



Cloud point-dispersive liquid-liquid microextraction for preconcentration and separation of mercury in wastewater samples by methylsulfanyl thiophenol material

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ABSTRACT

A efficient method based on 4-methylsulfanyl thiophenol (MSTP, $C_7H_8S_2$) and ionic liquid ([BMIM][PF₆]) was used for mercury (Hg) separation and preconcentration from wastewater of petrochemical industries. The 0.01 mole molar of MSTP, 80 mg of [BMIM][PF₆] was diluted with 0.2 mL of ethanol (Et 98%). The mixture was injected to 10 mL of wastewater samples, shaken by ultrasonic bath for 5.0 min and cloudy solution was achieved by ionic liquid micelles at pH=7.0. The mercury ions were complexed with MSTP and extracted on micelles (IL/Et) by cloud point dispersive liquid-liquid microextraction (CP-DLLME) at 50°C before determined by cold vapor atomic absorption spectrometry (CV-AAS). The favorite extraction for mercury with low LOD (15 ng L⁻¹) and good linear ranges (0.05- 6.2 µg L⁻¹) was achieved (RSD<5%). The main parameters such as, pH, sample volumes, amount of MSTP, amount of IL and ultra-sonic time were optimized. The method validated by spiking samples and certified reference material (CRM, NIST) in water sample.

1. Introduction

Mercury compounds (Hg, R-Hg) as toxic pollutants enter to environment from wastewater factories and cause different disease in humans. There are three forms of Hg (Hg⁰, Hg (II), R-Hg) which was used in different industries [1]. The high exposure of inorganic mercury damaged the human organs such as renal, liver and CNS [2]. Although the exposure to organic mercury or fish food can be created an main problem in blood brain barrier (BBB) and cortex of brain but is weaker than inorganic compounds

[3]. The hazardous defect in humans organs such as, CNS, respiratory, cells, renal and liver caused to different diseases, hypertension, chromosomal aberrations, tremor and MS [4]. So, as high toxicity, mercury determination in wastewaters is very important as industries samples. The mercury concentration in water is less than 6 µg L⁻¹ [5] and in blood is less than 1-2 µg dL⁻¹ [6]. So, the reliable, accurate and fast analytical methods must be used for wastewater samples. Among different analytical methods cold vapor atomic absorption spectrometry (CV-AAS) has been widely used for mercury determination in water samples due to simple, lower LOD and good sensitivity [7]. But,

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as low concentration of Hg and high interferences ions in wastewaters, the preconcentration and extraction processes must be done [8,9]. Recently, different extraction or microextraction mechanisms were used for this purpose. The micro-solid phase extraction (μ -SPE) [10], CPE [11], LLME based on ionic liquids [12], The DLLME and LLME are a strategy promotes the complexation processes between metal and ligand [13]. CP-DLLME technique can be assisted by ultrasonic accessory [14]. Solidified floating organic drop DLLME (SFO-DLLME) was developed by Kocurov et al and many other techniques introduced by liquid extraction procedure [15-22]. The cloud point extraction (CPE) caused to two phases for solution by temperature. The surfactants such as T-X100 were used for metal separation by clouding phenomena (S-CPE). The S-CPE has many advantages as compared to traditional extraction. The two components, salt and surfactant solutions separate into immiscible phases [23]. The metal mineral can analysis by different methods such as electrochemistry, ionic liquids and nano sorbents [24]. In the presence of salt, ionic liquids and surfactants self assemble in liquid phase at special temperature change to micelles [25-28]. Many metals interacted to micelles and so preconcentrated into the surfactant-rich phase. The aim of this study is to develop a new analytical method for rapid preconcentration and determination of trace mercury in wastewater samples based on the combination of CP-DLLME technique coupled to

CV-AAS. Ionic liquid of [BMIM][PF₆] dispersed in ethanol was used as trapping solvent for separation of MSTP from liquid phase. All factors which were affected on mercury extraction were studied and performance of the proposed method was validated.

