accurate determination of heavy

metals in food and environmental samples.[10−13] FAAS is widely used because of its good precision and selectivity, high speed, low cost, and simplicity. However, FAAS is limited by the matrix effect and low concentration levels of some analytes outside the detection limit of FAAS. Various separation/preconcentration techniques such as solid phase extraction, ion exchange, cloud point extraction, membrane filtration, and coprecipitation are used to solve these problems.[14−21]

Solid phase extraction (SPE) is popular for the enrichment of heavy metals due to its advantages such as high enrichment factor, rapid phase separation, reusability of adsorbents, simple operation, combination with different detection techniques, and low consumption of chemical reagents.[22]

In the present study, two new solid phase extraction methods were developed for separation and preconcentration of Cu(II) and Cd(II) ions by using ethyl [3-(cyanomethyl)-5-(4-methylphenyl)-4H-1,2,4-triazol-4-yl]carbamate (L1) and 4-(4-methylphenyl)-5-{[pyridine-4-yl-4H-1,2,4-triazole-3-yl)thio]methyl} -4H-1,2,4-triazole-3-thiol (L2) as complexing reagents prior to their flame atomic absorption spectrometry (FAAS) determination. The effects of various analytical parameters such as pH, ligand amount, eluent type and volume, and matrix ion were investigated. Then the method was applied to determine Cu(II) and Cd(II) amounts in some food and environmental samples.

2. Results and discussion

2.1. Effect of pH on recovery of Cu(II) and Cd(II)

The effect of pH on the recovery of Cu(II) and Cd(II) was evaluated in the pH range 2.0–10.0 in two enrichment methods separately. The effect of pH on the recovery of Cu(II) and Cd(II) ions is shown in Figure 1. Analyte ions were quantitatively separate from other metal ions at pH 6.0 in both methods. Hence the optimum pH of each method was determined as pH 6.0.
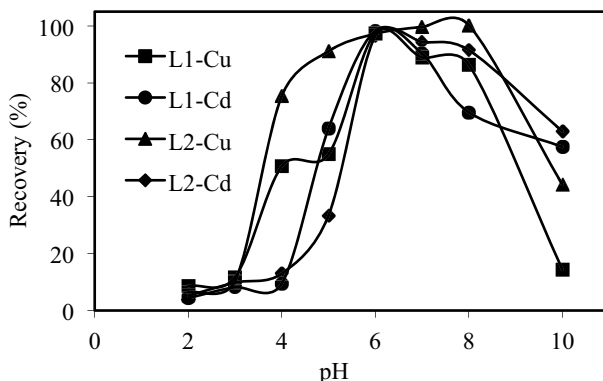

Figure 1. Effect of pH on the recovery of the analyte ions (N = 3, L1 and L2 amounts: 7.5 mg, eluent: 7.5 mL of 1 mol L^{-1}, final volume: 2.0 mL).

2.2. Effect of ligand amount

The effect of L1 amount on the recovery of Cu(II) and Cd(II) ions was examined in the L1 amount range 0–15.0 mg [0–3.0 mL (0.5% (w/v)] in the first method. Under the optimum conditions, the recovery of Cu(II) and Cd(II) ions was below 5.0% without L1 (Figure 2). The recovery of Cu(II) and Cd(II) was quantitative in the L1 amount ranges 3.0–15.0 mg and 7.4–15.0 mg, respectively. Hence all subsequent experiments were performed using 7.5 mg [1.5 mL (0.5% L1)]. In order to determine the effect of L2 amount on the recovery of

Cu(II) and Cd(II) ions, the L2 amount range 0–15.0 mg [0–3.0 mL (0.5% (w/v)] was examined in the second method. The recovery of Cu(II) and Cd(II) was quantitative when using 2.5 mg of L2 (Figure 2). Hence all subsequent experiments were performed using 2.5 mg [0.5 mL (0.5% L2)].
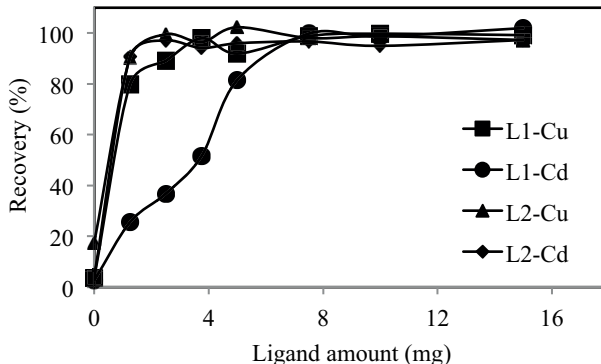

Figure 2. Effect of ligand 1 and ligand 2 concentration on the recovery of Cu(II) and Cd(II) (pH: 6.0, sample volume: 50 mL, N = 3, eluent: 7.5 mL of 1 mol L^{-1} HCl (in acetone)).

2.3. Eluent type and volume

Various solvents were tested as eluent solutions for elution of retained Cu(II) and Cd(II) from Amberlite XAD-1180 resin. Quantitative recovery was achieved using 1 mol L^{-1} HCl in acetone in both methods (Table 1). Afterward the effect of eluent volume was also tested in the eluent volume range 2.5–10.0 mL. When using 7.5 mL of elution solution, the recovery was quantitative in both methods. Hence 7.5 mL was selected as the elution volume.

