

Selective transport of cadmium(II) through hollow fiber-supported liquid membrane microextraction using diaza-18-crown-6 in ionic liquids as carrier

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Abstract A hollow fiber-supported liquid membrane microextraction (HF-SLME) system using diaza-18-crown-6 (DA18C6) in ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄MIM]PF₆) as an efficient carrier for the selective transport of cadmium(II) is described. The Cd(II) is ion paired with chlorine ion as a suitable counter into the membrane phase and then complexed with DA18C6; sodium thiosulfate (Na₂S₂O₃) is injected in the lumen of membrane as an acceptor phase to trap the Cd(II) into the acceptor phase. The influence of various experimental parameters in the extraction procedure is discussed using a three-level Box–Behnken experimental design with three factors to optimize. Under the optimum conditions, the selectivity and efficiency of Cd(II) transport from an aqueous sample containing different mixtures of Co²⁺, Ni²⁺, Fe³⁺, Cr³⁺, Mn²⁺, and Cd²⁺ are investigated. The enrichment factor of Cd²⁺ is 172, the limit of

detection is 0.13 ng L⁻¹, and the relative standard deviation is 5.1 %. The method has been successfully applied to the determination of Cd(II) in food and cosmetic samples.

Keywords Hollow fiber-supported liquid membrane microextraction · Ionic liquid · Crown ether · Cadmium

Introduction

Cadmium (Cd) is known to be an environmental pollutant heavy metal. In the human body, Cd(II) accumulates mainly in the kidneys and results in various diseases. Despite its toxicity, Cd(II) is widely used in different industries such as electroplating, pigmenting, metallurgy and in the fabrication of Ni–Cd batteries [1, 2]. Therefore, separating and determining Cd(II) in different environmental samples are of great importance. Sensitive analytical techniques will be necessary before Cd(II) determination due to its low content and complex matrix in these samples.

Several technologies can be used to remove toxic metals from liquid effluents, including solvent extraction, precipitation, ion exchange, etc. [3, 4]. Most of these methods may result in a large amount of waste solvents. Membrane-based separation processes do not require high energy consumption for their operation; they can be conducted under moderate operating conditions. Accordingly, they have been considered as a promising alternative to overcome the above drawbacks. Among membrane-based separation processes, supported liquid membranes (SLMs) have been used extensively in recent years [5]. Traditional SLMs are tested as flat sheets, but the membrane instability is one of the major disadvantages due to the partition of the organic solvent to the aqueous phases [6]. Some researchers begin testing SLMs with a hollow fiber [7, 8]. The hollow fiber

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geometry makes it have very high module packing densities, liquid membrane inside can resist great pressure, and the stability of SLMs is improved [9]. In addition, the high surface area of the hollow fiber-supported liquid membrane (HF-SLM) system can achieve high separation rates [10].

In order for selective extraction of the desired substances from the aqueous solution to the acceptor solution, the selection of an appropriate extractant-carrier is very important in the HF-SLM [11]. Macrocyclic compounds such as crown ethers have been well known for selective recognition of specific metal ions since their discovery nearly four decades ago [12]. Compared to alkali and alkaline earth metal cations, the selective transport of heavy metal ions using crown ethers as an ion carrier in liquid membrane is relatively scarce [13]. Some crown ethers containing nitrogen atoms or sulfur atoms, such as aza-crown ethers, seem to be suitable candidates for the selective transport of heavy metal ions [14]. Morteza et al. [15] have described a highly efficient and selective method for the transport of Cd^{2+} ions through a liquid membrane containing a mixture of aza-18-crown-6 (A18C6) and palmitic acid (PA). Compared with their method, we show here that a mixture of diaza-18-crown-6 (DA18C6) and IL $[\text{C}_4\text{MIM}]\text{PF}_6$ was used as the membrane phase in the hollow fiber-supported liquid membrane microextraction (HF-SLME). ILs are considered to be solvents which are beneficial for both the operator and the environment due to their good dissolving capacity for numerous compounds and excellent thermal stability.

