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A nanofiber functionalized with dithizone by co-electrospinning for lead (II) adsorption from aqueous media

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ABSTRACT

An electrospun nanofiber was utilized as a sorbent in packed fiber solid phase extraction (PFSPE) for selective separation and preconcentration of lead (II). The nanofiber had a polystyrene (PS) backbone, which was functionalized with dithizone (DZ) by co-electrospinning of a PS solution containing DZ. The nanofiber exhibited its performance in a cartridge prepared by packing 5 mg of nanofiber. The nanofiber was characterized by a scanning electron microscope and IR spectra. The diameter of the nanofiber was less than 400 nm. After being activated by 2.0 mol L^{-1} NaOH aqueous solution, the nanofiber quantitatively sorbed lead (II) at pH 8.5, and the metal ion could be desorbed from it by three times of elution with a small volume of 0.1 mol L^{-1} HNO_3 aqueous solution. The breakthrough capacity was 16 μg mg^{-1}. The nanofiber could be used for concentration of lead (II) from water and other aqueous media, such as plasma with stable recovery in a simple and convenient manner.

1. Introduction

Heavy metals, which are the main pollutants not only in the industrial sector, but also in our living environment, are causing severe public health problems. One typical example of it is lead. According to the Guidelines of the United States Center for Disease Control, a blood lead level below 10 μg dL^{-1} is interpreted as "safe", while medical evaluation and treatment are recommended for blood leads above 20 μg dL^{-1} [1]. However, many works have found that even low-level lead exposure is harmful to our health, especially for children who are more susceptible [2–5]. Therefore, the determination of heavy metal ions at trace level is very important in environmental protection and disease prevention.

The direct determination of heavy metal ions in complex matrices is limited due to their low concentrations and matrix interferences. Therefore, a preconcentration and separation procedure, such as liquid–liquid extraction, coprecipitation, and cloud point extraction [6–9], is necessary to improve the sensitivity and selectivity of the determination of heavy metal ions. Recently, solid phase extraction (SPE) has been the most common technique used for preconcentration of heavy metal ions because of its advantages of a high enrichment factor, high recovery, rapid phase separation and low consumption of organic solvents [10–13].

Among various types of SPE techniques, there is a new technique called packed fiber solid phase extraction (PFSPE) [14], which is based on the use of electrospun nanofiber as the sorbent. Although the electrospinning technique was invented in the early 1900s, electrospun nanofiber was reported as early as 1971 [15], and various types of electrospun nanofiber and various applications have been reported after that [16–18]; there are few reports related to the extraction. Compared to the conventional SPE technique, the nanofiber sorbent possesses a large surface area which facilitates the attachment of target molecules, so that less amounts of sorbent, and less volume of sample and eluent are required [19]. The PFSPE technique can perform perfectly in both environmental and biological sample pretreatment. Some successful applications of PFSPE have been reported in the extraction of target compounds, such as the cortisol in the saliva [19], vitamins in the plasma [20] and in the beverages [21], drugs [22] in the plasma, and aromatic pollutants in the environmental water [23]. The target molecules which have been reported were organic matters. However, the pretreatment of metal ions by PFSPE is rarely found to be reported.

In this work, a selective sorbent, polystyrene–dithizone composite electrospun nanofiber (PS–DZ nanofiber), was fabricated, characterized and applied to extraction of lead (II) in aqueous samples. Dithizone, as a well-known reagent, has been used for the determination of many metal ions [24]. It can be immobilized on the solid phase by synthetic reaction. The chelating resin containing

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s-bonded dithizone was reported to have good performance on SPE of metal ions [25], but the procedure of fabrication was not straightforward enough. The modification was also achieved by coating the solid phase with dithizone [26], however, the dithizone on the solid phase was possibly not stable enough. In this work, the immobilization of DZ on the solid phase was finished by co-electrospinning of a mixture solution of PS polymer and DZ, and adsorbing performance of the composite nanofiber was investigated.

2. Experimental

2.1. Reagents and solutions

All chemicals used in this work were of analytical reagent grade and were used without further purification. Doubly distilled deionized water was used throughout. The polystyrene (PS), the polyacrylonitrile (PAN) and the acrylic resin (AR) were obtained from Shanghai Chemical Agents Institute. The standard labware and glassware used were cleaned with HNO_3 and rinsed with double distilled water, according to Tuzen et al. [27].

