



Optimization of magnetic ionic based dispersive liquid-liquid microextraction of cadmium in water and food samples using experimental design prior to flame atomic absorption spectrophotometry

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ABSTRACT

A magnetic ionic based dispersive liquid liquid microextraction (MIL-DLLME) procedure was optimized for the analysis and extraction of cadmium in water and food samples by flame atomic absorption spectrophotometry (FAAS). Contribution of experimental variables were optimized through central composite design combined with response surface analysis. Under optimized conditions, the limit of detection was found 0.6 ng mL^{-1} with the relative standard deviation of 1.7%. Dynamic range was obtained in the concentration range of 2–700 ng mL^{-1} with correlation coefficient of 0.9983. Relative recoveries were ranged from 94% to 99% with enrichment factor of 172. The validation of the optimized method was successfully confirmed by reference material analysis. The optimized method allows the analysis of cadmium in water and food samples with good reliability of the determination. Compared with the conventional procedures, the method enabled a fast, green and simple determination of cadmium in the real sample with minimal solvent consumption and a higher extraction capability.

1. Introduction

Since cadmium (Cd) is the element with the highest water solubility among other heavy metals, its diffusion rate is quite high. (Hayat et al., 2019). Since cadmium has a high solubility in the aquatic ecosystem, it can be easily taken into the biological system by plants and sea creatures in the form of Cd(II). (Zuluaga et al., 2015). Cd accumulating in soil and water is transmitted to microorganisms in the water first, and then to animals and humans through food (Hamid et al., 2019). Ingestion of high levels of Cd with food causes acute toxicity. Depending on the intake of Cd, chronic obstructive pulmonary diseases, emphysema and chronic renal tubular disorders are formed (Ganguly et al., 2018); Mezynska and Brzoska (2018). Due to these disadvantages, the weekly acceptable dose for Cd determined by FAO/WHO is 0.007 mg/kg body weight (Jorhem et al., 2008). Therefore, it is important to develop fast, sensitive and simple analytical methods for monitoring of Cd in water and food samples.

A selective and efficient sample preparation procedure is required prior to the determination step to minimize the matrix effect and for easy analysis (Xia et al., 2019). So far, the most frequently applied sample preparation techniques, for the separation and pre-concentration of Cd(II) from food and water samples, were switchable water dispersive liquid-liquid microextraction (Tuzen and Kazi, 2016), single-solidified floating organic drop microextraction (Jalbani and Soyak, 2015), centrifuge-less deep eutectic solvent based

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magnetic nanofluid-linked air-agitated liquid–liquid microextraction (Shirani et al., 2019), ultrasonic assisted dispersive liquid–liquid microextraction (Ghorbani et al., 2018), magnetic stirring-assisted dispersive liquid–liquid microextraction (Mohammadzadeh et al., 2016), ultrasound-assisted emulsification solidified floating organic drop microextraction (Dias et al., 2018), heat-induced deep eutectic solvent microextraction (Altunay et al., 2020) and ultrasound-assisted alkanol-based nanostructured supramolecular solvent microextraction (Altunay and Elik, 2021). In the above sample preparation procedures, surfactant, organic solvent, supramolecules, deep eutectic solvents and switchable were used as extraction solvents.

Recently, dispersive liquid-liquid microextraction (DLLME) using magnetic ionic liquids (MIL) has been widely used for pre-concentration and determination of target analytes (Chatzimitakos et al., 2021). Compared to other microextraction methods, the MIL has a high extraction efficiency, fast separation, no centrifugation step, improved sensitivity and exhibits a simplified sample pre-treatment procedure (Trujillo-Rodríguez et al., 2022). The procedure is based on a three-component solvent system that is formed after a suitable mixture of a water-immiscible MIL and a hydrophilic dispersant solvent is injected into an aqueous sample solution (Llaver et al., 2021). The mixture quickly reaches equilibrium, which significantly shortens the extraction time. DLLMEs using MILs have significant advantages such as being easy to process, fast, inexpensive, quantitative recovery and high enrichment factor. (Alves et al., 2021). MILs are non-flammable so they can be used safely (Clark et al., 2016). MILs are easy to prepare and not expensive. MILs are less toxic when compared to low boiling point solvents (Sajid, 2019). Moreover, since MILs have very low vapor pressures, they are not volatile and therefore do not release toxic vapors into the atmosphere like organic solvents when used at high temperatures.

