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Isolation and preconcentration of Cd(II) from environmental samples using polypropylene porous membrane in a hollow fiber renewal liquid membrane extraction procedure and determination by FAAS

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ABSTRACT

The use of polypropylene porous membrane in a hollow fiber renewal liquid membrane (HFRLM) procedure for determination of Cd(II) in water samples was assessed. Ammonium *O,O*-diethyl dithiophosphate (DDTP) was used to complex cadmium (II) in an acid medium to obtain a neutral hydrophobic complex. The organic solvent introduced to the sample extracts this complex from the aqueous solution and carries it over the polypropylene membrane porous. The organic solvent is immobilized inside the polypropylene membrane porous, leading to an homogeneous phase. The complex strips the lumen of the membrane where, at higher pH, the complex Cd–DDTP is broken down and Cd(II) is released into the stripping phase. EDTA was used to complex the cadmium (II), helping to trap the analyte in the stripping phase. The optimized variables were: sample pH, DDTP concentration, stripping pH, EDTA concentration, extraction temperature and time, extractor solvent and addition of salt to saturate the sample. The sample volume used was 15 mL and the stripping volume was 165 μL. The analyte enrichment factor was 107, limit of detection 1.5 μg L^{-1}, relative standard deviation 4.0% (15 μg L^{-1}, $n = 7$) and the working linear range 5–30 μg L^{-1}.

1. Introduction

The interest in miniaturization in the area of analytical chemistry has led to the introduction of alternative techniques to substitute the conventional liquid–liquid extraction and solid-phase extraction procedures. Among these alternative techniques, liquid-phase microextraction (LPME) introduced firstly by Liu and Dasgupta [1] and by Jeannot and Cantwell [2] is becoming a widely accepted and applied sample preparation technique, as it is a simple, relatively fast extraction and preconcentration procedure and is particularly attractive for the replacement of techniques that use solvents [3].

Among the several possible configurations in which LPME can be performed, the use of a hollow fiber membrane (HFLPME) to stabilize the extracting phase was introduced by Pedersen-Bjergaard and Rasmussen [4]. HFLPME can be conducted in two-phase or three-phase configurations [5], being that the three-phase system consists of immobilizing a water-immiscible organic solvent in the wall pores of the HF while an aqueous acceptor solution is held within its lumen. Thus, analytes are extracted into the intermediary organic phase and subsequently into the aqueous phase. In case of metal ion determination, the mass transfer process from a donor to an acceptor solution through a liquid membrane involves several stages, which include: a complexation reaction between the metal ion and the extractant at the membrane/donor solution interface, diffusion of the complex formed through the liquid membrane and break down of the complex at the membrane/acceptor solution interface with the release of the metal ion to the acceptor solution. This mechanism enables the transfer process to be carried out even at low analyte concentrations and even against an analyte concentration gradient, known as facilitated transport [6–11].

Recently, Ren et al. [12–14] introduced the concept of HFRLM, where an extractor solvent is introduced not only into the membrane porous but also into the sample. Due to the wetting affinity of the organic phase and hydrophobic membrane, a thin organic film of solvent develops at the interface between the donor phase and the membrane. The shear force due to the sample agitation causes the formation of organic microdroplets on the surface of the liquid membrane layer, which separate from the surface of the liquid membrane. At the same time, the organic microdroplets present in the sample greatly increase the contact area between the extractor solvent and the sample. In addition, the presence of organic solvent into the sample provides the liquid membrane renovation. The HFRLM was used for simultaneous extraction and concentration of copper (II) from wastewater