2. Experimental

2.1. Apparatus and Reagents

Mercury was determined by atomic absorption spectrometer with a cold vapor accessory (GBC 932, CV-AAS, AUS), deuterium-lamp (UV), Hg HCL, and a unit of circulating cooling. The conditions of CV-AAS were shown in Table 1. The pH values of the solutions were measured by a digital pH meter Metrohm (744, Swiss). A Hettich centrifuge (Germany) and an ultra sonic accessory (Tecno-GAZ, Germany) were used. All reagents with high purity and analytical grade were purchased from Merck (Germany). All standard solutions were prepared with deionized water (DW) from Millipore (USA). The Hg (II) standard stock solution (1000 ppm in 1% HNO₃) was prepared from Sigma Aldrich, Switzerland. The experimental standard mercury were prepared daily by diluting of DW. The standards from 0.05- 6.2 ppb were freshly prepared and stored in a fridge (4 °C). A 0.5% (w/v) sodium borohydride (NaBH₄) was prepared daily by dissolving an appropriate amount of NaBH₄ in 0.5% (w/v) of NaOH and used for hydration of mercury (HgH₂). 1-Benzyl-3-methylimidazolium hexafluorophosphate $\geq 97.0\%$ ([BMIM][PF₆]; CASN: 39447), 1-Butyl-2,3-dimethylimidazolium hexafluorophosphate (CASN: 70869), 1,3-Diethoxyimidazolium hexafluorophosphate $\geq 97\%$ (CASN: 688649), 1,3-Dimethoxyimidazolium hexafluorophosphate 98% (CASN: 690821) were purchased from Sigma-Aldrich, Germany. The 4-methylsulfanyl thiophenol (CAS N: 1122-97-0, 96%, MSTP, C₇H₈S₂) was purchased from Sigma Aldrich, Germany. The pH adjusted to 6.5 by using sodium phosphate (Na₂HPO₄/NaH₂PO₄) as pH of 5.8-8.2. All the laboratory glasses were cleaned and washed by nitric acid and DW.

Table 1. The CV-AAS conditions for mercury analysis

Features	Value
Linear range, $\mu\text{g L}^{-1}$	1-62
Wavelength, nm	253.7
Lamp current, mA	3.0
Slit, nm	0.5
Mode	Peak Area
HCl carrier solution 37%, mol L ⁻¹	3.0
NaBH ₄ reducing agent, % (m/v)	0.5 (in 0.5% w/v NaOH)
Argon flow rate, mL min ⁻¹	10-15
Sample flow rate, mL min ⁻¹	3-5
Reagent flow rate, mL min ⁻¹	4-6

2.2. Sampling

Samples of wastewater (paint factory, Tehran, Iran), wastewater (industrial factories, Jajrood, Iran), oil company wastewater (Tehran, Iran) and chemical factory wastewater (Tehran, Iran) collected and filtered (0.45 μm) with polyethylene tubes and cellulose membrane (CMF), respectively before we used. The pH was tuned up to 7.0 with phosphate buffer solution. Then, the cloud point dispersive liquid-liquid microextraction (CP-DLLME) procedure was used for mercury extraction and determination in wastewater samples. The standard reference materials NIST NIST-SRM 1641e (total mercury in water) from the National Institute of Standard and Technology (NIST, Gaithersburg, USA) were also analyzed in a similar manner according to the general procedure.

2.3. CPE procedure

A simple procedure based on MSTP was used for separation of mercury ions from wastewater samples by cloud point dispersive liquid-liquid microextraction (CP-DLLME) at 50°C. The $10 \times 10^{-6} \text{ mol L}^{-1}$ of MSTP solution, 80 mg of [BMIM][PF₆] and 0.2 mL of ethanol was injected to 10 mL of wastewater samples. The samples were shaken

by ultrasonic bath for 10 min and cloudy solution was achieved by ionic liquid/ethanol micelles at pH=7.0. The pH of sample adjusted with 1 mL of buffer solution up to 7.0 which was added to 10 mL of wastewater samples. Based on ionic liquid/ethanol micelles, the cloud point extraction (CPE) for Hg(II) ions was obtained by adding, 0.08 g (120 μL) of [BMIM][PF₆] and 0.2 mL of ethanol as a dispersive solvent in wastewater samples. For optimizing and recovery, 10 mL of 0.02, 0.1, 0.5, 1.0, 3.0 and 6.0 $\mu\text{g L}^{-1}$ Hg(II) as working standard solution was prepared and used by CP-DLLME procedure. The cloudy solution was shaken for 5.0 min by ultrasonic shaking at 50 °C. In order to separate the phases, the turbid solution was centrifuged for 5.0 min at 4500 rpm and the liquid phase was removed with an auto-sampler of 10 mL. Hg(II) ions back-extracted from [BMIM][PF₆] with 0.5 mL of nitric acid (1.5 M) and after dilution with DW up to 1 mL determined by CV-AAS (Fig.1). The blank solutions proceeded the same way and are used for the preparation of the calibration solutions and for measurement of the blanks. The extraction mercury based on MSTP-CP-DILLME method was shown in Table 2.

