Polyelectrolyte Multilayers on Magnetic Silica as a New Sorbent for the Separation of Trace Silver in the Leaching Solutions of Antibacterial Products 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 was used for Magnetic Solid Phase Extraction (MSPE) of trace A$^+$ via Flame Atomic Absorption Spectrometry (FAAS). The experimental parameters for the MSPE procedure, such as the pH, type, and concentration of eluent, ultrasonic time and effects of co-existing ions were investigated. The detection limit of the developed method was 0.17 ng/mL for Ag$^+$ with an enrichment factor of 35. This method was also successfully applied to the determination of trace Ag$^+$ in the leaching solution of different antibacterial products with satisfactory results.*

KEYWORDS: *Polyelectrolyte multilayers; Magnetic solid phase extraction; Silver; Antibacterial products; FAAS.*

INTRODUCTION

Silver and silver ions are classified as broad-spectrum anti-microbial agents and are well-known to have strong inhibitory and bactericidal effects [1,2]. It is generally believed that silver reacts with proteins by combining with thiol groups, which leads to the inactivation of the protein[3]. Thus the delivery of silver is critical for the antibacterial effect of the materials. There is a great risk of silver leaching from antibacterial products into the environment, and drinking water and surface water quality standards in China are set to 0.05 ng/mL.

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Therefore, there is an increasing need to monitor silver levels in the leaching solution of antibacterial products at ever decreasing concentrations. For this purpose, highly sensitive, simple, rapid, and inexpensive analytical methods are necessary.

Flame Atomic Absorption Spectrometry (FAAS) is a widely-used elemental detector with the characteristics of good precision, simple operation, and low cost. However, its poor sensitivity limits its use for analysis of trace analytes in complicated matrices [4]. To solve this problem, combining the separation-preconcentration procedure with FAAS detection is were choice. Among the separation-preconcentration procedures, Solid Phase Extraction (SPE) has attracted more and more attention in the field of metal enrichment. The SPE technique has the following characteristics: A high preconcentration factor, rapid phase separation, and convenient combination with different elemental detectors [5]. However, the typical SPE procedure includes two separate operation steps (the adsorption [extraction] step and the elution step), a SPE cartridge and pump are required, and the procedure is often time-consuming particularly 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 [6-8]. Magnetic Solid Phase Extraction (MSPE) based on magnetic materials is now applied to the separation and preconcentration of metal ions in complicated samples [9-11]. Compared with the conventional SPE procedure using a cartridge, MSPE can greatly simplify the SPE procedure. Both the adsorption step and the elution step are completed in the same container assisted by a magnet. The whole operation time is greatly reduced, and the SPE procedure is less expensive and easier to perform.

The Layer-by-Layer (LbL) assembling technique [12, 13] is a convenient and versatile technique for the bottom-up assembly of multilayered polymer films 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[14, 15]. Recently, PolyElectrolyte Multilayers (PEMs) obtained by the LbL

technique have attracted the attention of researchers in analytical chemistry [16-22]. Unfortunately, the published reports have primarily investigated PEM applications in chromatography with organic analytes, while few of the studies report on PEM applications with metal ion analytes [23].

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 Ag^+ in the leaching solution of antibacterial products. The developed MSPE-FAAS method was successfully applied to the determination of silver leaching in antibacterial products.

EXPERIMENTAL SECTION
Apparatus
A TAS-986 atomic absorption spectrometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) with silver 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 PEMs 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.

