Polyelectrolyte multilayers on magnetic silica as a new sorbent for the separation of trace copper in food samples and determination by flame atomic absorption spectrometry

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ABSTRACT

A novel magnetic silica sorbent with polyelectrolyte multilayers (PEMs) on its surface was prepared, and the sorbent was used for the magnetic solid phase extraction (MSPE) of trace Cu^{2+} in drinking water with flame atomic absorption spectrometry (FAAS) as the detector. The experimental parameters for the MSPE procedure, such as the pH, desorption conditions, ultrasonic time and co-existing ions effects, were investigated. The adsorption capacity of the new sorbent was 14.7 mg g^{-1} for Cu^{2+}. The detection limit of the developed method was 0.23 ng mL^{-1} for Cu^{2+} with an enrichment factor of 95.7. The analytical data obtained from the certified reference water and rice samples were in good agreement with the certified values. This method was also successfully applied to the determination of trace Cu^{2+} in different food samples with satisfactory results.

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1. Introduction

Copper is an essential element not only for life in mammals but also for plants, and copper plays an important role in carbohydrate and lipid metabolism. Copper has many biological effects as an essential element, including toxic effects [1]. In general, a daily copper intake of 1.5–2 mg is essential, and a copper level of 40 ng mL^{-1} is required for the normal metabolism of many living organisms [1,2]. However, copper at higher levels is toxic, and severe oral intoxication primarily affects the blood and kidneys. Because of these and other copper effects on the taste of water and corrosion, the copper content in water and food must be controlled on a daily basis, and the European Commission has fixed a limit of 2 µg mL^{-1} for copper in drinking water. The allowed limit of copper is set to 1.3 µg mL^{-1} in the USA, which is similar to that established in Canada (1.0 µg mL^{-1}) [3,4]. Therefore, there is an increasing need to monitor copper levels in food samples at ever decreasing concentrations. For this purpose, highly sensitive, simple, rapid and inexpensive analytical methods are necessary.

FAAS is a popular elemental detection technique with the characteristics of good precision, simple operation and lower cost. However, this technique's poor sensitivity limits its applications for trace level analysis in complicated samples [5]. To solve this problem, combination of the separation–preconcentration procedure and FAAS detection is a popular choice. Among the separation–preconcentration procedures, solid phase extraction (SPE) has become increasingly popular for the enrichment of metal ions prior to their determination [6,7], many kinds of materials were developed as SPE sorbent for metal separation–preconcentration [8–11]. The SPE technique has the characteristics of a high preconcentration factor, rapid phase separation and convenient combination with different elemental detectors [12]. However, the typical SPE procedure includes two separate operation steps, the adsorption (extraction) step and the elution step. Additionally, an SPE cartridge and pump are needed for the SPE procedure, which increase the cost of the analysis. The SPE procedure is often time-consuming, and the analytical time is even longer for large sample volumes.

Recently, magnetic materials have received increasing attention due to their desired characteristics, such as unique magnetic response, low cytotoxicity, ease of chemical surface modification and great application potential in various fields [13–16]. Magnetic solid phase extraction (MSPE) based on the magnetic response of the magnetic materials is now applied to the preconcentration of metal ions in complicated samples [17–19]. Compared with conventional SPE based on a cartridge, MSPE can greatly simplify the SPE procedure. Both the adsorption step and the desorption step are completed in the same container assisted by a magnet. The whole operation time is greatly reduced, and the SPE procedure becomes inexpensive and easy to perform without an SPE cartridge and pump.

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The layer-by-layer (LbL) assembling technique [20,21] is a convenient and versatile technique for the bottom-up assembly of multilayered polymer films. This method allows the deposition of oppositely charged polyelectrolytes on different types of solid substrates. The versatility of the LbL process has allowed the fabrication of thin multilayer films made of synthetic polyelectrolytes, DNA, lipids and proteins, which has resulted in a boost of novel applications in recent years [22,23]. Recently, polyelectrolyte multilayers (PEMs) obtained by the LbL technique have attracted the attention of researchers in analytical chemistry [24–31]. Unfortunately, the published reports have primarily investigated the PEMs applications in chromatography with organic analytes. Reports describing PEMs as the extraction media for metal ions are rare.