In this work, we used DA18C6 and IL $[\text{C}_4\text{MIM}]\text{PF}_6$ as an extractant-carrier inside the hollow fiber pores. $\text{Cd}(\text{II})$ is ion paired with chlorine ion as a suitable counter into the membrane phase and then complexed with DA18C6. The sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) in the acceptor phase, which had a stronger complexing ability than DA18C6, stripped the $\text{Cd}(\text{II})$ to the acceptor phase. The acceptor phase was collected and analyzed by graphite furnace atomic absorption spectrometry (GFAAS) after the extraction process. The mechanism of the HF-SLME was discussed. And the effects of various experimental parameters in HF-SLME, such as DA18C6 concentration, incubation time, and $\text{Na}_2\text{S}_2\text{O}_3$ concentration, were studied using two optimization methods, one variable at a time and Box–Behnken design (BBD) of the response surface methodology (RSM). Under the optimal conditions, the proposed method was applied to the selective transport of $\text{Cd}(\text{II})$ in food and cosmetic samples.

Experimental

Instrumentation

A model TAS-986 graphite furnace atomic absorption spectrophotometer (General Instrument Company, Beijing,

China) equipped with deuterium lamp background correction (Hamamatsu Photonics, Japan), a cadmium hollow cathode lamp as a radiation source at the 228.8 nm wavelength with a slit width of 0.4 nm, 2.0 mA current was used for the determination of cadmium [16]. The temperature program used to determine the cadmium by GF-AAS is shown in Electronic Supporting Material (Table S, ESM). The sample solution was stirred by a DF-101S constant temperature magnetic stirring meter (Jintan, Medical Instrument Corporation, Jiangsu, China). 25- μL microsyringes (Anting Corporation, Shanghai, China) were used for sampling and washing the lumen of the hollow fiber.

Reagents and materials

All chemicals and reagents used in this study were of analytical grade, and all of them were purchased from the Shanghai Chemical Reagent Corporation, Shanghai, China, and double distilled water (DDW) was used to dilute all solutions. 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{MIM}]\text{PF}_6$) was purchased from Chengjie Chemistry Corporation (Shanghai, China). DA18C6 was purchased from J & K Chemical Technology Corporation, Beijing, China. The stock standard solution for $\text{Cd}(\text{II})$ (1 mg mL^{-1}) was prepared by dissolving appropriate amounts of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ in DDW. Working standard solutions were obtained daily by appropriate dilution of the stock standard solution. $1 \text{ mg mL}^{-1} \text{Na}_2\text{S}_2\text{O}_3$ was prepared by dissolving moderate $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in DDW. Another concentration of $\text{Na}_2\text{S}_2\text{O}_3$ used in the experiment was diluted with it step by step. $[\text{C}_4\text{MIM}]\text{PF}_6$ was used to dissolve DA18C6.

Accurel Q3/2 polypropylene hollow fiber membrane used for the extraction of cadmium was purchased from Membrana (Wuppertal, Germany). Its specifications are 600 μm internal diameter, 200 μm wall thickness and 0.2 μm pore size.

Extraction procedure

The purchased hollow fiber membrane was cut into 5.7 cm segments by scissors, then immersed in acetone and sonicated for a few minutes to remove the impurities. They were air-dried prior to use. 50 mL sample solution containing a certain amount of Cd^{2+} was placed in a vial; this vial was put into a constant temperature water bath. The lumen of the hollow fiber was washed with $\text{Na}_2\text{S}_2\text{O}_3$ contained in the 25- μL microsyringe. After flushing, one end of the hollow fiber was sealed using heated iron. On the other side, 15 μL $\text{Na}_2\text{S}_2\text{O}_3$ was injected into the lumen, and then the end was sealed in the same way. The hollow fiber was immersed in an ionic liquid $[\text{C}_4\text{MIM}]\text{PF}_6$ solution of crown ether for a while to immobilize the solution in the pores of

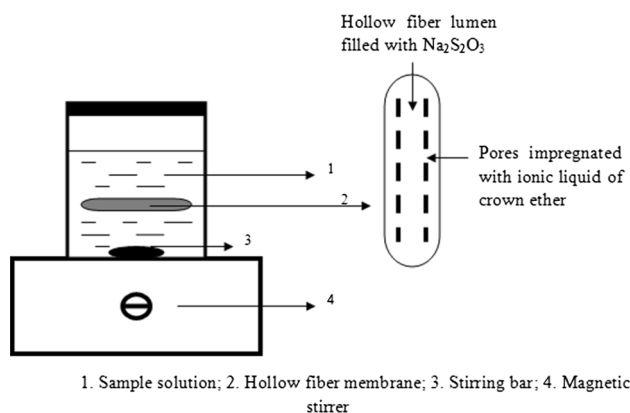


Fig. 1 Schematic diagram of the hollow fiber-supported liquid membrane microextraction

the hollow fiber. The excess solution on the wall of the hollow fiber was washed away with redistilled water. Lastly, the hollow fiber was completely immersed in the sample solution for extraction. The device used for extraction is shown in Fig. 1. Following extraction, the extracted solvent with analytes was put into the graphite furnace tubes for analysis.

