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On-site solid-phase extraction and application to in situ preconcentration of heavy metals in surface water

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Abstract An on-site solid-phase extraction, consisting of the sorption, the separation and the elution function units, was designed for in situ preconcentration of heavy metals ions. The D401 resin powder was employed as sorbent to capture Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+}, and then they desorbed with 2 mol/L nitric acid as eluent. Under the optimized conditions, these heavy metals ions in West Lake, Taihu Lake, and Yangtze River of China were captured and then determined by ICP-OES with the recovery of 92.5% to 111.5%. The on-site solid-phase extraction achieved a quick preconcentration of heavy metals to avoid the transport and storage of a large volume water sample. It is suitable for in situ monitoring of water quality in mountains, tablelands or other remote areas.

Keywords Solid-phase extraction · In situ preconcentration · Heavy metals · Sorbent · Water quality analysis

Introduction

The accumulation of toxic heavy elements may affect human health, because the human body cannot process and dispose the heavy metals. That too much deposit may cause adverse reactions and serious damage to the body is proven (Oliveira and Pampulha 2006). So the quantification of toxic metal ions in various water resources is important, especially in the environment monitoring and the assessment of environmental exposure to toxic metals. It is therefore important to develop accurate techniques to quantify heavy metals in water. However, due to the low concentrations in environmental samples and the complexity of matrices, it is usually difficult to detect heavy metals directly using some typical analytical techniques such as atomic absorption spectrometry and inductively coupled plasma (ICP). Prior to the determination, the preconcentration of metals ions from water sample is always necessary.

During the years, the classical solid-phase extraction (SPE) has evolved to meet such requirements because of several advantages, which include flexibility, low cost, absence of emulsion, simplicity, ease of automation and so on (Lloyd et al. 1998; Van Stee et al. 2002; Pecoraino et al. 2008; Zhang et al. 2010; Faraji et al. 2010; Vellaichamy and Palanivelu 2011; Yildiz et al. 2011). The traditional solid-phase extractor has some disadvantages. For example, a vacuum pump is used so that it is only used in laboratory. In addition, a water sample must keep at a low flow rate to pass through the column filling with sorbent to capture all the analytes. In this work, a portable solid-phase extraction (PSPE) device was developed, which consists of the sorption, separation and elution

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functional units. A quick in situ preconcentration of heavy metals ions from surface water was tried by the PSPE.

Various sorbents were employed for capturing heavy metals ions and organic chemicals in trace level, such as chelating resin (Narin et al. 2003; Furusho et al. 2009; Tokalioglu et al. 2009; Saygi et al. 2008; Sakamoto et al. 2006), macroporous resin (Yildiz et al. 2011), activated carbon (Zhang et al. 2010), nanoparticles (Faraji et al. 2010), and so on. Of these sorbents, the chelating resin is often used in extraction of heavy metals (Tunceli and Turker 2002), where the D401 resin with diglycolamidic acid group can adsorb bivalent metal ions selectively (Wang et al. 2009). In this work, the D401 chelating resin powder (DCRP) was used to capture heavy metals ions.

Materials and methods

Instruments and materials

A Model 2100DV Optima inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer Inc, USA) was used for determination of metal ions. A PSPE device was designed, manufactured (Shanghai GreenEmpire Environmental Protection S&T Co, China) and employed for in situ preconcentraction of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+}. A Model FD-1 lyophilizer (Shanghai Tianfeng Industrial Co., China) was used to dry the D401 resin.

A stock standard solution of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} (every metal in 1.00 mg mL^{-1}; Aladdin Reagents Co., China) was diluted into their working solutions (every metal in 1.00 mg L^{-1}) with doubly distilled water. 2 mol L^{-1} HNO_3 was prepared as eluent. The 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH were used to adjust pH of solution. The D401 resin (Shanghai Mosu Science Equipments, China) was used to capture metal ions fro aqueous solution. All chemical reagents are in GR grade.

Preparation of DCRP

The D401 chelating resin was selected as sorbent in this work. Prior to use, it was immersed into 2 mol L^{-1} HNO_3 for 2 h. After drying for 24 h in the lyophilizer, the resin was comminuted into powder with a Model FW 80-I disintegrator (Tianjin Taisite Instruments, China) and then the powder filtered through the standard sieves. The DCRP particles between 0.075 and 0.250 mm were collected as sorbent.