In this work, PEMs were successfully fabricated on a magnetic silica sorbent, and the obtained sorbent was used as an MSPE sorbent for the extraction of trace Cu^{2+} in water samples. The developed MSPE–FAAS method was successfully applied to the determination of Cu^{2+} in drinking water and rice samples.

2. Experimental

2.1. Apparatus

A TAS-986 atomic absorption spectrometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) with a copper hollow cathode lamp (KY-1) was used for the determination. The instrumental parameters used were those recommended by the manufacturer. Elemental component information of the polyelectrolyte multilayers on magnetic silica (PEMMS) sorbent was obtained by an Element Analyzer (Flash 2000, Thermo Electron). FT-IR spectra in KBr were recorded by a WQF-510 FT-IR spectrometer (Beijing Rayleigh Analytical Instrument Co., Ltd., Beijing, China). The pH values were measured with a PHS-3C pH meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). An ultrasonicator (KQ116, 40 kHz, Kun Shan Ultrasonic Instruments Co., Ltd., Beijing, China) was used to disperse the magnetic sorbent in solution. A magnet (Nd–Fe–B, 60 mm × 35 mm × 10 mm) was used for the magnetic separation.

Fig. 1. Schematic of the preparation of the PEMMS sorbent.

2.2. Standard solution and reagents

Poly(allylamine hydrochloride) (PAH, Sigma Aldrich, average $M_w \sim 58,000$), poly(ethylene-alt-maleic anhydride) (PEMA, Sigma Aldrich, typical M_w 100,000–500,000), N,N-dimethylformamide (DMF) (AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and tetraethoxysilane (TEOS, AR) were used without further purification. Ellman reagent (5,5-dithio-bis-(2-nitrobenzoic acid), Sigma Aldrich) was used for the determination of the thiol group on the sorbent. The stock standard solution (1.000 g L^{-1}) of Cu^{2+} was prepared by dissolving an appropriate amount of copper nitrate (AR, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) in deionized water. Acetate–acetic acid buffer (pH 3.0–5.0) and NaOH solution (0.1 mol L^{-1}) were used for pH adjustment. Different stock solutions (1.000 g L^{-1}) of potentially interfering ions were prepared according to the conventional method. Working solutions were prepared by appropriate dilution of the stock solutions. The laboratory glassware was kept in a 5% (v/v) nitric acid solution overnight. Afterwards, the glassware was rinsed thoroughly with deionized water and dried. Deionized water (18.2 MΩ cm) was used throughout the experiment.

2.3. Preparation of the sorbent

The preparation of the PEMMS sorbent is illustrated in Fig. 1. Firstly, the magnetic Fe_3O_4 particles were synthesized by co-precipitation of a mixture of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ with concentrated aqueous ammonia. The obtained magnetic Fe_3O_4 was embedded in silica microspheres to obtain $Fe_3O_4@SiO_2$ microspheres through a modified Stöber method [32]. Then, the polyelectrolyte multilayers were fabricated onto the surface of the magnetic $Fe_3O_4@SiO_2$ microsphere through a layer-by-layer (LbL) technique. PAH (5 mM) aqueous solution (with 0.3 M NaCl) was prepared as the cationic solution. The anionic solution was prepared by dissolving the appropriate amount of thiol modified PEMA (TMPEMA) in NaOH with stirring. The TMPEMA solution (5 mM, with 0.3 M NaCl) was obtained by step dilution. The TMPEMA was obtained by PEMA and ʟ-cysteine (1:1, molar ratio) reacting in DMF at 110 °C for 7 h with magnetic stirring. The details of the synthesis procedure are shown in the Supplementary information, Fig. S1. The PEMs were fabricated onto the magnetic $Fe_3O_4@SiO_2$ microspheres by the LbL technique as follows: the magnetic $Fe_3O_4@SiO_2$ microspheres were dispersed into PAH solution with ultrasonication for 10 min, and the particles were separated from the PAH solution by a magnet and rinsed with deionized water. Next, the particles were treated in the same manner as in the TMPEMA solution to form a PAH/TMPEMA bi-layer on the surface of the magnetic $Fe_3O_4@SiO_2$ microspheres. The whole procedure was repeated nine times to yield a magnetic silica sorbent with ten bi-layers on its surface.

