Regular Article

Combining Dispersive Solid Phase Extraction-dispersive Liquid-liquid Microextraction Using Walnut Green Husk as an Efficient Adsorbent for the Extraction of Lead and Cadmium Ions from Oil Samples Prior to Flame Atomic Absorption Spectrometry

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In this work, walnut green husk has been used as a simple, cheap, biodegradable, and efficient adsorbent in dispersive solid phase extraction of Cd(II) and Pb(II) ions from some oil samples including edible, fish oil, and butter. In the next step, a dispersive liquid-liquid microextraction method was used to enrich the extracted analytes before their analysis with flame atomic absorption spectrometry. For this purpose, the adsorbent was obtained from agricultural wastes, dried in an isolated environment at ambient temperature, and mechanically ground to obtain a homogeneous powder. The parameters affecting the efficiency of the method were optimized. Low detection limits (0.12 and 0.32 µg l^{-1} for Cd(II) and Pb(II), respectively), low relative standard deviations (3.8% and 4.2% for Cd(II) and Pb(II), respectively), and determination coefficients close to 1 (0.991 and 0.995 for Cd(II) and Pb(II), respectively) were achieved. Also, the extraction recoveries for the target analytes were 89 and 96% for Cd(II) and Pb(II), respectively.

Keywords: Heavy metal, Walnut green husk, Dispersive solid phase extraction, Dispersive liquid-liquid microextraction, Flame atomic absorption spectrometry, Oil

INTRODUCTION

For environmental protection, there is a need to determine heavy metals at trace levels in the samples such as water, food, and agricultural products. It is very important and necessary for human health and other environmental ecosystems [1,2]. As two important pollutants, Cd(II) and Pb(II) may be carcinogenic to humans, cause disturbances in the normal functioning of organs or cause diseases [3,4]. In edible oils, the maximum recommended contents for cadmium and lead are 50 and 100 µg kg^{-1}, respectively, with respect to national and international authorities [5,6]. Due to the low concentrations of the mentioned ions in complex food and environmental samples, there is a need for

preconcentration and extraction of these ions before instrumental analysis. For this purpose, solid phase extraction (SPE) is used as a conventional separation and enrichment method with features such as simplicity in operation, environmental friendliness, and providing high efficiency [7,8]. A key parameter in SPE is the selection of an efficient adsorbent with high adsorption capacity to reach the enrichment factor (EF). In the previous studies for the extraction/preconcentration of heavy metals, various materials such as modified TiO_2 [9], carbon nanotubes [10], graphene oxide [11], metal-organic frameworks [12,13], and ion imprinted polymers [14,15] have been used as adsorbents. The mentioned adsorbents have features such as providing large surface area, the ability to chemically modify the surface, and chemical and thermal stability. But sometimes they have long and complicated synthesis steps

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and need to use high-purity reagents or solvents. Therefore, finding a new group of materials seems necessary. The use of new adsorbents that are biodegradable, do not require synthetic steps, are cheap and available, and do not pose a threat to the environment, can be important [16-18]. Recently, a new version of SPE methods called dispersive solid phase extraction (DSPE) was used [19,20], in which extraction is performed by adding an adsorbent into the sample solution containing the target analytes. In the next step, the adsorbent is collected using centrifugation, and the adsorbed analytes are desorbed by a suitable solvent.

In common dispersive liquid-liquid microextraction (DLLME), a mixture of water-immiscible solvent (extraction solvent) and miscible solvent (dispersive solvent), is rapidly injected into a sample solution. Because of the dispersion of the extraction solvent into the sample solution a cloudy and turbid solution is formed [21]. A high contact area between the sample solution and the extraction solvent is obtained which results in a rapid and efficient extraction. This method can be easily coupled with the other extraction methods to increase the EFs of the analytes [22-25].

In this research work, a biodegradable adsorbent prepared from the residue of agricultural products was used. Walnut green husk (WGH) was obtained from agricultural waste. Due to being cheap, compatible with the environment, and having no risk to humans and the environment, it can be one of the most suitable options as the DSPE absorbent. The mentioned properties make WGH an ideal candidate in the DSPE method coupled with DLLME for the extraction and preconcentration of Cd(II) and Pb(II) from oil samples. The purpose of coupling two methods is the simultaneous beneficiation of the features of both methods such as the elimination of interferences from other materials in the sample matrix and increasing EFs. Also, simplicity of work, low cost, high extraction recovery (ER), and without the need for adsorbent synthesis steps are the other main advantages of the proposed method.