Preconcentration of heavy metals ions

One gram of DCRP was added into a solution containing heavy metal ions. After adjusting to around pH 5 with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH, the solution was stirred to facilitate the sorption of heavy metal ions to DCRP. After 15 min, the liquid was pumped through an empty column with a filter plate so that DCRP was separated from the liquid. Then, the DCRP was washed with 5.0 mL of eluent for 3 min with an ultrasonic unit combining to the PSPE device. The heavy metals released into the eluent were determined by ICP-OES.

Application to on-site monitoring of surface water

Prior to in situ preconcentration of heavy metals ions, surface water was filtered through millipore cellulose membrane (0.45 μm pore size). Heavy metals ions in three water samples, e.g., West Lake, Yangtze River, and Taihu Lake were captured and eluted with a PSPE device and then determined by ICP-OES.

Results and discussion

Design of portable SPE device

An PSPE device was designed, which consisted of the sorption of heavy metal ions, separation of sorbent and desorption of heavy metals (Fig. 1). Being different from the traditional SPE, it is suitable for in situ preconcentration of heavy metal ions in aqueous solution.

Effect of pH

DCRP (1.5 g) was added into 500 ml of solution containing six kinds of heavy metal ions: Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} (every metal in 0.100 mg L^{-1}), and the pH adjusted with 0.1 M HCl or 0.1 M NaOH. After the on-site SPE operation, these metals ions released into the eluent were determined

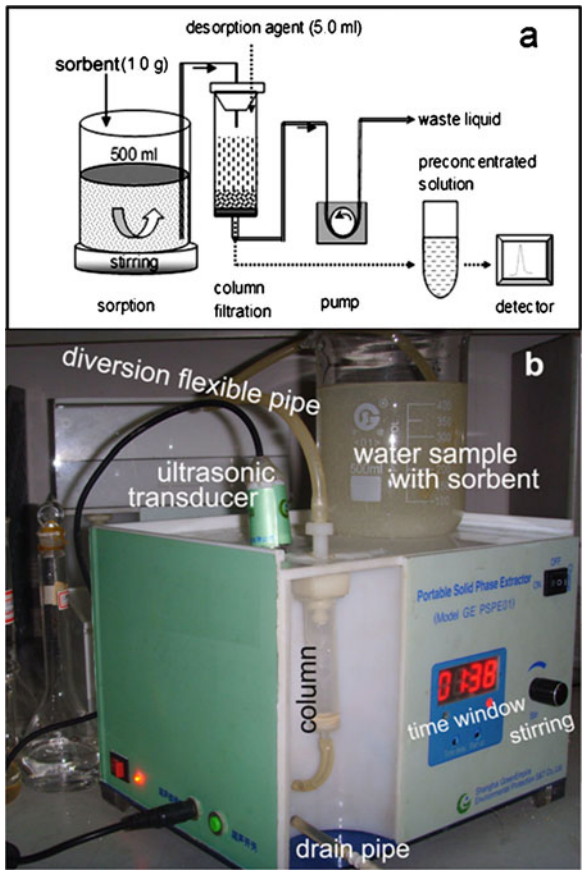

Fig. 1 Design of the PSPE device. **a** The function units and **b** photograph of the device working with marks

by ICP-OES. Effect of pH on the sorption of heavy metals is shown in Fig. 2. The acidity of solution exhibited an obvious effect. The recovery of heavy metals increased with increase of pH from 1 to 4 and remained constant between pH 5 and 7, e.g., 96% for Pb^{2+}, 96% for Zn^{2+}, 93% for Cd^{2+}, 84% for Co^{2+}, 81% for Ni^{2+} and 57% for Cu^{2+}. It demonstrated that the DCRP is suitable for quantitatively capturing heavy metal ions from aqueous liquid.