2.4. General procedure for MSPE

Two hundred milliliters of Cu^{2+} standard solution (or sample solution) was transferred to a 250 mL beaker, the pH of the solution was adjusted to 6.0, and 70 mg sorbent was added. After ultrasonication for 6 min, the magnetic sorbent was separated easily and quickly by a magnet, and the supernatants were decanted directly. For desorption of the target ion, the sorbent was mixed with 2.0 mL thiourea (2%, m/v) in nitric acid (0.1 M) solution. After 2 min ultrasonication of the mixture, the eluent was collected with a magnet outside the bottom of the beaker. Finally, the collected eluent was analyzed by FAAS.
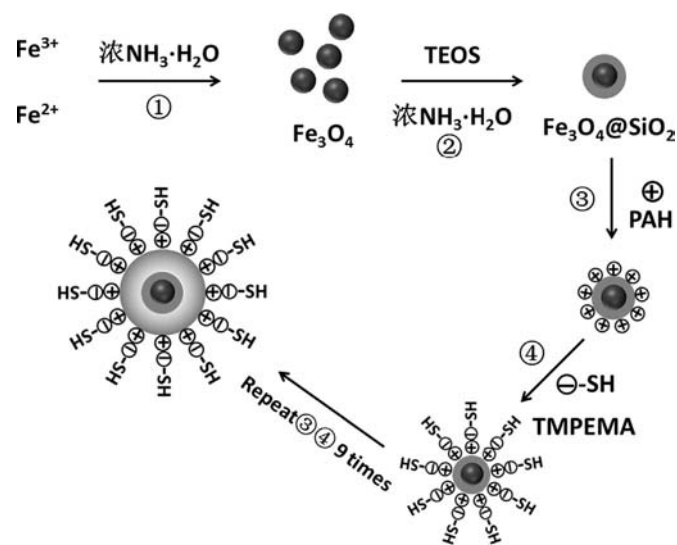
2.5. Sample preparation

Tap water and boiler water samples were collected from the campus (Henan University of technology, Zhengzhou, China). Well water was collected from a well in a village (Zhengzhou, China). The drinking water samples were filtered through filter paper, and subsequently filtered through a membrane (0.45 μm). The pH of the samples was adjusted to 6.0 before analysis.

Rice samples: The rice samples were digested by pressure assisted digestion method. 4.000 g of rice (purchased in the supermarket) was weighed into a 150 mL polytetrafluoroethylene (PTFE) digestion vessel, and 8.0 mL concentrated nitric acid and 24.0 mL H_2O_2 (30%, w/v) were added, then the vessel was placed overnight without cover. After that, the vessel was sealed, and then placed into a closed stainless steel container, and the container was heated in a drying oven at temperature of 100 °C for 1 h, then at temperature of 140 °C for 3 h. After that, the container was cooled to ambient temperature. The vessel was put out, and the digested solution was heated and evaporated to dryness on a hot plate. The residue was dissolved in 5% (v/v) nitric acid, and transferred into a 2000 mL volumetric flask and diluted to volume with deionized water.

Certified reference rice sample (GBW10044(GSB-22)): The sample was treated by the similar procedure for the rice sample above.

