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# *Pleurotus eryngii* immobilized Amberlite XAD-16 as a solid-phase biosorbent for preconcentrations of $Cd^{2+}$ and $Co^{2+}$ and their determination by ICP-OES

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ABSTRACT

This article reports a method that is used for the preconcentration and determination of $Cd^{2+}$ and $Co^{2+}$ in vegetables, using *Pleurotus eryngii* immobilized Amberlite XAD-16 as a solid-phase biosorbent. The concentrations of metals were determined by inductively coupled plasma-optical spectrometry (ICP-OES). Critical parameters, such as the pH of the solution, flow rate, the amount of biosorbent, type and volume of eluent, and the sample volume, that affect the solid-phase extraction (SPE) procedure were optimized. The optimum extraction conditions were determined as being a pH of 6.0 for $Cd^{2+}$ and of 5.0 for $Co^{2+}$; a sample flow rate of 2.0 mL $min^{-1}$; 200.0 mg of biosorbent; and 5.0 mL of 1.0 mol $L^{-1}$ HCl as eluent. The capacities of the biosorbent for metal uptake were found to be 11.3 and 9.8 mg $g^{-1}$ for $Cd^{2+}$ and $Co^{2+}$ ions, respectively. Limit of quantitations (LOQs) were found to be 0.67 and 0.82 ng $mL^{-1}$, respectively, for $Cd^{2+}$ and $Co^{2+}$. The linear working curves were observed to be in the linear range from 1.0 to 50.0 ng $mL^{-1}$, and possessed high correlation coefficients. The use of the SPE method showed 50.7- and 35.7-fold improvements in the sensitivities of ICP-OES. The developed method was successfully applied to NCS ZC-73014 (a certified reference tea sample). Relative standard deviations (RSD) were lower than 5.0%. The $Cd^{2+}$ and $Co^{2+}$ concentrations in the different parts (leave, root, stem, and fruit) of purslane, onion, rocket, okra, and aubergine were determined after microwave digestion and solid-phase extraction by *P. eryngii* immobilized on Amberlite XAD-16.

## 1. Introduction

Nowadays, the significance of heavy metal pollution in threatening the living system is well understood [1]. The main sources of heavy metal pollution in environmental samples are industrial facilities, traffic, and antrophogenic activities [2]. It was reported that some heavy metals, for example, manganese, copper, and cobalt, are required by humans, whereas other heavy metals such as lead, cadmium, and nickel have a toxic effect on human health, even at trace levels [3]. Although cobalt is toxic when used in large amounts, it is essential to humans at trace levels. Long-period exposure to cobalt is one of the reasons behind toxicity [4]. It is also well known that cadmium is a highly toxic element which has hazardous effects on human health [5]. Every country establishes its regulations by considering the tolerance limit of these metals.

Analytical techniques that have been used for the determination of heavy metal ions in the real samples include inductively coupled plasma-optical emission spectrometry (ICP-OES) [6], inductively coupled plasma-mass spectrometry (ICP-MS) [7], electrothermal atomic absorption spectrometry (ETAAS) [8], and flame atomic absorption spectrometry (FAAS) [9]. These techniques are both widely and routinely used for the determination of trace amounts of heavy metal ions. However, the direct determination of heavy metal ions at trace levels is limited due to their low concentrations and matrix effects. This limitation can be overcome by use of a separation and preconcentration step before instrumental analysis [10] if the sensitivity of the instrument is not enough for the analyte. Different techniques are used for the separation and preconcentration of metals in solutions. These techniques include solid-phase extraction (SPE), precipitation, liquid–liquid extraction, cation-exchange resins, and cloud-point extraction [11–15]. Among them, SPE is a routine extraction method that is used for obtaining the trace levels of contaminants in environmental samples. This technique has some advantages compared with other preconcentration methods, such as a higher preconcentration factor, better efficiency, greater reproducibility,

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and greater simplicity in handling and transfer [16]. SPE, the suitable adsorbent usage involves a critical factor in order to obtain a high enrichment factor [17]. Many substances have been used as solid-phase sorbents, such as chelating resin [18], bentonite [19], activated carbon [20], and biological substances [21]. The usage of biological substances for the preconcentration and separation of traces of heavy metals and some organic materials at trace levels is popular due to good adsorption properties such as high surface area and high adsorption capacities for biological substances [22].