Effect of sorption time

DCRP (1.5 g) was mixed into 500 ml of solution containing six kinds of heavy metal ions: Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} (every metal in 0.100 mg L^{-1}). The effect of sorption time from 0 to 30 min was investigated. From curves in Fig. 3, the recovery of metals increased with increase of the

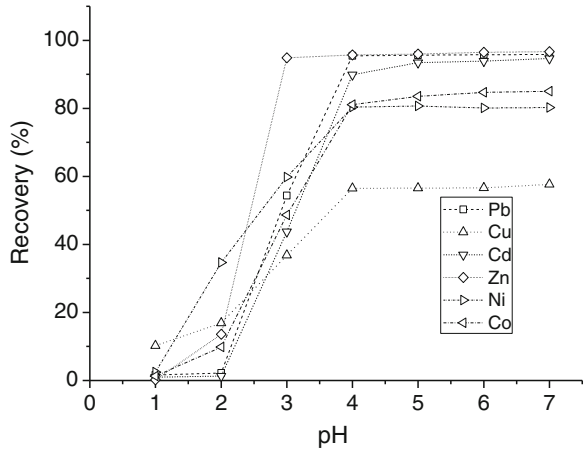

Fig. 2 Effect of pH on the sorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} (every metal in 0.100 mg L^{-1}). DCRP (1.5 g) was added as sorbent, the shaking time kept for 15 min and 5 ml of 2 mol L^{-1} HNO_3 used as eluent

shaking time in the first 15 min and then approached constant, for example 96.09% to 98.85% for Pb^{2+}, 58.47% to 61.08% for Cu^{2+}, 95.69% to 96.89% for Cd^{2+}, 96.89% to 98.74% for Zn^{2+}, 82.12% to 85.21% for Ni^{2+} and 85.78% to 86.98% for Co^{2+}.

Effect of sorbent

A known amount of DCRP from 0.1 to 1.8 g was added into 500 ml of solution containing Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} (every metal in

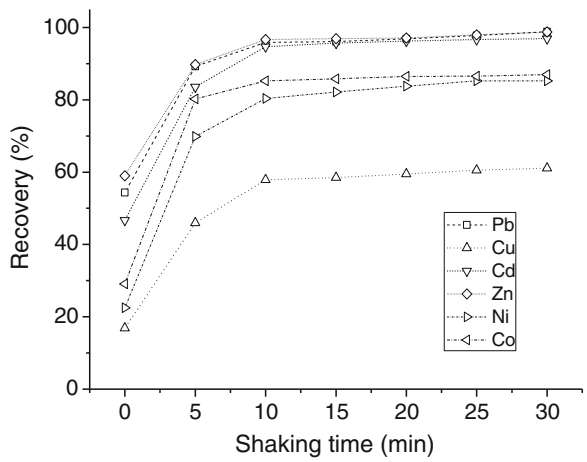

Fig. 3 Effect of the shaking time on the recovery of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} (every metal in 0.100 mg L^{-1}). DCRP (1.5 g) was added and 5 ml of 2 mol L^{-1} HNO_3 used as eluent

0.100 mg L^{-1}). After the sorption and elution, the recovery of metals was calculated and shown in Fig. 4. The recovery of metals increased up to 96.5% for Pb^{2+}, Cd^{2+} and Zn^{2+}, 86% for Ni^{2+} and Co^{2+} and 60% for Cu^{2+} with increase of DCRP from 0.1 to 1.0 g. More than 1.0 g of DCRP was added so that the recovery of metals approached constant maximum except for Cu(II).

Effect of eluent

The HNO_3 solution from 0.5 to 2.5 mol L^{-1} was used to elute the DCRP. The recovery of heavy metals increased with increase of acidity to 1.5 mol L^{-1} (Fig. 5) and then approached almost constant except for Cu(II) between 1.5 to 2.5 mol L^{-1} HNO_3. In the following experiments, 2.0 mol L^{-1} HNO_3 was used as the optimal eluent.

Effect of water volume

The effect of the sample volume from 200 to 1,000 ml on adsorption of heavy metals was investigated. The recovery of Pb^{2+}, Cd^{2+}, Zn^{2+}, and Co^{2+} remained almost constant, but that of Cu^{2+} decreased with increase of the sample volume (Fig. 6). It may be attributed to the fact that Cu^{2+} chelating to DCRP is weaker than the other metals ions. The recovery of Ni^{2+} decreased when the sample volume was more than 600 ml. If the sorption time or the sorbent addition increased, e.g., to 20 min or to 1.5 g, the recovery of Cu^{2+} and Ni^{2+} may increase.