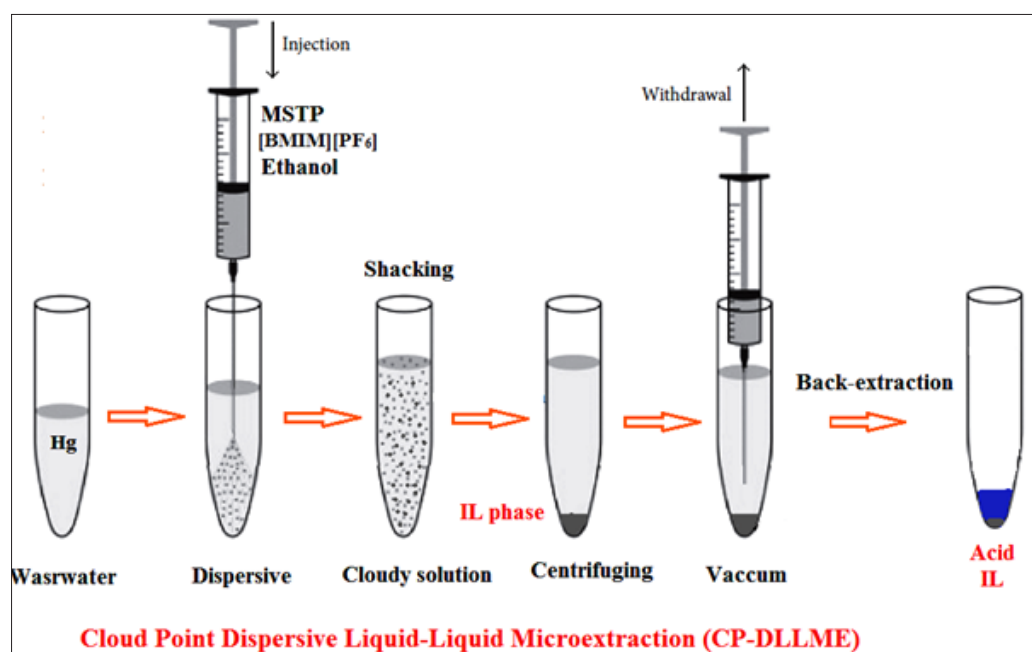


Fig. 1. The mercury extraction based on MSTP by cloud point dispersive liquid-liquid microextraction (CP-DLLME)

Table 2 The characteristics of the developed MSTP-CP-DILLME method for mercury extraction in wastewater samples (10 mL, pH=6.5, 0.02-6.2 $\mu\text{g L}^{-1}$)

Parameter (Inter-day)	Wastewater sample	Standard sample
PF ^a	9.8	10.2
LOD ^b (n=10, ng L ⁻¹)	15.8	15.2
LOQ (n=10, $\mu\text{g L}^{-1}$)	0.053	0.048
RSD ^c (n=6, %)	2.4	2.2
Linear range ($\mu\text{g L}^{-1}$)	0.05– 6.3	0.05-6.1
Working Range ($\mu\text{g L}^{-1}$)	0.05-14.5	0.05-14.2
Correlation coefficient	0.9993	0.9997

^a Preconcentration factor, ^b Limit of detection, ^c Relative standard deviation.