Experimental design is a form of process analysis in which experimental parameters are changed in a controlled manner to detect their effects on a response of interest (Curtis et al., 2018). Statistical experiment design methods (full factorial design, central composite, Box-Behnken, Doehlert matrix..etc) experimentally describe the regression model between one or more measurable input variables (Rakić et al., 2014). These methods provide great advantages in terms of optimizing the ambient conditions, increasing the efficiency, reducing the number of experiments and reducing the cost (Altunay et al., 2021).

The aim of this study was to introduce a selective, efficient and rapid DLLME method based on the magnetic ionic liquid (MIL) for the trace-level determination of Cd in water and food samples. An $[P_{6,6,6,14}]_2^+ [CoCl_4]^{2-}$ magnetic-IL was easily prepared and utilized as the extraction solvent in the DLLME process. To separate Cd(II) ions from aqueous solutions, neodymium magnet was used in this study. After the magnetically separating step, the analyte-containing phase was injected directly into the atomization section of flame atomic absorption spectrophotometry (FAAS). Important experimental parameters have been optimized by central composite design (CCD) combined with response surface methodology (RSM). The accuracy of the optimized method was checked by analysis of three reference materials.

2. Experimental

2.1. Instrumentation and software

Determination of cadmium was performed using a flame atomic absorption spectrometer (FAAS) Shimadzu® AA-6300 (Tokyo, Japan) equipped with a deuterium background correction. The hollow cathode lamp of Cd was operated at 0.7 nm spectral bandwidth, 228.8 nm measurement wavelength, 7 mm burner height and 8 mA lamp current. All pH measurements were performed by a digital pH meter (Metrohm® pH 827, Herisau, Switzerland) calibrated with standard buffer solutions. An ultrasonic water bath with temperature control (SK5210LHC Kudos, Shanghai, China) was used to achieve dispersion in the microextraction steps. Microwave system (Milestone Ethos, Italy) was used for the digestion of the food samples. A neodymium magnet (1.17 T magnetic field) was used for phase separation). A rotary evaporator BUCHI R-200 (BÜCHI Labortechnik AG, Flawil, Switzerland) was used for the preparation of the magnetic ILs. Design-Expert® software version 12.0.1 (Stat-Ease Inc., Minneapolis). was utilized for ANOVA analysis and experimental design.

2.2. Standard solutions and chemicals

All chemicals used were of analytical grade. The stock solution (1000 mg L^{-1}) of Cd(II) ion were prepared from its nitrate salt (Sigma-Aldrich, Steinheim, Germany) in the water. Serial dilutions of the stock solutions were used to prepare suitable working standard solutions. Acetate buffer solution (0.1 mol L^{-1} pH = 5.5) was prepared by mixing suitable volumes of 0.1 mol L^{-1} sodium hydroxide and 0.1 mol L^{-1} acetic acid. L-Cysteine was used as complexing agent and its 50 mmol L^{-1} concentration was prepared by dissolving the appropriate amount (Merck, Darmstadt, Germany) in the water. For the preparation of magnetic-ionic liquid, CYPHOS®IL 101 (triethyl(tetradecyl)phosphonium chloride) $[P_{6,6,6,14}]$ and cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) were purchased from Merck and Sigma, respectively.

2.3. Collection and preparation of samples

In our study, bottled water, mineral water, rice, wheat and black tea were collected from other supermarkets in Sivas/Turkey. Waste-waters were collected from different areas of the organized industrial zone in Sivas. Well-waters were collected from agricultural lands in Sivas. Flower honey and chestnut honey were purchased from local producers in Erzurum/Turkey. Vegetable samples (corn, leek, spinach, eggplant and tomato) were purchased from local grocery stores. Grilled meatballs, grilled meat and grilled chicken were collected from local restaurants in Sivas.

Water samples were prepared as follows. 100 mL of all water samples were filtered through a membrane filter and transferred to beakers. The beakers were then placed on the warming plate and evaporated until the final volume was reduced to approximately 5 mL. Finally, the optimized MIL-DLLME method was applied to the enriched water samples.