Table 1. Influence of eluent type and concentration on the recovery of Cu(II) and Cd(II) ions (N = 3; pH 6.0; L1 concentration: 7.5 mg; L2 concentration: 2.5 mg, and sample volume: 50 mL).

Eluent type and concentration	L1		L2	
	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)
	Cu	Cd	Cu	Cd
1 M HCl (in water)	35.9 ± 1.1	42.6 ± 1.9	69.2 ± 5.1	67.2 ± 1.1
1 M HNO$_3$ (in water)	35.1 ± 0.6	54.3 ± 2.0	70.4 ± 0.9	57.4 ± 06
2 M HCl (in water)	52.8 ± 2.3	59.8 ± 4.1	64.6 ± 2.3	68.3 ± 1.0
2 M HNO$_3$ (in water)	37.2 ± 1.3	62.9 ± 2.9	74.9 ± 2.1	70.2 ± 0.3
1 M HCl (in acetone)	98.9 ± 1.3	98.3 ± 4.1	102.7 ± 1.5	100.2 ± 0.8
1 M HNO$_3$ (in acetone)	86.6 ± 5.2	84.3 ± 1.4	75.8 ± 1.0	93.0 ± 0.9
2 M HCl (in acetone)	100.7 ± 0.9	98.8 ± 4.1	98.1 ± 0.3	95.5 ± 4.4
2 M HNO$_3$ (in acetone)	91.9 ± 6.1	89.4 ± 3.8	96.8 ± 1.1	95.5 ± 4.6
1 M HCl (in methanol)	98.4 ± 0.2	89.1 ± 2.4	101.7 ± 1.0	98.6 ± 0.1
1 M HNO$_3$ (in methanol)	96.8 ± 4.3	96.5 ± 5.9	86.5 ± 3.1	95.3 ± 1.6

2.4. Effects of sample volume

To evaluate the effect of sample volume on the recovery of Cu(II) and Cd(II), 50–1000 mL of sample solutions containing 7.5 μg of Cu(II) and 2.5 μg of Cd(II) were processed. In the first method, the recovery of analyte ions was quantitative up to 250 mL for Cu(II) and Cd(II) ions as can be seen from Figure 3. When the recovery

values were examined, the recovery of Cd using L1 ligand was very low in high volumes. This may be explained by the interaction between L1 and Cd being very weak because of high sample volume.
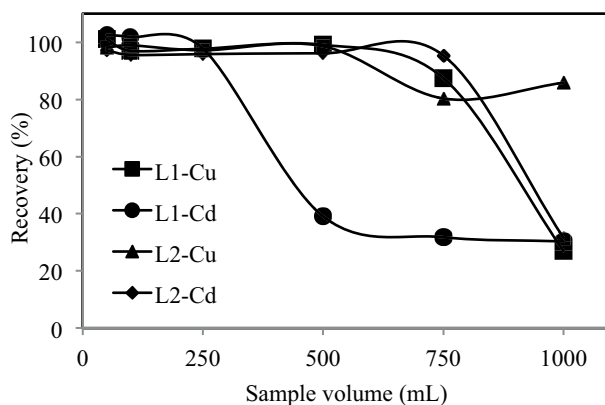

Figure 3. Effect of sample volume on the recovery of Cu(II) and Cd(II) ions (N = 3; pH 6.0; and eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone).

The preconcentration factor (PF) was calculated from the ratio of the highest sample volume and the lowest final volume, and it was 125 when the final volume was 2.0 mL.

In the second method, recovery was quantitative until 500 mL for Cu(II) and Cd(II) ions (Figure 3). The preconcentration factor was calculated as described above and it was 250 when the final volume was 2.0 mL.

2.5. Effects of foreign ions

The interference effects of some foreign ions on the separation and preconcentration of Cu(II) and Cd(II) were evaluated by mixing some common anions, cations, and trace metal ions at different concentrations. Recovery of Cu(II) and Cd(II) was generally higher than 90% in both methods. Hence, the proposed methods can be applied to samples containing high amounts of salt and some transition metal ions at concentration levels given in Table 2.

Table 2. Effect of matrix ions on the recovery of Cu(II) and Cd(II) ions (N = 3; pH 6.0; L1 concentration: 7.5 mg; L2 concentration: 2.5 mg; eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone; and sample volume: 50 mL).

