Abstract. New adsorbents PAMAM-n.0TMSG (n=1,2,3,4) with thiomalic acid as functional group has been prepared based on polyamidoamine dendrimer modified silica gel and characterized with FTIR, SEM and TG. Microcolumn enrichment and measurement of Pb²⁺ with graphite furnace atomic absorption spectroscopy (GFAAS) was investigated with PAMAM-n.0TMSG (n=1,2,3,4) as adsorbent. The adsorption conditions were optimized. The increase of grafted generation of PAMAM-n.0TMSG could effectively improved the adsorption performance of adsorbents. The adsorption capacity of adsorbents was 14.42, 16.19, 20.79 and 25.32 mg g⁻¹ respectively. With PAMAM-4.0TMSG as adsorbent, microcolumn enrichment and measurement of Pb²⁺ with GFAAS was proposed. The relative standard deviation (R.S.D.) was 1.4% (n=11) for 0.2 μg mL⁻¹ of Pb²⁺. The limit of detection (LOD) of 2.9 ng mL⁻¹ was achieved. The proposed column enrichment method was applied for detection of Pb²⁺ in tap water and sea water samples successfully.

1. Introduction

Because of the low concentration of lead and interference from co-existing substances in environmental sample, Solid-phase extraction (SPE) was often used to preconcentrate and separate trace metals from matrices [1-3] with macroporous adsorption materials such as silica-gel [4], chelating resin [5] and organic–inorganic hybrid materials [6,7]. Dendrimer-like polyamidoamine (PAMAM) has attracted considerable attention in metal ions adsorption due to its end amine and ester groups [8-11]. Considering that if silica-gel could be modified with dendrimer-like PAMAM and functional group for adsorption could be linked to the generous peripheral amine group of PAMAM, it would be possible to improve the adsorption capacity of silica-gel and selectivity.

In present work, silica-gel adsorbents PAMAM-n.0TMSG (n=1,2,3,4) with dendrimer-like PAMAM and thiomalic acid as functional groups have been prepared and characterized with FTIR, SEM, and TG, then micro-column adsorption of Pb²⁺ was investigated. The experiments results showed that modification of PAMAM and thiomalic...
acid could effectively improve the adsorption/desorption properties of adsorbent. With PAMAM-4.0 TMSG as adsorbent, GFAAS method for analysis of Pb^{2+} combined with micro-column enrichment was proposed and applied to analysis of Pb^{2+} of water samples.

2. Experimental

2.1 Apparatus and Reagents

Peristaltic pump (BT01S-YZ1515) of Yi Kang Xin Da Technology Co., Ltd (China) and a self made micro-column (7 cm × 0.5mm i.d.) were used. PTFE tubing (0.8mm i.d.) was used for connections. Atomic absorption spectrometer (TAS-990) of Beijing Purkinje General Instrument Co., Ltd. (China) was employed to detection of Pb^{2+}.

Silica gel (60–100 meshes, surface area 300-600 m^2 g^{-1}) was bought from Qingdao Shuoyuan Chemical Co. Ltd., China. \( \gamma \)-Aminopropyltriethoxysilane (Beijing Shenda Fine Chemical Co. Ltd., China) was purified by distillation at 123°C under 10 mm Hg. All of the other reagents were analytical reagent grade.

1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), thiomalic acid and N-Hydroxysuccinimide (NHS) were all bought from Aladdin Chemistry Co.Ltd. Stock solution of Pb^{2+} (1000 mg L^{-1}) was prepared by dissolving appropriate amounts of analytical pure Pb(NO₃)₂ in pH=2 HNO₃ solution. Standard solutions of Pb^{2+} were prepared by dilution of the stock solution just before use. Distilled water was used throughout.

2.2 Preparation of PAMAM-n.0TMSG

Pretreatment of silica-gel and synthesis of aminopropyl silica-gel (APSG) and dendrimer-like PAMAM modified silica-gel PAMAM-n.0SG (n=1,2,3,4) were followed as described previously [10]. PAMAM-n.0TMSG (n=1,2,3,4) was prepared as below. 4.505g thiomalic acid, 1.036 g NHSand 8.626g EDC were dissolved in 250 mL flask with appropriate amounts of N,N-Dimethylformamide (DMF). Then 10g PAMAM-n.0SG(n=1,2,3,4) was added into the flask. In room temperature the mixture was stirred for 24 h to obtain solid products PAMAM-n.0TMSG(n=1,2,3,4).