Solid samples and reference materials were prepared by microwave digestion method. All experimental steps were listed below

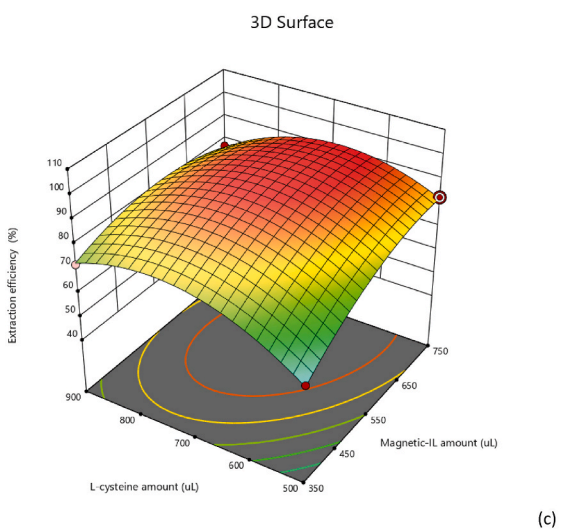
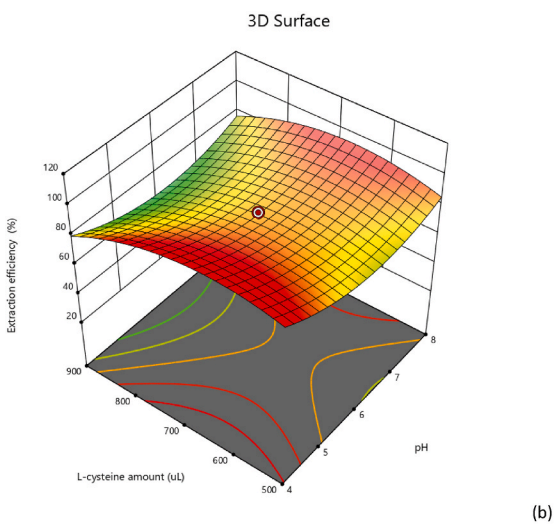
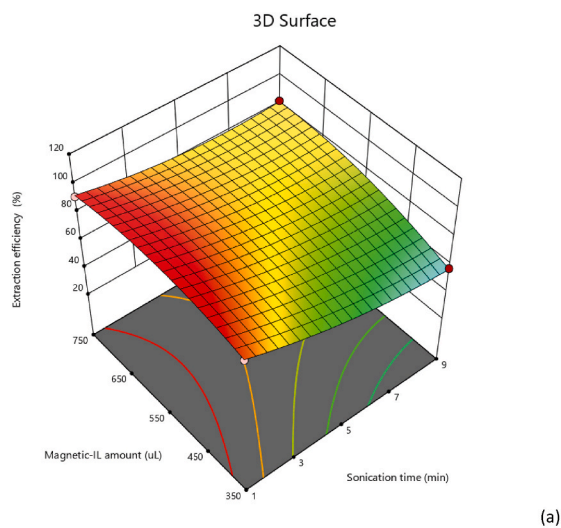


Fig. 1. a-c. 3D response surfaces for: (a) magnetic-IL -sonication time, (b) L-Cysteine amount-pH, (c) magnetic-IL amount- L-Cysteine amount.

(Tuzen et al., 2016). First, 1.0 g of the solid samples was carefully weighed and added to Teflon® flasks. Then, 6 mL of concentrated nitric acid and 2 mL of concentrated hydrogen peroxide were added to these flasks, respectively, and their lids were carefully closed, and then placed in the microwave system. The steps of 6 min for 250 W, 6 min for 400 W, 6 min for 550 W, 6 min for 250 W, ventilation: 8 min were applied to the tubes, respectively. After the digestion step, the final volume of the digested samples was made up to 10 mL using the water. Lastly, cadmium level in the prepared food samples were analyzed using the optimized MIL-DLLME method.

2.4. Optimization strategy

Important microextraction parameters of the MIL-DLLME method may affect the extraction efficiency of Cd(II). Therefore, central composite design (CCD) combined with response surface methodology (RSM) was used for the optimization of the important parameters such as association time (A), pH (B), amount of magnetic-IL (C) and amount of complexing agent (D). Each microextraction parameter was set at a low (-1), high value (+1), and the median (0). Totally, 30 experiments were designed by the CCD. Factor levels, symbols, and experimental design were shown in [Supplementary Material Table S1](#). The extraction efficiency obtained for Cd(II) ions as a result of the experimental plan of the CCD model was presented in [Supplementary Material Table 2](#).