Single-factor experiments of HF-SLME

The effects of concentration of DA18C6, sample pH, extraction temperature and stirring rate, extraction time, concentration of $\text{Na}_2\text{S}_2\text{O}_3$ were studied by a single-factor design as follows: one factor was changed while other factors were kept constant in each experiment. The effect of each factor was evaluated by determining the absorbance of Cd(II).

Experimental design of response surface methodology (RSM)

Optimization of HF-SLME by RSM

Box–Behnken design (BBD) with three independent variables was used for the optimization of the extraction of Cd(II). Experiments were established based on a BBD with three factors at three levels and each independent variable was coded at three levels: -1 , 0 , and $+1$. Three parameters including concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (ng mL^{-1}), concentration of DA18C6 (ng mL^{-1}), and extraction time (min) were chosen as key variables based on the results of single-factor experiments and designated as X_1 , X_2 , and X_3 , respectively. Absorbance (A) was taken as the response of the design experiments. Table S2 (ESM) lists the ranges of independent variables and their levels. The coding of the variables was undertaken using Eq. (1)

$$X_i = \frac{\chi_i - \chi_0}{\Delta\chi} \quad (i = 1, 2, 3) \quad (1)$$

where X_i and χ_i are the dimensionless and actual values of the independent variable i , respectively, χ_0 is the actual value in the center of the domain, and $\Delta\chi$ is the increment of χ_i corresponding to a variation of one unit of X_i .

The response function (Y) was partitioned into linear, quadratic, and interactive components:

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=1}^3 \beta_{ij} X_i X_j \quad (2)$$

where Y is the dependent variable, β_0 is the constant coefficient, β_i is the linear coefficient (main effect), β_{ii} is the quadratic coefficient, and β_{ij} is the two-factor interaction coefficient [17].

Verification of the predicted optimized conditions

Triplicate experiments were executed under optimal conditions to confirm the validity of the developed mathematical model. The average value of the experiments was compared to the predicted value of the developed model to ascertain the accuracy and suitability of the optimized conditions.

Sample preparation

Triplicate samples (0.5 g) of milk, honey, hand cream, face cream were accurately weighed in 100 mL conical flasks, respectively. About 10 mL of a freshly prepared mixture of concentrated HNO_3 – HClO_4 (4:1, v/v) was added to each flask and soak overnight. The next day, these samples were heated on a hot plate until releasing largely white smoke. When the heated solutions became clear, samples cooled naturally, then transferred to a 50 mL volumetric flask and diluted to scale with redistilled water. The extracts were filtered with a $0.45 \mu\text{m}$ membrane filter. The filtered solutions were stored at 4°C .

Results and discussion

The mechanism of the HF-SLME

The HF-SLME consists of three phases. The aqueous source phase initially contains chloride ion (Cl^-) and all the metal ions (M^{n+}), the hollow fiber membrane phase involves DA18C6 and $[\text{C}_4\text{MIM}]\text{PF}_6$ as the carrier (E), and the aqueous receiving phase $\text{Na}_2\text{S}_2\text{O}_3$ is present on the lumen of the hollow fiber.

The various steps which characterize the transport of metal species through HF-SLM are described in Fig. 2.

