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Magnetic stirring-assisted dispersive liquid–liquid microextraction in narrow neck glass tube for determination of cadmium in water, fruit and vegetable samples using response surface methodology

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ABSTRACT

Narrow neck glass tube-magnetic stirring-assisted dispersive liquid–liquid microextraction for extraction and preconcentration of trace amounts of cadmium ions as ammonium pyrrolidine dithiocarbamate complex was developed. In this method, a cloudy state is formed in a homemade glass syringe by magnetic stirring. Afterward the organic phase on top of the solution was transferred into narrow neck by moving the piston upwards, and withdrawn by the syringe for conventional injection to flame atomic absorption spectrometry. The experimental conditions were optimized by Plackett–Burman and Box–Behnken design methods. Under the optimum conditions (pH 5.5, chelating agent = 1×10^{-5} mol L^{-1}, sodium chloride (0.04% w/v), extraction solvent volume = 250.0 μL, stirrer rate = 1,200 rpm, and extraction time = 10 min), the calibration graph was linear over the range 10–1,000 μg L^{-1} and the limits of detection was 1.4 μg mL^{-1}. The relative standard deviation was 1.15% ($n = 10$, $C = 100$ μg L^{-1}) and the enrichment factor was about 280. The developed method was successfully applied to the extraction and determination of cadmium in wastewater, fruit, and vegetable samples.

Keywords: Narrow neck glass tube-magnetic stirring-assisted dispersive liquid–liquid microextraction (NNGT-MSA-DLLME); Cadmium; Water; Fruit and vegetable samples; Flame atomic absorption spectrometry

1. Introduction

Cadmium is classified as prevalent toxic metal even at very low concentration, causing damage to organs such as the liver, lung, and kidney [1]. Contaminated waters and foods are the main source of consumption of this metal. Therefore, rapid and sensitive methods need to be developed for its determination in water samples [2–4].

Dispersive liquid–liquid microextraction (DLLME), as liquid phase microextraction method, was developed in 2006 by Assadi and coworkers [5]. Although the first articles about DLLME have been related to determination of trace organic compounds with gas chromatography, but to date, this method coupled with atomic spectrometry has been suggested for a variety of elements [6–9]. DLLME provides many

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advantages of high enrichment factor, simplicity, rapidity, easy to operate, low sample volume, low cost, and consumption of organic solvents, but one of the serious drawbacks is its limited choices of extraction solvent. So lately, some researchers make great effort to use low-density solvents microextraction methods such as: vortex-assisted liquid–liquid microextraction, low-density extraction solvent-based solvent terminated DLLME [10,11], and ultrasound-assisted liquid–liquid microextraction [12]. In the mentioned methods, the neck of extraction vessel is relatively wide; therefore it is difficult to collect a thin layer of extractant floating on the top of the aqueous sample. Recently, several literatures about different narrow-necked apparatuses are published which eliminate this difficulty [13–16]. In 2012, Suárez and coworkers [17–19] introduced a robust in-syringe-stirring dispersive liquid–liquid microextraction (IS-DLLME) method for determination of aluminum in seawater and methylene blue in waste water and water samples. In this method, for the first time, a stirring bar placed into the syringe of a computer controlled syringe pump was used for magnetic stirring assisted DLLME. The extraction process was based on the disruption of the extraction solvent by the kinetic energy of the swirling stirring bar. This method could be automation and has good sensitivity and precision.

The aim of this paper is introduced a new IS-DLLME method which provides a simple and a rapid way to collect hydrophobic species from aqueous solutions. A homemade glass syringe vessel is used to perform the microextraction process through collecting the extraction solvent in narrow neck glass tube by moveable septum. The microvolume of organic solvents is poured on the surface of sample solution and then is magnetically agitated. After extraction, the extraction solvent is easily separated from the aqueous phase by leaving the extraction system statically for a several minutes and lifted it to the narrow section of syringe. Experimental parameters, which may affect the extraction performance, are identified by Plackett–Burman (P–B) and optimized by the Box–Behnken design (BBD). The developed method was successfully applied to the extraction and determination of cadmium in wastewater, fruit, and vegetable samples.

2. Experimental

2.1. Instrumentation

A Shimadzu flame atomic absorption spectrophotometer (AA-680) equipped with a deuterium lamp for the background correction was used to measure of absorbance. A cadmium hollow cathode lamp (analytical wavelength 228.8 nm) from Hamamatsu, Photonic Co. Ltd, L233-series was employed as the radiation source. Acetylene and air flow rates were 2.2 and 10.0 L min^{-1}, respectively. The nebulizer flow rate was 4.0 mL min^{-1}. A pH meter model Metrohm Lab-827 was used for solution pH adjustment.