2.5. Preparation of $[P_{6,6,6,14}]_2^+[CoCl_4]^{2-}$

The $[P_{6,6,6,14}]_2^+[CoCl_4]^{2-}$ magnetic-IL was prepared by the following experimental steps (Del Sesto et al., 2008). First, an equimolar concentration of $CoCl_2 \cdot 6H_2O$ and 50% (w/v) CYPHOS IL 101 solution dissolved in anhydrous dichloromethane was carefully added to a 100 mL beaker. In the second step, the resulting mixture was kept at room temperature under constant temperature for 24 h to complete the reaction. In the final step, a rotary evaporator was used to evaporate excess anhydrous dichloromethane and remove it from the solution. The obtained magnetic IL ($[P_{6,6,6,14}]_2^+[CoCl_4]^{2-}$) was dried in an oven at 50 °C.

2.6. Microextraction procedure for MIL-DLLME

The experimental steps of the optimized method were carried out as follows. The 5 mL of sample solution were transferred to a conical bottom tube including 50 ng mL⁻¹ of Cd(II) solution. Then, the pH of the sample solution was adjusted to 4.5 with acetate buffer solution. For the complexation of Cd(II) ions in the sample solution, 680 µL of the L-Cysteine (Cys, 50 mmol L⁻¹) was injected into the sample solution and the mixture was then homogenized by gentle shaking. After complexation, 560 µL of the $[P_{6,6,6,14}]_2^+[CoCl_4]^{2-}$ magnetic-IL (MIL) was added to the obtained solution to ensure the separation of Cys-Cd complex in the sample solution. Then, the conical bottom tube was sonicated for 2 min at room temperature to allow the $[P_{6,6,6,14}]_2^+[CoCl_4]^{2-}$ (as extraction solvent) to disperse into the sample solution. At this stage, the Cys-Cd complex in sample solution was successfully extracted into the MIL phase. The analyte-enriched MIL was then easily separated from the sample solution using a powerful neodymium magnet. After the collected MIL phase is redissolved in 1.0 mL of acidic ethanol, it is injected into the FAAS to determine the amount of cadmium. All studies were carried out with the sample blank.

3. Results and discussion

3.1. Optimization of extraction conditions by CCD

The effect of microextraction parameters on the extraction efficiency of Cd(II) ions was evaluated for optimization studies. The extraction efficiency was calculated according to the formula below.

$$\text{Extraction efficiency (\%)} = C_{\text{final}} V_{\text{final}} / C_o V_o \quad (1)$$

Where C_{final} and C_o were the Cd(II) amount in the final phase and the initial Cd(II) amount in the sample solution, respectively. In addition, V_{final} and V_o refer to the volume of the final phase and the volume of the sample solution, respectively.

The effect of the binary interactions of the optimized parameters on the extraction efficiency of Cd(II) ions was discussed by drawing 3D surface response graphs. [Fig. 1a](#) shows the effect of the interaction between magnetic-IL and sonication time on the extraction efficiency of Cd(II) ions. Here, the sonication application aims to effectively disperse the magnetic ionic liquid into the sample solution. If the $[P_{6,6,6,14}]_2^+[CoCl_4]^{2-}$ magnetic-IL does not effectively disperse into the sample solution, the extraction of Cd(II) ions will not be quantitative. When [Fig. 1a](#) was examined, it is seen that quantitative of Cd(II) extraction efficiency was provided in the range of 1–2.5 min and 375–700 µL of sonication time and magnetic-IL amount, respectively. In addition, no significant change was observed in the extraction efficiency of Cd(II) ions when the sonication time exceeded 5 min.

The second interaction examined is the effect of complexing agent amount (L-Cysteine) and pH on the extraction efficiency of Cd(II). The main purpose here is to determine the appropriate pH for the effective complexation of Cd(II) ions with L-cysteine. When [Fig. 1b](#) is examined, there was a decrease in the extraction efficiency of Cd(II) ions, especially in the pH range of 6–7.5. The reason for this is the interaction of L-cysteine with OH⁻ ions, and accordingly, the efficiency of complex formation of the Cd-L-cysteine is decreased. In addition, the extraction efficiency of Cd(II) ions decreased when the amount of L-cysteine exceeds 700 µL. This is because the amount of L-cysteine is insufficient to fully complex the Cd(II) ions in the sample solution.