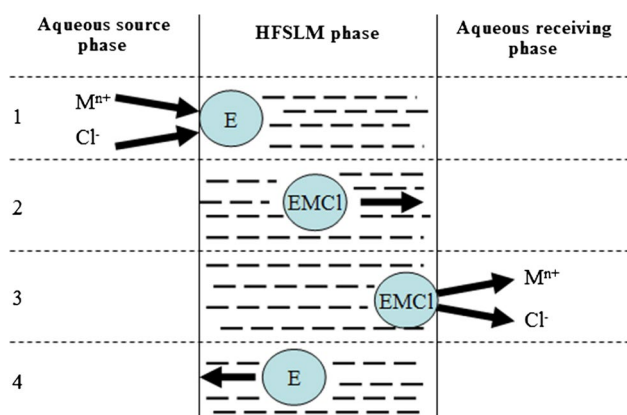


Fig. 2 Schematic transport of metal ions (M^{n+}) through a hollow fiber-supported liquid membrane. E represents the membrane carriers; Cl^- is an aqueous soluble counterion

Firstly, the metal ions (M^{n+}) react with the metal carrier (E) after diffusing into the aqueous source phase–HFSLM phase interface. Cl^- accompanies the M^{n+} into the membrane phase. Secondly, the complex diffuses across the membrane in the lower concentration gradient. Thirdly, at the HFSLM phase–aqueous receiving phase interface, another complexing agent, which has the stronger complexing ability than the carrier, will strip the M^{n+} into the receiving phase. Finally, the dissociated free carrier drives to aqueous source phase–HFSLM phase interface in its concentration gradient.

Single-factor tests of HF-SLME

Effect of the concentration of DA18C6

Extractions were carried out at the DA18C6 concentration varying from 100 to 350 $ng\ mL^{-1}$, while other extraction variables were set as follows: $Na_2S_2O_3$ concentration 250 $ng\ mL^{-1}$, extraction time 20 min, and the stirring rate 400 rpm. As shown in Fig. 3a, the absorbance of Cd(II) increased with increasing the DA18C6 concentration and reached its maximum absorbance when the DA18C6 concentration was 250 $ng\ mL^{-1}$. Therefore, 250 $ng\ mL^{-1}$ was selected as the center point for further study.

Effect of the concentration of $Na_2S_2O_3$

The nature and composition of the ligand in the receiving phase could have an important effect on the selectivity of metal ion. It was reported that the $S_2O_3^{2-}$ as a stripping ion had certain selective transport ability for cadmium [15]. In the HF-SLME, $Na_2S_2O_3$ was used as the stripping ligand in the receiving phase and the effect of

different concentrations of $Na_2S_2O_3$ on the absorbance of Cd(II) is shown in Fig. 3b for the DA18C6 concentration of 250 $ng\ mL^{-1}$ (other extraction variables kept constant as described above). It can be seen that the absorbance of Cd(II) increased with the increasing $Na_2S_2O_3$ concentration from 100 to 250 $ng\ mL^{-1}$, then leveled off up to the concentration of 350 $ng\ mL^{-1}$. Thus, the $Na_2S_2O_3$ concentration of 250 $ng\ mL^{-1}$ was considered to be optimal in the present experiment.

Effect of the extraction time

Extraction time was another important factor influencing the extraction efficiency and the selectivity of Cd^{2+} . The effect of extraction time on the absorbance of Cd(II) was investigated from 10 min to 50 min, when the other factors kept constant. The results shown in Fig. 3c indicated that the maximum absorbance of Cd(II) was achieved when the extraction time was 20 min. The absorbance of Cd(II) decreased continuously after 20 min due to the loss of ionic liquids over longer extraction time. Thus, the extraction time of 20 min was selected for the following experiment.

Effect of sample pH

The sample pH can affect the absorbance and the selectivity of Cd^{2+} since different metal ions had their own optimal pH. When the other factors kept constant, the effect of sample pH on the absorbance of Cd(II) was investigated in the pH range of 2–12, as shown in Fig. 3d. It was found that the absorbance of Cd(II) increased continuously at pH 2–7, and when the pH value was greater than 7, the absorbance of Cd(II) was almost constant. The possible reason for this phenomenon was that the NH^- of DA18C6 was an electron withdrawing group under the acidic condition, which reduced the complexing ability with Cd^{2+} [18]. Therefore, the sample pH would not be considered when selecting factors in RSM.

Effect of stirring rate

The stirring rate of the sample solution can reduce the dynamic equilibrium time and accelerate the extraction kinetics. The effect of stirring rate on the absorbance of Cd(II) was investigated in the range of 200–600 rpm. The maximum absorbance of Cd(II) was achieved at 400 rpm, and the absorbance of Cd(II) had no significant change after 400 rpm. A higher stirring rate may generate excess air bubbles on the hollow fiber surface, suspending the diffusion of analyte from the aqueous phase to the organic phase [19]. Thus, the stirring rate of 400 rpm was considered to be optimal in the experiment.