Standard stock solutions (1 mg mL^{-1}) of lead (II) were prepared by dissolving spectral pure grade chemicals $Pb(NO_3)_2$ in double distilled water. Buffer solutions (NH_3/NH_4Cl) were prepared by mixing appropriate volumes of 1 mol L^{-1} ammonium chloride and ammonia for pH 8–9. Phosphate buffer solutions for pH 6–7 were prepared from disodium hydrogen phosphate and citric acid, and the concentration of Na_2HPO_4 was approximately 1 mol L^{-1}. The acetic buffer solutions (HAc/NaAc) were prepared by mixing 1 mol L^{-1} sodium acetate and glacial acetic acid for pH 3–5. The sodium hydroxide solutions were prepared by dissolving sodium hydroxide in distilled water.

2.2. Instruments and apparatus

A high performance liquid chromatography, consisting of a LC-20A pump and a PDA detector (SHIMADZU, Japan) was used. A C18, 5 μm, 150 mm × 4.6 mm Rad-Pak reversed-phase column (SHIMADZU, Japan) was used to achieve fast separation and analysis of metal ions. A HPLC software package (SHIMADZU, Japan) was used for the data analysis.

A pH meter (Shanghai, China) with a glass electrode was used for all pH measurements. A high-voltage power supply (model DW-P403-1AC, Tianjin, China), and a syringe pump were used for the electrospinning. The nanofiber was examined using a Hitachi S-3000N scanning electron microscope (SEM, Tokyo, Japan). The IR spectra were carried out on a NICOLET 5700 FT-IR Spectrophotometer (Nicolet, US).

2.3. Fabrication of electrospun nanofiber and preparation of cartridge

The electrospun solution was prepared by dissolving an appropriate amount of PS (10%, w/v) and dithizone (5%, w/w of PS) in a mixture of dimethylformamide and tetrahydrofuran (4:6, v/v). At the beginning, PS was dissolved in the mixed solvent by magnetic stirring. The dithizone was added into the polymer solution after PS was dissolved completely. The solution continued to be stirred at room temperature for more than 10 h before electrospinning. This solution was loaded into a glass syringe which was fitted to a steel needle with a tip diameter of 0.5 mm whose tip was filed flat. Then electrospinning performance was shown in Fig. 1 in this condition: an anodic voltage of 17 kV, 25 cm from the tip of the needle to the collecting equipment, the feed rate of 1 mL h^{-1} for precursor solution. The nanofiber was collected on the collector which was covered by a piece of gauze pretreated by dilute HNO_3 (1 + 9) and rinsed with distilled water.

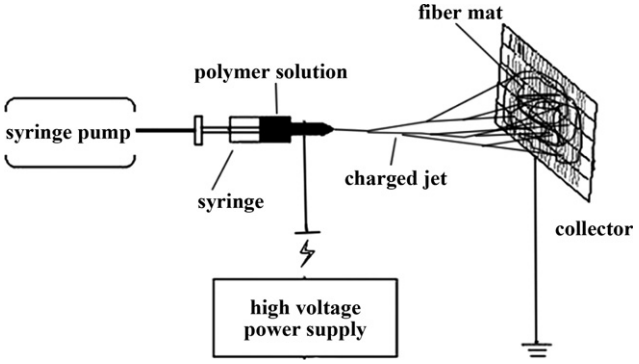

Fig. 1. The system of electrospinning.

The PAN–DZ nanofiber and the AR–DZ nanofiber were prepared in the following procedures: 8% (w/v) polyacrylonitrile (PAN) was dissolved in the dimethylformamide by magnetic stirring after ultrasonic processing for 30 min; and 8% (w/v) acrylic resin (AR) was dissolved in the ethanol by magnetic stirring. Then dithizone (5%, w/w of polymer) was dissolved in the polymer solution. The solutions continued to be stirred at room temperature for more than 10 h before electrospinning. Other procedures were similar to those of the PS–DZ nanofiber, except for a voltage of 14 kV for the PAN–DZ nanofiber and 10 kV for the AR–DZ nanofiber.

A novel cartridge, as shown in Fig. 2, was designed for pretreatment of the aqueous sample. 3–5 mg of nanofiber were packed into a column with an inside diameter of 1.5 mm. A conical liquid storage cartridge was attached to the column. The pressurizer was available by using a syringe with a modified tip which was fitted to the liquid storage cartridge.