In the present work, the analytical potential of *Pleurotus eryngii* as a solid-phase biosorbent for the preconcentration of trace levels of $Cd^{2+}$ and $Co^{2+}$ was studied, and experimental parameters were optimized through the study. The applicability of the method was tested against the certified reference sample and edible vegetables. The sensitivity of ICP-OES was also improved for the determination of $Cd^{2+}$ and $Co^{2+}$.

## 2. Experimental

### 2.1. Instrumentation

The concentrations of metal ions were determined by Perkin Elmer Optima 2100 DV inductively coupled plasma-optical emission spectrometry (ICP-OES). A Mettler Toledo MPC 227 (Polaris Parkway, Columbus) model digital pH meter was used to adjust the pH of the solutions. Filtration columns (1.0 cm × 10.0 cm) equipped with polypropylene frites were used for solid-phase extraction (SPE). A Waters Marlow 323 (Milford, MA) model peristaltic pump was used to enable the solutions to pass through the column. The operating conditions of the ICP-OES are displayed in Table 1.

### 2.2. Reagents and solutions

Analytical-reagent grade chemicals were used in experiments. The stock standard solutions containing 1000 mg $L^{-1}$ of $Cd^{2+}$ and $Co^{2+}$ (from Merck Darmstadt-Germany) were used to prepare lower concentrations. A certified reference tea sample (NCS ZC-73014) was supplied by the China National Analysis Center for Iron and Steel. The laboratory glasswares were kept overnight in a 1.0 mol $L^{-1}$ nitric acid solution before use; thoroughly rinsed with distilled-deionized water; and, finally, dried.

**Table 1**
Operating conditions of the ICP-OES.

| Parameter | |
|---|---|
| RF power (W) | 1450 |
| Plasma gas flow rate (L $min^{-1}$) | 15 |
| Auxiliary gas flow rate (L $min^{-1}$) | 0.2 |
| Nebulizer gas flow rate (L $min^{-1}$) | 0.8 |
| Sample flow rate (L $min^{-1}$) | 1.5 |
| View mode | Axial |
| Read | Peak area |
| Source equilibration time (s) | 15 |
| Read delay (s) | 50 |
| Replicates | 3 |
| Background correction | 2-point (manual point correction) |
| Spray chamber | Scott type spray chamber |
| Nebulizer | Cross-flow gem tip nebulizer (HF resistant) |
| Detector | CCD |
| Purge gas | Nitrogen |
| Shear gas | Air |
| Gas | Argon |
| Analytical wavelength (nm) | Cd 228.804<br>Co 228.616 |

Amberlite XAD-16 (polystyrene divinyl benzene) was supplied by Sigma. The organic and inorganic impurities in resin were removed by treatment with 4.0 mol $L^{-1}$ HCl. Then, the resin was rinsed with distilled water until its pH level was neutral, followed with a rinsing in an ethanol–water (1:1) solution. Finally, it was washed with distilled water again and was then stored in a polyethylene bottle.

### 2.3. Preparation of SPE columns

*Pleurotus eryngii* as biomass was collected from the south-eastern regions of Turkey. The fungal sample was washed twice with distilled water to remove contaminants and then dried at room temperature. The dried fungal biomass was ground in a porcelain mortar to obtain a fine powder. It was then dried at 80 °C in an oven for 24 h to assess the complete death of the dried cells. Finally, the cells were inoculated to malt agar at 25 °C for 24 h. The absence of mycelia in *P. eryngii* indicated positive results, which reflects the complete death of the fungus. Dry biomass powder (250.0 mg) was mixed with 1.0 g of Amberlite XAD-16 and 10.0 mL of double-distilled water, and then thoroughly mixed. The amount of biomass taken up by the resin was determined by measuring the increase in the weight of the resin after mixing the paste that had been heated in an oven at about 105 °C for 1 h to dry the mixture. The wetting and drying steps were repeated to maximize the contact between biomass and resin, thereby improving the immobilization efficiency. Finally, the product obtained was ground to get the original size (20–60 mesh) and was packed in a solid-phase column (1.0 cm × 10.0 cm).

