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Functionalization of silica-gel with polyamidoamine and 2-mercaptobenzothiazole and its adsorption property for lead

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Abstract. Adsorbents PAMAM-n.0MBTSG (n=1-4) have been prepared by immobilizing polyamidoamine (PAMAM) and 2-mercaptobenzothiazole (MBT) on silica-gel. Characterized with FTIR, SEM, TGA, the preconcentration of Pb²⁺ with PAMAM-n.0MBTSG(n=1-4) has been investigated by graphite furnace atomic absorption spectroscopy (GFAAS). SEM showed that the surface morphology of adsorbent changed with the generation increase of PAMAM. Adsorption capacity of PAMAM-n.0MBTSG for Pb²⁺ (n=1-4) reached 16.22, 19.84, 22.92 and 27.56 mg g⁻¹ respectively. Pb²⁺ (1.0 ng mL⁻¹) in 2000 mL solution could be quantitatively absorbed with PAMAM-4.0MBTSG and eluted to obtain a preconcentration factor (PF) of 200. GFAAS method for analysis of Pb²⁺ with PAMAM-4.0MBTSG as adsorbent was proposed and successfully applied to analysis of Pb²⁺ of standard reference material, sea water and squid sample.

1. Introduction

In recent years, the analysis of lead in environmental samples has become an important research field. In order to overcome the interference of co-existing substances in the determination of metal ions, Solid-phase extraction adsorbents, such as nano-materials [1,2], activated carbon [3], chelating resin [4], functionalized silica-gel [5] have been already applied to enrichment of lead in aqueous solution, fruits or salt, etc. Because of their special structure, dendrimer-like polyamidoamine (PAMAM) has been applied to silica-gel modification and metal ions adsorption [6,7]. EDTA modified Gn-PAMAM-SBA-15 (n=1-4) inorganic-organic hybrid materials were successfully used to absorb Pb²⁺[8]. In present work, dendrimer-like highly branched polyamidoamine (PAMAM) and 2-mercaptobenzothiazole (MBT) have been immobilized on silica-gel surface to prepare adsorbents PAMAM-n.0MBTSG (n=1-4). After characterized, PAMAM-n.0MBTSG (n=1-4) was used to preconcentrate Pb²⁺. With PAMAM-4.0MBTSG as adsorbent, micro-column enrichment-GFAAS method for determination of Pb²⁺ was proposed and applied to analysis of Pb²⁺ in standard reference material, sea water and squid sample.

2. Materials and methods

2.1 Reagents and instruments

Silica-gel (60-100 meshes, surface area: 300-600 m² g⁻¹) was bought from Qingdao Shuoyuan Chemical Co. Ltd., China. γ -aminopropyltriethoxysilane was bought from Beijing Shenda Fine Chemical Co. Ltd. and distilled at 123°C under 10 mm Hg. Standard reference material (GSB 04-1767-2004) was bought from General Research Institute for Nonferrous Metals, Beijing, China. 2-



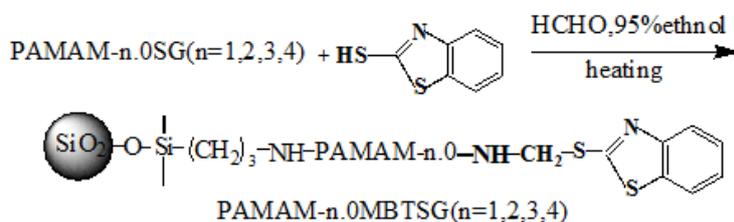
mercaptobenzothiazole (MBT) was bought from Aladdin Industrial Corporation. The other reagents used in preconcentration were analytical grade. Suitable amount of $\text{Pb}(\text{NO}_3)_2$ was dissolved in HNO_3 solution (pH=2) to obtain $1000 \text{ mg L}^{-1} \text{ Pb}^{2+}$ stock solution. Pb^{2+} stock solution was diluted step by step to obtain Pb^{2+} standard solutions.

Infrared spectra were obtained at room temperature with Thermo Nexus 470 FTIR spectrometer. The surface morphology of APSG and PAMAM-n.0MBTSG (n=1-4) were obtained by scanning electron microscopy (SEM, Hitachi S-4800). Thermal analyzer (SDT-Q600, Waters) was used to obtain thermogravimetric analysis (TA) curves of sample. Temperature range of TG analysis was from room temperature to $600 \text{ }^\circ\text{C}$ with heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ and N_2 atmosphere.