EXPERIMENTAL

Materials and Solutions

Ethyl acetate, ethanol, methanol, sodium diethyldithiocarbamate (SDDTC), 1,2-dibromoethane (1,2-DBE), 1,1,2-trichloroethane (1,1,2-TCE), chloroform, and 1,1,2,2-tetrachloroethane (1,1,2,2-TCE) were supplied from Sigma-Aldrich (St. Louis, Missouri, USA). Acetone, isopropanol, acetonitrile, $Pb(NO_3)_2.6H_2O$, and $Cd(NO_3)_2.6H_2O$ were obtained from Merck (Darmstadt, Germany). All materials used in this study were analytical grade ($\geq 99\%$). A mixture stock solution of Pb(II) and Cd(II) ions with a concentration of 100 mg l^{-1} of each ion was prepared by dissolving sufficient amounts of $Pb(NO_3)_2.6H_2O$ and $Cd(NO_3)_2.6H_2O$ in ethanol. The daily working solution was prepared with a concentration of 20 μg l^{-1} of Pb(II) and Cd(II) ions (of each) in ethyl acetate and used in the optimization stages of the method. Also, to ensure the accuracy of the detection system, a standard solution with a concentration of 10 mg l^{-1} of each cation was prepared in deionized water (Qazi Company, Tabriz, Iran) and injected into the flame atomic absorption spectrometry (FAAS) daily (n = 3). The obtained results were also used in the calculation of ERs of the target cations.

Real Samples

Fish oil capsules were obtained from domestic pharmacies (Tabriz, Iran). For the analysis of fish oil, the contents of the capsules were removed with the help of a syringe. Also, samples of butter and two edible oils (sunflower and colza oils) were obtained from a local supermarket (Tabriz, Iran). Before performing the analysis, the used butter sample was exposed to a temperature of 30 °C for 20 min to become liquid.

Apparatus

A Shimadzu AA-6300 flame atomic absorption spectrometer (Kyoto, Japan) equipped with a 100-mm torch head and an air-acetylene flame was used for the analysis of the selected cations. For the radiation sources, hollow cathode lamps of lead (resonance line = 283.3 nm) and cadmium (resonance line = 228.8 nm) from Hamamatsu Photonics (Shizuoka, Japan) with a current of 10 mA were used. Other devices used in the process of extracting target analytes were a Hettich centrifuge, model ROTOFIX 32A (Kirchlengern, Germany), a Labinco vortex, model L46 (Breda, the Netherlands), and a Metrohm pH meter, model 654 (Herisau, Switzerland).

Preparation of DSPE Adsorbent

In this study, the DSPE adsorbent was easily obtained from agricultural residues. For this purpose, WGH was collected and dried in an isolated environment at ambient temperature. In the next step, the dried WGH was mechanically ground to obtain a homogeneous powder and sieved through a sieve (63 μm, mesh No. 230). It was directly used in the sample preparation.

Extraction Procedure

In the DSPE step, 5 ml of a working solution containing 20 μg l^{-1} of each cation in ethyl acetate or oil sample solution (1.0 g diluted with ethyl acetate till 5 ml) and 500 μl of SDDTC solution (0.03 M) were added to a 10-ml glass test tube. SDDTC formed a complex with Cd(II) and Pb(II) ions facilitating the adsorption of the analytes onto the adsorbent surface. In the next step, 0.2 g of the powdered WGH was added to the solution. Then, for maximum interaction between the adsorbent and target analytes, the resulting mixture was vortexed for 4 min. After adsorption of the analytes by WGH, the mixture was centrifuged at 7000 rpm for 5 min. After discarding the supernatant, 1.5 ml of methanol was added to the adsorbent particles. Methanol was used as an elution/dispersing solvent. The resulting mixture was vortexed for 3 min for the complete desorption of analytes. By centrifuging the mixture at 7000 rpm for 5 min, the supernatant containing the analytes was separated.

In the DLLME step, to the supernatant obtained from the previous step, 250 μl of 1,1,2,2-TCE (extraction solvent) was added and the obtained mixture was rapidly injected into 5 ml of deionized water to form a cloudy solution. It was centrifuged for 6 min at a speed of 7000 rpm. To investigate the extraction efficiency of the proposed procedure, two 100-μl aliquots of the sedimented phase (1,1,2,2-TCE, 210 μl) were removed and separately injected into FAAS by the homemade microinjection system [26].

Calculation of Enrichment Factor (EF) and ER

EF is defined as the ratio between the analyte concentration in 1,1,2,2-TCE (C_{sed}) and the initial concentration of analyte (C_0) in ethyl acetate:

$$EF = C_{sed}/C_0 \tag{1}$$

C_{sed} is obtained from a calibration graph. ER is defined as the percentage of the total heavy metal ion (n_0) which is extracted into 1,1,2,2-TCE (n_{sed}).

$$ER = {n_{sed}}/{n_0} \times 100 = {C_{sed} \times V_{sed}}/{C_0 \times V_{aq}} \times 100 = EF \times {V_{sed}}/{V_{aq}} \times 100 \tag{2}$$

Where V_{sed} and V_{aq} are the volumes of the sedimented phase and sample solution, respectively.