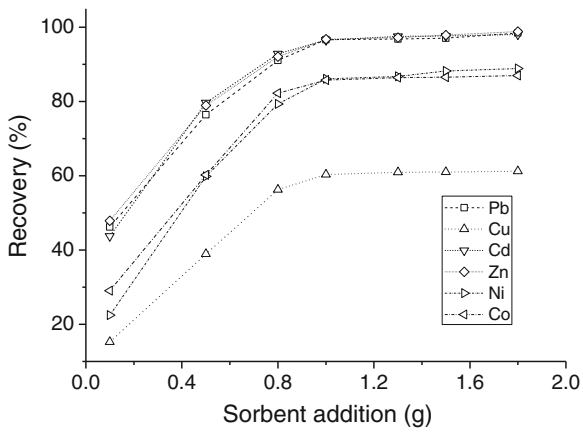

Fig. 4 Effect of DCRP on the recovery of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} in 500 ml of solution (every metal in 0.100 mg L^{-1}). The sorption time kept for 15 min and 5 ml of 2 mol L^{-1} HNO_3 used as eluent

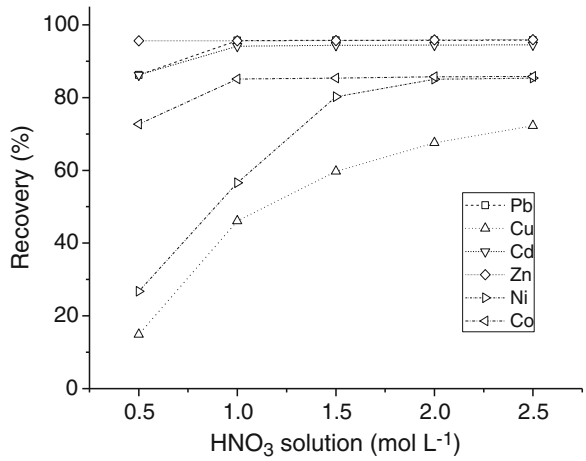

Fig. 5 Effect of HNO_3 concentration on the recovery of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} (every metal in 0.100 mg L^{-1}). DCRP (1.0 g) was added, the sorption time kept for 15 min and 5 ml of eluent used

Calibration graph for determination of heavy metals

In order to avoid the interference of common metal ions co-existing in water, 1000-fold K^+ and Ca^{2+} and 500-fold Mg^{2+} were added into a series of heavy metals standard solutions. According to the recommended procedures, these metal ions were captured and then determined by ICP-OES. From

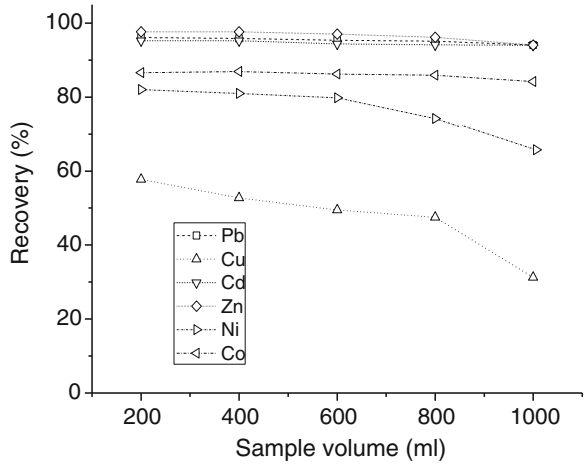

Fig. 6 Effect of volume on the recovery of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} (every metal in 0.100 mg L^{-1}). DCRP (1.0 g) was added, the sorption time kept for 15 min and 5 ml of 2 mol L^{-1} HNO_3 used as eluent

curves in Fig. 7, this method released a quantitative preconcentration of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, and Co^{2+}.