2.2 Preparation of adsorbents

PAMAM modified silica-gel PAMAM-n.OSG (n=1-4) were synthesized according to reference [7]. According to acid-base titration method described in reference [6], $-\text{NH}_2$ content of γ -aminopropyltriethoxysilane modified silica-gel (APSG) and PAMAM-n.OSG (n=1-4) was 0.60, 0.86, 1.30, 1.70 and 1.97 mmol g^{-1} respectively. PAMAM-n.0MBTSG (n=1-4) was prepared as below according to reference [9]. 5.85 g (about 35.0 mmol) 2-mercaptobenzothiazole was dissolved with 60 mL 95% ethanol in a 250 mL flask. 4.5 mL formaldehyde solution (37%) and 20.0 g PAMAM-1.OSG were added to the flask. Then the flask was placed in $50 \text{ }^\circ\text{C}$ oil bath and the mixture was stirred for 8 h to prepare PAMAM-1.0MBTSG.

PAMAM-n.0MBTSG (n=2,3,4) were prepared as PAMAM-1.0MBTSG. The above solid products PAMAM-n.0MBTSG (n=1-4) were filtrated and washed with 95% ethanol for 3 times. After extracted with 95% ethanol for 5 hours in Soxhlets, solid products were dried at $50 \text{ }^\circ\text{C}$ under vacuum and yellow adsorbents PAMAM-n.0MBTSG (n=1-4) were obtained respectively. The ideal synthetic route of adsorbents was illustrated in Scheme 1.



Scheme 1. The ideal synthetic route to PAMAM-n.0 MBTSG (n=1,2,3,4)

2.3 Preconcentration experiment

Preconcentration of Pb^{2+} was completed in a self-made micro-column ($7.0 \text{ cm} \times 0.5 \text{ mm}$ i.d., packed with about 0.6 g adsorbent) and peristaltic pump (BT01S-YZ1515) (Yi Kang Xin Da Technology Co., Ltd, China). PTFE tubing (0.8 mm i.d.) was used for connection.

The preconcentration experiment was carried out as below. (1) micro-column was cleaned with blank solution. (2) Pb^{2+} solution was driven through micro-column and the outflow solution was collected. (3) Blank solution was driven through micro-column for 30 s to remove the matrix ions. (4) Pb^{2+} was desorbed with eluent in the reverse direction and effluent solution was collected. Pb^{2+} in outflow solution and effluent solution was determined by atomic absorption spectrometer (TAS-990, Beijing Purkinje General Instrument Co., Ltd.) to obtain adsorption percentage and desorption percentage of Pb^{2+} .

3. Results and discussion

3.1 Characterization

In FTIR spectra of PAMAM-n.0MBTSG (n=1-4), the characteristic absorption of stretching vibration of C=O in amide groups and N-H scissoring vibration appeared at 1658 cm^{-1} and 1558 cm^{-1} respectively, which suggested that PAMAM was introduced onto the surface of silica-gel. Absorption at 1508 cm^{-1}

and 1452cm^{-1} , attributed to characteristic vibration of aromatic rings, indicated that 2-mercaptobenzothiazole was linked to the surface of PAMAM-n.0SG.

Figure 1 presents SEM images of APSG and PAMAM-n.0MBTSG ($n=1-4$). As the increase of PAMAM grafting generation, many surface pores became smaller and the surface became smoother gradually, representing that some of micropore could be closed by PAMAM. The phenomenon indicated that PAMAM has successfully grafted onto silica-gel surface and played a dominant role in the changing of the surface morphology.