Ion	Added as (mg L^{-1})	Cons.	L1		L2	
			Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)
			Cu	Cd	Cu	Cd
Na$^+$	NaCl	10000	100.5 ± 2.0	100.4 ± 0.6	99.9 ± 1.1	98.8 ± 0.9
K$^+$	KCl	1000	97.3 ± 3.2	99.7 ± 0.9	96.9 ± 1.6	97.1 ± 1.0
Ca^{2+}	CaCl$_2$	1000	91.2 ± 4.2	91.3 ± 0.5	90.9 ± 1.9	94.2 ± 4.3
Mg^{2+}	Mg(NO$_3$)$_2$	1000	91.1 ± 3.5	98.7 ± 2.7	99.2 ± 0.8	102.3 ± 2.8
NO$_3^-$	NaNO$_3$	5000	95.1 ± 3.5	96.2 ± 2.3	98.7 ± 4.2	93.9 ± 2.2
CO$_3^{2-}$	Na$_2$CO$_3$	1000	94.5 ± 1.9	99.3 ± 0.9	97.5 ± 0.8	93.2 ± 1.3
SO$_4^{2-}$	Na$_2$SO$_4$	1000	95.2 ± 2.8	97.0 ± 0.5	94.6 ± 0.6	98.0 ± 2.8
PO$_4^{3-}$	Na$_3$PO$_4$	1000	88.8 ± 5.4	98.7 ± 0.5	95.3 ± 0.1	96.1 ± 0.8
I$^-$	KI	250	96.7 ± 1.2	97.2 ± 2.9	96.0 ± 2.2	98.5 ± 1.3
F$^-$	NaF	250	94.5 ± 4.8	98.1 ± 2.6	96.6 ± 1.1	99.8 ± 3.1
Mixed *			97.0 ± 2.4	96.2 ± 0.6	95.3 ± 0.3	96.8 ± 1.4

[*]10760 mg L^{-1} Na^+, 16110 mg L^{-1} Cl^-, 2030 mg L^{-1} NO_3^-, 250 mg L^{-1} K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, PO_4^{3}, I^-, F^-, 10 mg L^{-1} Cu(II), Cd(II), Ni(II), Al(III), Pb(II), Cr(III), V(V).

2.6. Adsorption capacity of the resin

To determine the capacity of Amberlite XAD-1180 resin in the first SPE method, the pH of 50 mL of solution containing Cu(II) and Cd(II) at concentrations in the range 250–5000 μg was adjusted to 6.0. After adding a sufficient amount of L1, this solution stood for 20 min. Then the final solution was loaded to the column containing 250 mg of resin. Analyte ions were eluted with 7.5 mL of 1 mol L^{-1} HCl in acetone. Final solutions were appropriately diluted and Cu(II) and Cd(II) were analyzed by FAAS. The Langmuir isotherms were plotted in order to determine the resin capacity, where q_e (mg g^{-1}) is the amount of element adsorbed per unit mass of adsorbent, and C_e (mg L^{-1}) is the equilibrium element concentration in aqueous solution (Figures 4a and 4b). The maximum amount of Cu(II) adsorbed on 1.0 g of resin and the adsorption equilibrium constant were calculated as 2.24 mg g^{-1} and 0.060 L mol^{-1}, respectively. The maximum amount of Cd(II) ions adsorbed on 1.0 g of resin and the adsorption equilibrium constant were 2.29 mg g^{-1} and 0.081 L mol^{-1}, respectively.

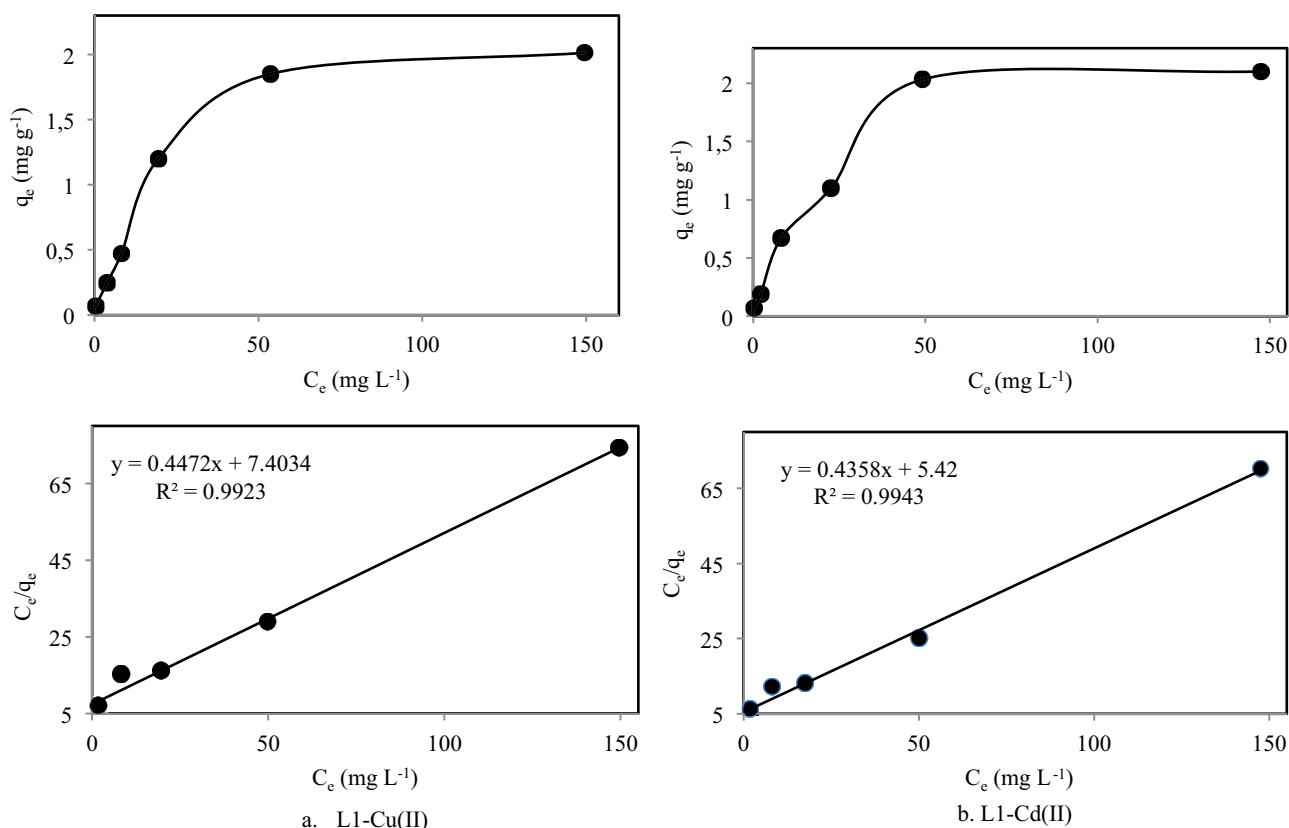**Figure 4.** Langmuir isotherm plots for the determination of resin capacity a. L1-Cu(II), b. L1-Cd(II).