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[12], citric acid from dilute solutions [13] and penicillin G from aqueous solution [14]. The system of di(2-ethylhexyl) phosphoric acid in kerosene (extractor phase) + HCl (stripping phase); 30% N235 (trialkyl amine, R_3N, $R = C_8 - C_{10}$):20% *n*-octanol:50% kerosene (extractor phase) + NaOH (stripping phase) and 7% di-n-octylamine:30% iso-octanol:kerosene (extractor phase) + Na_2CO_3 (stripping phase) were used to study the mass transfer characteristics of HFRLM process for each application aforementioned. In all these cases, a PVDF hollow fiber (effective length 29.8 cm, internal diameter 814 μm, external diameter 886 μm and membrane porosity 0.82), as well as a self-designed system with two 0–1 $dm^3\ min^{-1}$ peristaltic pumps and flow meters specifically designed for the experimental purposes were used. More recently, Carasek and coworkers [15] simplify the HFRLM presented by Ren et al. [12–14] adapting it to a U-shape configuration. In this new configuration a poly(dimethyl siloxane) membrane was used to determine cadmium (II) from aqueous samples. DDTP was used to complex the Cd(II) to a neutral hydrophobic complex which was extracted by a solvent mixture N-butyl acetate and hexane (60/40%, v/v) and re-extracted into EDTA pH 8.5.

In continuation to our previous communication [15], the purpose of this work is to assess the feasibility of the use of polypropylene porous membrane for HFRLM procedure in an U-shape configuration for determination of Cd(II) with FAAS. The method has been applied on environmental samples and the proposed system showed good results.

2. Experimental procedure

2.1. Instrumentation

A Varian Model SpectrAA 50 (Mulgrave, Australia) flame atomic absorption spectrometer equipped with a deuterium lamp as a background corrector and a cadmium cathode lamp (Hitachi HLA-4S, Tokyo, Japan) was used for the analysis. The instrument was operated under the conditions recommended by the manufacturer. The analytical signals were measured as peak area. A 320 Mettler Toledo pH meter was used to adjust the pH of the solutions. A Microquímica MQAMA 301 stirrer (Santa Catarina, Brazil) was used to agitate the solutions and a Microquímica MQBTC 99-20 bath system was used to control the temperature. A Q 3/2 accurel polypropylene hollow fiber membrane (600 μm id, 200 μm wall thickness and 0.2 μm pore size) was purchased from Membrana GmbH (Wuppertal, Germany). The hollow fiber was cut into 8.0 cm segments and was cleaned in acetone and dried before use. It was used as the barrier between the donor phase and the acceptor phase.

2.2. Reagents

Ultrapure water from a Milli-Q® (Bedford, MA, USA) water purification system (Millipore®) was used to prepare all solutions. All chemicals were of analytical grade and were used without previous purification, except for DDTP. The laboratory glassware was kept overnight in a 2% (v/v) Extran® (Merck, Darmstadt, Germany) solution and then again overnight in a 10% (v/v) hydrochloric acid solution. Before use, the glassware was washed with deionized water and dried in a dust-free environment.

Cadmium (II) working standard solutions were prepared daily by dilution of a 2000 $mg\ L^{-1}$ cadmium (II) stock solution (atomic absorption grade, Carlo Erba, Italy).

Ammonium sulfate (Nuclear, São Paulo, Brazil) and sodium chloride (Nuclear) were used to evaluate the salting-out effect. Toluene (Tedia, Fairfield, OH, USA), hexane (Tedia, Fairfield, OH, USA) and n-butyl acetate (Vetec, São Paulo, Brazil) were used as extractor solvents.

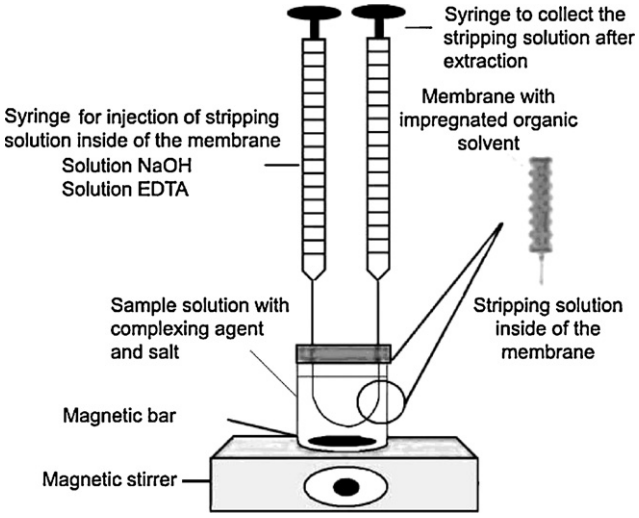

Fig. 1. Schematic illustration of three-phase HFRLM.