2.4. Procedures

2.4.1. Adsorption and desorption procedures

The nanofiber should be activated before being used. Before activation, the pretreatment device consisted of the column and the liquid storage cartridge was washed with 0.1 mol L^{-1} nitric acid and water, so as to clean up the metal ion remaining in the device.

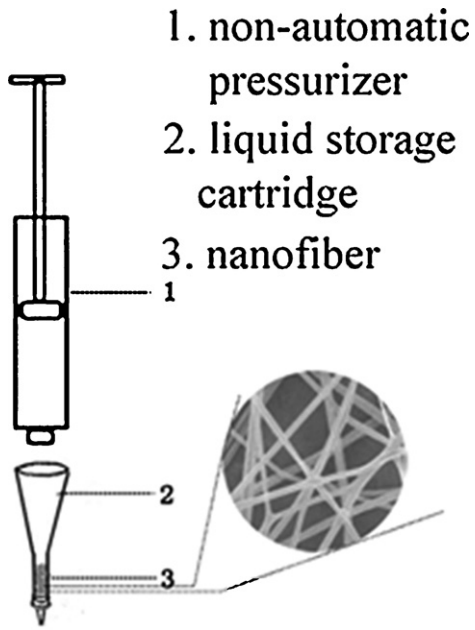

Fig. 2. The component of the pretreatment device.

2 mol L^{-1} sodium hydroxide aqueous solution was used to activate the nanofiber. After had been washed with water, the nanofiber was ready for sample pretreatment. Test solutions containing lead (II) were adjusted to the desired pH before being loaded into the cartridge. After loading and elution, the column was washed with buffer solutions (pH 8.5–9.0), and then desorbed with the one and the same 0.1 mol L^{-1} nitric acid solutions in a small volume (0.1 mL) throughout 3 times. The flow rate was carefully controlled in a slow dropwise manner in the adsorption and desorption procedures.

2.4.2. Chromatographic procedures

Analysis of metal ions by high performance liquid chromatography had been extensively reported before [28–30]. Based on the works of Dilli et al. [31] and Wang and Wai [32], we used the sodium dimethylaminaocarbodithioate as chromogenic agent. The mobile phase was composed of methanol, acetonitrile and water (40:35:25, v/v/v). The HPLC flow rate was 1.5 mL min^{-1}. The detection wavelength was 260 nm.

2.5. Application

The tap water, the lake water and the plasma provided by The Nanjing Blood Donor Service (Nanjing, China), which was donated from a healthy volunteer, were collected in the polytetrafluoroethylene centrifugal tube. 10 mL of water samples were adjusted to the desired pH with the buffer solution. A 0.5 mL nitric acid solution (5%, v/v) was added into 1 mL of the plasma sample. After agitation for 1 min and ultrasonic processing for 10 min, the mixture was centrifuged at 12,000 rpm for 5 min. The supernatant then was transferred into another centrifugal tube. The precipitate was washed with a 0.5 mL nitric acid solution twice. Then the supernatant which was collected into the same centrifugal tube was adjusted to the desired pH with sodium hydroxide solutions and buffer solutions. The pretreatment and the detection procedures given above were applied to the samples.

3. Results and discussion

3.1. Characterization

Identified by scanning electron microscope, illustrated in Fig. 3a and b, the diameter of the PS–DZ nanofiber was 200–400 nm, and the nanofiber was dense with network structure. Though PS was modified with dithizone, no morphological change was observed in the view of the SEM images shown in Fig. 3c.

PS–DZ nanofiber was also identified by the IR spectra, as shown in Fig. 4. Compared to the IR spectra of the PS nanofiber (Fig. 4a), many new peaks appeared in the IR spectra of PS–DZ nanofiber (Fig. 4b) from 1000 to 2000 cm^{-1}, which were similar to the IR spectra of dithizone. According to the literature [33], the new peaks at 1257 cm^{-1}, 1172 cm^{-1} and 1522 cm^{-1} were respectively due to C–N stretching vibration, C=S stretching vibration and N=N