### 2.4. General sorption studies

The 50.0-mL model solutions containing 50.0 ng $mL^{-1}$ of $Cd^{2+}$ and $Co^{2+}$ were prepared by diluting the stock solution of metals. The pH of the model solution was adjusted to the desired value, and then, this solution was passed through the solid-phase extraction (SPE) column by means of a peristaltic pump. After completing this, 10.0 mL of distilled water was passed through the column. The retained $Cd^{2+}$ and $Co^{2+}$ ions on the biosorbent were then eluted from the solid phase with 5.0 mL of 1.0 mol $L^{-1}$ HCl. The concentrations of the $Cd^{2+}$ and $Co^{2+}$ ions in solution were simultaneously determined by ICP-OES. *Pleurotus eryngii* immobilized on XAD-16 was repeatedly used (up to 20) after washing with 1.0 mol $L^{-1}$ HCI solution and distilled water, respectively.

### 2.5. Preparation of samples

Samples of the edible vegetables were randomly collected along the cultivated banks of the Tigris River, Diyarbakır, Turkey. All of the samples were stored in polyethylene bags according to their type and brought to the laboratory for sample preparation and digestion. All the vegetables were washed in fresh running water to eliminate dust, dirt, possible parasites, and their eggs. After the prewashing step, they were washed with deionized water, and then oven dried at 80 °C for 24 h before grinding them. Edible vegetables and certified reference samples of tea (NCS ZC-73014) were digested in a temperature- and pressure-controlled analytical microwave oven. A 2.0-g portion of tea was weighted and inserted in a beaker. A pre-digestion step was performed because of the low level of $Cd^{2+}$ in the certified leave sample. Then, 5.0 mL of concentrated $HNO_3$:HCl (1:1) was added and carefully shaken with a clean glass bar for 30.0 min until the achievement of dryness. This procedure was repeated twice; then, a 6.0-mL mixture of concentrated $HNO_3$:HCl:$H_2O_2$ (1:1:0.2) was added to the beaker and transferred to the microwave vessel (speedwave MWS-3, Berghof). It was digested by a procedure recommended by the manufacturer. The same microwave program was directly applied to a 0.5-g portion of edible vegetables without the pre-digestion procedure. The final volume was completed at 50.0 mL, and the developed biosorption method was applied to the samples. The concentrations of analytes in the samples were determined by ICP-OES.

### 2.6. Loading capacity

With the aim of determining the loading capacity of *Pleurotus eryngii* immobilized on Amberlite XAD-16, 50.0 mg of *P. eryngii* immobilized on Amberlite XAD-16 was added to a 100.0-mL solution containing 10.0 mg $Cd^{2+}$ and $Co^{2+}$ at pH 6.0 and 5.0 for $Cd^{2+}$ and $Co^{2+}$, respectively. The mixture was shaken at 25 °C for 2 h. After centrifugation, the $Cd^{2+}$ and $Co^{2+}$ ions in the centrifuged solution were determined by ICP-OES. The loading capacity of the resin was calculated from the equation provided in the literature [23].

## 3. Results and discussion

### 3.1. Effect of pH on recovery

The initial pH of solutions is the most important parameter that is used for biosorption studies [23]. The solution pH strongly influences the solution chemistry of metals, the activity of functional groups (carboxylate, phosphate, and amino groups) on the cell wall, and the competition of metallic ions for the binding site [23,24]. The effect of pH on the recovery of $Cd^{2+}$ and $Co^{2+}$ onto *Pleurotus eryngii* immobilized on Amberlite XAD-16 was examined in the pH range of 2.0–8.0. For this purpose, column experiments were performed by using 50.0 mL of test solutions containing 2.5 μg of $Cd^{2+}$ and $Co^{2+}$ ions. In Fig. 1, the effects of the initial pH on the biosorption of $Cd^{2+}$ and $Co^{2+}$ ions in aqueous solution are depicted. The removal efficiencies of $Cd^{2+}$ and $Co^{2+}$ ions in the solution at a pH of 2.0 were found to be 43.1% and 39.2%, respectively, and they increased when the solution pH increased from 2.0 to 4.0. At a pH of 4.0, the removal rates of $Cd^{2+}$ and $Co^{2+}$ ions were 75.6% and 89.4%, respectively. Thus, a pH of 6.0 was selected for $Cd^{2+}$, whereas a pH of 5.0 was optimum for $Co^{2+}$. Maximum biosorption capacities were also calculated at a pH of 6.0 and 5.0 for $Cd^{2+}$ and $Co^{2+}$, respectively.