2.2. Reagents

All solutions were prepared using ultrapure water (18.2 MΩ). The glassware was kept in a 5% (v/v) nitric acid solution overnight and subsequently washed with deionized water. All reagents were used in analytical grade. Analytical grade cadmium nitrate and nitrate salts of other cations (all from Merck, Darmstadt, Germany) were available with high purity and used without further purification. Working solutions of cadmium at μg mL^{-1} level were prepared daily by diluting a 1,000 μg mL^{-1} stock solution. The pH of cadmium solutions was adjusted with the aid of acetate (pH 4.0–6.0), phosphate (pH 2.0–3.0, 7.0–9.0), and ammonia (pH 10.0–12.0) buffer solutions. Toluene, 1-octanol, 1-decanol, 1-dodecanol, 1-undecanol, hexane, and heptane were purchased from Merck Darmstadt, Germany and were used in the proposed microextraction method as extraction solvents. Ammonium pyrrolidine dithiocarbamate (APDC) as chelating agent, at a concentration of 10^{-3} mol L^{-1}, was prepared by dissolving an appropriate amount of reagent (Merck, Darmstadt, Germany) in water.

2.3. General procedure

According to Fig. 1(a) 50 mL solution containing cadmium ions in the dynamic range, APDC as complexing agent (1×10^{-5} mol L^{-1}) and sodium chloride (0.04% w/v) was adjusted to pH 5.5 with acetate/

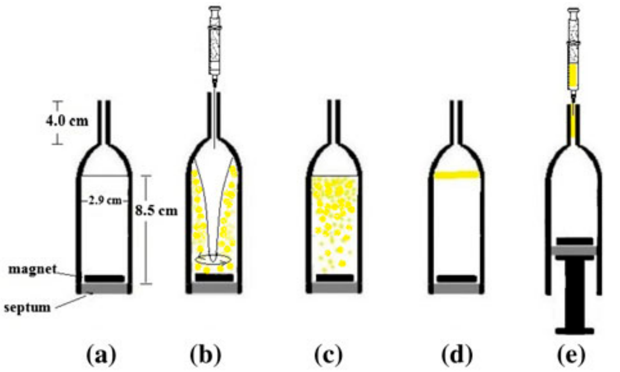


Fig. 1. Schematic representation of the presented NNGT-MSA-DLLME set up and procedure.

acetic acid buffer. Next, the prepared solution was poured in a glass syringe (8.5 cm × 2.9 mm i.d.) in which end of the syringe was closed with a movable septum (Fig. 1(a)). Then, while the solution is magnetically stirred, 250.0 μL of toluene was injected through the top of the glass syringe into the sample solution by Hamilton gas-tight syringe (Fig. 1(b)). Afterwards, the solution was firmly stirred for 10 min and a cloudy solution is formed, due to the dispersion of many fine droplets of toluene (Fig. 1(c)). After a few second, the organic phase was collected on the top of the solution (Fig. 1(d)), and then it was lifted up in the narrow section of the tube by moving the septum to the top of the syringe (Fig. 1(e)). Finally, 80 μL of extraction solvent was manually removed by microsyringe, and was poured into the eppendorf vial and diluted with 100 μL of methanol. Next, the resulting solution was introduced to the flame atomic absorption spectrometer for further analysis.

2.4. Sample preparation

The water samples were collected from different part of river and sewage samples in Kermanshah and Arak, Iran. The water samples were filtered using 0.45-μm micropore membranes and were kept in glass containers at 4°C. Fruit and vegetables samples were purchased in local market in Arak, Iran. The fruit and vegetables samples were washed with double-distilled water for several times, dried at 100°C for 24 h, and homogenized by grinding. Next, the wet digestion was applied for analysis of fruits and vegetables. Hence, 1.0 g of each above sample were weighted in porcelain crucible and placed into the electrical furnace. The temperature was increased gradually to 600°C and maintained for 7 h. Afterward, the appropriate amount of HCl solution (20%) was added to digest ash powder. The digested powder was diluted by distilled water to 25 mL in volumetric flask [20]. The obtained solutions were applied to analyses the cadmium contents of each fruit and vegetables sample by narrow neck glass tube-magnetic stirring-assisted dispersive liquid–liquid microextraction (NNGT-MSA-DLLME) method.