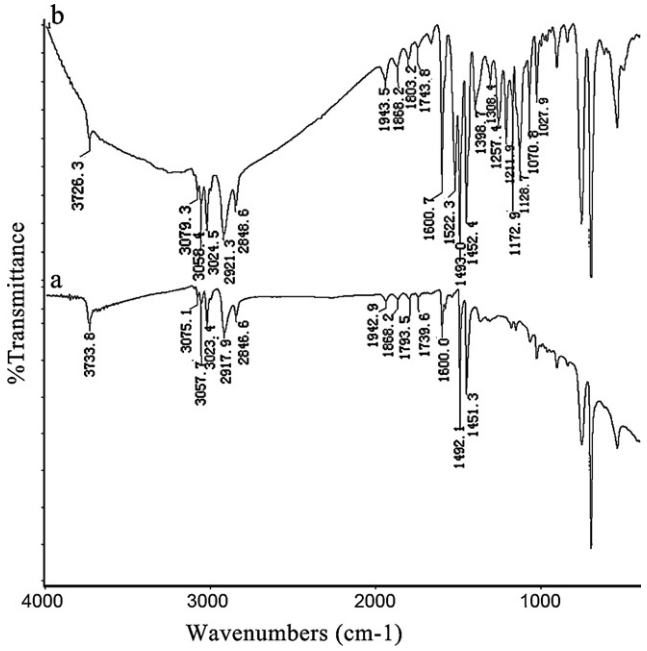

Fig. 4. IR spectra of PS nanofiber (a) and PS–DZ nanofiber (b).

stretching vibration donated by dithizone. It seems that dithizone was successfully impregnated in the PS nanofiber.

3.2. Activation of nanofiber

The PS–DZ nanofiber performed poorly without activation. The recovery of lead (II) was less than 20%. The commonly used activating solvent for PFSPE, such as methanol [14], did not improve the recovery very much. The sodium hydroxide aqueous solutions were found to activate the PS–DZ nanofiber effectively. Furthermore, the absorption was influenced by the concentration of sodium hydroxide aqueous solutions (Fig. 5). With 0.1–5.0 mol L^{-1} of sodium hydroxide aqueous solutions, the recovery improved correspondingly when the concentration of the sodium hydroxide aqueous solution increased, and was stable when the concentration of sodium hydroxide aqueous solutions was higher than 1 mol L^{-1}. In addition, the activation efficiency decreased when the methanol was added into the sodium hydroxide solutions. Finally, the 2.0 mol L^{-1} of sodium hydroxide aqueous solution was selected as the activating solution throughout the following work.

Dithizone is an S, N-donating ligand as shown in Fig. 12a. It can easily react with many heavy metal ions at particular pH [34]. Primary dithizonate is formed when dithizone reacts with the metal ion as an anion of monobasic acid (HDz^-) [35]. And dithizone dissolves in the alkaline aqueous medium in the form of the dithizonate whose polarity is stronger than that of the dithizone, but is undissolved in the neutral aqueous medium [36]. When

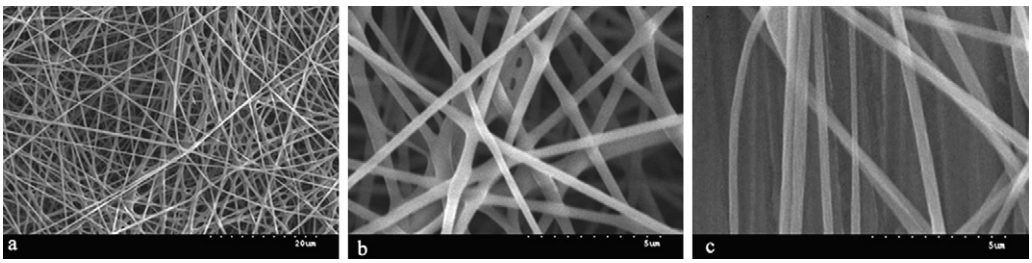

Fig. 3. Scanning electron microscope images of nanofiber: (a) PS–DZ nanofiber magnified 2k times, (b) PS–DZ nanofiber magnified 10k times, and (c) PS nanofiber magnified 10k times.