Ammonium *O,O*-diethyl dithiophosphate (DDTP) was supplied by Aldrich (Milwaukee, WI, USA) and used after purification with silica gel C18 column (Merck).

The working solutions were prepared by the addition of proper amount of salt, organic solvent and DDTP solution 1% (v/v) to 20 mL of a working standard solution containing 100 $\mu g\ L^{-1}$ of Cd(II). An EDTA solution (Vetec) was used as stripping phase.

Water samples collected from Araranguá River (Araranguá, Santa Catarina, Brazil), Carreiro River (Serafina Corrêa, Rio Grande do Sul) and sea water sample (Rio Vermelho beach, Florianopolis, Santa Catarina, Brazil) were used to verify the accuracy of the proposed method.

2.3. Extraction procedure

An aliquot of 20 mL of sample and an adequate amount of salt, DDTP and extractor solvent were added to a 40 mL vial. A polypropylene hollow fiber was cut carefully into 8 cm pieces and the two ends of each piece were connected to needles each with a 250 μL microsyringe. One of these microsyringes contained 165 μL of the acceptor solution, which was used to fill the lumen of the hollow fiber. The vial contain the sample was introduced into the temperature-controlled bath unit at the appropriate temperature. The extraction was carried out by placing the hollow fiber in the sample vial. After stirring for a predetermined time, the acceptor solution was collected by the second microsyringe and the solution was directly injected into the FAAS. Fig. 1 represents schematically the three-phases of the HFRLM system used in this study.

3. Results and discussion

Firstly, the optimum experimental conditions for extraction of Cd(II) from aqueous solutions using the HFRLM system was determined. For this purpose a multivariable optimization was adopted. The best extracting organic solvent on the extraction efficiency was studied by triangular surface mixture design. Sample pH, DDTP concentrations, acceptor phase pH, EDTA concentrations, organic solvent volume and extraction temperature and time were optimized using a three-level full factorial design that generates surface response plots. In the optimized condition, the analytical figures of merit were obtained and the proposed method was applied to the determination of Cd(II) in real water samples.

3.1. Effect of salting-out

The addition of salts to the samples results in increase of the ionic strength of the solution influencing significantly the extraction process. In some cases, an increase in the ionic strength of the sample phase can decrease the solubility of the analytes in an aqueous medium because of the effect called salting-out [16]. In this process, the water molecules hydrate ions reducing the molecules of analytes dissolved in the aqueous medium through a competition mechanism. In other words, increasing the salt concentration in the donator phase the water molecules will have more interaction to salt ions, releasing the DDTP–Cd(II) complex to interact to the organic solvent.

In order to evaluate the salting-out effect, some preliminary experiments using sodium chloride and ammonium sulfate were carried out. The results have shown that both salts presented an improvement in the extraction efficiency. However, a saturated ammonium sulfate solution showed a very distinct improvement in the analytical signal as demonstrated previously in our recent work [15]. The possible explanation is the high solubility and the presence of double charge in the ammonium sulfate which increase considerably the ionic strength of the solution. Despite the difference in ionic strength of feed aqueous solution and stripping solution, there was no osmotic process observed in the proposed system. Probably, because of the fact that the polypropylene membrane was completely filled with organic solvent which prevents permeability of the water molecules. Thus, this condition was adopted in the subsequent tests.

3.2. Effect of extractor solvent

An organic solvent suitable for the HFRLM should have low solubility in water, good compatibility with polypropylene hollow membrane and high partition coefficient between the analytes and the solvent [17]. In this case, the polarity between the organic solvent and the DDTP–Cd(II) complex should be similar, so a high partition coefficient could be reached. The effect of some extractor solvents on the extraction efficiency was studied. The mixture of organic solvents was optimized through triangular surface mixture design, where toluene, hexane and butyl acetate were evaluated individually, through binary mixtures with 33% and 67% (v/v) of one solvent and a ternary mixture containing 33% of each solvent. The results obtained from this design can be seen in Fig. 2. Here, there is a region in which the response reaches high values, corresponding to the use of toluene. This condition was selected to continue the optimization of the proposed method.