Standard solution and reagents
Poly(allylamine hydrochloride) (PAH, Sigma-Aldrich, average M_w ~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) of Ag^+ was prepared by dissolving an appropriate amount of silver nitrate (AR,
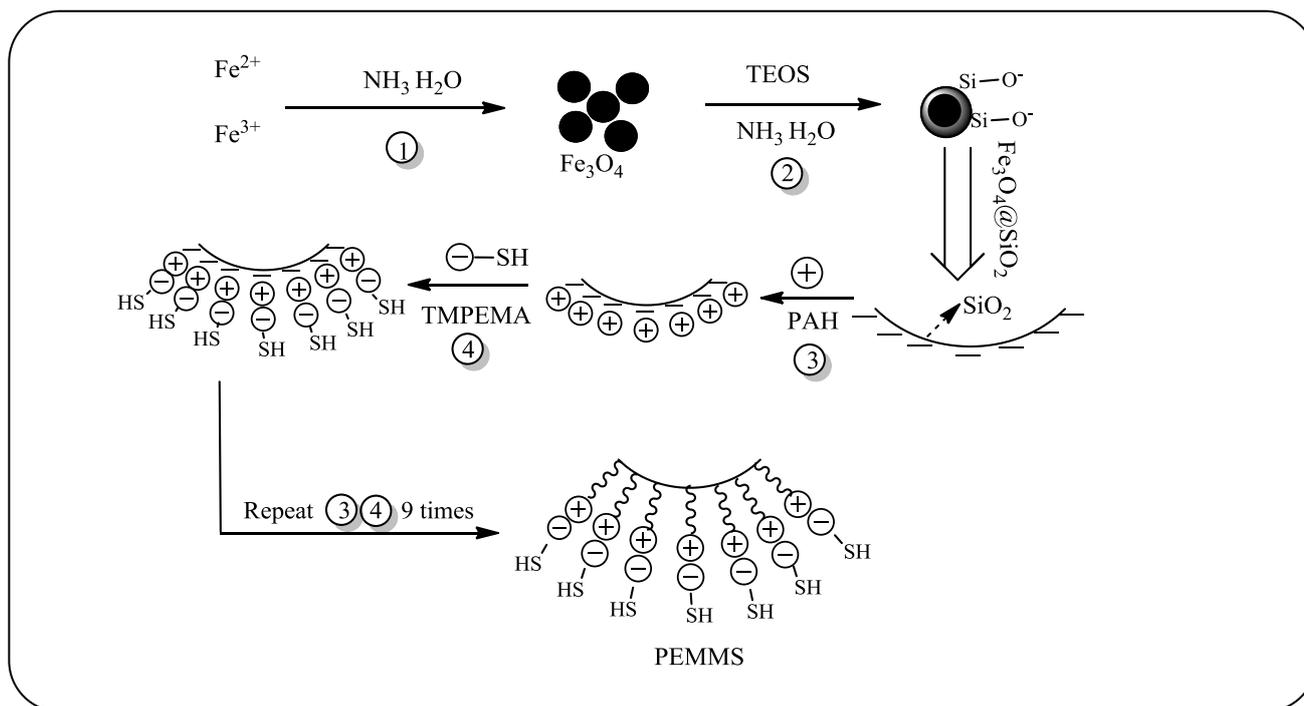
Fig. 1: Schematic of the preparation of the sorbent.

Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) in deionized water. An acetate-acetic acid buffer (pH 3.0-5.0) and NaOH (0.1 mol/L) were used for pH adjustments. Different stock solutions (1.000 g/L) 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. Afterward, the glassware was rinsed thoroughly with deionized water and dried. Deionized water (18.2 MΩ·cm) was used throughout the experiment.

Preparation of the sorbent

The preparation of the PEMMS sorbent was similar with our previous report [23] and is illustrated in Fig. 1. First, the magnetic Fe_3O_4 particles were synthesized by co-precipitation of a mixture of $FeCl_3·6H_2O$ and $FeCl_2·4H_2O$ with concentrated aqueous ammonia. The obtained magnetic Fe_3O_4 was embedded in silica microspheres to obtain $Fe_3O_4@SiO_2$ through a modified Stöber method [7]. The polyelectrolyte multilayers were then fabricated onto the surface of the magnetic $Fe_3O_4@SiO_2$ microsphere using the LbL technique.

A 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. The synthesis of TMPEMA was according to our previous report [23].

General procedure for MSPE

One hundred milliliters of the Ag^+ standard solution (or sample solution) was transferred to a 250 mL beaker, the pH of the solution was adjusted to 6.0, and 100 mg of the sorbent was added. After ultrasonication for 8 min, the magnetic sorbent was separated easily and quickly using a magnet, and the supernatants were decanted directly. For elution of the analyte, 2.0 mL of thiourea (2%, m/v) in nitric acid (0.2 M) was mixed with the sorbent. The eluent was collected using a magnet after ultrasonication for 5 min. Finally, the collected eluent was analyzed using FAAS.

Sample preparation

The following antibacterial products were purchased from a local supermarket and used for the leaching experiment: antibacterial fresh-keeping film (polyethylene),
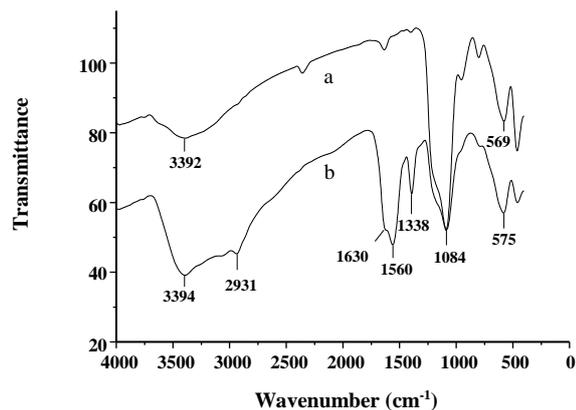
Fig. 2: The FT-IR spectra of (a) Fe₃O₄@SiO₂ and (b) PEMMS sorbent.