In the second SPE method, to determine the capacity of Amberlite XAD-1180 resin different amounts of Cu(II) and Cd(II) in the range of 250–5000 μg were loaded onto a column containing 250 mg of resin. The analytes in the eluents were determined by FAAS as the first method and the adsorption capacity of resin

calculated from Langmuir isotherms (Figures 5a and 5b). The maximum amounts of Cu(II) and Cd(II) ions adsorbed on 1.0 g of resin were 2.28 mg g^{-1} and 2.19 mg g^{-1}, respectively. The adsorption equilibrium constant for Cu(II) and Cd(II) ions was 0.071 L mol^{-1} and 0.082 L mol^{-1}, respectively.
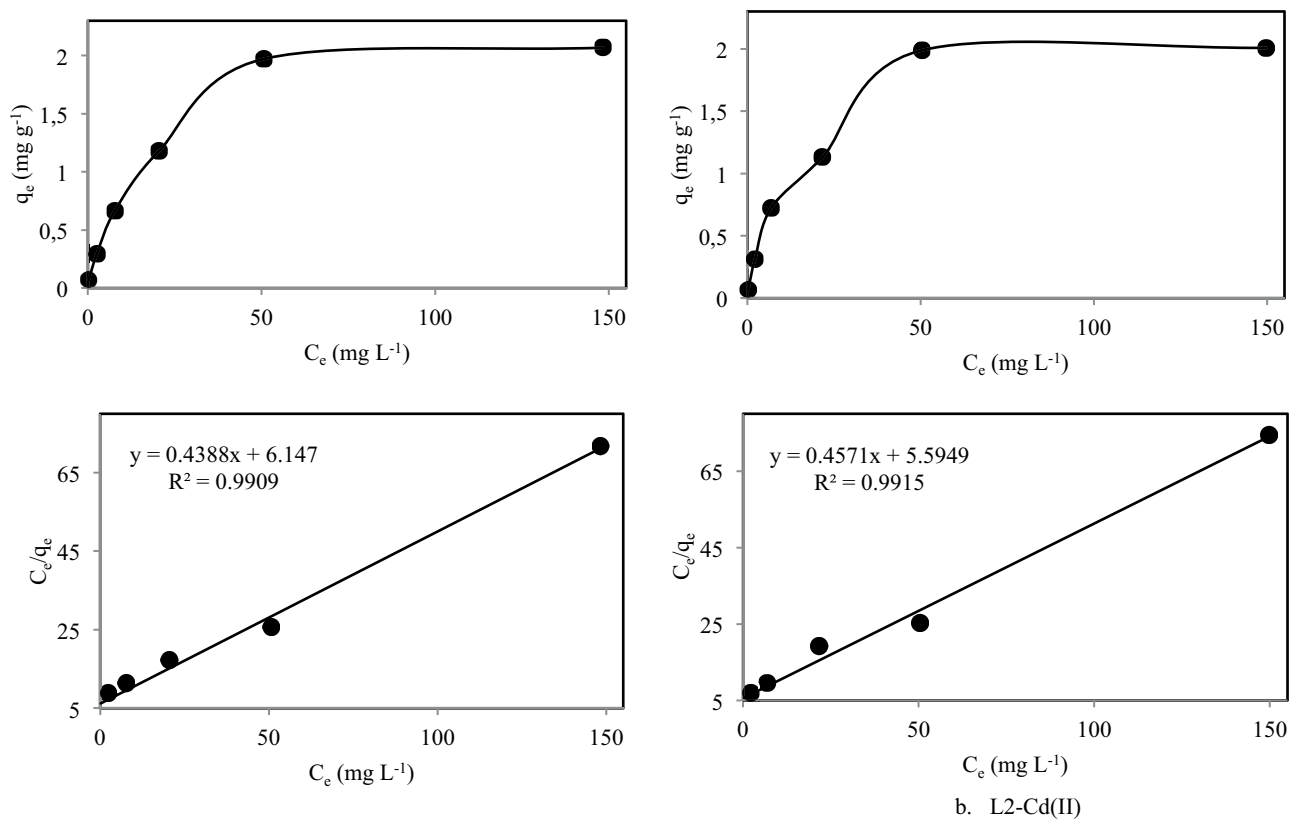

Figure 5. Langmuir isotherm plots for the determination of resin capacity a. L2-Cu(II), b. L2-Cd(II).