2.5. Experimental design strategy

In this research, instead of several numbers of experiments in one-at-a-time method, which is time-consuming and expensive, the experimental design was used to reduce experiments runs and to get effective factors. The P–B design was used to clarify the effective factors in extraction of cadmium by

Table 1
Factors, levels, and their coded for PBD

Factor	Low	Levels central	High
(X_1) pH	2	5.5	9
(X_2) Extractor volume (μL)	50	175	300
(X_3) Stirrer rate (rpm)	400	800	1,200
(X_4) Extraction time (min)	2	8.30	15
(X_5) concentration of APDC (mol L^{-1})	0.0001	0.05	0.1
(X_6) Salt effect (mL of NaCl (10%))	0	2	4

Runs	(X_1)	(X_2)	(X_3)	(X_4)	(X_5)	(X_6)
1	2.0	300	1,200	2.0	0.00010	4
2	2.0	50	1,200	15.0	0.00010	4
3	9.0	300	1,200	15.0	0.10000	0
4	5.5	175	800	8.5	0.05005	2
5	9.0	300	400	15.0	0.00010	4
6	9.0	300	400	2.0	0.00010	0
7	2.0	300	1,200	2.0	0.10000	0
8	9.0	50	1,200	2.0	0.10000	4
9	9.0	50	1,200	15.0	0.00010	0
10	9.0	50	400	2.0	0.10000	4
11	2.0	50	400	2.0	0.00010	0
12	5.5	175	800	8.5	0.05005	2
13	5.5	175	800	8.5	0.05005	2
14	2.0	300	400	15.0	0.10000	4
15	2.0	50	400	15.0	0.10000	0

NNGT-MSA-DLLME method from aqueous solution. The P–B design is a useful method to determine of effective parameters by a few tests [21]. Table 1 shows the factors, their levels, and the runs of P–B design. After implementation of the P–B design, the effective factors were analyzed by BBD to achieve optimum conditions, the investigation of the variables interaction and the significance of factors. The widely use of BBD is based on the following advantages:

1. Finding effective factors in the experiment.
2. Studying the factors influencing on responses.
3. Investigating the interactions among the variables.
4. Obtaining the optimum conditions for further studies.

In the BBD, the total number of experimental runs is equal to Eq. (1)

$$N = 2K\ (K - 1) + C \tag{1}$$

where N, K, and C are number of experimental runs, the number of central points, and the number of variables, respectively [22]. In this study, after P–B design, four factors were chosen and analyzed by BBD on two levels and at a triplicate central point (Table 1). By considering Eq. (1), the experimental runs were 27 runs (Table 2). In the BBD, for minimizing the systematic error, experiments were conducted randomly and all runs were replicated three times. All the statistics were carried out by Minitab (Version 16.0) software. According to Table 2, these factors include: the pH of

Table 2
Design matrix by BBD

Factor		Levels		
		Low	central	High
(X_1) pH		2	5.5	9
(X_2) Extractor volume (μL)		50	150	250
(X_3) Stirrer rate (rpm)		400	800	1,200
(X_4) Extraction time (min)		2	6	10
Runs	X_1	X_2	X_3	X_4
1	5.5	50	1,200	6
2	2.0	150	1,200	6
3	2.0	150	800	2
4	2.0	150	400	6
5	9.0	50	800	6
6	5.5	150	800	6
7	9.0	150	1,200	6
8	5.5	50	800	10
9	5.5	150	400	2
10	9.0	150	400	6
11	5.5	150	800	6
12	5.5	250	800	10
13	5.5	250	800	2
14	5.5	150	800	6
15	5.5	50	800	2
16	5.5	250	1,200	6
17	5.5	50	400	6
18	9.0	150	800	10
19	5.5	150	1,200	2
20	5.5	150	400	10
21	2.0	150	800	10
22	5.5	250	400	6
23	2.0	50	800	6
24	2.0	250	800	6
25	9.0	250	800	6
26	9.0	150	800	2
27	5.5	150	1,200	10

solution (X_1), the extractor volume (μL, X_2), the stirrer rate (rpm, X_3), and the extraction time (min, X_4).

3. Results and discussion

3.1. Selection of extracting and diluting agent

Solvents of the lower density than water including toluene, 1-octanol, 1-decanol, 1-undecanol, 1-dodecanol, hexane, and heptane were tested. As shown in Fig. 2, toluene has highest extraction efficiency compared to non-aromatic ones. This behavior may be due to the unsuccessful demulsified process when non-aromatic organic solvents were employed. Additionally, it seems the ring structure and aromatic group of organic solvents benefit the extraction of the Cd–PDC complex, which have aromatic group in the molecular structure. Accordingly, toluene was selected for subsequent experiments [23–25]. In addition, among of various diluting solvent; ethanol, methanol, and nitric acid in methanol were investigated. According to obtained results, methanol was selected as a diluting agent.