# RESULTS AND DISCUSSION

Optimization of Parameters

Sorbent amount. In order to achieve the highest ER, it is inevitable to optimize the amount of the adsorbent. For this purpose, different quantities of the absorbent in the range of 50-500 mg were added to the working solution and then the processes of extraction and analysis were done. Based on the obtained results (Fig. 1), the ERs increase with the increase of the amount of adsorbent from 50 to 200 mg. By increasing the amount of adsorbent, more surface area is achievable for the analytes. At amounts greater than 200 mg, the ERs decrease slightly. It seems that by increasing the amount of adsorbent due to the constant volume of the desorbing solvent, the ability of the solvent to elute the adsorbed analytes from the surface of the adsorbent decreases. Also, agglomeration of the adsorbent particles is possible at high amounts.
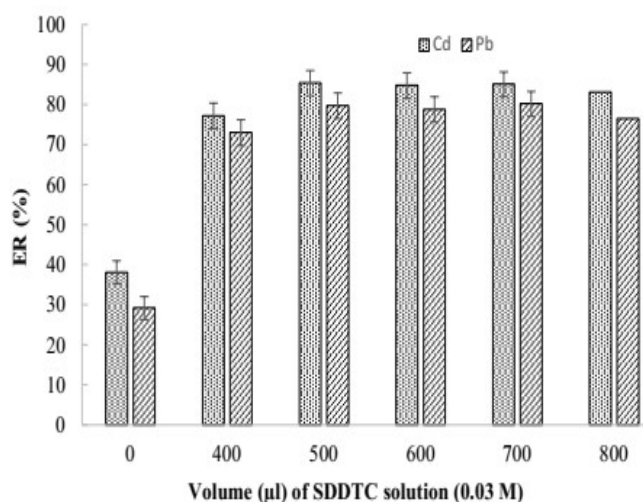
SDDTC Solution Volume

SDDTC is a non-specific chelating agent that can form stable complexes with Cd(II) and Pb(II) ions. The reason for choosing SDDTC was to achieve multi-element analysis for the simultaneous determination of Cd(II) and Pb(II) using the studied method. The effect of the volume of SDDTC solution used (at a constant concentration of 0.03 M) on the ERs of Cd(II) and Pb(II) is shown in Fig. 2. According to these results, increasing the volume of SDDTC solution from 0 to 500 μl leads to enhancement of the ERs of the target analytes. With further increases in the amount of the chelating agent, there are no noticeable changes in the values of ERs.

Vortexing Time in Adsorption Step

Considering that the analytes are spread uniformly in all
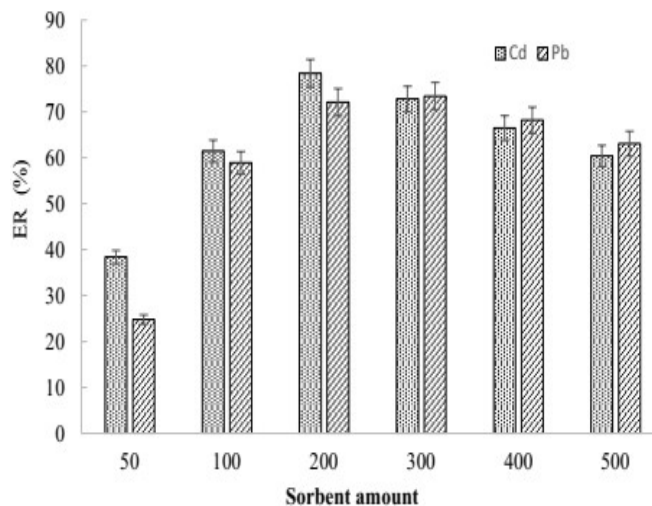
Fig. 1. Sorbent amount optimization. Conditions: DSPE step: volume of aqueous solution, 5 ml deionized water spiked with 20 µg l^{-1} each of Cd(II) and Pb(II) ions; SDDTC solution volume, 400 µl (0.03 M); adsorption time, 5 min; elution/disperser solvent (volume), methanol (1.0 ml); and desorption time (vortex time), 2 min. DLLME step: aqueous phase, 5 ml deionized water; extraction solvent (volume), 1,2-DBE (250 µl); and centrifugation rate and time, 5000 rpm and 4 min, respectively. The error bars indicate the standard deviations of three repeated determinations.
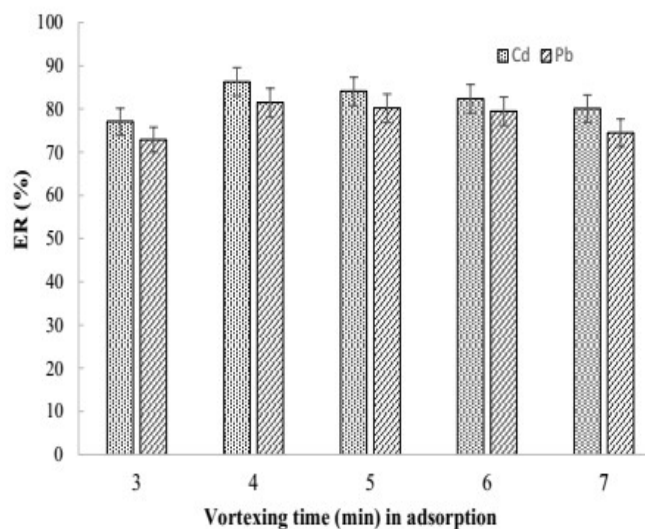
parts of the sample solution, in order to increase the ER, the adsorbent must be able to contact all of the analytes. Therefore, it is necessary to stir the mixture of adsorbent and analytes. Vortexing is a commonly used method in laboratories to mix samples inside tubes with a small volume and has a rotational movement and an orbital state on its axis. In this method, vortexing was used for mixing. Its optimization in terms of time can be important. Vortexing time has a direct effect on the efficiency of the procedure since it changes the number of contacts between the analytes and adsorbent. For this purpose, the vortexing time (considered as adsorption time) was evaluated in the range of 3-7 min. The obtained results are summarized in Fig. 3. According to the results, with the increase of vortexing time, ERs increase, and adsorption equilibrium is achieved at 4 min. At times higher than 4 min, the changes in ERs are not significant. Therefore, 4 min was chosen as the optimum adsorption time.