The third evaluated is the interaction of magnetic-IL amount and the complexing agent amount. As can be seen in [Fig. 1c](#), quantitative extraction efficiency of Cd(II) ions was achieved in the range of magnetic-IL and L-cysteine in the range of 550–700 µL and 650–750 µL, respectively. Especially at low magnetic-IL volumes, since full phase separation could not be achieved, there were severe decreases in the extraction efficiency of Cd(II) ions. In order to ensure high extraction efficiency of Cd(II), optimum values for the sonication time, pH, magnetic-IL amount and L-cysteine amount by CCD were established as 2 min, 4.5, 560 µL and 680 µL,

Table 1
ANOVA analysis for the extraction efficiency of the Cd(II) obtained by the CCD.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2991.24	14	213.66	152.57	<0.0001	significant
A	247.90	1	247.90	177.02	<0.0001	
B	121.68	1	121.68	86.89	<0.0001	
C	280.06	1	280.06	199.98	<0.0001	
D	14.58	1	14.58	10.41	0.0056	
AB	20.25	1	20.25	14.46	0.0017	
AC	424.36	1	424.36	303.02	<0.0001	
AD	484.00	1	484.00	345.61	<0.0001	
BC	59.29	1	59.29	42.34	<0.0001	
BD	70.56	1	70.56	50.38	<0.0001	
CD	432.64	1	432.64	308.93	<0.0001	
A ²	73.79	1	73.79	52.69	<0.0001	
B ²	467.79	1	467.79	334.03	<0.0001	
C ²	122.04	1	122.04	87.14	<0.0001	
D ²	415.47	1	415.47	296.67	<0.0001	
Residual	21.01	15	1.40			
Lack of Fit	13.71	10	1.37	0.9388	0.5661	not significant
Pure Error	7.30	5	1.46			
Cor Total	3012.25	29				
Std. Dev	1.18		R ²	0.9930		
Predicted R ²	0.9865		Adjusted R ²	0.9694		

Table 2
Analytical characteristics of the MIL-DLLME procedure for determination of Cd.

Parameters	Analytical value
Calibration equation	A = 0.0078[Cd amount. ng mL ⁻¹]+0.0012
Correlation coefficient	0.9983
Dynamic range (ng mL ⁻¹)	2–700
Limit of detection (ng mL ⁻¹)	0.6
Quantification of detection (ng mL ⁻¹)	2.0
Repeatability (for 10 ng mL ⁻¹ of Cd(II), N:3)	1.5
Recovery (for 10 ng mL ⁻¹ of Cd(II), N:3)	98±3
Enrichment factor	172

respectively. Experimental extraction efficiency obtained using these optimum values showed statistically high agreement with the value predicted by the CCD model. A value less than 0.9% represents a strong correlation between the experimental and predicted values. Therefore, these data were chosen as optimum for the studied parameters.

3.2. Statistical analysis

The ANOVA analysis was given in Table 1. In the evaluation of significance for the CCD model, the explanations of R² values were made as follows. The quality parameters R², adjusted- R² and predicted- R² values of the CCD model were 0.9930, 0.9865 and 0.9694, respectively, indicating that the model had a high potential for predicting the response. The p-value for lack of fit was calculated as 0.5661, indicating that the lack of fit was not significant compared to pure error. When Table 1 is examined, it is seen that the p-value (<0.0001) of the CCD model is considerably lower than 0.05. This showed that the established CCD model was significant. In addition, all interactions were significant. The magnitude of the F-value is directly proportional to the contribution to the CCD model. In this context, the linear, binary and quadratic interactions that contribute the most to the CCD model are C (F-value: 199.98), AD (F-value: 345.61) and B² (F-value: 334.03), respectively. The relationship between the optimized parameters and the extraction efficiency of Cd (II) can be calculated according to the equation below.

$$\text{Extraction efficiency (\%)} = +75.23 - 3.71A - 2.60B + 3.94C - 0.9D + 1.13AB + 5.15AC + 5.50AD + 1.93BC + 2.10BD - 5.20CD + 534 A^2 + 13.44 B^2 - 6.86C^2 - 12.66 D^2$$

In Supplementary Material Fig. S1, a straight line can be seen for the normal probability plot of the extraction efficiency of Cd(II) ions. Also, this figure represents a normal distribution for experimental results and the reliability of the CCD model.

3.3. Analytical parameters of optimized method

The analytical performance of the optimized method was investigated using the optimal conditions obtained using CCD. The analytical results were listed in Table 2. The optimized method was applied by adding standard Cd(II) solution in different concentrations to the real samples. As a result of these studies, calibration equation was obtained as A = 0.0078[Cd amount, ng mL⁻¹]+0.0012 (A, measured absorbance) with correlation coefficient of 0.9983. In addition, the dynamic range for Cd(II) was determined as

Table 3
Tolerance limit of foreign ions for determination and extraction of Cd(II) (100 ng mL⁻¹).