3. Results and discussion

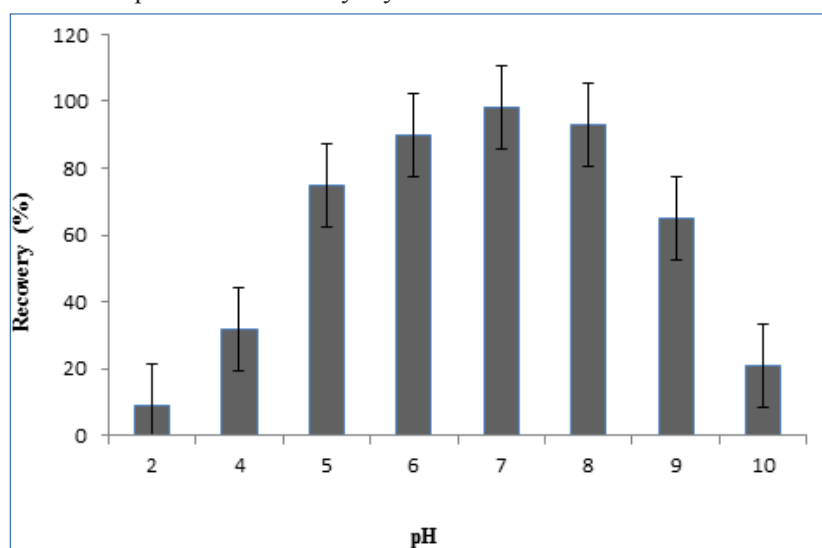
3.1. Optimization of pH

The effect of pH on complexation of mercury ions based on MSTP was investigated in different pH from 2 to 10 for 0.05 $\mu\text{g L}^{-1}$, 0.5 $\mu\text{g L}^{-1}$, 6.2 $\mu\text{g L}^{-1}$ Hg(II) as a LLOQ, MLOQ and ULOQ ranges. The complexation was strongly depended on the pH sample and subsequently caused to increase the extraction efficiency of mercury in wastewater samples. Based on results, the maximum extraction efficiency for mercury was obtained at pH=7.0 and the recovery were below 5% in acidic or basic pH. Therefore, the pH=6-8 was selected as optimum pH for mercury extraction from wastewater samples by the developed MSTP-CP-DILLME method with high recovery (Fig. 2). In pH=6-10, the sulfur (-) has negative charge but mercury based on positive charge (+) can be complexed with sulfur in pH more of 6 and less than 8. The results showed the maximum extraction was achieved at pH=7 for mercury by

coordinating covalent bond of sulfur ($\text{Hg}^{2+} \cdots \text{S}^{2-}$).

3.2. Optimization of ionic liquid

By procedure, the wastewater samples were shaken by ultrasonic bath for 10 min and cloudy solution was achieved by ionic liquid/ethanol micelles at pH=7.0. So the kind and amount of ionic liquid has critical role as generation micelles in liquid phase and extraction process by MSTP-CP-DILLME method. For this purpose, different ILs such as, 1-Benzyl-3-methylimidazolium hexafluorophosphate, 1-Butyl-2,3-dimethylimidazolium hexafluorophosphate, 1,3-Diethoxyimidazolium hexafluorophosphate, 1,3-Dimethoxyimidazolium hexafluorophosphate were selected and used for mercury extraction in optimized conditions. Based on results, the extraction efficiency was remarkably affected by amount ionic liquid amount, so it was examined within the range of 20-200 mg. Quantitative extraction was achieved more than 60 mg of