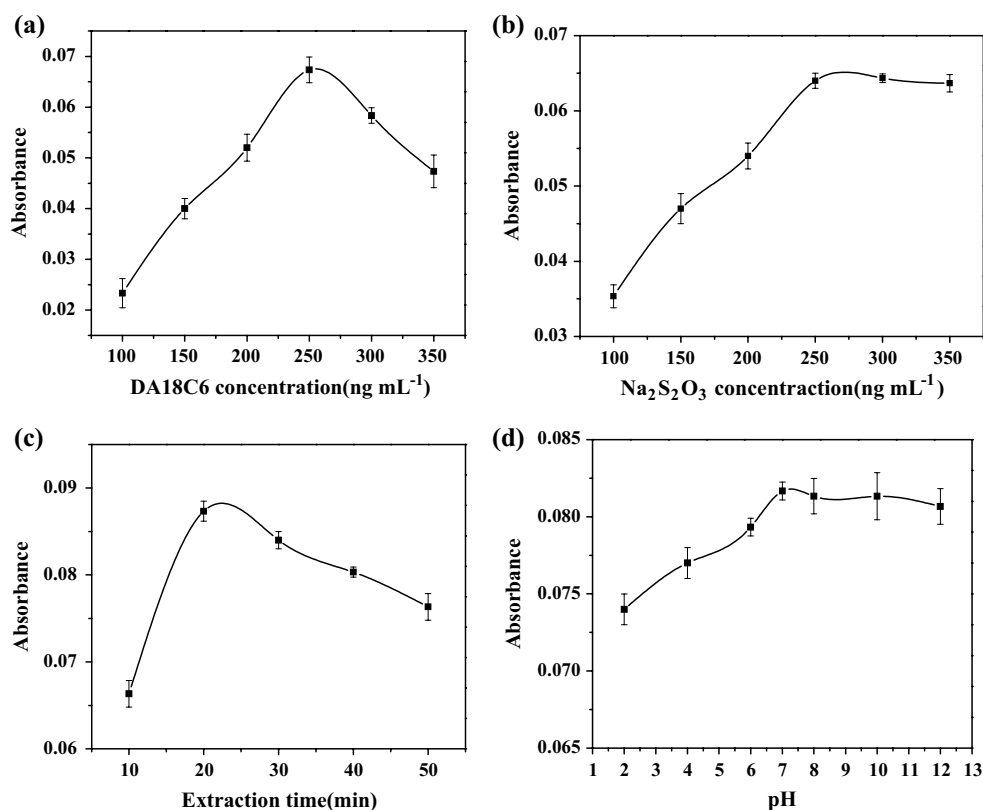


Fig. 3 Effect of various factors on the absorbance of Cd(II). **a** DA18C6 concentration, **b** Na₂S₂O₃ concentration, **c** Extraction time, **d** pH of the aqueous solution

Table 1 ANONA results of response surface quadratic model for Cd(II) extraction in HF-SLME

Source	Sum of squares	df	Mean square	F value	Prob > F
Model	2.988E-003	9	3.320E-004	251.23	<0.0001
X ₁	2.761E-004	1	2.761E-004	208.96	<0.0001
X ₂	3.645E-004	1	3.645E-004	275.84	<0.0001
X ₃	4.061E-004	1	4.061E-004	307.34	<0.0001
X ₁ X ₂	2.500E-007	1	2.500E-007	0.19	0.6767
X ₁ X ₃	9.000E-006	1	9.000E-006	6.81	0.0349
X ₂ X ₃	6.250E-006	1	6.250E-006	4.73	0.0661
X ₁ ²	3.603E-004	1	3.603E-004	272.63	<0.0001
X ₂ ²	8.853E-004	1	8.853E-004	669.93	<0.0001
X ₃ ²	4.866E-004	1	4.866E-004	368.22	<0.0001
Residual	9.250E-006	7	1.321E-006		
Lack of fit	3.250E-006	3	1.083E-006	0.72	0.5891
Pure error	6.000E-006	4	1.500E-006		
Cor total	2.997E-003	16			
R ² = 0.9969		R ² _{Adj} = 0.9929			