Foreign ions	Recovery (%)	RSD (%)	Tolerable limit ^a
SO ₄ ²⁻	99.5	2.5	2000
Cl ⁻	99.0	2.6	1000
Mg ²⁺	99.4	2.9	1000
NO ₃ ⁻	98.6	3.0	1000
HCO ₃ ⁻	98.5	2.4	1000
K ⁺	98.3	2.6	500
Mn ²⁺	98.1	2.9	500
Ni ²⁺	97.7	3.1	500
Zn ²⁺	97.4	2.9	500
Co ²⁺	96.0	2.3	500
Fe ³⁺	96.7	2.6	500
Cu ²⁺	95.5	2.6	250
As ³⁺	95.4	3.0	250
Pb ²⁺	95.7	2.8	250
Cr ³⁺	94.2	2.7	250
Mixture of equivalent concentrations of all foreign ions	93.8	3.2	100

^a [Foreign ion concentration]/[Cd(II) ion concentration].

Table 4a
Results for the analysis of Cd in reference materials (N = 5) by the optimized method.

Reference material	Certified value (mg kg ⁻¹)	Measured value (mg kg ⁻¹)	Recovery (%)	*t-value
INCT-TL-1 Tea leaves	0.030 ± 0.004	0.028 ± 0.06	93.3	0.75
NIST1573A Tomato leaves	1.52 ± 0.04	1.48 ± 0.11	97.4	0.81
CRM 7502-a: Trace Elements in White Rice Flour (Cd Level II)	0.548 ± 0.020	0.540 ± 0.015	98.6	1.19

* The one paired critical t-value is 2.78 for four degrees of freedom at probability level of 0.05.

2–700 ng mL⁻¹. The detection limit (LOD) and quantification limit (LOQ) of the optimized method were calculated from the formulas of 3 s/m and 10 s/m, respectively. The s and m symbols in the formulas were the standard deviation of the blank samples and the slope of the calibration graphs, respectively. LOD and LOQ were calculated as 0.6 and 2.0 ng mL⁻¹, respectively. As a result of three repetitions of 10 ng mL⁻¹ Cd(II) solution, the relative standard deviation (RSD) and recovery were found to be 1.5% and 98±3%, respectively. The enrichment factor (EF) was calculated as 172 by dividing the sensitivity before and after the MIL-DLLME procedure.

3.4. Interference effect

Optimization studies were carried out on model solutions. Therefore, different chemical species may affect the extraction procedure. For this reason, foreign ions in Table 3 were added to the model solutions at different concentrations and then the optimized method was applied to these prepared solutions. In this study, tolerable limit, recovery and RSD values were calculated for each foreign ion. The tolerable limit was calculated from the ratio of the amount of foreign ion added to the amount of added Cd(II), causing a ±5% change in the analytical signal of Cd(II). As a result, the tolerable limit ranged from 100 to 2000. Furthermore, the recovery and RSD% in presence of foreign ions varied in the range of 93.8–99.5% and 2.4–3.2%, respectively. All these quantitative results showed that the optimized chemical conditions had high selectivity for Cd(II) ions.

3.5. Intraday/inter-day precision

The precision of the optimized method was evaluated by intraday and inter-day studies. In these studies, different concentrations of standard Cd(II) solution were added to the selected samples. Intraday precision was estimated via studying five replicate solutions of Cd(II) at three concentration levels (10, 200 and 400 ng mL⁻¹). The RSD were obtained 3.1%, 2.4% and 2.0% for 10, 200 and 400 ng mL⁻¹ of Cd(II), respectively. Inter-day precision was estimated by running the same concentrations in five replicates on five consecutive days. The result of the study, the RSD were obtained 4.6%, 3.5% and 2.9% for 10, 200 and 400 ng mL⁻¹ of Cd(II), respectively. The fact that the RSDs obtained as a result of all studies were below 5% indicated that the precision of the method was acceptable.