2.7. Analytic performance of the presented method

Limit of detection (LOD) was defined as the concentration that gives a signal equivalent to three times the standard deviation for 10 replicate measurements of the blank samples. LOD was 0.15 μg L^{-1} for Cu(II) and 0.11 μg L^{-1} for Cd(II) in the first SPE method. Linear dynamic ranges were 0.06–8.00 μg/mL and 0.05–2.25 μg/mL for Cu(II) and Cd(II), respectively. In the second method LOD was 0.47 μg L^{-1} for Cu(II) and 0.06 μg L^{-1} for Cd(II). The linear dynamic ranges of Cu(II) and Cd(II) were 0.39–8.50 μg/mL and 0.05–2.50 μg/mL, respectively. In order to evaluate the precision of the procedures, expressed as the relative standard deviation (RSD), the procedures were repeated 10 times under optimum conditions. From the results the RSD was 3.90% for Cu(II) and 4.49% for Cd(II) ions in the first method. In the second method the RSD was 6.94% for Cu(II) and 3.12% for Cd(II).

2.8. Method validation and applications to real samples

In order to evaluate the accuracy of the method, different amounts of Cu(II) and Cd(II) ions were spiked in 50-mL seawater and stream water samples, and 0.750-g rice, lentil, tea, tobacco, bulgur, chickpea, wheat, red

Table 3. Spiked recoveries of Cu(II) and Cd(II) ions from water samples (L1) (N = 3; pH 6.0; L1 concentration: 7.5 mg; eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone; and sample volume: 50 mL).

Element	Added (μg)	River water		Seawater	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cu(II)	0	BDL*	-	BDL*	-
	10.0	9.38 ± 0.25	94.0	9.44 ± 0.14	94.4
	20.0	19.66 ± 0.14	98.3	19.46 ± 0.16	97.3
Cd(II)	0	BDL*	-	BDL*	-
	1.0	0.95 ± 0.02	95.0	0.95 ± 0.01	95.0
	2.0	1.86 ± 0.02	93.0	1.90 ± 0.05	95.0

*Below detection limit

Table 4. Spiked recoveries of Cu(II) and Cd(II) ions from water samples (L2) (N = 3; pH 6.0; L2 concentration: 2.5 mg; eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone; and sample volume: 50 mL).

Element	Added (μg)	River water		Seawater	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cu(II)	0	BDL*	-	BDL*	-
	10.0	9.47 ± 0.31	94.7	9.27 ± 0.42	92.6
	20.0	19.26 ± 0.18	96.3	19.25 ± 0.25	96.2
Cd(II)	0	BDL*	-	BDL*	-
	1.0	0.94 ± 0.01	94.0	0.95 ± 0.03	94.5
	2.0	1.90 ± 0.05	95.0	1.86 ± 0.04	93.0

*Below detection limit

pepper, black pepper, peppermint, and dried eggplant samples. Then the SPE methods given above were applied to the samples. Good agreement was obtained between the added and measured analyte amounts in both SPE methods (Table 3–6). The results showed that the presented SPE methods can be applied for separation and preconcentration of Cu(II) and Cd(II) ions in environmental samples. Certified reference materials (CRM-SA-C Sandy Soil C and CRM-TMDW-500 Drinking Water) were also used for method validation and good agreement was obtained between analytical and certified values in both methods (Table 7).

After the accuracy of the methods was verified, the procedures were applied for the determination of trace Cu(II) and Cd(II) ions in rice, lentil, tea, tobacco, bulgur, chickpea, wheat, red pepper, black pepper, peppermint, and dried eggplant samples as solid samples and seawater and stream water as liquid samples (Tables 8 and 9).

The developed methods, based on the adsorption of the L1-Cu(II), L1-Cd(II), L2-Cu(II), and L2-Cd(II) complexes on Amberlite XAD-1180 resin provide simple, rapid and low cost separation and preconcentration methods for accurate and precise determination of analyte ions in environmental and food samples. The proposed methods are not influenced by various common ions present together with analyte ions. The procedures were also successfully employed for the determination of analyte ions in some environmental and food samples. The procedures were compared with other SPE methods in terms of pH, preconcentration factor, limit of detection, relative standard deviation, type of sample, and determination techniques (Table 10). The two proposed methods have high preconcentration factor, and low RSD and LOD values when compared to some other methods reported in Table 10.[23−30] Additionally, adsorption capacity of the resin for Cu(II) and Cd(II) is broadly similar to that of some other methods in the literature.[14,23,24,26] When these two methods are compared

Table 5a. Spiked recoveries of Cu(II) and Cd(II) ions from solid samples (L1) (N = 3; pH 6.0; ligand concentration: 7.5 mg; eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone; sample quantity: 0.750 g; and final volume: 2.0 mL).