**Fig. 2.** The effect of pH on mercury extraction in wastewater samples by MSTP-CP-DILLME method

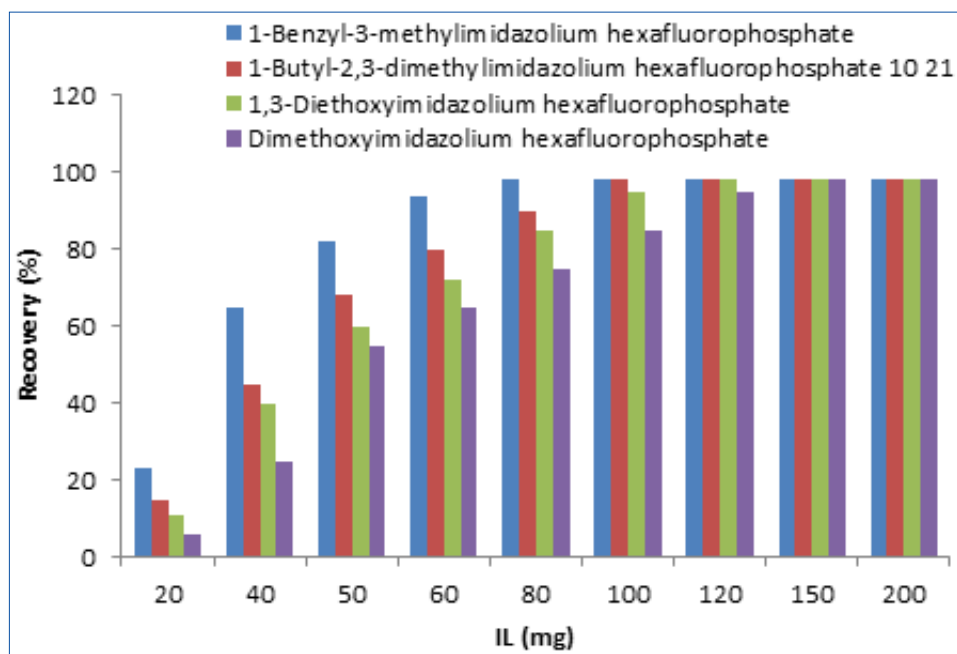


Fig. 3. The effect of different ionic liquids on mercury extraction by MSTP-CP-DILLME method

[BMIM][PF₆]. Therefore, 80 mg (120 μ L) of [BMIM][PF₆] was chosen as optimum leading to a final IL (Fig. 3).

3.3. Optimization of amount of MSTP

The amount of methylsulfanyl thiophenol (MSTP, C₇H₈S₂) was evaluated by CP-DLLME. By procedure, The concentration of MSTP between 1.0×10^{-6} - 50.0×10^{-6} mol L⁻¹ was prepared and optimized for maximum extraction mercury in wastewater samples in pH=7.0. The results showed the recovery has high extraction more than 5.7×10^{-6} and then no effected on mercury extraction by

increasing MSTP. In fact, the 5.7×10^{-6} mol L⁻¹ of MSTP was the minimum concentration which was necessary for high recovery for mercury extraction from wastewater samples. So, the 10×10^{-6} mol L⁻¹ of MSTP was selected as optimum concentration as interference ions in wastewater and more than the signal remained constant (Fig. 4).

3.4. Optimization of acids

The ionic liquids cannot directly use by CV-AAS, because of high viscosity and low interaction with redacting reagents such as NaBH₄. By MSTP-CP-DILLME procedure, the Hg-MSTP loaded on

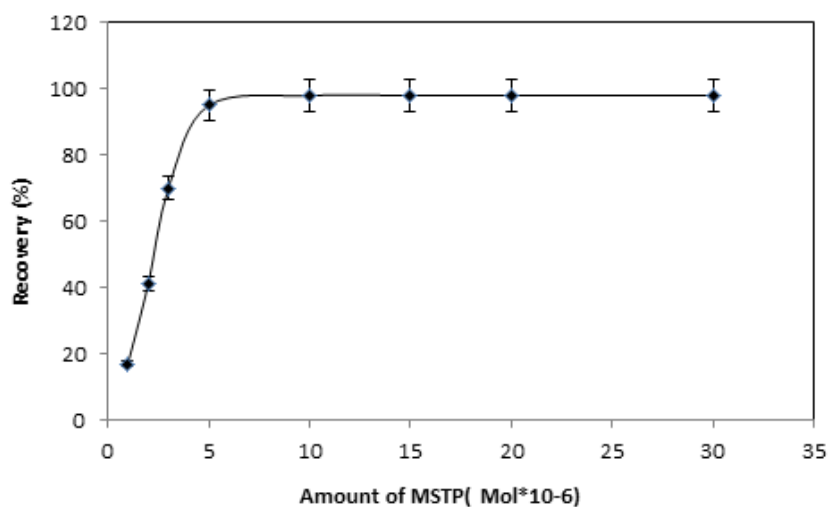


Fig. 4. The effect of MSTP ligand on mercury extraction in wastewater samples by MSTP-CP-DILLME method

[BMIM][PF₆] was back-extraction by the mineral acidic/basic solution. By changing of pH, the covalence bond between sulfur and mercury leads to dissociation and mercury ions release to liquid phase of acid. Different concentration of mineral reagents from 0.1-3 mol L⁻¹ (HCl, HNO₃, CH₃-COOH, NaOH) were used for back-extraction mercury from IL. The results showed that 1.5 mol L⁻¹ of HNO₃ can back-extracted of Hg(II) from the IL phase. Then, different of volume of reagents between 0.1-1.0 mL was studied and optimized. The results showed, 0.5 mL, 1.5 M of HNO₃ had maximum back-extraction mercury in wastewater samples (Fig. 5).