3. Results and discussion

3.1. Characterization of the PEMMS sorbent

The PEMMS sorbent was characterized by FT-IR (Fig. 2). As shown in Fig. 2, the comparison of the typical absorption peaks of the PEMMS sorbent and $Fe_3O_4@SiO_2$ confirmed the successful assembling of PEMs on the surface of $Fe_3O_4@SiO_2$. The peaks at 569 (575) cm^{-1} and 1090 (1084) cm^{-1} are attributed to the Fe–O stretching band of Fe_3O_4 and the Si–O stretching band of silica, respectively. Furthermore, the presence of the C–H bond of SH–CH_2–CH_2–CH_2– was reflected by the peaks at 2931 cm^{-1}. The peaks at 1630 cm^{-1}, 1560 cm^{-1}, and 1338 cm^{-1} were attributed to the C=O, N–H and C–N bands of the amide.

The most important functional group of the prepared sorbent for MSPE was the thiol group, and the amount on the surface of the sorbent was a key factor for its analytical performance. The amount of thiol groups on the PEMMS was 0.26 mmol g^{-1},
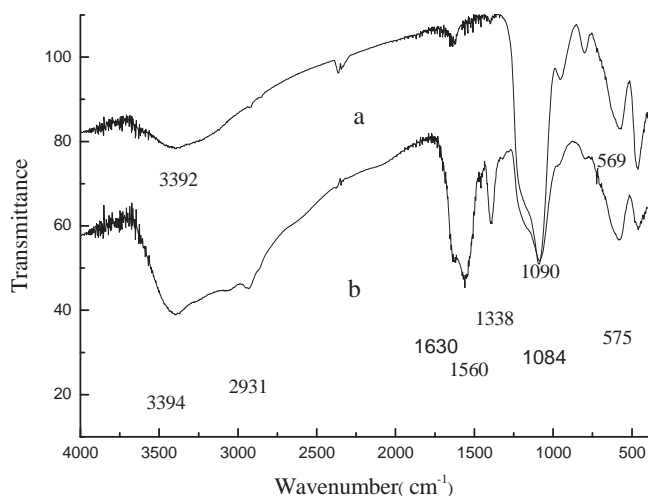
according to the Ellman method [33], which was in a good agreement with the result (0.25 mmol g^{-1}) obtained by the elemental analyzer (the full results of the elemental analysis are shown in the Supplementary information, Table S1). This brings the sorbent great potential for the application of trace metal preconcentration with large adsorption capacity. The magnetic properties were also characterized, and the results are shown in the Supplementary information (Fig. S2).

3.2. Effect of pH

The pH value plays a key role in the MSPE procedure. The adsorption behavior of Cu^{2+} on the PEMMS sorbent was studied according to the general procedure for MSPE. Fig. 3 shows the effect of pH on the extraction efficiency (R%) of Cu^{2+} on the PEMMS sorbent. It could be observed that Cu^{2+} was adsorbed quantitatively (R larger than 90%) on the PEMMS sorbent within a pH range of 5.5–7.0. For further experiments, pH 6.0 was chosen for the preconcentration of Cu^{2+}.

3.3. Optimization of desorption conditions

From the results in Fig. 3, it can be seen that the extraction efficiency of Cu^{2+} sharply decreased at the lower pH range. Thus, a typical acid eluent is a possible choice for the quantitative desorption of the adsorbed analyte. Unfortunately, when using nitric acid solution with different concentrations (0.1–1.0 M) as the eluent, the recoveries of Cu^{2+} were approximately 40–70%. To improve the desorption recovery of the analyte, a mixture of thiourea and nitric acid solution was selected as the eluent. The concentration of the mixture was optimized, and quantitative desorption could be obtained by using thiourea (2%, m/v) in nitric acid solution (0.1 M) as the eluent.

Using thiourea (2%, m/v) solution in nitric acid (0.1 M) solution as the eluent, the effect of the eluent volume on the desorption of Cu^{2+} was studied with eluent volume varying from 1.0–5.0 mL. The results showed that 2.0 mL was sufficient to recover Cu^{2+} quantitatively. Therefore, 2.0 mL eluent was selected for the subsequent experiment.