		Rice		Lentil		Tea	
Element	Added (μg)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
	0	2.62 ± 0.3	-	1.06 ± 0.42	-	1.25 ± 0.24	-
Cu(II)	10.0	11.1 ± 0.19	93.2	10.45 ± 0.30	94.0	11.04 ± 0.3	97.0
	20.0	21.1 ± 0.04	92.5	18.93 ± 0.18	94.6	20.85 ± 0.2	98.0
	0	0.23 ± 0.08	-	0.14 ± 0.05	-	0.17 ± 0.04	
Cd(II)	1.0	1.13 ± 0.02	90.0	1.1 ± 0.03	95.5	1.08 ± 0.02	92.0
	2.0	2.11 ± 0.05	94.0	2.08 ± 0.03	97.3	2.01 ± 0.09	91.75
		Bulgur		Chickpea		Wheat	
	0	1.18 ± 0.72	-	3.7 ± 0.3	-	1.26 ± 0.8	-
Cu(II)	10.0	10.46 ± 0.11	92.8	13.11 ± 0.18	94.1	10.96 ± 0.5	97.0
	20.0	20.29 ± 0.18	95.5	22.94 ± 0.12	96.2	20.56 ± 0.4	96.5
	0	0.13 ± 0.01	-	0.19 ± 0.03	-	0.16 ± 0.08	
Cd(II)	1.0	1.08 ± 0.04	95.0	1.15 ± 0.03	95.0	1.01 ± 0.07	91.0
	2.0	2.02 ± 0.08	94.5	2.07 ± 0.02	94.0	2.08 ± 0.05	95.8

Table 5b. Spiked recoveries of Cu(II) and Cd(II) ions from solid samples (L1) (N = 3; pH 6.0; ligand concentration: 7.5 mg; eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone; sample quantity: 0.750 g; and final volume: 2.0 mL).

		Red pepper		Black pepper		Peppermint	
Element	Added (μg)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
	0	1.6 ± 0.45	-	1.6 ± 0.6	-	1.8 ± 0.2	-
Cu(II)	10.0	11.01 ± 0.25	94.7	10.96 ± 0.31	93.6	11.5 ± 0.2	97.0
	20.0	20.68 ± 0.08	95.4	21.03 ± 0.86	97.0	21.4 ± 0.5	98.0
	0	0.15 ± 0.03	-	0.27 ± 0.01	-	0.19 ± 0.06	-
Cd(II)	1.0	1.07 ± 0.06	91.5	1.22 ± 0.04	94.5	1.11 ± 0.04	92.0
	2.0	2.03 ± 0.06	94.0	2.14 ± 0.06	93.3	2.06 ± 0.05	93.5
		Dried eggplant		Tobacco			
	0	2.16 ± 0.28	-				
Cu(II)	10.0	11.68 ± 0.24	95.2				
	20.0	21.42 ± 0.5	96.3				
	0	0.21 ± 0.05	-	0.98 ± 0.08	-		
Cd(II)	1.0	1.15 ± 0.01	94.0	1.92 ± 0.03	94.0		
	2.0	2.12 ± 0.03	95.5	2.87 ± 0.05	94.5		

with each other, both methods have the same optimum pH, but the second method has a high preconcentration factor. While the LOD of the second method is lower than that of the first method for Cd(II), the LOD of first method is lower for Cu(II). Moreover, the first solid phase extraction method has a better RSD than the second method.

3. Experimental

3.1. Instrument

The analyte measurements were performed using a Unicam model AA-929 flame atomic absorption spectrometer with an air/acetylene flame. The instrumental parameters were determined according to the manufacturer's recommendations. The pH measurements were made on a Hanna pH-211 (Hanna Instruments, Romania) digital pH meter with a glass electrode. A Sigma 3-16P (Sigma Laborzentrifugen GmbH, Germany) model centrifuge

Table 6a. Spiked recoveries of Cu(II) and Cd(II) ions from solid samples (L2) (N = 3; pH 6.0; ligand concentration: 2.5 mg; eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone; sample quantity: 0.750 g; and final volume: 2.0 mL).

		Rice		Lentil		Tea	
Element	Added (μg)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
	0	2.38 ± 0.12	-	1.47 ± 0.35	-	1.16 ± 0.52	-
Cu(II)	10.0	11.98 ± 0.06	96.0	11.07 ± 0.16	96.0	11.48 ±0.12	98.75
	20.0	22.05 ± 0.21	98.1	21.11 ± 0.12	98.2	21.03± 0.28	98.5
	0	0.21 ± 0.03	-	BDL*	-	0.16 ± 0.06	-
Cd(II)	1.0	1.11 ± 0.02	93.0	1.15 ± 0.03	92.0	1.1 ± 0.05	93.5
	2.0	2.09 ± 0.05	94.0	2.2 ± 0.06	94.5	2.05 ± 0.04	95.0
		Bulgur		Chickpea		Wheat	
	0	1.06 ± 0.56	-	3.18 ± 0.35	-	1.51 ± 0.21	-
Cu(II)	10.0	10.9 ± 0.17	98.4	12.73 ± 0.4	95.6	11.08 ± 0.24	95.7
	20.0	21.13 ± 0.01	98.4	22.1 ± 0.94	94.6	21.13 ± 0.13	98.1
	0	0.15 ± 0.06	-	0.18 ± 0.02	-	BDL*	
Cd(II)	1.0	1.07 ± 0.04	92.0	1.13 ± 0.03	95.0	1.09 ± 0.03	96.0
	2.0	2.10 ± 0.05	97.3	2.01 ± 0.03	96.3	2.07 ± 0.04	97.0

*Below detection limit

Table 6b. Spiked recoveries of Cu(II) and Cd(II) ions from solid samples (L2) (N = 3; pH 6.0; ligand concentration: 2.5 mg; eluent: 7.5 mL of 1.0 mol L^{-1} HCl in acetone; sample quantity: 0.750 g; and final volume: 2.0 mL).