3.3. Effect of sample pH and DDTP concentration

Several factors were responsible for the choice of DDTP as complexing agent such as its solubility in water, high stability in acid medium and high formation constant to Cd(II) complexes [18]. The best experimental conditions for sample pH and DDTP concentration were determined through a three-level experimental design. From these results, a response surface was generated as shown in Fig. 3. Increasing the DDTP concentration from 0.025% to approximately 0.07% we can see an enhancement in the analytical signal. This indicates that with a DDTP concentration below 0.025% the extracting solvent does not contain enough DDTP to complex Cd(II), reducing the Cd(II) flux through the membrane. On the other hand, high DDTP concentrations lead to an increased membrane viscosity and, consequently, a lower extraction efficiency due to a reduced Cd(II) flux through the membrane. Also, high DDTP concentrations can lead to the formation of charged complexes like ML_3^- (where M is the metal ion and L is the DDTP ligand). Thus, the amount of the analyte extracted decreases, since the neutral complexes are preferentially extracted into the organic solvent. Fig. 3 also shows an antagonistic effect between the sample pH and the DDTP concentrations. As can be observed, reducing the sample pH a higher DDTP concentration is required for the complexation of Cd(II), probably because the protonation of DDTP is increased. In accordance with this study the optimum values for the two variables are sample pH of 3.5 and DDTP concentration of 0.055% (m/v).

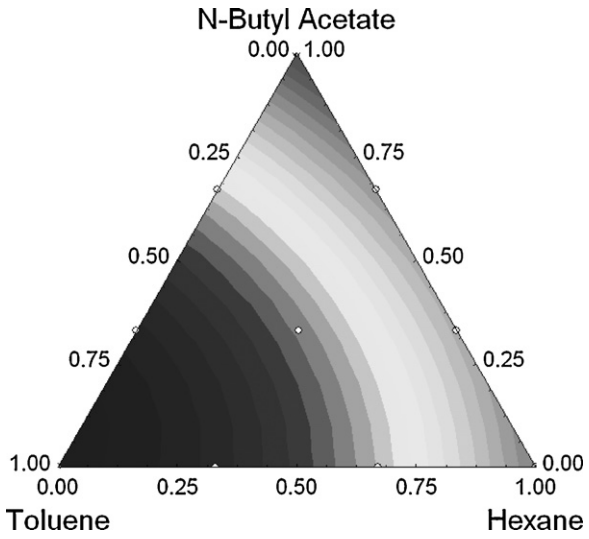

Fig. 2. Study of the effect of solvent choice on Cd(II) extraction by HFRLM with polypropylene membrane and detection by FAAS. Experimental conditions: 100 μg L^{-1} Cd(II), extraction time 30 min, sample pH 3.5, DDTP concentration 0.01% (m/v), stripping pH 8.5, EDTA concentration 5×10^{-2} mol L^{-1}, saturated solution $(NH_4)_2SO_4$ and extracting solvent volume 300 μL.

3.4. Effect of acceptor phase pH and EDTA concentration

As in the three-phase HFRLM system the DDTP–Cd(II) complex is formed in an acid medium, the pH acceptor phase should be basic promoting the broken down of the complex and releas-