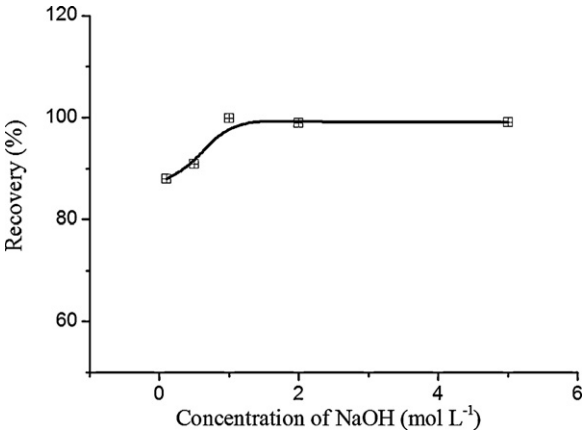

Fig. 5. Effect of the concentration of NaOH in the activation solution. Other conditions: sample pH = 8.5. eluent: 100 μL of 0.1 mol L^{-1} HNO_3 aqueous solution eluted 3 times with the same eluent. $N = 3$.

the dithizone was impregnated in the fiber, it was expected that the chelation between dithizone and lead (II) became more difficult in the neutral aqueous medium because of phase interfacial resistance, which caused the poor adsorption efficiency without activating the PS–DZ nanofiber. When the PS–DZ nanofiber was treated by strong alkaline aqueous solutions, dithizone on the nanofiber transformed into dithizonate (NaHDz), which was possibly easier to react with lead (II). That may be the reason that treating with methanol did not activate the PS–DZ nanofiber.

3.3. Effect of pH

The pH of the sample solutions is usually the most critical parameter on the SPE studies of metal ions [37,38]. Especially for the SPE of lead (II) in this trial based on the chelation, the pH of the sample solution is one of the decisive parameters for quantitative recovery of the analytes [39]. The effect of pH was investigated in the pH range of 3–9. As shown in Fig. 6, stable recoveries were obtained in the pH range of 7–9. For dithizone chelated respectively with zinc at the neutral pH, and cadmium in the strong alkaline solution [40], the investigation was carried out at pH 8.5.

3.4. Effect of organic solvent in the medium

The effect of the organic solvent was also investigated with methanol as a model solvent. The sample solutions containing 0–20% (v/v) of methanol were carried out to find out how the

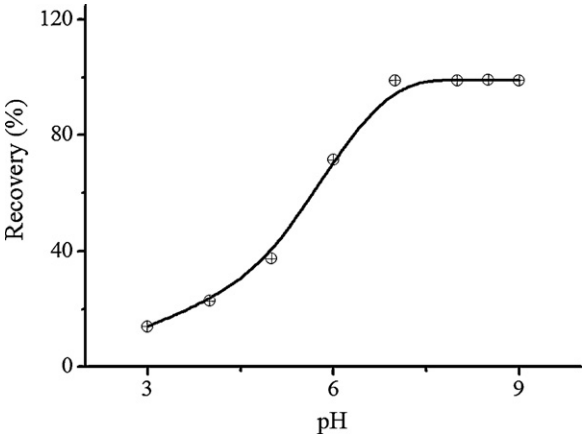

Fig. 6. Effect of pH on the retention of lead (II).

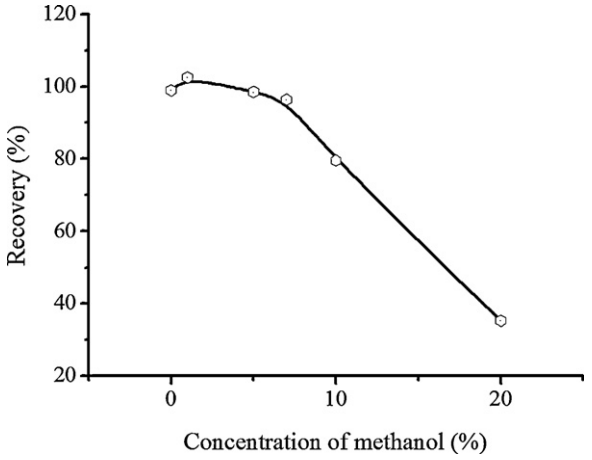

Fig. 7. Effect of organic solvent in the medium on the retention of lead (II).

organic solvent influenced the quantitative recovery. The result was given in Fig. 7. The existence of methanol impacted the absorption efficiency of the PS–DZ nanofiber notably when the concentration of methanol was higher than 7% (v/v). To obtain a good recovery, the ratio of organic solvent in the sample should be as less as possible.