Type and Volume of Elution Solvent

Choosing an ideal elution solvent is important in the proposed DSPE-DLLME method. The solvent selected as the elution solvent in the DSPE step will be used as a dispersing

Fig. 2. Volume of SDDTC solution (0.03 M). Conditions: the same as those used in Fig. 1, except the WGH amount was fixed at 200 mg.
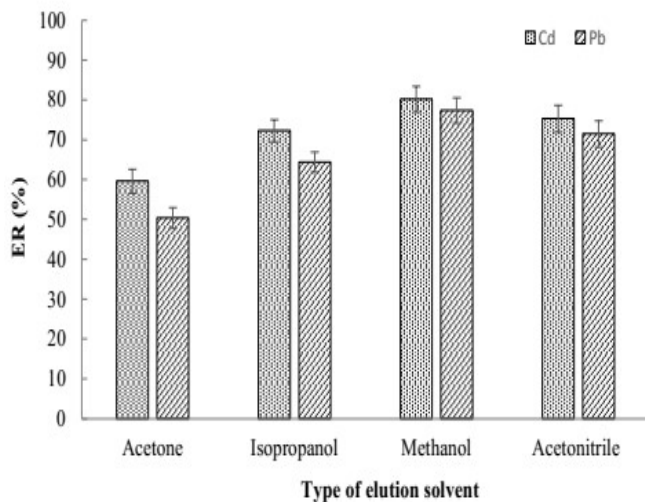

Fig. 3. Vortex time (adsorption step) optimization. Conditions: the same as those used in Fig. 2, except the volume of SDDTC solution was fixed at 500 µl.
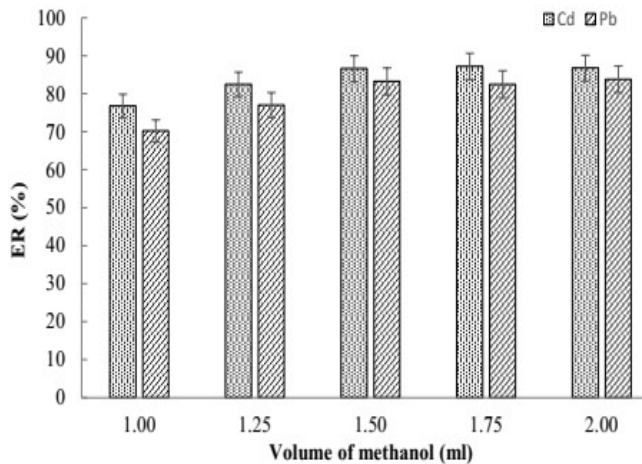
solvent in the DLLME step. Therefore, it should have the ability to elution of the analytes adsorbed onto the adsorbent particles and also be able to dissolve in the aqueous phase and extraction solvent used in the DLLME step. For this purpose, acetone, isopropanol, methanol, and acetonitrile were tested. By using 1.0 ml of each solvent, the highest ERs are related to methanol (Fig. 4). The amount of desorption solvent is another parameter that should be investigated. It can affect the desorbed amounts of the analytes and the quality of the extraction solvent dispersion in the following DLLME step. Therefore, to obtain the optimal volume of elution solvent, the volume of methanol was changed in the range of 1.00-2.00 ml (at 0.25-ml intervals). Based on the obtained results (Fig. 5), 1.5 ml of methanol is preferred to the other used volumes.

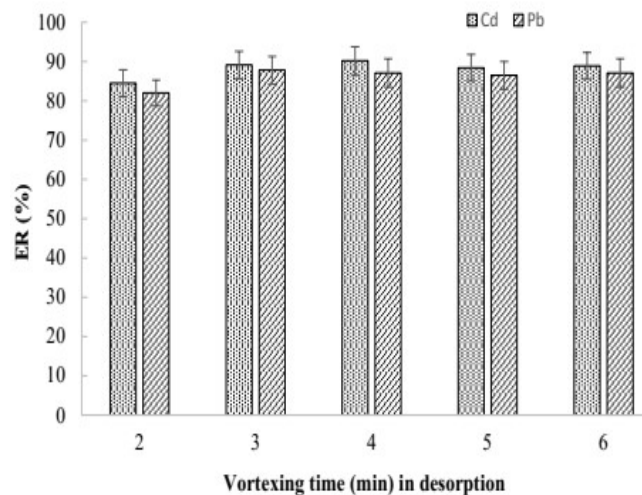## Vortexing Time in Desorption Step

Vortexing can accelerate the desorption of the analytes from the WGH surface, and hence it leads to decreasing desorption time. In the desorption step, vortexing time (elution time of the analytes from the adsorbent) should be optimized. This optimization was done by changing the vortexing time between 2 and 6 min, and the results are shown in Fig. 6. The duration of 3 min was chosen as the

Fig. 5. Elution solvent volume optimization. Conditions: the same as those used in Fig. 4, except methanol was used as the elution solvent.