3.2. Plackett–Burman design

In order to select the effective factors in extraction of cadmium by NNGT-MSA-DLLME method, the Plackett–Burman design (PBD) was applied for six factors (Table 1). To this purpose, in three times, 15 experiments were performed and the average of them was examined. According to the result, the Pareto chart with confidence limit of 95%, (Fig. 3), four factors: (1) the pH of solution, (2) the volume of extraction solvent (μL), (3) the stirrer rate (rpm), and (4) the extraction time (min) were significant in extracting process. Based on Pareto chart, the stirring rate was the most effective factor. The concentration of APDC (mol L^{-1}) and ionic strength provided to have no significant effect. Therefore, ligand concentration and ionic strength were fixed at a middle level and must be eliminated to optimization with BBD.

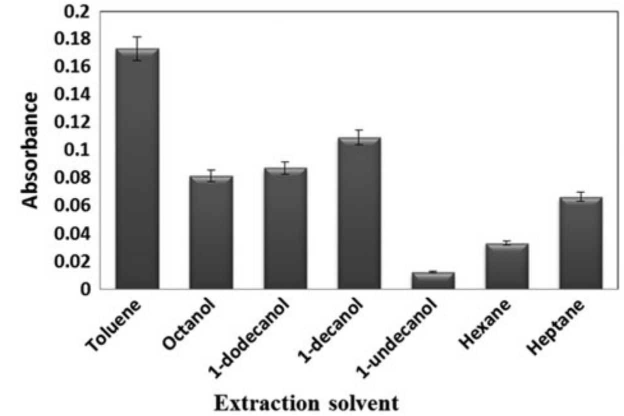


Fig. 2. Influence of extraction solvent type in the extraction efficiency in NNGT-MSA-DLLME. Condition: solution volume, 50 mL; APDC concentration, 1×10^{-3} mol L^{-1}; pH 7.0; extraction volume, 200 μL; stirring rate, 1,000 rpm; extraction time, 5 min.

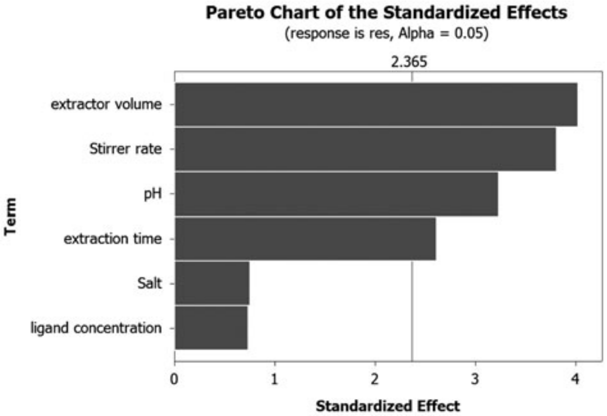


Fig. 3. Standardized main effect Pareto chart for the PBD of screening experiment. Vertical line on the graph indicate that the corresponding factor terms are significant ($p < 0.05$).

3.3. Box–Behnken design

The analysis of variance (ANOVA) was shown in Table 3 (the significant criteria is $p < 0.05$). Lack of fit (LOF) and the p-value are important parameters in ANOVA table. Based on the p-value, stirring rate has a more significant effect on the extraction process by NNGT-MSA-DLLME method, and was followed by: pH of solution > extraction solvent volume > extraction time. The LOF parameter in ANOVA table shows the variation of signals around the fitted model. If the results were well fitted with the model, LOF will not be significant. As the Table 3 shows, the p-value for LOF parameter is 0.211 which confirms a good fitting of model to responses. By referring to the coefficients of R^2 (99.9%) and adjusted R^2 (99.9%), this model shows a good relationship between responses and the fitted model, it reveals a high fitness too. Regression analysis of BBD was carried out and thereby the following equation was obtained Eq. (2):