3.5. Optimization of sample volume

The different sample volume for extraction mercury was studied. The effect of sample volume was evaluated between 5.0 to 35 mL of wastewater/standard samples for 0.05 µg L⁻¹ and 6.0 µg L⁻¹ of Hg(II). Quantitative extraction was achieved less than 15 mL. In addition, the higher sample volumes caused to trace soluble the ionic liquid in liquid phase and lead to non-accurate results. So, a sample volume of 10 mL was selected for further work by CP-DLLME procedure (Fig. 6).

3.6. Interferences Ions

For analytical application of the CP-DLLME procedure, the effect of interference of coexisting

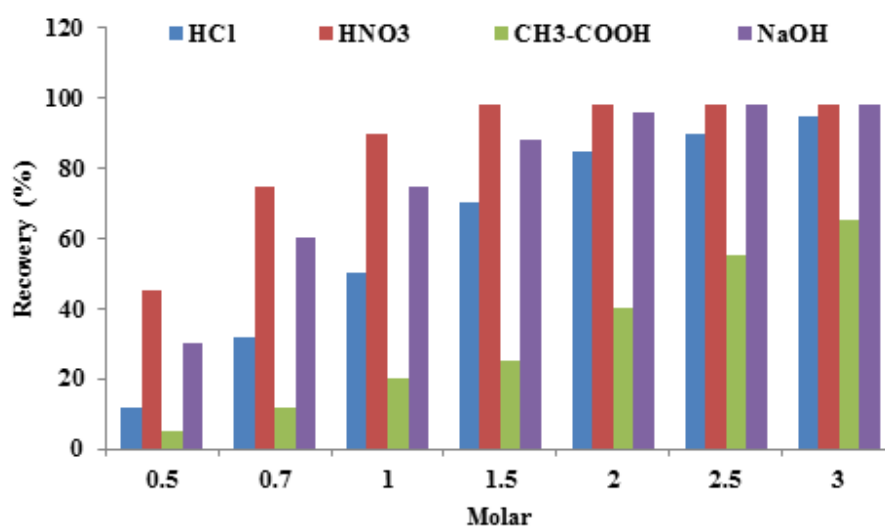


Fig. 5. The effect of different reagents for back-extraction of mercury from MSTP by CP-DILLME method

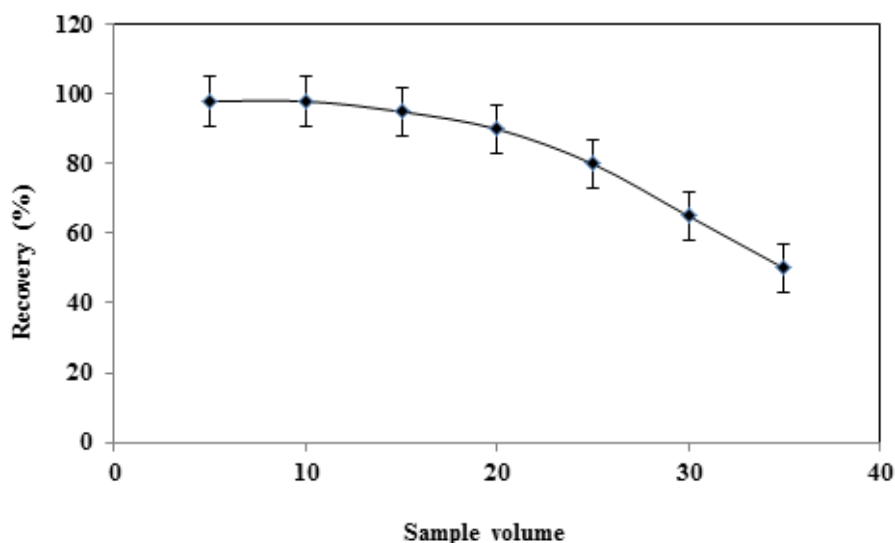


Fig. 6. The effect of sample volume on mercury extraction by MSTP-CP-DILLME method