Fig. 3: The effect of pH on the adsorption of Ag⁺ on the PEMMS sorbent.

an antibacterial key cover (thermoplastic urethane), and antibacterial cleaning sponges (polyurethane). Each of the antibacterial products was cut into 15 g pieces, and the pieces were immersed in deionized water (1000 mL, pH 6.0) for 24 h. The corresponding soak solutions were collected and transferred into brown volumetric flasks for analysis.

RESULTS AND DISCUSSION
Characterization of the PEMMS sorbent

The PEMMS sorbent was characterized by FT-IR (Fig. 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 to the Si-O stretching band of silica, respectively. Furthermore, the presence of the C-H bond of $SH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$ was reflected by the peak 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. From this, the successful assembling of PEMs on the surface of the magnetic silica ($Fe_3O_4@SiO_2$) was confirmed.

The most important functional group of the prepared sorbent for MSPE was the thiol group, and its amount on the surface of the sorbent was a key factor for the analytical performance. A number of thiol groups on the PEMMS was 0.26 mmol g^{-1}, according to the Ellman method[25], and this was in a good agreement with the result (0.25 mmol/g) obtained using the elemental analyzer. The full results of the elemental analysis were: C 15.58%, N 3.37%, H 3.11%, and S 0.81%. Thus, the sorbent has great potential for the application of trace metal preconcentration with a large adsorption capacity.
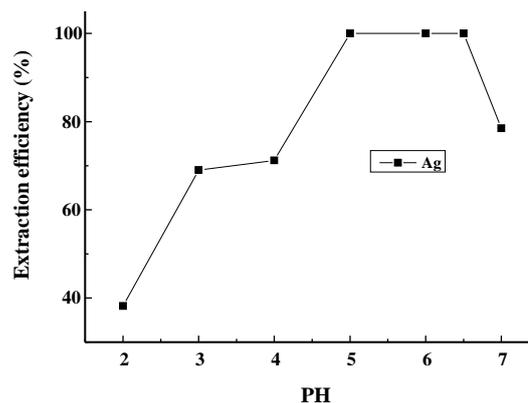
Effect of pH

The pH value plays a key role in the MSPE procedure. The adsorption behavior of Ag^+ 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 Ag^+ on the PEMMS sorbent. It could be observed that Ag^+ was adsorbed quantitatively (R larger than 90%) on the PEMMS sorbent within a pH range of 5.0-6.5. For further experiments, a pH of 6.0 was chosen for the preconcentration of Ag^+.

Optimization of elution conditions

Inorganic acid is a popular eluent in the SPE procedure for metal ions. Unfortunately, when using nitric acid with different concentration (0.1-1.0 M), the recoveries of Ag^+ were approximately 40%-70%. To improve the elution recovery of the analyte, a mixture of thiourea and nitric acid was used as the eluent. The concentration of the mixture was optimized, and quantitative elution was obtained using thiourea (2%, m/v) in nitric acid (0.2 M).

Using this eluent, the effect of the eluent volume on desorption of Ag^+ was studied with the eluent volumes varying from 1.0-5.0 mL. The results showed that 2.0 mL was sufficient to recover Ag^+ quantitatively. Therefore, 2.0 mL was used as the eluent volume for the subsequent experiment.

Effect of ultrasonic time

To minimize the analysis time, the ultrasonic times for the adsorption process and the elution process were
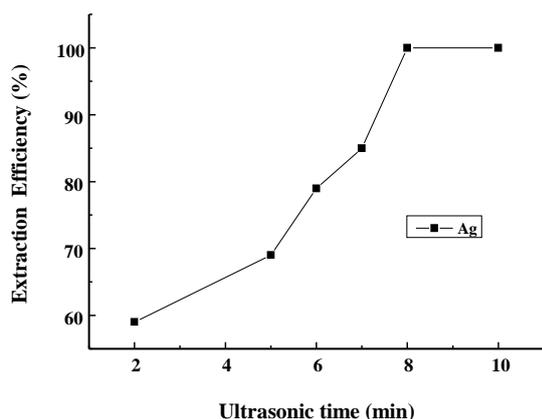
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Fig. 4: The effect of ultrasonic time for adsorption of Ag⁺ on the PEMMS sorbent.

also investigated. For the adsorption process, the effect of the ultrasonic time on the extraction efficiency of Ag^+ was studied according to the general procedure for MSPE, with the ultrasonic time varying from 2-10 min. Fig. 4 shows that quantitative extraction can be obtained with ultrasonic times greater than 8 min. For the elution process, the experimental results showed that 5 min was adequate for quantitative recovery of Ag^+ adsorbed on the PEMMS sorbent with thiourea (2%, m/v) in nitric acid (0.2 M) as the eluent. Therefore, 8 min of ultrasonic time for adsorption and 5 min of ultrasonic time for elution were chosen.