Table 3
ANOVA for BBD

Source	Df[a]	Seq. SS	Adj. SS	Adj. MS	*F*-value[b]	*p*-value
X_1	1	0.037185	0.037185	0.037185	8.45	0.013
X_2	1	0.022969	0.022969	0.022969	5.22	0.041
X_3	1	0.082502	0.082502	0.082502	18.74	0.001
X_4	1	0.025208	0.025208	0.025208	5.73	0.034
${X_1}^2$	1	0.001735	0.000002	0.000002	0.00	0.985
${X_2}^2$	1	0.000023	0.001227	0.001227	0.28	0.607
${X_3}^2$	1	0.009355	0.011615	0.011615	2.64	0.130
${X_4}^2$	1	0.002475	0.002475	0.002475	0.56	0.468
X_1X_2	1	0.003249	0.003249	0.003249	0.74	0.407
X_1X_3	1	0.002916	0.002916	0.002916	0.66	0.432
X_1X_4	1	0.003844	0.003844	0.003844	0.87	0.369
X_2X_3	1	0.009900	0.009900	0.009900	2.25	0.160
X_2X_4	1	0.001444	0.001444	0.001444	0.33	0.577
X_3X_4	1	0.000289	0.000289	0.000289	0.07	0.802
LOF	10	0.050375	0.050375	0.005038	4.11	0.211
Pure error	2	0.002453	0.002453	0.001226	–	
Total SS	26	0.255922				

[a] DF: degrees of freedom.

[b] Test for comparing variance of model with variance of residual (error).

$$
\begin{aligned}
A = {} & 0.124333 + 0.055667\ X_1 + 0.043750\ X_2 \\
& + 0.082917\ X_3 + 0.045833\ X_4 + 0.000542\ X_1^2 \\
& + 0.015167\ X_2^2 + .046667\ X_3^2 + 0.021542\ X_4^2 \\
& - 0.028500\ X_1X_2 + 0.027000\ X_1X_3 + 0.031000\ X_1X_4 \\
& + 0.049750\ X_2X_3 - 0.019000\ X_2X_4 \\
& - \ 0.008500\ X_3X_4
\end{aligned}
\tag{2}
$$

By solving of Eq. (2), it is possible to improve the extraction of cadmium by NNGT-MSA-DLLME method. Other results of BBD are plotted in Fig. 4. Fig. 4(a) and (b) show the percentage of value vs. the residual value and the residual value vs. the fitted value, respectively. Fig. 4(a) illustrates that the residuals have a normal distribution around the line and indicates a response which is well fitted to the model. Fig. 4(b) also reveals that the residuals do not follow a specific pattern of responses. Fig. 5(a)–(f) shows the response surface plots between the paired factors in BBD. Based on surface the plots, there isn't any interaction between factors; similar to the results of ANOVA table (Table 3). In this table, each factor with negative or positive coefficient shows its effect on the extraction efficiency. The surface plots show that, at a high stirring rate, a high volume of extraction solvent, and a high extraction time, the extraction efficiency is increased. Therefore, it could illustrate that when the stirring rate is increased, the dispersion of extraction solvent was increased, and, when there is

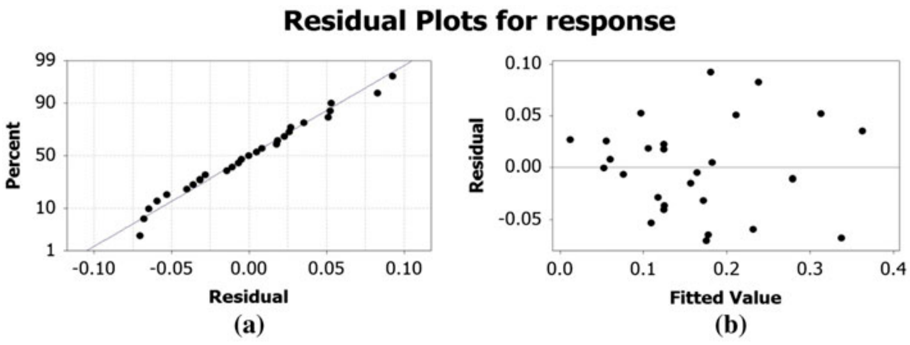
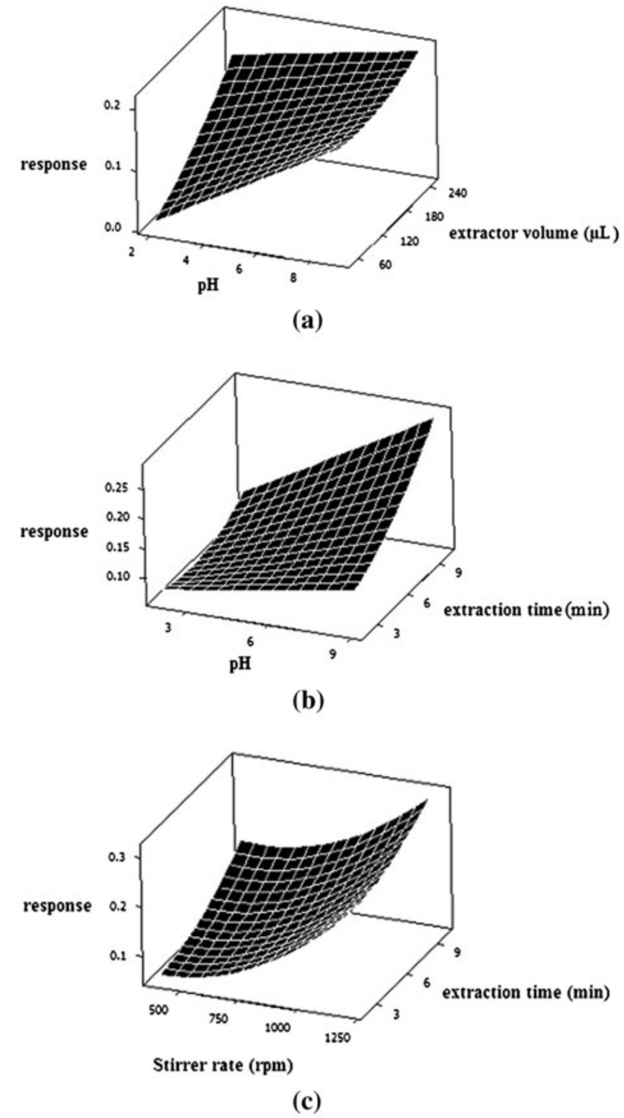