3.4. Effect of ultrasonic time

To minimize the pretreatment time, the ultrasonic time for the adsorption process and desorption process was also investigated. For the adsorption process, the effect of the ultrasonic time on the extraction efficiency of Cu^{2+} was studied according to the general
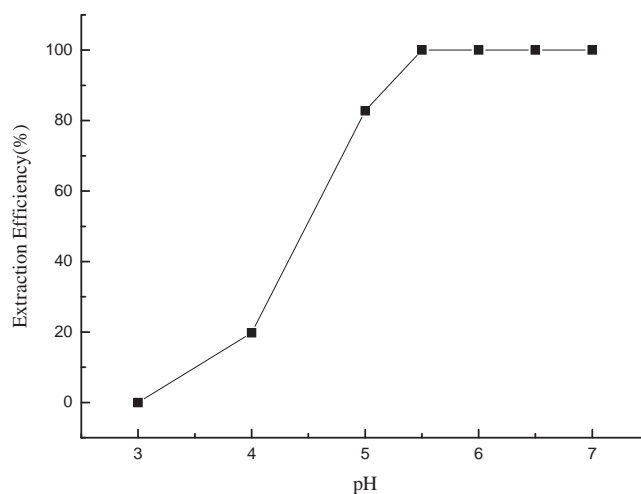
Fig. 2. FT-IR spectra of the sorbents. (a: FT-IR spectra of $Fe_3O_4@SiO_2$; b: FT-IR spectra of PEMMS sorbent).

Fig. 3. Effect of pH on extraction efficiency of Cu^{2+} on the PEMMS sorbent.

procedure for MSPE, with the ultrasonic time varying from 3 to 10 min. Fig. 4 shows that quantitative extraction could be obtained with ultrasonic times greater than 5 min. For the desorption
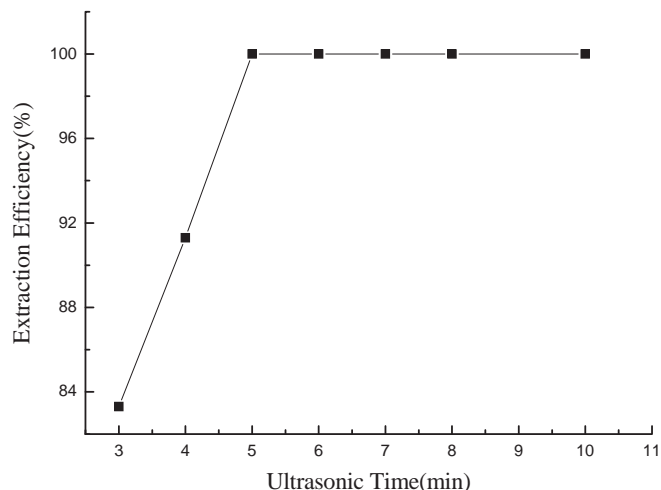

Fig. 4. Effect of ultrasonic time on extraction efficiency of Cu^{2+} on the PEMMS sorbent.

Table 1
Tolerance limits of co-existing ions.

Ions	Tolerable concentration ($\mu g\,mL^{-1}$)	Recovery (%)
K^+	2000	92.9
Na^+	2000	101.8
Mg^{2+}	1000	107.5
Zn^{2+}	50	102.6
Ni^+	50	95
Co^+	20	91.49
Ca^{2+}	20	94.7
Pb^{2+}	20	91.48
Cd^{2+}	20	95.8
Ag^+	1.0	102.5
AsO_2^-	1.0	102.4
AsO_4^{3-}	10	101.6
Hg^{2+}	0.2	100

process, the experimental results showed that 2 min was adequate for quantitative recovery of Cu^{2+} adsorbed on PEMMS sorbent with thiourea (2%, m/v) in nitric acid solution (0.1 M) as the eluent. Therefore, 6 min of ultrasonic time for adsorption and 2 min of ultrasonic time for desorption were chosen.