* Significant at *p* < 0.05

Optimization of HF-SLME procedure by RSM

Analysis of variance (ANOVA) and regression estimation

According to the results of single-factor research, the concentration of DA18C6, the concentration of Na₂S₂O₃, and the extraction time were adopted for RSM experiments. The analyzed results are listed in Table S2 (ESM). The regression analysis was carried out on the experimental data to find an optimal region of factors for the responses studied. The analysis applied allows determination of quadratic statistical models that describe the relation between the responses and factors. Obtained regression models can be described by the following equations:

$$\begin{aligned}
 Y = & 0.091 + 5.875E - 003X_1 + 6.750E - 003X_2 \\
 & + 7.125E - 003X_3 + 2.500E - 004X_1X_2 \\
 & + 1.500E - 003X_1X_3 - 1.250E - 003X_2X_3 \\
 & - 9.250E - 003X_1^2 - 0.014X_2^2 - 0.011X_3^2
 \end{aligned}$$

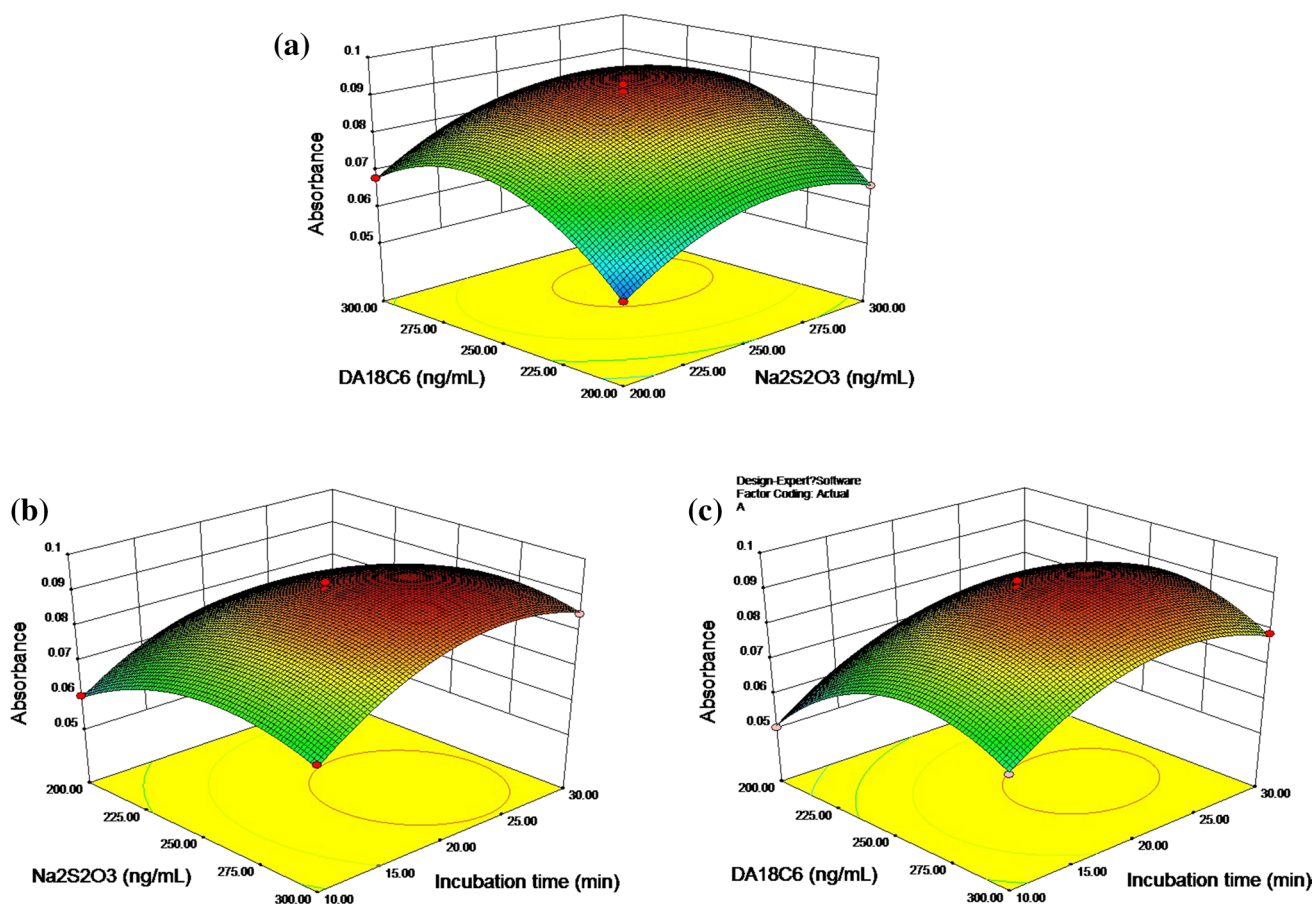


Fig. 4 Response surfaces plots for Cd(II) extraction in HF-SLME as a function of **a** DA18C6 concentration and Na₂S₂O₃ concentration, **b** incubation time and DA18C6 concentration, **c** incubation time and Na₂S₂O₃ concentration

Significant regression coefficients are determined by the statistical analysis of *t* test and *p* values. The estimation value of regression coefficient in the regression equation is shown in Table 1. For the experimental design model, the X_1 , X_2 , X_3 , X_1X_3 , X_1^2 , X_2^2 , X_3^2 were the significant regression coefficients in the HF-SLME procedure of Cd(II). ANOVA results showed that the test model was extremely significant ($p < 0.0001$), and the R^2 was 0.9969, indicating the goodness-of-fit of the model. The lack-of-fit *p* value of 0.5891 was insignificant which meant that the model was sufficiently accurate for predicting the relevant response.

Response surface plots and response optimization