Selectivity of PEMMS sorbent

The effect of co-existing ions on the preconcentration and determination of the studied analyte was investigated. In this experiment, the Ag^+ standard solution (20.0 ng/mL) containing the added interfering ions was treated according to the general procedure for MSPE. The content of Ag^+ 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 ions that would achieve >90% recovery of Ag^+, are given in Table 1. Most of the cations had a largely tolerable concentration under the selected conditions. However, the tolerable concentrations of Hg^{2+} and Cu^{2+} were much smaller than the other metal ions. This is because 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 smaller tolerable concentrations of Hg^{2+} and Cu^{2+} for Ag^+ determination. However, the tolerable concentrations of Hg^{2+} (0.1 μg/mL) and Cu^{2+} (5 μg mL⁻¹) were still acceptable in most application cases. Therefore, it was concluded that the PEMMS sorbent is fairly selective.

Sorbent renewability and analytical performance

The renewability and stability of the sorbent was investigated by testing the Ag^+ standard solution according to the general procedure for MSPE using the same portion of sorbent (100 mg). The sorbent could be reused up to 20 times while maintaining recoveries of analyte greater than 90%.

Under the optimized experimental conditions, the analytical performance of this method was evaluated. Based on the IUPAC definition, the limit of detection (3σ) of this method was 0.17 ng mL⁻¹ for Ag^+, and the relative standard deviation (RSD) was 2.0% (c=20 ng/mL, n=9). The calibration graph for the preconcentration procedure was $A=0.0056C+0.0091$ ($r^2=0.9981$) with a linear range of 1.0~60 ng/mL. The Enrichment Factor (EF) was calculated as the ratio of the slopes of the calibration graphs with and without the preconcentration procedure and was determined to be 35.

A comparison of the MSPE-FAAS method and some of the published similar method for extraction and determination of Ag^+ are summarized in Table 2. Comparing to the other literature, detection limit and precision of the method are comparable or better than that of published methods.

Sample analysis

The proposed method was also applied to the determination of trace Ag^+ in the leaching solution of different antibacterial products. The analytical results and the recoveries for antibacterial products are given in Table 3. The recovery for the leaching solution samples was between 91.5% and 100.0%.

CONCLUSIONS

A new type of sorbent for MSPE was prepared through the LbL assembling method. The prepared PEMMS sorbent exhibited fast adsorption kinetics and high selectivity for Ag^+. MSPE based on the PEMMS sorbent was a combination of a simple preparation technique

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Table 1: Tolerance limits of co-existing ions.

Ions	Tolerable Concentration (μg/mL)	Recovery (%)
K^+	2000	90.3
Na^+	5000	103.7
Mg^{2+}	1000	96.9
Zn^{2+}	20	110.0
Ni^{2+}	20	107.0
Co^{2+}	50	97.6
Ca^{2+}	20	100.7
Pb^{2+}	10	88.0
Cd^{2+}	5	103.6
Cu^{2+}	5	110.1
Hg^{2+}	0.1	97.4

Table 2: Comparison of current method characteristics with those of previously developed methods.

Analyte	Extraction method	Detection System	Detection limit (ng/mL)	Linear Range (ng/mL)	RSD (%)	Ref.
Ag^+	MSPE	FAAS	1.1	2-250	2.7	25
Ag^+	MSPE	ICP-OES	0.2	0.75-100	4.2	26
Ag^+	MSPE	ICP-OES	0.12	-	5.31	27
Ag^+	MSPE	FAAS	0.17	1.0-60	2.0	This work

Table 3: Analytical results for Ag+ in water samples (mean±sd, n=3).

Sample	Added (ng/mL)	Founded (ng/mL)	Recovery (%)
Antibacterial fresh-keeping film	0	7.9±0.26	—
	20	26.2±0.86	91.5
	40	44.8±1.12	92.3
Antibacterial key cover	0	9.6±0.30	—
	20	28.2±0.82	93.0
	40	49.0±1.36	98.5
Antibacterial cleaning sponges	0	4.0±0.20	—
	20	24.0±0.89	100.0
	40	41.8±1.10	94.5

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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.

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