3.5. Selectivity of the ion imprinted sorbent

The effect of co-existing ions on the preconcentration and determination of the studied analyte was investigated. In this experiment, the Cu^{2+} standard solution ($10.0\,ng\,mL^{-1}$) containing the added interfering ions was treated according to the general procedure for MSPE. The content of Cu^{2+} in the eluent was determined to calculate the recovery of the analyte. The tolerable concentration of the co-existing ions, defined as the maximum concentration of co-existing ion that would achieve $> 90\%$ recovery of Cu^{2+}, are given in Table 1. Most of the cations had a large tolerable concentration under the selected conditions. However, the tolerable concentrations of Hg^{2+}, Ag^+ and AsO_2^- were much smaller than the other metal ions. This could be explained by the fact that the binding ability of metal ions to the –SH group sorted in descending order is as follows: $Hg^{2+} > Ag^+ > Cu^{2+} >$ other metal ions. Stronger binding ability to the –SH group led to (Hg^{2+}, Ag^+) smaller tolerable concentration for Cu^{2+} determination and AsO_2^- was also showed great affinity to SH group. Fortunately, the tolerable concentrations of Hg^{2+} ($0.2\,\mu g\,mL^{-1}$) AsO_2^- ($1.0\,\mu g\,mL^{-1}$) and Ag^+ ($1.0\,\mu g\,mL^{-1}$) were still acceptable in most application cases. Therefore, it could be concluded that the PEMMS sorbent is fairly selective.

3.6. Sorbent regenerability and adsorption capacity

The regenerability and stability of the sorbent was investigated by testing Cu^{2+} standard solution according to the general procedure for MSPE using the same portion of sorbent (70 mg). The sorbent could be reused up to 20 times while maintaining recoveries of analyte greater than 90%.

The adsorption capacity of the PEMMS sorbent was studied to evaluate the amount of sorbent required to quantitatively concentrate the analytes from a given solution. The adsorption isotherm of Cu^{2+} on the PEMMS sorbent could be simulated by the Langmuir equation, and the maximum adsorption capacity

Table 2
Comparative data from recent studies on offline SPE/FAAS systems.

Analyte	Absorbent	Adsorption capacity ($mg\,g^{-1}$)	Detection limit ($ng\,mL^{-1}$)	Enrichment factor	Sample volume and extraction time	Eluent/volume
Cu^{2+}	Multi-walled carbon nanotubes	–	1.46	60	600 mL 2.0 mL min^{-1}	10 mL HNO_3 (2.0 M) [34]
Pb^{2+} Cu^{2+} Cd^{2+}	Gallic acid modified silica gel	Pb:12.63 Cu:15.38 Cd:6.09 Ni:4.62	Pb:0.58 Cu:0.86 Cd:0.65	200	2000 mL	10 mL HCl (0.05–0.5 M, 0.1–0.5 M) [35]
Cu^{2+} Fe^{3+} Zn^{2+}	Modified Dowex optipore V-493	Cu:2.55 Fe:4.05 Zn:2.82	Cu:1.14 Fe:2.01 Zn:0.14	37	250 mL 5.0 mL min^{-1}	7 mL HCl (1.0 M) [36]
Cu^{2+} Zn^{2+} Mn^{2+}	2,6-dichlorophenyl-3,3-bis(indolyl) methane loaded on Amberlite XAD-16	Cu:70.6 Zn:64.3 Mn:60.1	Cu:1.9 Zn:1.5 Mn:2.6	35	1350 mL	6 mL HNO_3 (4.0 M) in acetone[37]
Cu^{2+} Ni^{2+}	MWCNTs impregnated with D2EHPA-TOPO mixture	Cu:4.90 Ni:4.78 Zn:4.82	Cu:50 Ni:40 Zn:60	25	100 mL	10 mL HNO_3 (2.0 M) [38]
Cu^{2+}	Modified soybean hull	18.0	0.8	18	50 mL 3.0 mL min^{-1}	2.0 mL HCl (1.0 M)[39]
Cu^{2+}	PEMs on magnetic silica	14.7	0.23	95.7	200 mL 6 min	2.0 mL HCl (1.0 M) (this work)

Table 3
Analytical results for Cu^{2+} in drinking water and rice samples (mean $\pm$ SD, $n=3$).