RSM was used to determine the optimal response for Cd(II) extraction using HF-LPME. Three-dimensional (3D) surface plots and contour plots for Cd(II) extraction are shown in Fig. 4. The 3D surface plots can be clearly seen the interaction between the other two variables when the third independent variable was fixed at the central experimental level of zero. Each of these plots allows the visualization of the

significant factors derived from the statistical analysis [20]. The optimal conditions correspond to the concentration of DA18C6 (261.06 ng mL⁻¹), the concentration of Na₂S₂O₃ (267.40 ng mL⁻¹), extraction time (23.42 min), the maximum absorbance of cadmium (0.093).

Experiments were repeatedly done 6 times under optimal conditions to validate the model prediction. The average absorbance of cadmium was 0.089, which was close to the predicted value. Therefore, the optimization model of the BBD is able to predict the average absorbance of cadmium.

Selectivity of the HF-SLME

Under the optimum conditions, the selective transport of cadmium(II) from an aqueous sample containing different mixtures of Co²⁺, Ni²⁺, Fe³⁺, Cr³⁺, Mn²⁺, Cd²⁺ was investigated using the DA18C6 as a transport carrier in the HF-SLME. The results are shown in Fig. 5. As can be seen from it, DA18C6 had an efficient selectivity for Cd²⁺ transport, and other coexistent metal ions could hardly be

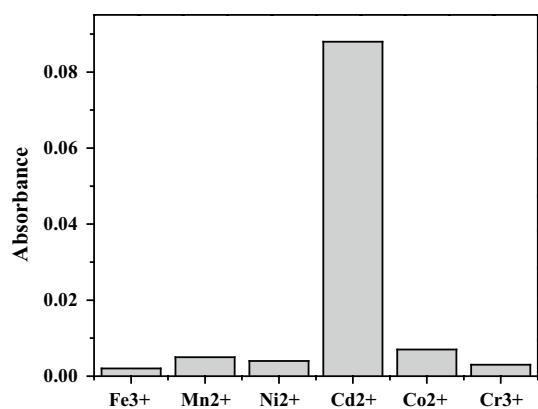


Fig. 5 The results of selective transport of Cd²⁺ using DA18C6-IL as carrier in HF-SLME

extracted. It could be explained by the following reasons. On the one hand, the ionic radius of Cd²⁺ ($r = 0.95 \text{ \AA}$) was larger than the other coexistent metal ions [Co²⁺ ($r = 0.74 \text{ \AA}$), Ni²⁺ ($r = 0.69 \text{ \AA}$), Fe³⁺ ($r = 0.55 \text{ \AA}$), Cr³⁺ ($r = 0.615 \text{ \AA}$), Mn²⁺ ($r = 0.67 \text{ \AA}$)], and it was also close to the cavity size of DA18C6 ($r = 1.43 \text{ \AA}$). On the other hand, based on the Hard and Soft acid–base concept, the Cd²⁺ as a soft acid had a stronger complex with the nitrogen atom of DA18C6 as a soft base [21, 22].