3.5. Eluent

Chelation of dithizonate is pH sensitive. Plumbous dithizonate is instable in an acidic solution. For selection of the best eluent, various acidic solutions were studied for desorption of lead (II). The result revealed that nitric acid performed better on desorption of lead (II). Moreover, the addition of methanol was favorable for desorption (Table 1). However, a small amount of dithizone was swilled out from the nanofiber by absolute methanol which was an environmental pollutant. Therefore, the nitric acid aqueous solution was considered as the most suitable eluent. The concentration of nitric acid was an influential factor in the desorption procedure. As shown in Fig. 8, recovery was lower than 95% while the concentration of nitric acid was lower than 0.08 mol L^{-1}. Hence, 0.1 mol L^{-1} nitric acid was selected as a suitable desorption solution.

A decreased volume of eluent was good for detection sensitivity, but a small volume of eluent, for example, a 100 μL of 0.1 mol L^{-1} nitric acid aqueous solutions could not desorb the adsorbate entirely. To solve this problem, multi-washing processes which repeatedly used the one and the same acid solution were carried out. As presented in Table 2, the frequency of eluting should be at least twice, but in order to ensure the entire recovery, three times was more suitable.

3.6. Effect of the sample volume

In order to find out the effect of the sample volume on the sorption behavior of lead (II) on the PS–DZ nanofiber, 1–20 mL of lead (II) aqueous solutions containing 500 ng mL^{-1} of lead (II) in the desired

Table 1
Effect of eluent on the recoveries of lead (II). Eluent volume: 100 μL, eluting for 3 times. $N = 3$.

Type of eluent	Recovery (%)
0.05 M HNO_3	91.36 ± 2.31
0.1 M HNO_3	98.99 ± 2.34
0.1 M HCl	81.46 ± 1.90
0.1 M H_2SO_4	85.52 ± 2.53
0.05 M HNO_3 with 20% (v/v) MeOH	98.74 ± 2.68
0.05 M HNO_3 with 20% (v/v) MeOH	99.10 ± 2.46
MeOH	8.28 ± 3.67

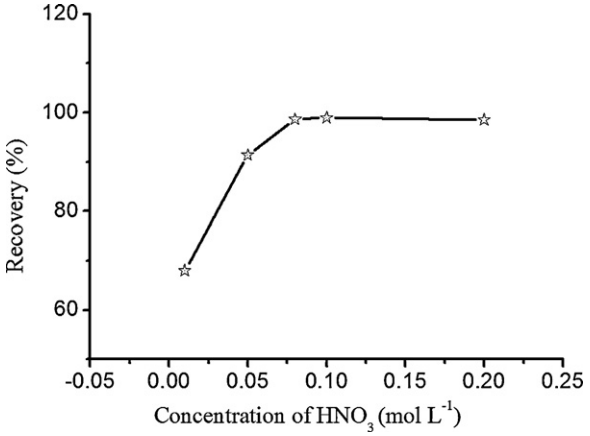

Fig. 8. Eluting effect of HNO_3 aqueous solution of different concentrations.

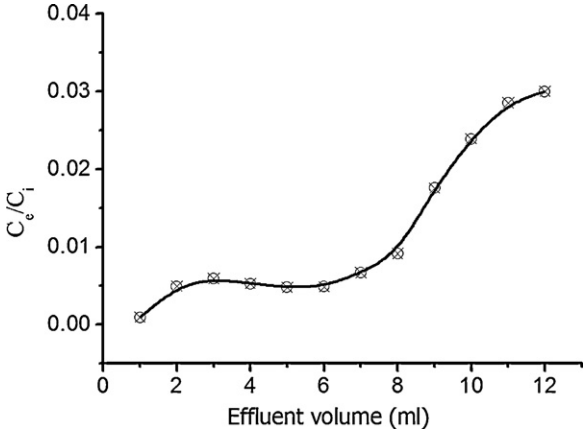

Fig. 10. Breakthrough volume of lead (II).

Table 2
Effect of the frequency of eluting. $N = 3$.

Times of eluting	Recovery (%)
1	91.35 ± 2.73
2	98.67 ± 1.79
3	98.99 ± 2.34
4	98.52 ± 3.13
5	98.61 ± 3.04

Table 3
Reutilization of PS–DZ nanofiber. $N = 3$.