Application to monitoring surface water

The PSPE device was used for on-site monitoring of West Lake, Taihu Lake, and Yangtze River of China. According to the recommended method, six kinds of heavy metals ions in these surface waters were determined as given in Table 1, where Zn^{2+} is from 3.82 to 89.31 μg L^{-1}, Pb^{2+} from 1.39 to 3.52 μg L^{-1}, Co^{2+} from 0.23 to 0.25 μg L^{-1}, Cd^{2+} from 0.26 to 0.46 μg L^{-1}, Ni^{2+} from 0.93 to 1.94 μg L^{-1}, and Cu^{2+} from 2.14 to 7.17 μg L^{-1}. The direct ICP-OES determination of Zn in the Yangtze River sample accorded with that obtained by the PSPE method. In addition, a known amount of heavy metal ions was added into these water samples for examination of recovery. The recovery was between 102.5% and 111.5% for Zn^{2+}, 92.5% and 101% for Pb^{2+}, 94.4% and 100.5% for Co^{2+}, 94% and 103.5% for Cd^{2+}, 95% and 100.5% for Ni^{2+} and 96.8% and 108.5% for Cu^{2+} (Table 1). It indicated that the PSPE device is accurate for in situ preconcentration of heavy metals ions in surface water.

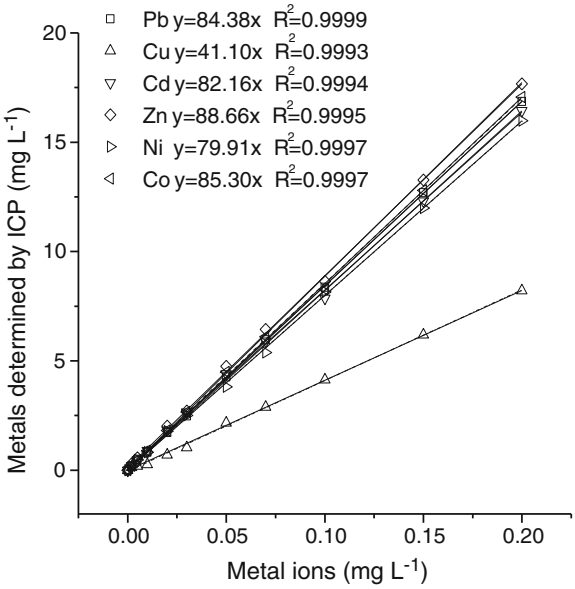

Fig. 7 Calibration graphs for heavy metals determination. DCRP (1.0 g) was added, the sorption time kept for 15 min and 5 ml of 2 mol L^{-1} HNO_3 used as eluent

Table 1 Determination of heavy metals ions in surface water (n=3)

Sampled from	Metal ions	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Yangtze River	Zn	0	89.3	–
		0	89.7[a]	–
	Pb	0	3.52	–
		2	5.37	92.5
	Co	0	0.25	–
		2	2.23	99
	Cd	0	0.26	–
		2	2.23	98.5
	Ni	0	0.93	–
		2	2.89	98
	Cu	0	7.17	–
		2	9.34	108.5
West Lake	Zn	0	3.82	–
		2	6.05	111.5
	Pb	0	1.39	–
		2	3.41	101
	Co	0	0.23	–
		2	2.16	96.5
	Cd	0	0.29	–
		2	2.32	101.5
	Ni	0	1.00	–
		2	2.98	99
	Cu	0	4.7	–
		2	6.72	101
Taihu Lake	Zn	0	5.31	–
		2	7.36	102.5
		5	10.4	102.6
	Pb	0	1.88	–
		2	3.74	93
		5	6.61	94.6
	Co	0	0.23	–
		2	2.24	100.5
		5	4.95	94.4
	Cd	0	0.46	–
		2	2.53	103.5
		5	5.16	94
	Ni	0	1.94	–
		2	3.95	100.5
		5	6.69	95
	Cu	0	2.14	–
		2	4.09	97.5
		5	6.98	96.8

[a] Zn(II) in Yangtze River was determined directly by ICP-OES

Conclusion

A PSPE device was designed for in situ preconcentration of heavy metal ions at trace levels in water. The D401 resin was used to capture Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} in trace level from water samples. The results indicated that the PSPE device can capture heavy metals ions rapidly and entirely. Also, DCRP may be recycled after acid washing. The PSPE device provided an on-site water quality monitoring method. By comparing with the normal SPE, it has advantages, e.g., portability, timesaving and avoiding the transport and storage of a large volume water sample. It is suitable to use in mountains, tableland, and other remote areas. Predictably, if this device is to combine with a metal detection unit, e.g., anodic stripping voltammetry, an in situ determination of metal ions in $<0.5\ \mu g\ L^{-1}$ level will be realized. If a favorable sorbent is used instead of DCRP, the on-site PSPE method may capture trace amounts of harmful organic chemicals in aqueous solution.

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