### 3.2. Effect of flow rate of sample solution on recovery

Flow rate of the metal ions solution, which is directly related to the contact of the solution with the solid phase, is one of the important factors affecting the amount of metals in the eluent [25,26]. The influence of the flow rate of the sample solution on $Cd^{2+}$ and $Co^{2+}$ (II) biosorption onto *P. eryngii* immobilized on Amberlite XAD-4 was investigated in the range of 1.0–6.0 mL min$^{-1}$. Recovery results depend on the flow rate of the solution and are displayed in Fig. 2. It was found that the recovery of $Cd^{2+}$ and $Co^{2+}$ ions was not significantly changed in approximately 3.0 mL min$^{-1}$ of the flow rate. At a flow rate of 3.0 mL min$^{-1}$, recoveries of $Cd^{2+}$ and $Co^{2+}$ ions were found to be 95.6% and 96.6%, respectively. However, when the flow rate of metal solutions increased above 3.0 mL min$^{-1}$, the recovery of the analytes decreased. All further studies were performed at 2 mL min$^{-1}$ flow rates for sample solutions.

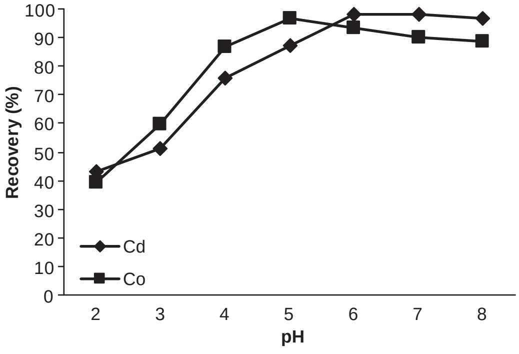

**Fig. 1.** Effect of pH on solid phase extractions of $Cd^{2+}$ and $Co^{2+}$.

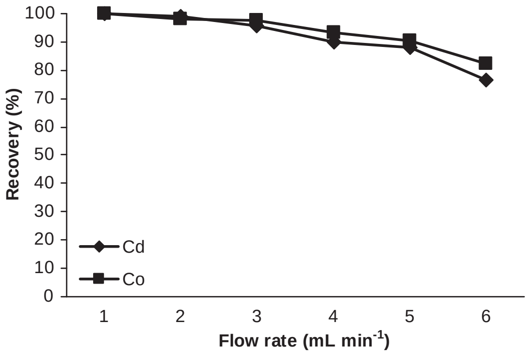

**Fig. 2.** Effect of flow rate of sample solution on solid phase extractions of $Cd^{2+}$ and $Co^{2+}$.

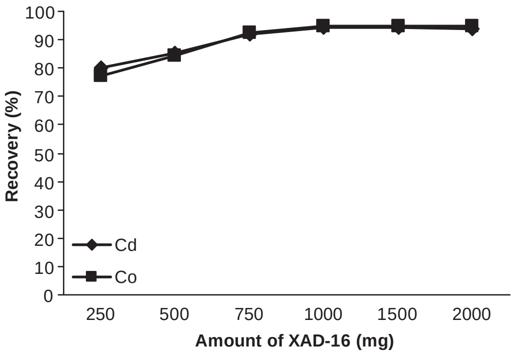

**Fig. 3.** Effect of amount of Amberlite XAD-16 on solid phase extractions of $Cd^{2+}$ and $Co^{2+}$.

### 3.3. Effect of amounts of Amberlit XAD-16 on the solid-phase extraction (SPE) procedure

The effects of the amounts of Amberlit XAD-16 on solid-phase extraction (SPE) were also examined. The results were represented in Fig. 3. The amount of Amberlit XAD-16 was increased from 250.0 mg to 1000.0 mg. The highest recoveries were obtained when the resin amount was 1000.0 mg. No change was observed in the recoveries of $Cd^{2+}$ and $Co^{2+}$ above 1000.0 mg. Therefore, 1000.0 mg of Amberlit XAD-16 was used for further SPE experiments.

### 3.4. Effect of amounts of Pleurotus eryngii on metal ion recoveries

The effects of the amounts of *P. eryngii* on the biosorption of $Cd^{2+}$ and $Co^{2+}$ ions were studied both at a sample flow rate of 2.0 mL min$^{-1}$ and at their individual pH values, respectively. The different amounts of *P. eryngii* (100.0–400.0 mg) for the solid-phase extraction (SPE) process were examined in the recoveries of $Cd^{2+}$ and $Co^{2+}$ ions. As observed in Fig. 4, the recovery values of $Cd^{2+}$ and $Co^{2+}$ ions increased by increasing the amounts of *P. eryngii* added and reached a constant value with at least 200.0 mg of the biosorbent. From that point of view, in all further experiments, 200.0 mg of *P. eryngii* loaded on 1000.0 mg of XAD-16 resin was used as an optimum amount of the biosorbent in the column.