Table 3. Effect of interfering ions on the recovery of Hg (II) ions by CP-DLLME procedure

Interfering ions C_M	Concentration ratio	Recovery (%)
	$(C_M/C_{Hg^{2+}})$	
Co^{2+} , Ni^{2+} , Pb^{2+} , Mn^{2+} , Cd^{2+}	750	98.3
PO_4^{3-} , CO_3^{2-} , NO_3^-	1000	97.7
Na^+ , K^+ , Ca^{2+} , Mg^{2+}	900	98.4
Ag^+ , Au^{3+}	40	96.5
Cu^{2+} , Zn^{2+}	300	97.2
Cr^{3+} , As^{3+} , Fe^{3+} , Al^{3+}	500	99.3
F-, Cl-, Br-, I-	1100	98.8

ions for mercury extraction in wastewater samples was studied. The various amounts of the interfering ions were added to 10 mL of wastewater sample containing $6.2 \mu\text{g L}^{-1}$ of Hg (II). As Table 3, the most of the probable concomitant ions have no considerable effect on the recovery efficiencies of Hg (II) ions under optimized conditions.

3.7. Real sample analysis

The developed CP-DLLME procedure was used for mercury determination in wastewater samples. The results showed the three separate determinations mercury in water samples. The results was verified by spiking of samples with standard concentration of Hg mercury. Table 4 showed, high recovery (more than 95%) between the added and found of mercury amount by procedure which confirms the accuracy of the procedure. The recoveries of spiked samples for mercury were ranged from 96% to

105%, which demonstrated satisfactory of mercury results. In order to validate the method described, the certified standard reference materials, NIST-SRM 1641e (total mercury in water), was analyzed and the results were given in Table 5. The results of the SRM were satisfactorily in agreement with the certified values.

4. Conclusions

A simple, fast and sensitive method based on MSTP was used for preconcentration and speciation of mercury in wastewater samples by CP-DILLME procedure. After extraction, the mercury concentration was determined by CV-AAS. The [BMIM][PF6] as ionic liquid was used as trapping agent of MSTP-Hg for rapid separation in short time. Utilizing ionic liquid micelles and MSTP together introduced a CPE procedure based on environmentally friendly for mercury extraction

Table 4. Validation of methodology based on MSTP for mercury analysis by CP-DILLME

Sample	Added ($\mu\text{g L}^{-1}$)	*Found ($\mu\text{g L}^{-1}$)	Recovery(%)
^a Wastewater Factory	-----	0.86 ± 0.04	-----
	0.8	1.64 ± 0.62	97.5
Wastewater oil	-----	1.01 ± 0.05	-----
	1.0	1.98 ± 0.09	97.0
^a Wastewater paint	-----	1.76 ± 0.09	-----
	1.5	3.28 ± 0.16	101.3
^a Wastewater Chemical	-----	1.12 ± 0.06	-----
	1.0	2.10 ± 0.11	98.0
Well water	-----	0.15 ± 0.01	-----
	0.2	0.36 ± 0.01	105.0

* Mean of three determinations \pm confidence interval ($P = 0.95$, $n = 5$).

^a Dilution (1:10)

Table 5. Validation of developed CP-DILLME method by standard reference material

Sample	Certified ($\mu\text{g L}^{-1}$)	Added ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Recovery (%)
CRM	1.016 \pm 0.017	-----	0.986 \pm 0.057	-----
		0.5	1.475 \pm 0.057	97.8
		1.0	1.971 \pm 0.069	98.5

^a Mean of three determinations \pm confidence interval ($P = 0.95$, $n = 5$).

^b NIST, SRM 1641e, total mercury in water ($p = 0.95$).

from wastewaters. This procedure provides low LOD values as well as good RSD with quantitative recoveries more than 95% in optimized conditions. The CP-DILLME procedure based on MSTP and [BMIM][PF₆] can be considered as effective sample preparation for mercury extraction from wastewater samples.

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