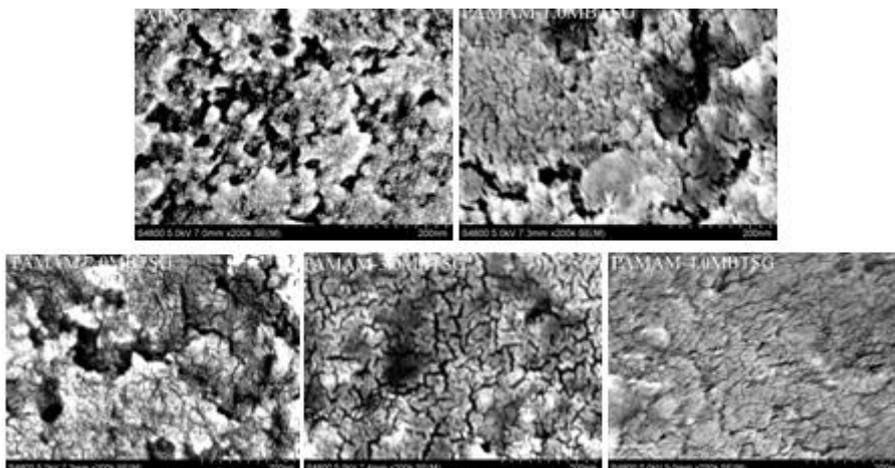


Figure 1. The SEM images of APSG and PAMAM-n.0 MBTSG ($n=1,2,3,4$)

TG curves in Figure 2 shows the weight loss of APSG and PAMAM-n.0MBTSG ($n=1-4$). The weight loss of 2.09-3.90% at about $110\text{ }^{\circ}\text{C}$ was due to evaporation of physically adsorbed water. While the temperature reached $600\text{ }^{\circ}\text{C}$, decomposition of organic molecular layer and condensation of the existing silanol groups [10] brought an obvious total weight loss of 11.69%, 19.54%, 23.76%, 27.84% and 29.18% for APSG and PAMAM-n.0MBTSG ($n=1-4$) respectively.

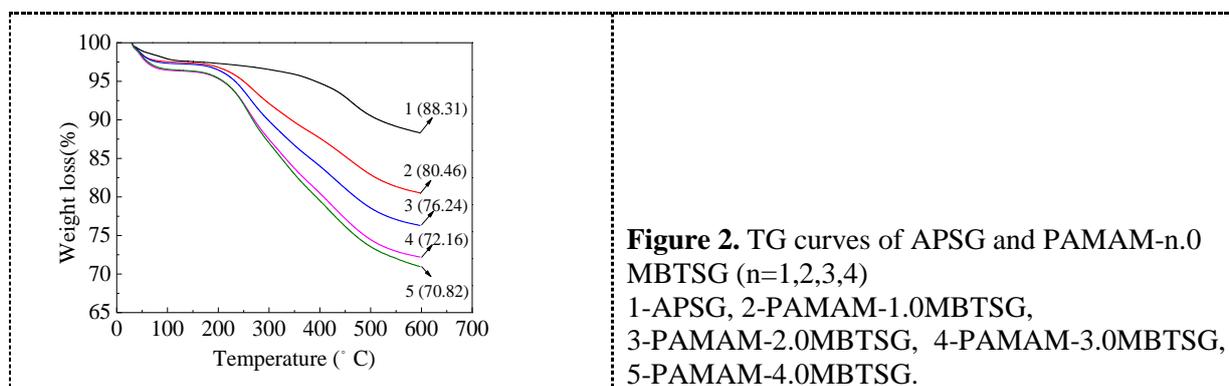


Figure 2. TG curves of APSG and PAMAM-n.0 MBTSG ($n=1,2,3,4$)
 1-APSG, 2-PAMAM-1.0MBTSG,
 3-PAMAM-2.0MBTSG, 4-PAMAM-3.0MBTSG,
 5-PAMAM-4.0MBTSG.

3.2 Effect of pH

$0.2\ \mu\text{g mL}^{-1}\ \text{Pb}^{2+}$ solutions with pH in the range of 3-9 were used to investigate the adsorption of Pb^{2+} on PAMAM-n.0MBTSG. While with silica-gel or APSG as adsorbent, adsorption percentage of Pb^{2+} were all less than 70.0% in pH range of 3-9, which indicated silica-gel or APSG was not suitable for quantitative enrichment of Pb^{2+} in the system. With PAMAM-1.0MBTSG as adsorbent, adsorption percentage of Pb^{2+} gradually increased with increase of pH from 3.0 to 6.0 and then was kept about 100% while solution pH from 6.0 to 9.0. With PAMAM-n.0MBTSG ($n=2-4$) as adsorbents, adsorption percentage of Pb^{2+} gradually increased with increase of pH from 3.0 to 5.0 and then was kept about 100% while solution pH from 5.0 to 9.0. The experiment results indicated that the surface modification of silica-gel with PAMAM and 2-mercaptobenzothiazole could effectively improve

silica-gel adsorption property for Pb^{2+} . Based on the above facts, only the adsorption of Pb^{2+} with PAMAM-n.0MBTSG (n=1-4) as adsorbent was studied and pH 6.0 medium solution was selected for Pb^{2+} adsorption in further experiments.