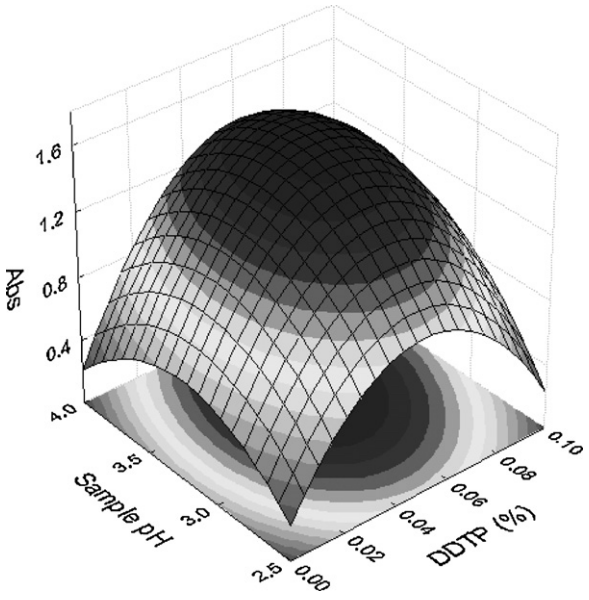

Fig. 3. Study of effect of sample pH and DDTP concentration on Cd(II) extraction by HFRLM with polypropylene membrane and detection by FAAS. Experimental conditions: 100 μg L^{-1} Cd(II), extraction time 30 min, stripping pH 8.5, EDTA concentration 5×10^{-2} mol L^{-1}, saturated solution $(NH_4)_2SO_4$ and extraction solvent 200 μL of toluene.

ing the analyte to the acceptor phase [19]. Due to the fact that EDTA can form a complex Cd(II) with a high formation constant, the addition of this quelant agent can change the equilibrium to the acceptor phase, trapping the analyte and improving the extraction efficiency. The optimum pH stripping phase and EDTA concentration were obtained using a three-level experimental design and the result of this study is illustrated in Fig. 4. As can be seen in Fig. 4, under optimum pH conditions the EDTA concentration has little effect on the analytical signal. However, for higher pH the effect of the medium on the analytical signal becomes more accentuated, due to the relation between the free EDTA (Y^{-4}) available to complex Cd(II) and the pH. Also, a lower analytical signal is obtained using a more acid medium probably because of a less efficiency broken down of the complex. The optimum values for the two variables were: EDTA concentration 1.5×10^{-2} mol L^{-1} (log EDTA = −1.82) and pH stripping phase 8.5.

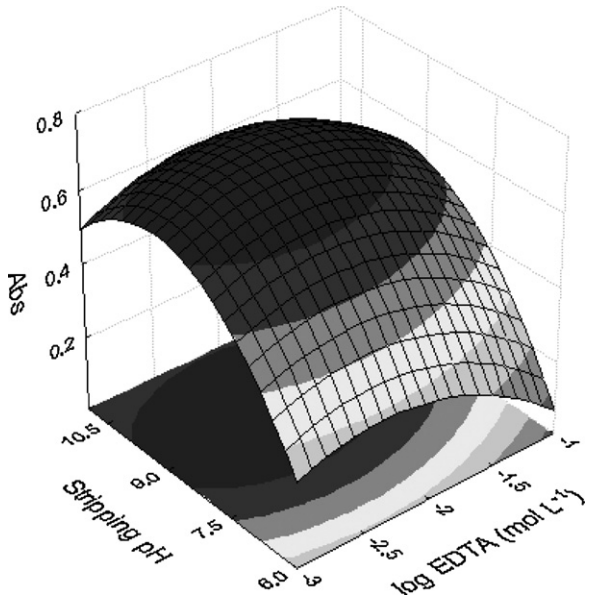

Fig. 4. Study of the effect of stripping pH and EDTA concentration on Cd(II) extraction by HFRLM with polypropylene membrane and detection by FAAS. Experimental conditions: 100 μg L^{-1} Cd(II), extraction time 30 min, sample pH 3.5, DDTP concentration 0.055% (m/v), saturated solution $(NH_4)_2SO_4$ and extraction solvent 200 μL of toluene.

3.5. Effect of solvent volume and extraction time and temperature

For the extraction techniques based on the diffusion of the analytes, it is expected that the extraction temperature exercises a significant effect on the extraction efficiency. In addition to the influence of the diffusion, the temperature affects the sample viscosity and the solubility of the extractor solvent in the sample, causing the degradation (degeneration) of the liquid membrane in the SLM. In the case of the HFRLM technique, this degradation should not occur because of the excess of solvent present in the sample, which constantly renews the liquid membrane. In general, supported membrane extractions need a long time to reach equilibrium, reducing the analytical frequency [17]. In this study, the volume of solvent, extraction time and extraction temperature were optimized using a three-level full factorial design that generates three response surfaces (Fig. 5).