		Red pepper		Black pepper		Peppermint	
Element	Added (μg)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
	0	1.14 ± 0.42	-	1.02 ± 0.26	-	1.72 ± 0.60	-
Cu(II)	10.0	10.91 ± 0.22	97.7	10.73 ± 0.3	99.1	11.1 ± 0.35	94.0
	20.0	20.87 ± 0.21	98.7	20.6 ± 0.41	97.7	21.15 ± 0.8	97.1
	0	0.16 ± 0.03	-	0.24 ± 0.07	-	0.16 ± 0.04	-
Cd(II)	1.0	1.11 ± 0.04	95.0	1.19 ± 0.01	95.0	1.09 ± 0.04	93.0
	2.0	2.01 ± 0.05	92.5	2.19 ± 0.03	97.5	2.07 ± 0.06	95.5
		Dried eggplant		Tobacco			
	0	2.89 ± 0.83	-				
Cu(II)	10.0	12.4 ± 0.48	95.1				
	20.0	21.94 ± 0.9	95.3				
	0	0.21 ± 0.02	-	0.97 ± 0.05	-		
Cd(II)	1.0	1.17 ± 0.03	96.0	1.92 ± 0.04	94.5		
	2.0	2.15 ± 0.04	96.8	2.86 ± 0.06	94.5		

Table 7. Determination of Cu(II) and Cd(II) ions in certified reference material for accuracy test of the method (pH 6.0, CRM-SA-C Sandy Soil C amount: 0.250 g, CRM TMDW-500 Drinking Water: 50.0 mL final volume: 2.0 mL).

L1					L2			
	CRM-SA-C Sandy Soil C		CRM TMDW-500 Drinking Water		CRM-SA-C Sandy Soil C		CRM TMDW-500 Drinking Water	
Element	Certified value (μg g^{-1})	Found value (μg g^{-1})	Certified value (μg g^{-1})	Found value (μg g^{-1})	Certified value (μg g^{-1})	Found value (μg g^{-1})	Certified value (μg g^{-1})	Found value (μg g^{-1})
Cu(II)	63.6 ± 4.0	62.44 ± 2.8	20.0 ± 0.2	18.5 ± 0.7	63.6 ± 4.0	62.19 ± 1.8	20.0 ± 0.2	19.03 ± 1.3
Cd(II)	109 ± 8	104.7 ± 0.3	10.0 ± 0.1	9.02 ± 0.2	109 ± 8	105.8 ± 0.4	10.0 ± 0.1	9.18 ± 0.6

Table 8. Analyte levels in real liquid samples after treatment with the proposed SPE procedure (N = 3 and final volumes: 2.0 mL).

Element	L1 Liquid samples (μg L^{-1})		L2 Liquid samples (μg L^{-1})	
	Seawater	River water	Seawater	River water
Cu(II)	5.2 ± 0.21	5.4 ± 0.35	6.2 ± 0.65	5.6 ± 0.32
Cd(II)	4.16 ± 0.03	5.04 ± 0.05	5.16 ± 0.3	4.34 ± 0.06

Table 9. Analyte levels in real solid samples (μg g^{-1}) after treatment with the proposed SPE procedure (N = 3 and final volumes: 2.0 mL).

L1						
Element	Rice	Lentil	Tea	Bulgur	Chickpea	Wheat
Cu(II)	3.5 ± 0.16	1.4 ± 0.28	1.7 ± 0.14	1.6 ± 0.37	4.9 ± 0.63	1.68 ± 0.33
Cd(II)	0.31 ± 0.1	0.19 ± 0.03	0.23 ± 0.4	0.17 ± 0.01	0.25 ± 0.02	0.21 ± 0.04
Element	Red pepper	Black pepper	Peppermint	Dried eggplant	Tobacco	
Cu(II)	2.1 ± 0.72	2.1 ± 0.26	2.4 ± 0.18	2.88 ± 1.2	-	
Cd(II)	0.2 ± 0.02	0.36 ± 0.04	0.25 ± 0.06	0.28 ± 0.03	1.31 ± 0.02	
L2						
Element	Rice	Lentil	Tea	Bulgur	Chickpea	Wheat
Cu(II)	3.2 ± 0.21	1.96 ± 0.15	1.55 ± 0.34	1.41 ± 0.23	4.24 ± 0.11	2.01 ± 0.13
Cd(II)	0.28 ± 0.2	BDL	0.21 ± 0.04	0.2 ± 0.03	0.24 ± 0.08	BDL
Element	Red pepper	Black pepper	Peppermint	Dried eggplant	Tobacco	
Cu(II)	1.5 ± 0.56	1.36 ± 0.06	2.29 ± 0.13	3.85 ± 0.18	-	
Cd(II)	0.21 ± 0.2	0.32 ± 0.03	0.21 ± 0.05	0.28 ± 0.02	1.29 ± 0.06	

Table 10. Comparison of the developed procedures with some recent studies based on SPE reported in the literature.