3.3 Effect of eluent concentration

The effect of concentration of HCl solution on desorption of Pb^{2+} from PAMAM-n.0MBTSG was investigated in the range of 0.05-4.0 mol L⁻¹. HCl solution with concentration of 0.05-1.0 mol L⁻¹ was sufficient for elution of Pb^{2+} . While HCl solution was more than 1.0 mol L⁻¹, the existing HCl solution in micro-column could not completely eluted with blank solution and would decreased adsorption of Pb^{2+} in the next enrichment cycle. In order to guarantee elution of Pb^{2+} and adsorption of Pb^{2+} in the next cycle, 0.5 mol L⁻¹ HCl solution of was used as eluent for the elution of Pb^{2+} in further experiments.

3.4 Effect of flow rate

In the range of 0.6-6.0 mL min⁻¹, effect of flow rate on adsorption and desorption of Pb^{2+} was investigated when 10 ml Pb^{2+} solution (0.2 $\mu\text{g mL}^{-1}$) was used. The adsorption of Pb^{2+} was complete and then kept over 95% until the sampling flow rate increased to 3.0 mL min⁻¹. While flow rate was more than 3.0 mL min⁻¹, adsorption percentage of Pb^{2+} on PAMAM-4.0MBTSG was obviously higher than that on PAMAM-n.0MBTSG (n=1-3). In the following experiments, 2.4 mL min⁻¹ was chose as flow rate for quantitative enrichment of Pb^{2+} .

Desorption percentage of Pb^{2+} reached more than 95% respectively with flow rate not more than 3.6 mL min⁻¹. Desorption percentage of Pb^{2+} with PAMAM-4.0MBTSG as adsorbent was higher than that with PAMAM-n.0MBTSG (n=1,2,3) as adsorbent if the same flow rate was used. Therefore, 3.0 mL min⁻¹ was selected as flow rate for desorption of Pb^{2+} .

3.5 Effect of solution volume

With 0.2 $\mu\text{g mL}^{-1}$ Pb^{2+} solution as sample solution, the effect of solution volume (5.0, 10.0, 15.0, 20.0, 30.0 mL respectively) on adsorption of Pb^{2+} was studied. When Pb^{2+} solution volume was not more than 10.0 mL, adsorption percentage of Pb^{2+} on PAMAM-n.0MBTSG (n=1-4) were all more than 95% respectively. In further experiments 10.0 mL solution was applied to preconcentration of Pb^{2+} .

The effect of eluent volume on recovery of Pb^{2+} was studied with 0.5 mol L⁻¹ HCl solution (5.0, 10.0, 15.0, 20.0, 25.0 mL respectively) as eluent. When the volume of eluent was more than 10.0 mL, the recoveries of Pb^{2+} were all more than 95%. 10.0 mL HCl solution (0.5 mol L⁻¹) was used for desorption of Pb^{2+} in the further experiments.

3.6 Effect of co-existing substance

Anions such as Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} (added as sodium salt) and ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Mn^{2+} , Al^{3+} , Cu^{2+} , Co^{2+} , Cr^{3+} , Cd^{2+} , Ni^{2+} , Ba^{2+} , Sr^{2+} , Fe^{3+} , Ag^+ , NH_4^+ (added as nitrate) were added respectively when 10 mL solution of 0.2 $\mu\text{g mL}^{-1}$ Pb^{2+} was enriched. Interference from Fe^{3+} of 5.0 $\mu\text{g mL}^{-1}$ could be masked by triethanolamine. The tolerance of ions and anions could reaches no less than 5 $\mu\text{g mL}^{-1}$ or 500 $\mu\text{g mL}^{-1}$ respectively with relative error not more than 5.0%. The results indicated that it was hopeful to enrich Pb^{2+} of trace level selectively with PAMAM-n.0MBTSG (n=1-4) as adsorbent.