As can be seen in Fig. 5A and B, on increasing the extraction temperature from 10 °C to 40 °C the extraction process becomes faster,

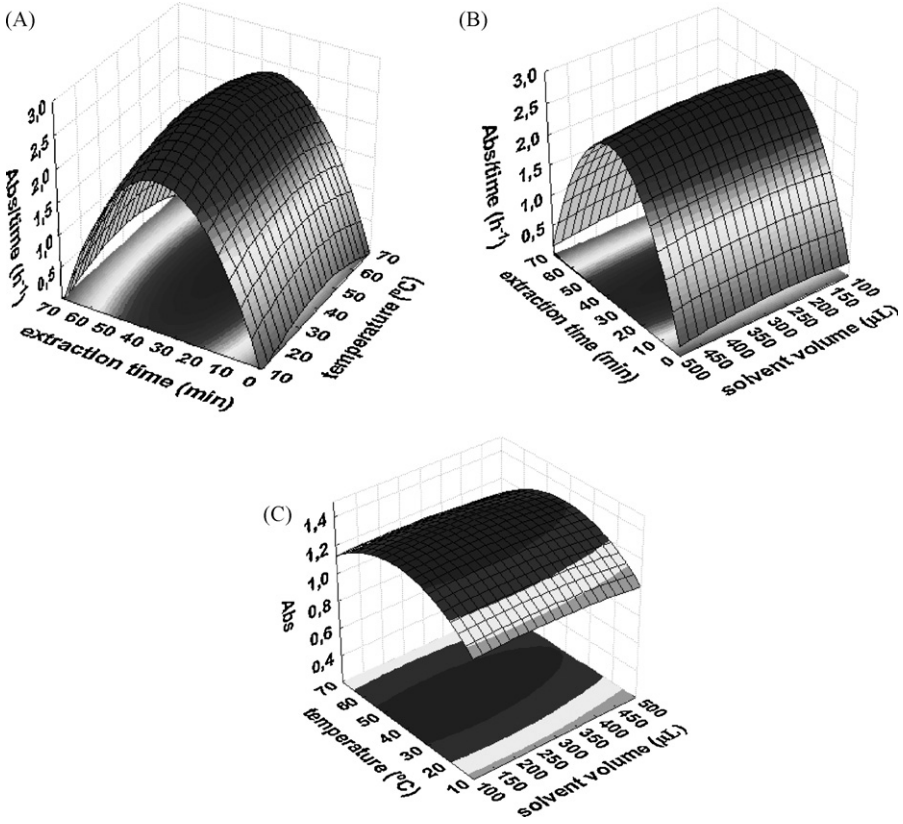

Fig. 5. Study of the effect of (A) temperature and extraction time, (B) solvent volume and extraction time and (C) solvent volume and temperature (time fixed in 30 min) on Cd(II) extraction by HFRLM with polypropylene membrane and detection by FAAS. Experimental conditions: Cd(II) 100 μg L^{-1}, sample pH of 3.5, DDTP concentration of 0.055% (m/v), saturated solution of $(NH_4)_2SO_4$, stripping pH of 8.5, EDTA concentration of 1.5×10^{-2} mol L^{-1} and extraction solvent 100 μL of toluene.

Table 1
Analytical figures of merit for determination of Cd(II) using the HFRLM extraction system with polypropylene membrane under optimized conditions and detection by FAAS.