Fig. 6. Vortexing time (desorption step) optimization. Conditions: the same as those used in Fig. 5, except the volume of methanol was used 1.5 ml.

Fig. 4. Elution solvent kind. Conditions: the same as those used in Fig. 3, except vortex time in the adsorption step was fixed at 4 min.

optimum desorption time of the analytes. Increasing the vortexing time up to 3 min causes an increase in the desorption of the analytes and the ER values increase. As the vortexing time increases to more than 3 min, no significant changes in the ERs are observed. Therefore, the time of 3 min was ideal for the desorption step.

Type and Volume of Extraction Solvent in DLLME

It seems that the most important parameter in the DLLME step is the choice of extraction solvent kind. Because it has a vital role in the extraction efficiency of the studied method, therefore, it should be carefully selected. The important features of the extraction solvent are the high ability the extract of the target analytes and the creation of a cloudy solution (a two-phase system) when its mixture with the eluate obtained from the DSPE step is injected into an aqueous phase. According to the properties mentioned for the extraction solvent, the solvents including 1,2-DBE, 1,1,2-TCE, chloroform, and 1,1,2,2-TCE were investigated. Maximum ERs are obtained for both cations using 1,1,2,2-TCE (Fig. 7), so it was chosen as the optimal extraction solvent for the next tests. The used volume of 1,1,2,2-TCE is another important parameter that has a direct effect on the volume of the final sedimented phase and therefore it can affect the amount of the obtained signals and efficiency of the developed method. Optimization of 1,1,2,2-TCE volume was done by using different volumes including 220, 250, 300, 400, and 500 µl. The obtained results showed that the analytical signals obtained for both cations were maximum in the volume of 250 µl. At higher volumes, the concentration of the analytes in the sedimented phase decreased because of the dilution effect. As a result, the analytical signals of the analytes decreased.
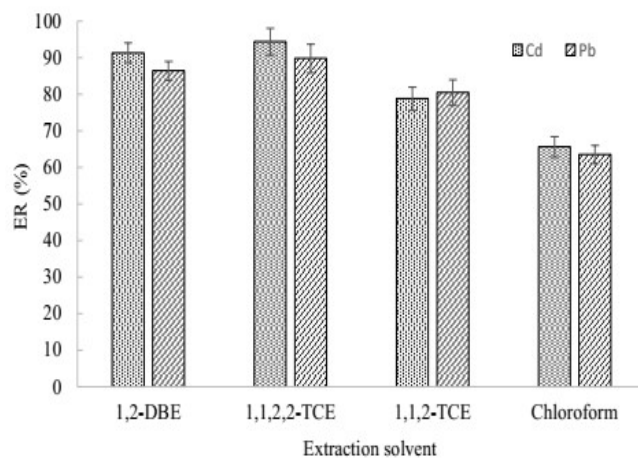
Fig. 7. Selection of extraction solvent type. Conditions: the same as those used in Fig. 6, except the vortexing time of the desorption step was fixed at 3 min.

Centrifugation Conditions

Centrifugation is a common procedure that is utilized to accelerate the separation of solid particles/extraction solvent droplets from aqueous solution. Therefore, in the proposed method, centrifugation was used in two stages. In the DSPE stage, the speed and time of centrifugation were optimized to collect the adsorbent particles after adsorbing the analytes, as well as after desorption of the analytes by the elution solvent. The optimal values obtained for speed and time were 7000 rpm and 4 min, respectively. In the DLLME step, it was necessary to optimize the speed and time of centrifugation for quick collection of fine droplets of the extraction solvent dispersed into the aqueous phase. For this purpose, the ranges of 2000-8000 rpm and 4-7 min were studied for speed and time of centrifugation, respectively. The values chosen as the optimal for the speed and time of centrifugation were 7000 rpm and 6 min, respectively.

Effect of Coexisting Ions

The presence of other ions may change the ERs of the analytes in the presented method. Therefore, the effect of some cations and anions on the extraction efficiency of the method was tested. For this purpose, the proposed extraction method was performed according to the optimized conditions on the solutions of the analytes (20 µg l^{-1} for each analyte) containing various concentrations of coexisting ions. If the presence of the added ion led to a ±5% variation in ERs of the analytes, it was considered as an interfering ion. The results are collected in Table 1. They show that the suggested method can be performed on real samples without significant interferences from the studied coexisting anions and cations.