Evaluation of the method

Various characteristics of this method were investigated under the optimum conditions. The enrichment factor (EF), which was calculated using the ratio of analyte concentration in the acceptor phase after HF-SLME to the initial concentration of analyte in the donor phase, was 172. The calculated calibration was in the range of 6–29 ng L⁻¹ with a correlation coefficient of 0.9991. Limit of detection (LOD) was 0.13 ng L⁻¹. The repeatability of this method expressed as the relative standard deviation (RSD) was 5.1 %.

Comparison of the HF-SLME with other methods for extraction of Cd(II)

To exhibit the merits of the HF-SLME, the proposed method was compared with other methods for extraction of Cd(II). The results are given in Table 2. Although the EF of the proposed method was not the highest, the LOD was lower than other methods. The hollow fiber could effectively avoid the interference of high weight molecular species and particles in the sample solution. In addition, in this experiment, crown ether ionic liquid as the carrier, the proposed method can realize the selective extraction of Cd²⁺ from the aqueous sample containing different mixtures of

Table 2 Comparison of the HF-SLME with other methods for extraction of Cd(II)

Method	EF	LOD (ng L ⁻¹)	References
CPE-FAAS ^a	27	500	[23]
SPE-FAAS ^b	32	1700	[24]
US-TC-IL-ME-FAAS ^c	40	100	[25]
RTIL-DLME-FAAS ^d	50	50	[26]
HF-SLM-GFAAS ^e	387	0.8	[27]
HF-SLME-GFAAS ^f	172	0.13	This work

^a Cloud point extraction—flame atomic absorption spectrometry

^b Solid phase extraction—flame atomic absorption spectrometry

^c Ultrasound-assisted temperature-controlled ionic liquid microextraction—flame atomic absorption spectrometry

^d Room temperature ionic liquid-based dispersive liquid phase microextraction—flame atomic absorption spectrometry

^e Hollow fiber-supported liquid membrane extraction—graphite furnace atomic absorption spectrometry

^f Hollow fiber-supported liquid membrane microextraction—graphite furnace atomic absorption spectrometry

Table 3 Analytical results of Cd(II) in real samples (mean \pm S.D., $n = 3$)

Sample	Added (ng L ⁻¹)	Found (ng L ⁻¹)	Recovery (%)
Milk	0	80 \pm 1	–
	100	180 \pm 2	100 % \pm 2
	300	400 \pm 2	107 % \pm 2
Honey	0	60 \pm 3	–
	100	150 \pm 1	90 % \pm 1
	300	370 \pm 4	103 % \pm 4
Face cream	0	100 \pm 2	–
	100	210 \pm 3	110 % \pm 3
	300	380 \pm 1	93 % \pm 1
Hand cream	0	90 \pm 3	–
	100	190 \pm 2	100 % \pm 2
	300	360 \pm 4	90 % \pm 4

Co²⁺, Ni²⁺, Fe³⁺, Cr³⁺, Mn²⁺, Cd²⁺. The stability of HF-SLME was improved using the DA18C6-IL as transport carrier.

Analytical application

Under the optimized conditions, the developed HF-SLME method was applied to preconcentration and selective extraction of Cd(II) in milk, honey, face cream and hand cream. To verify the accuracy of this method, recovery experiments were done by adding different amounts of metal ions into the samples. The analytical results are shown in Table 3. The range of recoveries was 90–110 %, indicating the good reliability and validity of this method.

Conclusions

A three-phase HF-SLME system using DA18C6 in IL as an efficient carrier for the selective transport of Cd(II) in food and environmental sample is developed. DA18C6 as a membrane carrier can be used for the selective extraction of Cd(II) from the source phase containing different mixtures of Co^{2+} , Ni^{2+} , Fe^{3+} , Cr^{3+} , Mn^{2+} , Cd^{2+} . ILs are considered as green solvents, which can improve the stability of the HF-SLME system. Given the advantages of a low detection limit, high selectivity, low cost and environmental friendship of the method presented, it is believed that the proposed method has broad application prospects in the sample pretreatment technology.

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