3.7 Adsorption capacity

Under the selected experimental conditions, 40.0 $\mu\text{g mL}^{-1}$ Pb^{2+} solution with hydro-chloric acid as medium (pH=6.0) was driven through micro-column with a flow rate of 2.4 mL min⁻¹. The outflow solution through micro-column was collected every 5 minutes and Pb^{2+} concentration was determined until Pb^{2+} concentration in outflow solution was not changing. The adsorption capacity of PAMAM-n.0MBTSG (n=1-4) were 16.22, 19.84, 22.92 and 27.56 mg g⁻¹ respectively. After used for no less

than 100 cycles of adsorption and desorption, the adsorption performance of PAMAM-n.0MBTSG has not changed yet.

3.8 Low concentration enrichment

According to enrichment procedure, solutions (containing 2.0 µg Pb²⁺) of different volume (10 mL, 100 mL, 1000 mL or 2000 mL) flowed through micro-column, and then Pb²⁺ adsorbed on PAMAM-4.0MBTSG was eluted and determined. 2.0 µg Pb²⁺ in solutions (solution of volume than 2000 mL was not tested) could be quantitatively absorbed on PAMAM-4.0MBTSG and eluted to obtain a preconcentration factor (PF) of 200, which makes it possible for analysis of ng mL⁻¹ Pb²⁺ with GFAAS and higher sample solution volume. In order to decrease enrichment time, 10 mL Pb²⁺ solution was still selected as sample solution.

3.9 Analytical performances

GFAAS method for determination of Pb²⁺ combining microcolumn preconcentration system with PAMAM-n.0MBTSG (n=1-4) as adsorbent was proposed. The limit of detection (LOD) for Pb²⁺ was 4.4 ng mL⁻¹ with 10 mL sample solution and a loading flow rate of 2.4 mL min⁻¹. RSD was 2.1% by 11 times parallel preconcentration and determination of Pb²⁺ (0.2 µg mL⁻¹). The calibration graph using the proposed method was linear in the range of 0.05-0.25 µg mL⁻¹ with the regression equation of A=2.6783×C+0.0177 (where C is the concentration of Pb²⁺ in µg mL⁻¹) with a correlation coefficient (R) of 0.9993. If a sample solution of 2000 mL was used, the analytical concentration range of Pb²⁺ was lower to 0.25-1.25 ng mL⁻¹, obtained by dividing the linear concentration (0.05-0.25 µg mL⁻¹) by preconcentration factor of 200. Sample frequency reached 10 samples h⁻¹.

3.10 Sample analysis

With the proposed method, standard reference sample (GSB 04-1767-2004), sea water and squid sample were analyzed. 0.10 µg mL⁻¹ solution A (pH=6.0) (pH was adjusted with 0.01mol L⁻¹ NaOH and HCl solution) was obtained by dilution of standard reference sample solution step by step. Pb²⁺ in 10.0 ml solution A was enriched and determined. The analysis result shown in Table 1 was in good agreement with certified value.

Table 1. Analysis of Pb²⁺ in standard reference sample

Sample	Certified Value /(µg)	Found ^a /(µg)	RSD /(%)	Relative error /(%)
Solution A	1.0	0.98	0.3	-2.00

^a Mean (n=6)

Pb²⁺ in 100.0 ml sea water (pH = 6.0) was enriched and determined. A suitable amount squid sample was digested to obtain sample solution (pH was adjusted to 6.0), Pb²⁺ in 100 ml squid sample solution was enriched and determined. The analysis results are shown in Table 2. The above results of analysis indicate that the proposed method is reliable for the preconcentration and detection of Pb²⁺ in environmental sample.

Table 2. Analysis of Pb²⁺ in sea water and addition-Recovery test

Sample	Added /(µg)	Determined ^a /(µg)	RSD / (%)	Recovery /(%)
Sea water	0	0.38	2.21	--
	0.2	0.58	1.72	101.0
	0.5	0.80	1.12	102.4
	0.8	1.17	0.47	99.8

^a Mean (n=6)

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