Method Validation

By examining parameters such as ER, accuracy, precision, limit of quantification (LOQ), limit of detection (LOD), coefficient of determination (r^2), and linear range (LR), the efficiency of the studied method was evaluated. By performing repeated tests, relative standard deviation (RSD) was obtained, which is a measure of the repeatability of the studied method. Also, based on the introduced method (section 2.5), calibration graphs were drawn by preparation of a working solution with different concentrations, and LR and r^2 values were calculated (Table 2). RSDs were evaluated in two cases: inter-day (n = 4) and intra-day (n = 6)

Table 1. Tolerance Limit of Interferent/analyte Ratios of Coexisting Ions in the Determination of Cd(II) and Pb(II) Using the Proposed Method

Species	Tolerance limit of interferent/analyte ratio	
	Cd(II)	Pb(II)
Zn^{2+}	800	6000
Cr^{3+}	750	1000
Co^{2+}	1200	1000
Ni^{2+}	1000	1000
Al^{3+}	1200	1000
K^{+}	1400	1400
Cu^{2+}	800	1000
Co^{2+}	1000	1250
Ni^{2+}	1000	1000
Hg^{2+}	500	500
SO_4^{2-}	1250	750
NO_3^{-}	2500	2500

Table 2. Quantitative Characteristics of the Method for the Studied Heavy Metals

Analyte	LR ($\mu g\ l^{-1}$)[a]	r^{2b}	LOD ($\mu g\ l^{-1}$)[c]	LOQ ($\mu g\ l^{-1}$)[d]	RSD (%)[e]		ER ± SD[f]	EF ± SD[g]
					Intra-day (n = 6)	Inter-day (n = 4)		
Cd(II)	0.40-30	0.991	0.12	0.40	3.8	4.6	89.3 ± 3.4	21.3 ± 0.8
Pb(II)	1.1-30	0.995	0.32	1.1	4.2	5.1	95.7 ± 4.0	22.8 ± 1.0

[a]Linear range. [b]Coefficient of determination. [c]Limit of detection. [d]Limit of quantification. [e]Relative standard deviation at a concentration of 20 $\mu g\ l^{-1}$ of each cation. [f]Extraction recovery ± standard deviation (n = 3). [g]Enrichment factor ± standard deviation (n = 3).

precisions. Based on the results (low LODs, LOQs, and RSDs, r^2 values close to 1, and wide LRs) the presented method is an efficient and reliable method for preconcentration and extraction of Pb(II) and Cd(II) ions. The accuracy of the developed procedure was also studied by comparing the obtained concentrations of Cd(II) and Pb(II) ions in a certified reference sample (Enviro MAT HU-1 oil) with the certificate values. It was concluded that the obtained concentrations (14.4 ± 0.6 and 19.2 ± 0.9 $\mu g\ g^{-1}$ for Cd(II) and Pb(II), respectively) have good coordination with the certified values (15 ± 1 and 20 ± 1 $\mu g\ g^{-1}$ for Cd(II) and Pb(II), respectively) at a confidence level of 95% [t-values of 1.04

for Cd(II) and 1.38 for Pb(II) are lower than $t_{critical}$ (4.30)].

Real Samples Analysis and Study of Matrix Effect

To evaluate the accuracy and validity of the proposed method, real samples including two samples of edible oils (sunflower and colza oils), fish oil, and butter were analyzed according to section 2.5. The influence of the sample matrix effect on the performance of the method was investigated by spiking the analytes at three different concentrations (2.5, 7 5, and 15 $\mu g\ l^{-1}$ of each cation). With a look at the results obtained from the studied method (Table 3), the potential of the proposed method for the analysis of Pb(II) and Cd(II) ions

is well revealed. Based on the results, the sample matrices do not have a significant effect on the efficiency of the method. The recovery for Pb(II) and Cd(II) ions in different samples was obtained in the acceptable ranges of 88.1-96.3 and 89.7-96.3%, respectively.

Comparison of the Proposed Method with other Studied Methods

By comparing the figures of merit obtained from the studied method (DSPE-DLLME-FAAS) and previously published methods summarized in Table 4, it can be

Table 3. Results of Assays to Check the Sample Matrices Effect for the Selected Cations and Concentrations of the Detected Analytes