### *3.5. Effect of sample volume on the solid-phase extraction (SPE) procedure*

The sample volume is one of the most important parameters that is used for the preconcentration of metals in a real sample [27]. The effects of sample volume on the retention of $Cd^{2+}$ and $Co^{2+}$ ions onto *Pleurotus eryngii* immobilized on Amberlite XAD-16 were investigated by varying the sample volume from 25.0 mL to 500.0 mL. The concentrations of $Cd^{2+}$ and $Co^{2+}$ ions were kept constant at 50.0 ng mL$^{-1}$. The recovery values as a function of the sample volume are represented in Fig. 5. The quantitative recoveries ($>97\%$) for $Cd^{2+}$ and $Co^{2+}$ were achieved in approximately 400.0 mL of the sample solution. When sample volume was increased, the concentrations of metal ions in the solution were decreased. This may be the reason for the decreased recovery of ions by increasing the sample volume.

### *3.6. Effect of type and volume of eluent on recovery*

A suitable eluent should be used to obtain a high enrichment factor. The eluent should quantitatively elute the sorbed analytes in a small volume. It should not affect the accurate determination of the analytes and destroy the life time and reusability of the solid phase [15]. HCl and $HNO_3$ were tried as eluents for the desorption of $Cd^{2+}$ and $Co^{2+}$ ions from the solid-phase extraction column. The results of this experiment are displayed in Table 2. It can be said that 5.0 mL of 1.0 mol L$^{-1}$ HCl was sufficient to simultaneously, quantitatively, and quickly recover the studied metal ions. In the studies described next, 1.0 mol L$^{-1}$ HCl and 5.0 mL, respectively, were selected as the eluent concentration and volume.

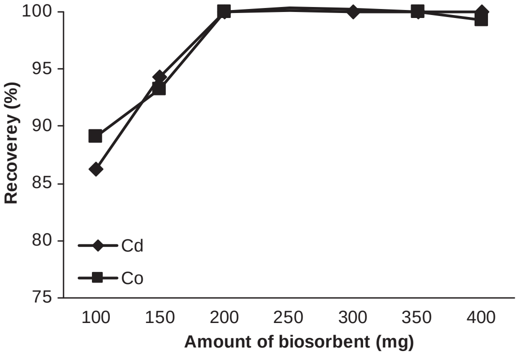

**Fig. 4.** Effect of amount of biosorbent on solid phase extractions of $Cd^{2+}$ and $Co^{2+}$.

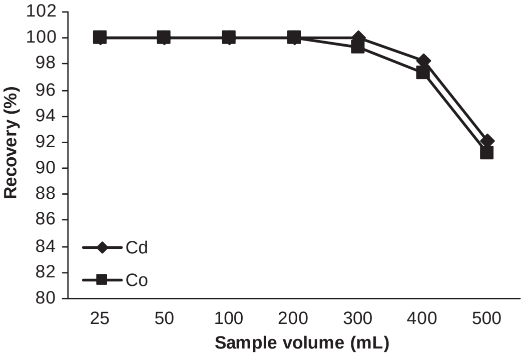

**Fig. 5.** Effect of volume of sample solution on solid phase extractions of $Cd^{2+}$ and $Co^{2+}$.

**Table 2**
Effect of type and volume of elution solutions on the recovery of $Cd^{2+}$ and $Co^{2+}$.

| Type of elution solution | Volume (mL) | Concentration (mol L$^{-1}$) | Recovery (%) | |
|---|---|---|---|---|
| | | | $Cd^{2+}$ | $Co^{2+}$ |
| HCl | 3 | 0.5 | 92.3 ± 0.2 | 91.4 ± 0.3 |
| | 5 | 0.5 | 96.2 ± 0.4 | 95.9 ± 0.1 |
| | 3 | 1 | 95.4 ± 0.3 | 94.3 ± 0.5 |
| | 5 | 1 | 99.8 ± 0.2 | 99.7 ± 0.4 |
| $HNO_3$ | 3 | 0.5 | 87.5 ± 0.6 | 86.9 ± 0.2 |
| | 5 | 0.5 | 95.7 ± 0.5 | 94.8 ± 0.6 |
| | 3 | 1 | 92.7 ± 0.2 | 91.6 ± 0.4 |
| | 5 | 1 | 97.9 ± 0.3 | 97.4 ± 0.5 |