Analytes	pH	PF		LOD (μg L^{-1})		RSD %		Techniques	Reference
		Cu	Cd	Cu	Cd	Cu	Cd		
Ni, Cd, Co, Zn	5.0	-	50	-	0.23	-	2.71	FAAS	23
Cd, Pb	9.0	-	250	-	0.19	-	< 7	FAAS	24
Cd	4.8	-	160	-	0.38	-	3.2	FAAS	25
Cd	8.0	-	50	-	3.15*	-	4.9	HG-AFS**	26
Cd, Hg, Ag, Cu	6.0	100	400	0.39	0.10	< 10	< 10	ICP–OES	27
Cu, Ni	8.0	50	-	1.03	-	7	-	FAAS	28
Cu	7.0	60	-	1.46	-	-	-	FAAS	29
Cu, Cd, Pb, Ni	6.0	50	50	0.18	0.18	< 7	< 7	FAAS	30
Cu, Cd	6.0	125	125	0.15	0.11	3.90	4.49	FAAS	This work (L1)
Cu, Cd	6.0	250	250	0.47	0.06	6.94	3.12	FAAS	This work (L2)

*ng L^{-1} **Hydride generation atomic fluorescence spectrometry

was used to centrifuge solutions. A Milestone Ethos D (Milestone Inc., Italy) closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was operated for digestion of the solid samples.

3.2. Reagents and solutions

All of the chemicals used in this study were analytical grade chemicals from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Distilled/deionized water was obtained from Sartorius Milli-Q system (arium®611UV)

and used in all experiments. Diluted HNO_3 and NaOH solutions were used for pH adjustments. CRM-SA-C Sandy Soil C and CRM-TMDW-500 Drinking Water certified reference materials were purchased from High Purity Standard Inc. Amberlite XAD-1180 resin was purchased from Sigma. Standard solutions of metal ions were prepared by diluting the stock solution in appropriate amounts. L1 and L2 were synthesized according to the literature in an organic chemistry research laboratory (Chemistry Department, Faculty of Science, Karadeniz Technical University) and 0.5% (w/v) L1 and L2 solutions were prepared in ethanol.[31,32] Synthesized ligands are easily reproducible and stable at room temperature.[33,34]

3.3. Column preparation

Amberlite XAD-1180 resin was washed with 0.1 mol L^{-1} HNO_3, water 0.1 mol L^{-1} NaOH, water, acetone, and water consecutively and dried at 105 °C in an oven. Then 50 mg of washed resin was slurred in water and poured into a glass column (length: 10 cm and diameter: 1.0 cm) with a porous disk and stopcock. After each use, the resin in the column was thoroughly washed with water and then stored in water for further application.

3.4. Sample preparation

Seawater (Black Sea, Trabzon, Turkey) and stream water (River Sana, Trabzon) samples were collected in prewashed polyethylene bottles. After filtration through a cellulose nitrate membrane of pore size 0.45 nm, the samples were acidified with 1 mL of 1% v v^{-1} HNO_3, and stored at 4 °C in a refrigerator.

Rice, lentils, tea, tobacco, bulgur, chickpeas, wheat, red pepper, black pepper, peppermint, and dried eggplant were purchased from the local market. Each sample (0.750 g) was weighed with sensitivity of 0.1 mg into a Teflon vessel, separately. Next 4.5 mL of HCl, 1.5 mL of HNO_3, 2 mL H_2O_2, and 1 mL of HF were added to the vessels and, to perform digestion with the microwave system, cycles of 6 min (each at 46 bar) were applied at 250 W, 400 W, 650 W, and 250 W, vent: 3 min. After microwave digestion the volumes of the samples were made up to 50.0 mL with distilled water.

3.5. Preconcentration procedure and FAAS analysis

The pH of 50-mL sample solution containing 7.5 μg of Cu(II) and 2.5 μg of Cd(II) was adjusted to 6.0 by addition of diluted NaOH and HNO_3, and 1.5 mL (0.5% (w/v)) of L1 was added in the first method. After waiting 15 min, the final solution was passed through the Amberlite XAD-1180 column at a flow rate 20 mL min^{-1}. The retained metal ions on the columns were eluted by 7.5 mL of 1 mol L^{-1} HCl solution in acetone. After the eluent was evaporated approximately to dryness on the hot plate, volume was made up to 2.0 mL with distilled water. The final solution was analyzed by FAAS for determination of analyte elements.

The second method, with L2, was carried out in the same protocol with one exception: 0.5 mL (0.5% (w/v)) of L2 was added instead of L1. The pH of the model solution was adjusted to 6.0 and left for 15 min. The final solution was passed through the Amberlite XAD-1180 column and retained metal ions were eluted by 7.5 mL of 1 mol L^{-1} HCl solution in acetone. The final solution was analyzed by FAAS for determination of analytes.

3.6. Application of real samples

The presented methods were applied to rice, lentils, tea, tobacco, bulgur, chickpeas, wheat, red pepper, black pepper, peppermint, and dried eggplant as solid samples and seawater and stream water as liquid samples.

The methods were also applied to CRM-SA-C Sandy Soil C as certified reference material. After microwave digestion, the volumes of the samples were diluted with distilled water (up to 50 mL) and each proposed method was applied separately.

CRM TMDW-500 Drinking Water was also analyzed as certified reference material. For this, 25 mL of CRM-TMDW-500 Drinking Water was taken and the solid phase extraction methods given above were applied separately.

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