Times of reutilization	Recovery (%)
0	98.99 ± 2.34
1	98.75 ± 2.16
2	99.03 ± 3.72
3	98.26 ± 2.58

pH were pretreated by the PS–DZ nanofiber. The result illustrated in Fig. 9 revealed that the recoveries of lead (II) from different sample volumes (1–20 mL) were quantitative.

3.7. Breakthrough capacity

To evaluate the amount of lead (II) sorbed per milligram on PS–DZ nanofiber under the operating conditions, the breakthrough capacity was calculated with the assumption that breakthrough occurs at $C_e/C_i = 0.01$; C_e is the concentration of lead (II) in the effluent, and C_i is the concentration of lead (II) in the influent [41]. 10 μg mL^{-1} of lead (II) solutions at the desired pH passed through the column packed with 5 mg of PS–DZ nanofiber. The concentration of lead (II) in each milliliter of the effluent was determined. The breakthrough capacity presented in Fig. 10 was calculated to be 16 μg mg^{-1} for the PS–DZ nanofiber.

3.8. Reutilization

The reutilization of PS–DZ nanofiber was also investigated. Sufficient nitric acid solution and water were used to clean the device before reutilization. Then the trial followed the optimum activation, adsorption and desorption procedures given above. The result was given in Table 3. The recoveries in three times of reutilization were quantitative. Although the PS–DZ nanofiber was reutilizable, it is recommended to be throwaway when used for determination of the trace of lead (II).

3.9. Effect of amounts of dithizone

The effect of amounts of dithizone in electrospun solutions was investigated in 0–20% mass ratio of PS. The result was given in Fig. 11. The nanofiber rarely sorbed lead (II) without dithizone, in contrast, the nanofiber modified with dithizone performed well. The recovery was over 98% in a mass ratio range of 5–20%. However, a little dithizone visibly brushed off from PS–DZ nanofiber whose contents of dithizone were over 10% when the nanofiber was being activated.

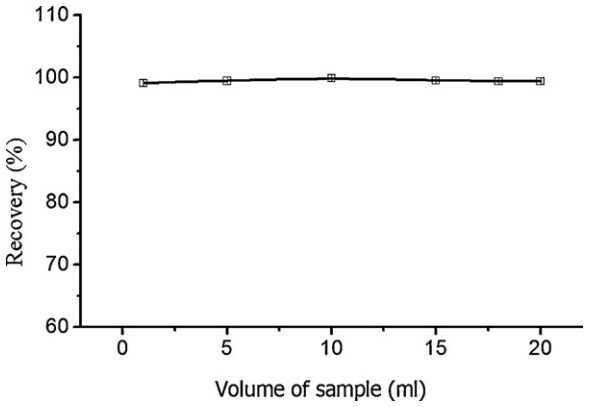

Fig. 9. Effect of the sample volume.

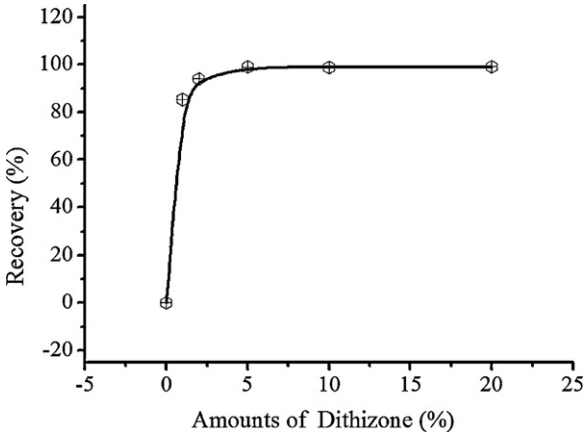

Fig. 11. Effect of amounts of dithizone in PS–DZ nanofiber. Each electrospun solution was electrospinned in the same conditions.

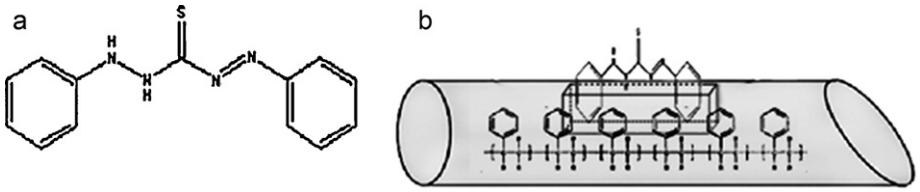

Fig. 12. The molecular structure of dithizone (a) and the representative schema of PS–DZ nanofiber (b).