Fig. 4. (a) Normal probability plot for residuals, (b) Plot of residual vs. fitted value.



(a)

(b)

(c)

Fig. 5. Response surface plots: (a) pH vs. extraction volume (μL), (b) pH vs. extraction time (min), (c) ligand concentration (m L^{-1}) vs. extraction time (min), (d) ligand concentration (m L^{-1}) vs. extraction volume (μL), and (e) extraction time (min) vs. extraction volume (μL).

a low volume of extraction solvent, the interaction and surface contact between organic and aqueous phase are also decreased. Moreover, when the extraction time is low, the time needed to complete dispersion of the organic solvent in the solution and extraction of Cd-APDC complex, is not adequate. Based on the surface plots in Fig. 5(a)–(c), the pH is the only factor that is optimum in the middle value, which indicates the best pH condition for complexing the cadmium ions with APDC. The results of BBD showed that the most extraction efficiency by the NNGT-MSA-DLLME method is related to the following conditions: pH 5.27, stirrer rate = 1,200 rpm, extraction solvent volume = 250 μL, and extraction time = 10 min.

3.4. Regression analysis

For statistic description of one or several predictors and responses, the regression analysis includes making of an equation using least square method Eq. (2). In addition, the regression should achieve to normality between responses. According to this matter, the normality of the responses for the two cases, without preconcentration (type 1) vs. with preconcentration (type 2) must be mentioned. Therefore, the regression was applied to investigate the effect of preconcentration with NNGT-MSA-DLLME method in the extraction of cadmium. Based on obtained results in Table 4, R^2 for both of the two calibrations showed the normality of the response. Comparing the slopes of the calibration type 2 vs. the slops of the calibration type 1, it indicates a positive effect of preconcentration on the extraction. Moreover, the residual error for the type 2 is lower than the type 1; which indicates a lower residual error in type 2, even by adding a preconcentration step in the present study. PRESS variable which is more than type 2 is also difference between the predicted values in regression equation and observed value. This analysis indicates that the type 2 is more normalized than the type 1. *p*-value also shows a significant preconcentration effect on the

Table 4
Regression analysis for NNGT-MSA-DLLME method

Variable	With preconcentration (type 2)	Without preconcentration (type 1)
Regression equation	$=1.797 \times X + 0.1191$	$=0.0802 \times X + 0.063$
R^2	99.93%	99.91%
p-value	0.000	0.000
Residual error	0.0007	0.0012
PRESS	0.0050	0.0101

extraction. Therefore, all variables reveal a completely positive preconcentration effect in the extraction.