Limit of detection (LOD)	1.5 μg L^{-1}
Limit of quantification (LOQ)	5.1 μg L^{-1}
RSD (15.0 μg L^{-1}, n = 7)	4.0% (n = 7)
Linear range	5–30 μg L^{-1}
Linear correlation coefficient (R)	0.9983
Enrichment factor (EF)	107

probably due to an increase in the analyte diffusion through the membrane. However, a higher extraction temperature is not appropriate because of the exothermic effect of the membrane extraction process. The extraction temperature also directly affects the solvent solubility in the sample, leading to degradation of the liquid membrane in HFSLM. Fig. 5B indicates that the undesirable membrane degradation effect can be overcome by adding a higher volume of extracting solvent to the sample. Thus, in the case of the HFRLM technique, the degradation of the liquid membrane does not occur because of the excess of extracting solvent in the sample, which renews the liquid membrane through the extraction period. The optimized extraction conditions used to continue this study were: extraction temperature 36 °C, extraction time 36 min and extracting solvent volume 310 μL.

3.6. Analytical figures of merit and accuracy

The analytical data of interest for the optimized proposed method are summarized in Table 1. Calibration curves were constructed to estimate the sensitivity, enrichment factor, correlation coefficients, limit of detection (LOD) and limit of quantification (LOQ) of the proposed method. The enrichment factor (EF) was calculated through the ratio between the slope of a calibration curve with and without preconcentration. The amount of cadmium extracted in the optimum experimental conditions can be estimate through the EF. In case of all analytes have been extracted, the EF should be 121 (calculated by ratio between the sample volume and stripping volume). As it was obtained an EF of 107, this value corresponds to 88% of cadmium extracted. The working linear range for the optimized procedure was between 5 and 30 μg L^{-1}. The detection limit was calculated as three times the standard deviation of ten blank readings divided by the slope of the calibration function. The method precision of 4.0% assessed as relative standard deviation was determined by submitting 20 mL of sample solution containing 15 μg L^{-1} of Cd(II) to the optimized procedure (n = 5).

A comparison between the LOD of the proposed method and several others found in the literature, including our previous work in which was used a PDMS membrane in a HFRLM technique [15], for determination of Cd(II) is presented in Table 2. It can be observed that the detection limit obtained in this study is compatible with that of other studies which used AAS as the detection system. In addition, the HFRLM technique is competitive in terms of sensitivity when compared with widely employed sample preparation techniques, such as solid-phase extraction (SPE) and cloud point extraction (CPE).

Table 2
A comparison between the results obtained in this study and those published in the literature.

Matrix	Separation and detection system	LOD	References
Water	LPME and GF AAS	6.5 ng L^{-1}	[20]
Water	LPME and GF AAS	3.5 ng L^{-1}	[21]
Urine	GF AAS	0.12 μg L^{-1}	[22]
Urine	ET AAS	0.08 μg L^{-1}	[23]
Water	SPE–FAAS	1.34 μg L^{-1}	[24]
Water/milk	SPE–FAAS	4.71 μg L^{-1}	[25]
Water	HFRLM and FASS	1.3 μg L^{-1}	[15]
Water	HFRLM and FAAS	1.5 μg L^{-1}	This study

Table 3
Recovery tests for Cd(II) extraction by HFRLM with polypropylene membrane and detection by FAAS under optimized conditions.

Samples	Spiked (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Araranguá river	15	14.3 ± 0.3	95.3
Carreiro river	15	14.1 ± 0.2	94.0
Rio Vermelho beach	15	16.9 ± 0.2	112.6

To verify the accuracy of the proposed procedure recovery tests were carried out using water samples from the Araranguá River (Araranguá, Santa Catarina, Brazil), Carreiro River (Serafina Corrêa, Rio Grande do Sul, Brazil) and seawater from Moçambique Beach (Florianópolis, Santa Catarina, Brazil). In all samples the analyte concentration was below the limit of detection of the method. In order to evaluate the accuracy of the preconcentration procedure, recovery experiments were carried out with spiked water samples (15 μg L^{-1}). As shown by the results in Table 3, good agreement between spiked and found values was obtained at a 95% confidence level, indicating that the calibration carried out using aqueous standard solutions submitted to the HFRLM procedure resulted in good accuracy.

4. Conclusions

The polypropylene porous membrane shows high stability and adequate to be used in a method based on a HFRLM. The proposed method allows the effective recovery of cadmium (II) in a single stage, with extraction and back-extraction occurring at the same time. This procedure can be successfully applied to the analysis of water samples in the study of cadmium (II) contamination.

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