Analyte	Spiked concentration ($\mu g\ Kg^{-1}$)	Edible oil (1) (sunflower oil)		Edible oil (2) (colza oil)		Butter		Fish oil	
		Found concentration ($\mu g\ Kg^{-1}$) ± S.D. [a] (n = 3)	Recovery ± S.D. [a] (n = 3)	Found concentration ($\mu g\ Kg^{-1}$) ± S.D. (n = 3)	Recovery ± S.D. (n = 3)	Found concentration ($\mu g\ Kg^{-1}$) ± S.D. (n = 3)	Recovery ± S.D (n = 3)	Found concentration ($\mu g\ Kg^{-1}$) ± S.D. (n = 3)	Recovery ± S.D. (n = 3)
Cd (II)	-	6.8 ± 0.3	-	5.3 ± 0.2	-	3.1 ± 0.1	-	0.6	-
	2.5	9.1 ± 0.4	91.9 ± 0.4	7.6 ± 0.3	93.8 ± 3.7	5.3 ± 0.2	89.7 ± 3.4	2.9 ± 0.1	92.2 ± 4.1
	7.5	13.8 ± 0.6	93.0 ± 4.0	12.4 ± 0.5	94.2 ± 4.0	10.0 ± 0.4	92.6 ± 3.7	7.5 ± 0.3	92.4 ± 3.9
	15.0	21.1 ± 0.9	95.4 ± 3.9	19.7 ± 0.8	96.3 ± 4.1	17.1 ± 0.7	93.2 ± 3.6	14.6 ± 0.6	93.5 ± 3.8
Pb(II)	-	2.6 ± 0.1		4.7 ± 0.2		N.D.[b]		1.2 ± 0.1	
	2.5	4.8 ± 0.2	89.5 ± 4.1	7.0 ± 0.3	91.2 ± 4.2	2.3 ± 0.1	93.2 ± 4.3	3.4 ± 0.1	88.1 ± 3.8
	5.0	7.1 ± 0.3	90.7 ± 4.0	9.4 ± 0.4	93.8 ± 3.8	4.7 ± 0.2	94.7 ± 4.3	8.1 ± 0.3	91.8 ± 3.8
	15.0	16.8 ± 0.7	94.9 ± 4.0	19.1 ± 0.8	96.3 ± 3.9	14.3 ± 0.6	95.7 ± 4.1	14.8 ± 0.6	91.0 ± 3.6

[a] Standard deviation. [b] Not detected.

Table 4. Evaluation of the Proposed Method by Comparing it with Similar Works

Adsorbent	LOD [a] ($\mu g\ L^{-1}$)		LOQ [b] ($\mu g\ L^{-1}$)		LR [c] ($\mu g\ L^{-1}$)		r^{2} [d]		RSD [e] (%)		Sample	Method	Ref.
	Cd(II)	Pb (II)	Cd(II)	Pb(II)	Cd (II)	Pb(II)	Cd(II)	Pb(II)	Cd(II)	Pb(II)			
TETA- MWCNT [f]	0.30	3.70	-	-	0.1-6.0	1.0-20.0	-	-	4.2	1.4	Water, cigarette, and fertilizer	SPE- FAAS [g]	[27]
MMOF [h]	0.20	1.10	1.0	2.5	1.0-80.0	2.5-125.0	0.998	0.997	3.6	4.3	Fish, sediment, and water samples	MSPE- FAAS [i]	[28]
MMOF	0.12	1.20	1.0	4.0	1.0-110.0	4.0-140.0	0.997	0.998	3.6	4.3	Fish, sediment, soil, and water samples	MSPE- FAAS	[29]
-	0.12	-	0.3	-	0.3-20.0	-	0.997	-	2.9	-	Oil samples	RP-DLLME-FAAS [j]	[30]
Fe₃O₄@TAR/HKUST-1 [k]	0.15	0.80	0.5	2.0	0.5-90.0	2.0-200.0	0.998	0.995	5.6	6.4	Sea food and agri food	MSPE- FAAS	[31]
MGO/SiO₂@coPPy-Th [l]	0.21	0.65	-	-	-	-	0.995	0.995	< 6	< 6	Fruit, vegetable, and water samples	MSPE- FAAS	[32]
WGH [m]	0.12	0.32	0.30	1.0	0.3-30	1.0-30	0.991	0.995	3.8	4.2	Oils and butter	DSPE-DLLME-FAAS [n]	This work

concluded that the proposed method provides lower LODs, LOQs, RSDs, acceptable LRs, and good linearity. It has the ability to be used for the determination of Cd(II) and Pb(II) cations in food samples. In addition to the mentioned cases, the most important advantage of the proposed method is the use of a safe, cost-effective, environmentally friendly adsorbent obtained from the wastes of agricultural products.

CONCLUSIONS

A combination of dispersive solid phase extraction and dispersive liquid-liquid microextraction was introduced as a highly effective approach for rapidly preconcentrating and extracting metal ions from different types of samples. In this study, a straightforward, cost-effective, and environmentally friendly adsorbent known as WGH was employed in the DSPE step to extract Pb(II) and Cd(II) ions from oil samples. Subsequently, DLLME was utilized to further enrichment of the analytes prior to analysis using FAAS. The use of two extraction techniques resulted in achieving low LODs and excellent selectivity. Moreover, it offered a simple and fast sample preparation method for the extraction and preconcentration of Cd(II) and Pb(II) without the need for complex extraction procedures, which can introduce contamination or errors during the analysis. By comparing the figures of merit obtained from the studied method and previously published methods, it was found that the proposed method provided lower LODs, LOQs, RSDs, acceptable linear range, and good determination coefficients. The simplicity and repeatability of the method make it a reliable choice for determining the desired analytes in various oil samples.

ACKNOWLEDGMENTS

REFERENCES

[1] X. Hu, Y. Zhang, Z. Ding, T. Wang, H. Lian, Y. Sun, J. Wu, Atmo. Environ. 57 (2012) 146.