Table 5
Analytical characteristic for determination of Cd with NNGT-MSA-DLLME method

Parameter	Value
Linear range (μg L^{-1})	10–1,000
LOD (μg L^{-1})	1.4
Correlation coefficient (r^2)	0.999
Enrichment factotor	280
R.S.D (%) ($n = 7$)	1.15
Sample volume (mL)	50
Solvent volume (μL)	250

3.5. Effect of interference ions

The interference studies were performed using various possible interfering ions on the extraction of cadmium ions. The critical scale for interference of each coexisting ion was set at ± 5.0% by the analytical signal. For this purpose, influences of some cationic and anionic species were investigated. In these experiments, solutions of 100 μg L^{-1} of Cd in the presence of 1,000 μg L^{-1} of Hg^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+}, Pd^{2+}, Mn^{2+}, Fe^{3+},Ag^{+}, NO_3^{-}, Cl^{-}, SO_4^{2-} ions and 100 μg L^{-1} of Zn^{2+}, Cu^{2+}, Ni^{2+} were treated according to the preconcentration procedure. The results showed that at these concentrations, the other metal ions did not interfere in the proposed procedure. Furthermore, the high concentration of common anions, alkali, and

Table 6
Determination of cadmium in water, fruit and vegetables samples

Samples	Certified (μg L^{-1})	Added (μg L^{-1})	Founded (μg L^{-1})	Recovery (%)
GSBZ 50009-88 (μg L^{-1})	150.0 ± 6.0	–	146.2 ± 3.7	97.4
River water (Ghareh Sou river, Kermanshah, Iran)		–	18.0 ± 2.0[a]	–
		100	119.0 ± 3.2	101
		150	167.5 ± 3.5	99
River water (Raz Avar River, Kermanshah, Iran)		–	17.0 ± 1.8	–
		100	118.7 ± 2.5	102
		150	169.0 ± 3.1	101
Cucumber		–	113.2 ± 2.2	–
		100	211.0 ± 3.1	98
		150	259.1 ± 2.8	97
Tomato		–	134.1 ± 2.9	–
		100	231.2 ± 1.7	97
		150	287.2 ± 3.2	102
Potato		–	148.3 ± 1.5	–
		100	249.2 ± 2.2	101
		150	296.4 ± 3.4	98
Rice		–	186.4 ± 2.6	–
		100	285.2 ± 1.7	99
		150	334.3 ± 3.1	98
Black tea		–	174.5 ± 1.3	–
		100	271.1 ± 2.3	97
		150	322.3 ± 2.6	98
Flour		–	123.3 ± 2.1	–
		100	224.5 ± 2.6	101
		150	275.1 ± 1.8	101
Spinach		–	210.3 ± 3.2	–
		100	308.3 ± 2.5	98
		150	357.4 ± 3.4	98
Parsley		–	152.1 ± 1.4	–
		100	249.1 ± 2.3	98
		150	298.3 ± 3.7	97
Tobacco		–	312.3 ± 2.6	–
		100	410.5 ± 1.8	98
		150	460.5 ± 2.7	99

[a] Errors correspond to standard deviations of three replicate measurements.

alkaline earth metal ions do not interfere with determination of cadmium.

3.6. Analytical figures of merits

Analytical figures of merit of the established NNGT-MSA-DLLME method were obtained by response surface modeling and are given in Table 5. Calibration graph was obtained by preconcentrating 50 mL of a sample containing known amounts of analyte under the optimized conditions. Under the specified experimental conditions, the calibration curve for Cd was linear from 10 to 1,000 μg L^{-1}. The regression equation for the calibration curve after NNGT-MSA-DLLME was $A = 1.7969\ C_{Cd} - 0.1191$ with a correlation coefficient (R^2) of 0.9991. Based on the definition of IUPAC, the limit of detection (LOD) (3σ) and limit of quantity (10σ) of this method were 1.40 and 4.66 μg L^{-1}, respectively. The precision of method (RSD) as within-run (repeatability) and between-run (reproducibility) were 1.15 and 1.89% ($C = 100$ μg L^{-1}, $n = 10$), respectively. Sensitivity enhancement factor (EF) was about 280, calculated by the slope ratio of the calibration curves for cadmium determination with and without NNGT-MSA-DLLME.

3.7. Comparison of NNGT-MSA-DLLME with other methods

Determination of cadmium in the water samples by the proposed microextraction method was compared with those of some of the best previously preconcentration methods used for this purpose, and the results are shown in Table 6. As it is shown from Table 7, although the proposed method possess some improved features including high EF low RSD and good dynamic range, some of the previously reported methods have also several advantageous properties such as better LOD and low sample consumption. Moreover, the simplicity in collecting and withdrawing by a microsyringe is another advantage of this method. If NNGT-MSA-DLLME is combined with sensitive techniques like, ICP–MS or atomic fluorescence spectrometry, its LOD can be significantly improved. The analytical characteristics make the method a good alternative to those of the previous methods used for determination of cadmium in routine analyses.-

3.8. Application of the method

The applicability of the method was used for the determination of cadmium in several water, fruit and