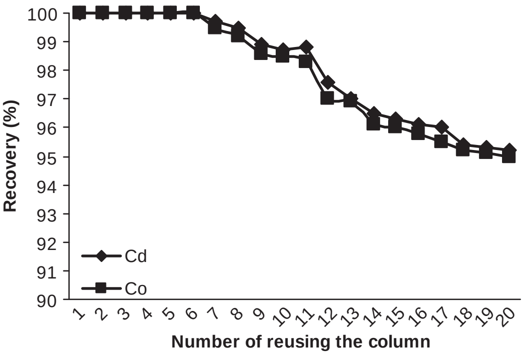

**Fig. 6.** Reusing the column for solid phase extraction of $Cd^{2+}$ and $Co^{2+}$.

### *3.7. Biosorption capacity of biosorbents*

The biosorption capacities of *Pleurotus eryngii* immobilized onto XAD-16 resin for $Cd^{2+}$ and $Co^{2+}$ ions were also examined. The batch method was used for the calculation of the biosorption capacity of biosorbents. 50.0 mg of biosorbents was added to 100.0 mL of the solution containing 10 mg $Cd^{2+}$ and $Co^{2+}$ ions at a pH of 6.0 and 5.0, respectively. Before analysis, the samples were centrifuged at 10,000 rpm for 10.0 min. Then, the supernatant fractions were separated and analyzed for the remaining metal ions. The supernatant was used to estimate the residual metal concentration by using inductively coupled plasma-optical emission spectrometry (ICP-OES). The capacities of the biosorbent were found to be 11.3 and 9.8 mg g$^{-1}$ for the $Cd^{2+}$ and $Co^{2+}$ ions, respectively.

### *3.8. Analytical features and applicability of methods*

The stability of the solid-phase extraction (SPE) column was tested using 2.5 µg $Cd^{2+}$ and $Co^{2+}$ ions, maintaining a sample volume of 50.0 mL. The biosorbed $Cd^{2+}$ and $Co^{2+}$ ions were eluted with 5.0 mL of 1.0 mol L$^{-1}$ HCl solution. It can be observed from Fig. 6 that the column was stable for approximately 20 cycles and could be used with good, susceptible, and quantitative recoveries ($>95\%$) for 20 cycles. It was observed that the recoveries of the Cd$^{2+}$ and Co$^{2+}$ ions were decreased beyond 20 cycles.

Optimized parameters of methods were employed to determine the linear application range of the method. For this purpose, 200.0 mL of the solution containing 1.0–50.0 ng mL$^{-1}$ of Cd$^{2+}$ and Co$^{2+}$ solutions were applied in the optimized method. A higher sample volume with the aim of reducing the analysis time was not employed. Direct linear calibration plots for Cd$^{2+}$ and Co$^{2+}$ in the concentration ranges of 0.020–1.0 μg mL$^{-1}$ were found to be $y=92960x+1067.0$, $r^2=0.9999$ and $y=98090x+443.2$, and $r^2=0.9999$, respectively. By considering the slope ratio of the calibration plots, sensitivity enhancements were calculated to be 50.7 for Cd$^{2+}$ and 35.7 for Co$^{2+}$. Limit of quantitations (LOQs) were found to be 0.67 and 0.82, respectively, for Cd$^{2+}$ and Co$^{2+}$. 200.0 mL of 1.0 ng mL$^{-1}$ of Cd$^{2+}$ and Co$^{2+}$ solutions were subjected to the solid-phase extraction procedure five times. Relative standard deviations (RSDs) were found to be 5.5 and 9.4%, respectively, for Cd$^{2+}$ and Co$^{2+}$. Regression coefficients were found to be higher than 0.9968. The preconcentration factor was calculated to be 40 from the ratio of the initial to the final sample volume.