[2] H. Ali, E. Khan, Hum. Ecol. Risk Assess. 25 (2019) 1353.

[3] M.C. Leung, M.H. Silva, A.J. Palumbo, P.N. Lohstroh, S.E. Koshlukova, S.B. DuTeaux, Reprod. Toxicol. 85 (2019) 12.

[4] N. Eevers, J.C. White, J. Vangronsveld, N. Weyens, Adv. Bot. Res. 83 (2017) 277.

[5] M. Behbahani, P.G. Hassanlou, M. M. Amini, F. Omidi, A. Esrafili, M. Farzadkia, A. Bagheri, Food Chem. 187 (2015) 82.

[6] European Commission. European Drinking Water Directive. (2018). http://ec.europa.euenvironment/water/water-drink/legislation_en.html. Accessed 2 May 2022.

[7] T. Daşbaşi, H. Muğlu, C. Soykan, A. Ülgen, J. Macromol. Sci. A 55 (2018) 288.

[8] N. Manousi, A. Kabir, K.G. Furton, G.A. Zachariadis, A. Anthemidis, Sep. 8 (2021) 100.

[9] G. Alpdogan, S. Dinc Zor, A. Peksel, Curr. Anal. Chem. 12 (2016) 642.

[10] M. Fayazi, M.A. Taher, D. Afzali, A. Mostafavi, M. Ghanei-Motlagh, Mater. Sci. Eng. C, 60 (2016) 365.

[11] N. Ghorbanian, Sh. Seidi, J.B. Ghasemi, S.J. Sadeghi, J. Iran. Chem. Soc. 16 (2019) 1411.

[12] F. Maya, C.P. Cabello, R.M. Frizzarin, J.M. Estela, G.T. Palomino, V. Cerda, Trend. Anal. Chem. 90 (2017) 142.

[13] M. Hemmati, M. Rajabi, A. Asghari, Microchim. Acta 185 (2018) 1.

[14] T. Madrakian, B. Zadpour, M. Ahmadi, A. Afkhami, J. Iran. Chem. Soc. 12 (2015) 1235.

[15] Z. Sadat Hashami, A. Taheri, M. Alikarami, Anal. Chim. Acta 1204 (2022) 339262.

[16] D. Ozdes, N. Tilki, S. Seker, C. Duran, J. Anal. Sci. Tech. 13 (2022) 1.

[17] A.E. Martins, M.S. Pereira, A.O. Jorgetto, M.A. Martines, R.I. Silva, M.J. Saeki, G.R. Castro, Appl. Sur. Sci. 276 (2013) 24.

[18] Q. Zhang, M. He, B. Chen, B. Hu, Spectrochim. Acta B, 121 (2016) 1.

[19] M. Rajabi, S. Arghavani-Beydokhti, B. Barfi, A. Asghari, Anal. Chim. Acta 957 (2017) 1.

[20] M. Ghalebi, S. Hamidi, M. Nemati, S. Sheykizadehd, F. Lotfipour, N. Alipour Ghorbani, A. Farjam, Anal. Bioanal. Chem. Res. 9 (2022) 431.

[21] S.M. Sorouraddin, M.A. Farajzadeh, H. Dastoori,

Talanta 208 (2020) 120485.

[22] F. Vela-Soria, J. García-Villanova, V. Mustieles, T. Haro, P. Antignac, M.F. Fernandez, Talanta 221 (2021) 121577.

[23] K. Parvizzad, S.M. Sorouraddin, M.A. Farajzadeh, J. Food Compos. Anal. 112 (2022) 104654.

[24] Zh. Zhong, G. Li, Zh. Luo, B. Zhu, Talanta 194 (2019) 46.

[25] A. Abbasalizadeh, S.M. Sorouraddin, M.A. Farajzadeh, E. Marzi, M.R. Afshar Mogaddam, J. Sep. Sci. 45 (2022) 1550.

[26] S.M Sorouraddin, M.A. Farajzadeh, A. Hassanyani, M.R. Afshar Mogaddam, RSC Adv. 6 (2016) 108603.

[27] Z.A. ALOthman, E. Yilmaz, M.A. Habila, I.H. Alsohaimi, A.M. Aldawsari, N.M. AL-Harbi, M. Soylak, RSC Adv. 5 (2015) 106905.

[28] M.R. Sohrabi, Z. Matbouie, A.A. Asgharinezhad, A. Dehghani, Microchim. Acta 180 (2013) 589.

[29] M. Taghizadeh, A.A. Asgharinezhad, M. Pooladi, M. Barzin, A. Abbaszadeh, A. Tadjarodi, Microchim. Acta 180 (2013) 1073.

[30] S.M. Sorouraddin, M.A. Farajzadeh, T. Okhravi, J. Food Compos. Anal. 93 (2020) 103590.

[31] E. Ghorbani-Kalhor, Microchim. Acta 183 (2016) 2639.

[32] K. Molaei, H. Bagheri, A.A. Asgharinezhad, H. Ebrahimzadeh, M. Shamsipur, Talanta 167 (2017) 607.