3.6. Analysis of reference materials

The accuracy of the optimized method was checked by analysis of three reference materials such as INCT-TL-1 Tea leaves, NIST1573a-Tomato leaves and CRM 7502-a: Trace Elements in White Rice Flour (Cd Level II). The reference materials were prepared according to the recipe in section 2.3 for the application of the optimized method. As a result of the application of the optimized method, it was seen that the experimental values found for all reference materials were compatible with the certified values and there was no significant difference between the results at the 95% confidence interval. When the t-value, which is an important parameter in the statistical evaluation, was examined, it was seen that the experimental t-values (0.75, 0.81 and 1.19) obtained from the analysis of the three reference materials were smaller than the statistical t-value (2.78 for four degrees of freedom at probability level of 0.05).

Table 4b
Analysis results of Cd(II) in various water samples (N:5) by the optimized method.

Samples	Spiked (ng mL ⁻¹)	Measured (ng mL ⁻¹)	Recovery (%)
Bottled water-1	–	nd*	–
	50	48.5 ± 1.2	97 ± 4
	200	244.5 ± 4.6	98 ± 3
Bottled water-2	–	nd	–
	50	49.0 ± 2.4	98 ± 3
	200	198.0 ± 5.6	99 ± 2
Well-water-1	–	9.1 ± 0.5	–
	50	56.1 ± 1.4	94 ± 4
	200	201.1 ± 3.9	96 ± 3
Well-water-2	–	12.5 ± 0.7	–
	50	61.0 ± 2.3	97 ± 4
	200	210.5 ± 5.2	99 ± 2
Waste water-1	–	33.4 ± 1.8	–
	50	81.4 ± 2.6	96 ± 3
	200	227.4 ± 4.4	97 ± 2
Waste water-2	–	25.9 ± 1.1	–
	50	72.9 ± 2.7	94 ± 5
	200	219.9 ± 5.8	97 ± 3
Mineral water	–	nd	–
	50	48.0 ± 2.4	96 ± 4
	200	198.0 ± 4.7	99 ± 4

* Below the determination limit.

Table 4c
Analysis results of Cd(II) in various food samples (N:5) by the optimized method.

Samples	Spiked amount (µg)	Measured amount (µg g ⁻¹)	Recovery (%)
Corn	–	1.7 ± 0.04	–
	15	16.0 ± 0.07	95.3
Rice	–	0.8 ± 0.2	–
	15	15.5 ± 0.9	98.0
Wheat	–	0.6 ± 0.06	–
	15	15.4 ± 1.1	98.7
Leek	–	1.3 ± 0.4	–
	15	16.1 ± 0.9	98.7
Spinach	–	2.2 ± 0.05	–
	15	16.6 ± 1.2	96.0
Eggplant	–	0.7 ± 0.03	–
	15	14.9 ± 1.3	94.6
Tomato	–	0.9 ± 0.02	–
	15	15.4 ± 0.7	96.7
Flower honey	–	1.3 ± 0.08	–
	15	15.9 ± 0.9	97.3
Chestnut honey	–	1.9 ± 0.07	–
	15	15.8 ± 1.0	92.7
Black tea	–	2.3 ± 0.6	–
	15	17.0 ± 0.8	98.0
Grilled meatballs	–	45.5 ± 1.2	–
	15	59.8 ± 2.0	95.3
Grilled meat	–	39.4 ± 1.7	–
	15	53.8 ± 2.3	96.0
Grilled chicken	–	54.2 ± 2.6	–
	15	68.8 ± 3.4	97.3

These results indicate that the optimized method exhibits high accuracy. Comprehensive analytical results were presented in Table 4a.

3.7. Application to the selected samples

After validation studies of the optimized method, its applicability was tested on selected water and food samples. In order to minimize the possible matrix effect in the analysis of water samples, two different concentrations (50 and 200 ng mL⁻¹) of the Cd(II) solution were added to the water samples including bottled water, well-water, waste water and mineral water. As a result of the application, cadmium could not be detected in the bottled waters and mineral water. The recovery for these samples was also found in the range of 97 ± 4%- 99 ± 2%. In addition, the highest cadmium was detected in wastewater-1 as 33.4 ± 1.8 ng mL⁻¹. Quantitative recoveries were obtained from the analysis of all water samples. All results were presented in Table 4b.

While the optimized method was applied to the food samples, 50 µg of cadmium was added to the samples including corn, rice, wheat, leek, spinach, eggplant, tomato, flower honey, chestnut honey, black tea, grilled meatballs, grilled meat and grilled chicken. As

Table 5

A comparison of analytical performance of the optimized method with other analytical methods in literatures.