The applicability of the method was validated through the analysis of certified reference tea samples (NCS ZC 73014). The results are presented in Table 3. The relative standard deviation (RSD) was found to be lower than 5.0%. Known amounts of Cd$^{2+}$ and Co$^{2+}$ were spiked to leave sample before analysis. The recovery values of spiked amounts of metals were directly calculated from the calibration plots. Results showed that the spiked amounts of metals could be quantitatively recovered. As a result, it can be said that the method can be applied to real samples without the loss of analytes.

**Table 3**
Results for Cd$^{2+}$ and Co$^{+2}$ in certified reference tea sample NCS ZC-73014 ($n=3$).

| Metal ion | Added (μg g$^{-1}$) | Certified (μg g$^{-1}$) | Found (μg g$^{-1}$) |
|---|---|---|---|
| Cd$^{2+}$ | – | 62.0 ± 4.0 | 61.2 ± 3.4 |
| | 200 | – | 259.6 ± 6.5 |
| | 400 | – | 460.5 ± 4.5 |
| Co$^{2+}$ | – | 220.0 ± 20.0 | 200.5 ± 16.6 |
| | 200 | – | 410.6 ± 20.4 |
| | 400 | – | 620.7 ± 18.7 |

**Table 4**
The level of total Cd$^{2+}$ and Co$^{2+}$ in vegetables ($n=3$).

| Vegetables | | Heavy metals ng g$^{-1}$ | |
|---|---|---|---|
| | | Cd$^{2+}$ | Co$^{2+}$ |
| Purslane | Leave | < LOQ | 38.3 ± 1.2 |
| | Root | 50.4 ± 1.4 | 140.6 ± 6.5 |
| | Stem | < LOQ | 195.5 ± 6.2 |
| Onion | Leave | < LOQ | 40.7 ± 6.1 |
| | Root | 29.5 ± 3.4 | 345.8 ± 14.5 |
| | Stem | 24.5 ± 1.2 | 51.3 ± 1.2 |
| Rocket | Leave | 50.1 ± 3.4 | 60.5 ± 4.5 |
| | Root | 54.1 ± 5.6 | 79.7 ± 1.8 |
| | Stem | 65.4 ± 1.9 | 48.0 ± 3.4 |
| Okra | Leave | 84.3 ± 0.9 | 98.8 ± 2.3 |
| | Root | 32.9 ± 3.7 | 362.2 ± 25.5 |
| | Stem | 34.0 ± 6.5 | 46.3 ± 3.5 |
| | Fruit | 28.4 ± 2.9 | 91.8 ± 8.4 |
| Aubergine | Leave | < LOQ | 39.7 ± 2.9 |
| | Root | 123.6 ± 12.9 | 52.4 ± 1.9 |
| | Stem | 125.6 ± 9.6 | < LOQ |
| | Fruit | 27.1 ± 5.8 | 7.3 ± 1.1 |

< LOQ: Under the limit of quantitation.

The Cd$^{2+}$ and Co$^{2+}$ concentrations in different parts of edible vegetables (leave, root, stem, and fruit) were determined after the solid-phase extraction procedure (Table 4). Cd$^{2+}$ was not determined in the leaves of purslane, onion, and aubergine. The lowest amount of Cd$^{2+}$ was detected in the root of onion, whereas the highest amount was found in the root of aubergine. It was found that the Cd$^{2+}$ content in aubergine fruit was lower than in its other parts. The Co$^{2+}$ levels in the roots of edible vegetables were higher than in other parts of the samples. The Co$^{2+}$ concentrations varied from 38.3 to 98.8 ng g$^{-1}$ in leaves, and from 51.3 to 195.5 ng g$^{-1}$ in stems.

## 4. Conclusions

A preconcentration method based on the use of *Pleurotus eryngii* immobilized on Amberlite XAD-16 as a biosorbent for solid-phase extraction was developed for Cd$^{2+}$ and Co$^{2+}$. It was found that Cd$^{2+}$ and Co$^{2+}$ were sorbed on a column at a pH of 6.0 and 5.0, respectively. In addition to pH, other experimental parameters were also optimized. The applicability of the method was validated through the analysis of certified reference tea samples. Results showed that founded concentrations for Cd$^{2+}$ and Co$^{2+}$ agreed with certified values. Edible vegetables were collected along the cultivated banks of the Tigris River. Cd$^{2+}$ and Co$^{2+}$ concentrations in different parts (leave, root, and stem) of purslane, onion, rocket, okra, and aubergine were determined after microwave digestion and solid-phase extraction by *P. eryngii* immobilized on Amberlite XAD-16.

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