Sample	Added	Founded	Recovery (%)
Boiler water (ng mL^{-1})	0	2.4 $\pm$ 0.05	
	5	7.11 $\pm$ 0.14	95
	10	12.71 $\pm$ 0.32	103
Tap water (ng mL^{-1})	0	2.46 $\pm$ 0.30	
	5	7.31 $\pm$ 0.13	97
	10	12.53 $\pm$ 0.43	100
Well water (ng mL^{-1})	0	1.41 $\pm$ 0.10	
	5	6.73 $\pm$ 0.03	106
	10	12.54 $\pm$ 0.38	111
Thai fragrant rice (µg g^{-1})	0	1.03 $\pm$ 0.12	
	2.5	3.88 $\pm$ 0.13	114.1
	5	5.80 $\pm$ 0.20	95.4
Glutinous rice (µg g^{-1})	0	0.90 $\pm$ 0.06	
	2.5	3.26 $\pm$ 0.23	94.4
	5	5.89 $\pm$ 0.15	99.8
Rice from Northeast China (µg g^{-1})	0	0.96 $\pm$ 0.08	
	2.5	3.45 $\pm$ 0.09	99.6
	5	5.90 $\pm$ 0.06	98.9

was 14.7 mg g^{-1} (the adsorption isotherm curve is shown in the Supplementary information, Fig. S3).

3.7. Analytical performance

Under the optimized experimental conditions, the analytical performance of this method was evaluated. Based on the definition of IUPAC, the limit of detection (3σ) of this method was 0.23 ng mL^{-1} for Cu^{2+}, and the relative standard deviation (RSD) was 2.1% ($c=10$ ng mL^{-1}, $n=5$). The calibration graph for the preconcentration procedure was $A=0.01137C+0.0096$ ($r^2=0.9922$) with a linear range of 1–30 ng mL^{-1}. The enrichment factor (EF, calculated as the ratio of the slopes of the calibration graphs with and without the preconcentration procedure, respectively) was 95.7.

Compared with other reported offline SPE/FAAS systems (Table 2), the developed method exhibited a lower detection limit with a larger enrichment factor. The significant difference of the extraction time must be addressed. The extraction time was longer than 50 min in most reported offline SPE/FAAS methods; however, the extraction time was only 6 min for the developed method, which benefits from the characteristics of MSPE. A simple and selective analytical method with better analytical performance was developed by coupling the simple LbL technique with a fast MSPE procedure.

3.8. Sample analysis

For real sample analysis, the standard calibration curve method was employed. To evaluate the validity of the procedure, the method was applied to the determination of Cu^{2+} in two certified reference samples (GBW08607 water sample and Certified reference rice sample (GBW10044(GSB-22))). The analytical results showed a good agreement between the determined values (water sample 10.52 $\pm$ 0.20 ng mL^{-1}, rice sample 2.71 $\pm$ 0.22 µg g^{-1}) and the certified values (water sample 10.45 $\pm$ 0.10 ng mL^{-1}, rice sample 2.60 $\pm$ 0.10 µg g^{-1}).

The proposed method was also applied to the determination of trace Cu^{2+} in drinking water and rice samples. The analytical results and the recoveries for the drinking water samples are given in Table 3. The recovery for the food samples was between 94.4% and 114.1%.

4. Conclusions

A new type of sorbent for MSPE was prepared through the layer-by-layer assembling method. The prepared PEMMS sorbent exhibited fast adsorption kinetics, high selectivity, and high adsorption capacity for Cu^{2+}. MSPE based on the PEMMS sorbent was a combination of a simple preparation technique and a quick extraction procedure, and this approach might provide an effective and quick solution to the separation of trace metal ions in samples with complicated matrices.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.07.003.

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