Table 7
Comparison of proposed method with other preconcentration methods for determination of cadmium

Method	Detection technique	Reagent	Solvent	LOD (μg L^{-1})	EF/PF	RSD (%)	Linear range (μg L^{-1})	References
DLLME	FAAS	DPTH	Chloroform	0.40	55.0	2.70–1.90	5–100	[26]
IL-DLLME	FAAS	Ligandless	$[C_4mim][PF_6]$	0.40	50.0	4.30	10–200	[27]
CIAME	FAAS	DDTP	$[C_6mim][PF_6]$	0.12	70.0	2.40	0.4–35	[28]
SDME	UV–Vis	Dithizone	CCl_4	5×10^{-4}	128	3.2	0.05[a]	[29]
CPE	FAAS	Ligandless	Triton X-114	1.00	55.6	3.20	3–300	[30]
CPE	FAAS	KI, MG	Triton X-114	0.90	13.5	4.20	2–200	[31]
UASEME-SFO	FAAS	Dithizone	1-dodecanol	0.011	64.0	1.98	0.3–100	[12]
VALLME	FAAS	APDC	$[C_4mim][PF_6]$	0.50	20	4.2	10–200	[32]
DLLME	ICP-OES	BTAC	Trichloroethylene	0.30	13	0.9	–	[33]
IL-USA-DLLME	ETAAS	DDTC	$[C_6mim][PF_6]$	0.0074	63	3.3	0.020–0.150	[34]
SDME	ETAAS	(5-Br-PADAP	Nitrobenzene	0.0065	390	6.4	0.01–1	[35]
NNGT-MSA-DLLME	FAAS	APDC	Toluene	1.40	280.0	1.15	10–1,000	This work

Notes: LOD: limit of detection; RSD: relative standard deviation; EF: enhancement factor; PF: preconcentration factor; CPE: cloud point extraction; VA-LLME: vortex assisted dispersive liquid–liquid microextraction; UASME-SFO; ultrasound-assisted surfactant-enhanced emulsification microextraction solidification floating organic drop; DLLME: dispersive liquid–liquid microextraction; IL-DLLME: ionic liquid dispersive liquid–liquid microextraction; CIAME; cold induced aggregation microextraction: BTAC: 2-(2´- benzothiazolylazo)-p-cresol; ICP-OES: inductively coupled plasma optical emission spectrometry; MG: methyl green; DDTP: diethyldithiophosphate; TAO: 4-(2-thiazolylazo)-orcinol; Triton X-114: octylphenoxypolyethoxyethanol; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol.
[a]Upper linear range.

vegetables samples, and the results along with the recovery for the spiked samples were given in Table 7. The accuracy of the method was verified by the analysis of the samples spiked with the known amount of cadmium. Based on obtained results, the recoveries for the addition of different concentrations of cadmium were in the range 97–104%, which it showed that the matrices of the samples have little effect on the NNGT-MSA-DLLME method for determination of cadmium. In order to evaluate the accuracy of the proposed method, the cadmium content of National Standard Reference Material for Environmental Water (GSBZ 50009-88) was tested. As can be seen from Table 7 that good agreement between the determined and certified values was obtained. In addition, the cadmium content of wastewater was determined by ET-AAS ($17.8 \pm 1.3\ \mu g\ L^{-1}$), and the result is compared with that obtained by the proposed method ($17.1 \pm 2.4\ \mu g\ L^{-1}$). The *t*-test showed that there is no significant difference between the result obtained by the proposed and that was obtained by ET-AAS.

4. Conclusion

In this proposed method, the magnet stirring was successfully used as a dispersing agent of extraction solvent for preconcentration of cadmium complex. The PBD and BBD were successfully carried out to optimize the affective parameters in extraction efficiency. This methodology has several advantages compared to the classical methods. Firstly, classical methods are time-consuming and a large number of experiments are needed to explain the behavior of a system, while in this method, a large amount of information was achieved from a small number of experiments. Secondly, in RSM, it is possible to observe the interaction effect of the independent variables on the response. This method provides several merits, such as: excellent enrichment factors, simplicity, good repeatability and recoveries, economic and low consumption of organic solvents. Furthermore, it doesnot need to dispersive solvent and centrifuging step, and separation and preconcentration can be done in one step. The above mentioned advantages and good analytical characteristics make this method to be successfully applied to determination of cadmium ions in water, fruit and vegetables samples. Finally, while this method is primarily focused on cadmium determination, the system may be readily applied for the determination of other metals with various chelating agents and organic solvents.

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