Samples	Microextraction procedure	Determination technique	Dynamic range (ng mL ⁻¹)	LOD (ng mL ⁻¹)	RSD (%)	Extraction time (min)	EF	References
Waters and Foods	MIL-DLLME	FAAS	2–600	0.6	1.5	2	172	Optimized method
Honey	DLLME	ETAAS	2–250	0.4	3.8	–	112	Fiorentini et al. (2018)
environmental samples	VA-SW-LLME	FAAS	60–1000	31	8.4	4	45	Firat et al. (2018)
Wine samples	DES-UA-DLLME	FAAS	0.50–8.0	0.08	4.5	10	–	Ji et al. (2021)
Water samples	IL-UA-DLLME-SAP	LC-UV	0.2–75.0	0.03	4.0	60	209	Werner (2018)
Vegetables	AA-DLLME	FAAS	1.7–50	0.51	6.6	6	79	Fontes et al. (2020)
Water and canned food	EA-SS-LPME	HR-CS-FAAS	20–1500	6.8	1.64	8	2.6	Chaikhan et al. (2021)
Waters and Foods	HDES-LPME	FAAS	5–200	1.6	3.3	5	43	(Çatak and Sabancı, 2021)

MIL-LPME: Magnetic ionic liquid dispersive liquid liquid microextraction; DLLME: dispersive liquid-liquid microextraction; VA-SW-LLME: Vortex-assisted switchable liquid-liquid microextraction; DES-UA-DLLME: deep eutectic solvent based on ultrasonic-assisted dispersive liquid-liquid microextraction; LC-UV: Liquid chromatography; IL-UA-DLLME-SAP: Ionic liquid ultrasound-assisted dispersive liquid liquid microextraction based on solidification; AA-DLLME: air-assisted dispersive liquid-liquid microextraction; HR-CS-FAAS: High-resolution continuum source flame atomic absorption spectrometry; EA-SS-LPME: Effervescent tablet-assisted switchable solvent based liquid phase microextraction; HDES-LPME: hydrophobic deep eutectic. Solvent based liquid phase microextraction.

a result of the application, the highest and lowest cadmium contents were observed in grilled chicken ($54.2 \pm 2.6 \mu\text{g g}^{-1}$) and rice ($0.8 \pm 0.2 \mu\text{g g}^{-1}$), respectively. As a result of the analysis of these samples, recovery in the range of 92.7–98.7% was obtained. Quantitative recoveries from experimental studies indicate the low matrix effect of the optimized method. Detailed results were presented in Table 4c.

3.8. Comparison with other methods

The analytical efficiency of the optimized method was compared with a number of previously reported analytical techniques for the determination of Cd and summary results were given in Table 5. Among all the compared methods, the optimized method was exhibited lower extraction time and lower RSDs. In particular, a wider dynamic range and lower LOD were obtained compared to the ETAAS and HR-CS-FAAS techniques, which are more sensitive than FAAS. A very high EF was obtained with the optimized method compared to other studies. This was due to the high efficiency of the magnetic-IL used in the study. As a result, the dynamic range, LOD, EF, and RSD values of the optimized method for the analysis and extraction of cadmium were better than many reported analytical techniques. The fact that toxic chemical reagents are not needed in this method provides a significant advantage over other methods. Moreover, the most important advantage of the optimized method compared to other microextraction procedures is that it does not require a heating step in the extraction step.

4. Conclusions

An easy, efficient, and green analytical method on the basis of the MIL-DLLME procedure combined with FAAS technique was optimized for extraction, preconcentration and determination of cadmium in real samples. The easily prepared $[\text{P}_{6,6,6,14}]_2^+ [\text{CoCl}_4]^{2-}$ magnetic-IL was tested for the first time for the extraction and preconcentration of Cd(II) ions. Contribution of experimental variables such as sonication time, pH, amount of magnetic ionic liquid, and amount of complexing agent were optimized through central composite design (CCD) combined with response surface analysis (RMS). The application of the RMS-CCD was a rapid, economical and efficient way of an optimization strategy of the MIL-DLLME procedure. Quantitative recovery results from standard addition experiments were proved the optimized method's accuracy for analyzed water and food samples. The optimized method is precise, reproducible, fast and can be safely used for analysis of trace levels of cadmium. As a result, it can be said that the optimized method has short extraction time, minimum amount of organic solvent requirement, simple computer application, high selective and good accuracy.

Author contributions section

Nail Altunay: Writing -original draft, Investigation. **Adil Elik:** Supervision, Validation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scp.2022.100697>.

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