3.10. Effect of foreign ions

In order to evaluate the possibility of selective recovery of analyte ions, the effect of coexisting ions needs to be considered. Various amounts of metal ions were added to an aqueous solution containing 500 ng mL^{-1} of lead (II), and the optimum procedure was followed. The result including the tolerance limit and the relevant recovery was given in Table 4. The metal ions normally present in natural water and biological samples did not interfere under the optimized experimental conditions, which implied the method was desired in view of applications on real samples.

3.11. Difference of polymers backbone

Dithizone was impregnated in different sorts of polymer nanofiber, and the performance on the adsorption of lead (II) was investigated. AR–DZ nanofiber was destroyed when activated by a sodium hydroxide solution for high solubility of acrylic resin in alkaline solution. PAN–DZ nanofiber performed almost as well as PS–DZ nanofiber in the adsorption and desorption procedure. However, a part of the dithizone from the PAN–DZ nanofiber was brushed off in the activation procedure. It was suggested that dithizone in PAN–DZ nanofiber was just inlayed on the surface of the nanofiber, in contrast, dithizone in PS–DZ was not only inlayed on the surface of the nanofiber but also immobilized by the conjugation of the benzene ring of dithizone and polystyrene (Fig. 12b). Therefore, the PS–DZ nanofiber was more stable than PAN–DZ nanofiber, and it was selected as the absorbent in our work.

3.12. Applications

The real samples, including lake water in a tourism area, tap water and plasma donated from a healthy volunteer, were used to investigate how PS–DZ nanofiber performed in the real samples. Various amounts of lead (II) were added to the real samples to examine recovery of lead (II). As illustrated in Table 5, PS–DZ nanofiber performed well in the water samples with quantitative recoveries. However, the performance in the plasma was not as good as in the water samples. Probably, a part of lead (II) coprecipitated with the protein, which could not be released by the nitric acid solution without digestion.

Table 4
Effect of coexisting ions on the recoveries of lead (II). $N = 3$.

Ions	Added as	Concentration (mg mL^{-1})	Recovery (%)
Na^+	NaCl	5	93.53 ± 2.58
K^+	KCl	3	96.61 ± 2.40
Mn^{2+}	$MnSO_4$	0.2	93.24 ± 3.36
Zn^{2+}	$ZnNO_3$	0.2	91.79 ± 3.53
Hg^{2+}	$HgAc_2$	0.5	98.85 ± 2.39
Cu^{2+}	$CuSO_4$	0.5	97.12 ± 2.44
Ca^{2+}	$CaAc_2$	0.3	93.41 ± 3.13
Al^{3+}	$AlCl_3$	0.4	98.83 ± 2.96
Fe^{3+}	$FeCl_3$	0.4	98.03 ± 3.38

Table 5
The determination of lead (II) in some real sample. $N = 3$.

Sample	Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
Lake water	–	10.26 ± 1.73	–
	50	59.37 ± 2.18	98.22
	100	108.95 ± 1.85	98.69
Tap water	–	ND	–
	50	49.63 ± 2.35	99.26
	100	98.71 ± 1.89	98.71
Plasma	–	ND	–
	50	39.68 ± 2.81	79.36
	100	80.54 ± 2.52	80.54

ND: not detected.

4. Conclusions

The PS–DZ nanofiber was used as the sorbent for solid phase extraction of lead (II). The most important characteristic of the PS–DZ nanofiber was its excellent selectivity towards lead (II). A novel modification for sorbent by co-electrospinning of the polymer solution containing functional molecules was developed, which was simple and rapid. The performance of the functional PS–DZ nanofiber in retaining lead (II) was investigated by packing it into a novel sample pretreatment device. The conditions relevant to the performance of PS–DZ nanofiber were optimized for the quantitative recovery of lead (II). The pretreatment device was practicable in the analysis of water samples. The enrichment factor of PS–DZ nanofiber for lead (II) was higher than that of other SPE materials [42–44] when used in pretreatment of the same volume of liquid samples. Though the application in plasma without digestion was not as efficacious as in the water samples, this device with the PS–DZ nanofiber could be applicable in screening blood lead or lead in urine, for the simple and rapid procedures and small sample volumes it required.

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