PAMAM-n.0TMSG (n=1,2,3,4) were washed with DMF at least for 3 times, then washed with ethanol at least for 3 times. PAMAM-n.0TMSG (n=1,2,3,4) were dried at 70 °C. The ideal synthetic route of PAMAM-n.0TMSG(n=1,2,3,4) was illustrated in Scheme 1.
2.3 Enrichment Procedure

One end of the micro-column was packed with polypropylene fiber, PAMAM-n.0TMSG (n=1,2,3,4) was packed in micro-column, then the other end of the micro-column was packed with polypropylene fiber, two ends were connected with silicone tubing. In Step 1, the blank solution (its pH is the same as Pb²⁺ solution) was pumped through micro-column. In Step 2, the Pb²⁺ solution was pumped through micro-column and was collected for determination of Pb²⁺. In Step 3, the blank solution was pumped through micro-column. In Step 4, the eluent solution was pumped through micro-column in the reverse direction and was collected for determination of Pb²⁺. Pb²⁺ concentration was determined with GFAAS. Pb²⁺ adsorption percentage (A) and desorption percentage (R) were calculated according to (1) and (2).

\[
A = \frac{C_0 V_0 - C_1 V_1}{C_0 V_0} \times 100 \% \quad (1)
\]
\[
R = \frac{C_2 V_2}{C_0 V_0 - C_1 V_1} \times 100\% \quad (2)
\]

While \(C_0\) and \(C_1\) (\(\mu\)g mL⁻¹) are concentration of Pb²⁺ in the sample solution before and after adsorption, \(C_2\) (\(\mu\)g mL⁻¹) is concentration of Pb²⁺ in elutant through micro-column in step 4; \(V_0\) and \(V_1\) (mL) are the volume of sample solution before and after adsorption, \(V_2\) (mL) is elutant volume.
3. Results and Discussion

3.1 Characterization of Adsorbent

The Fourier transmission infra-red (FTIR) spectra of PAMAM-n.0TMSG (n=1,2,3,4) are shown in Fig.1. The absorption at 3346 cm⁻¹ is characteristic of –NH₂ and –OH stretching vibration and the absorption at 2946 cm⁻¹ is characteristic of –CH₂–stretching vibration. The absorption at 1644 cm⁻¹ and 1575 cm⁻¹ is characteristic of C=O stretching vibration in amide groups and N-H scissor vibration respectively. The absorption at 2614 cm⁻¹ and 2558 cm⁻¹ is characteristic of -SH vibration. The appearance of these characteristic absorptions suggested that PAMAM and thiomalic acid were successfully introduced onto the surface of silica-gel.

Fig.2 presents SEM images (magnified fifty thousand times) of PAMAM-n.0TMSG (n=1,2,3,4). On the rough surface of APSG there are many pores with kinds of diameter. As the increase of PAMAM grafting generation, more surface was covered by PAMAM, indicating that dendrimer-like PAMAM had been successfully grafted onto the surface of silica gel.

TG analysis was applied to evaluate the grafting effectiveness of PAMAM onto the surface of silica gel. Under N₂ atmosphere, temperature range was from 30 to 600 °C with heating rate of 5 °C min⁻¹ during TG analysis. When the temperature reached 100 °C, the weight loss were about 2.09-8.23%, which represented the evaporation of water adsorbed on silica-gel. When the temperature reached 600 °C, the total weight loss of APSG, PAMAM-n.0TMSG(n=1,2,3,4) were 11.69, 22.42, 26.46, 27.43 and 33.08% respectively, suggesting that grafting percentage of PAMAM increased with the increase of grafting generation number of PAMAM.

3.2 Effect of pH

In the range from 2.0 – 9.0, adsorption rate of Pb²⁺ reached more than 95% when pH is in the range of 5-8. The solution of pH=5.0 was selected as the sample medium.
3.3 Effect of Eluent concentration

In the range of 0.05-4.0 mol L⁻¹, Pb²⁺ could be eluted by 1.0 mol L⁻¹ HCl solution with PAMAM-n.0TMSG (n=1,2) as adsorbent and by 0.1 mol L⁻¹ HCl solution with PAMAM-n.0TMSG (n=3,4) as adsorbent. In order to guarantee the elution of Pb²⁺, 1.0, 1.0, 0.1 and 0.1 mol L⁻¹ HCl solution was used as eluent respectively in further experiments.

3.4 Effect of Flow Rate

In the sample solution flow rate range of 0.6–6.0 ml min⁻¹, adsorption rate of Pb²⁺ reached more than 95%. So 4.2 mL min⁻¹ was used as the sample solution flow rate.

In the eluent solution flow rate range of 0.6–6.0 ml min⁻¹, recovery of Pb²⁺ reached more than 95% with a flow rate of 3.0 mL min⁻¹ and with PAMAM-1.0TMSG or PAMAM-2.0TMSG as absorbent. Recovery of Pb²⁺ reached more than 95% with a flow rate of 3.6-4.8 mL min⁻¹ and with PAMAM-3.0TMSG or PAMAM-4.0TMSG as absorbent. In order to guarantee the elution of Pb²⁺, 3.0, 3.0, 4.2 and 4.2 mL min⁻¹ was used as eluent solution flow rate respectively in further experiments.

Fig.2 The SEM images of APSG and PAMAM-n.0TMSG (n=1,2,3,4)
3.5 Effect of Sample and Eluent Solution Volume

Under the above selected conditions, different volume (5.0-40.0 ml) sample solution of 0.2 μg mL^{-1} Pb^{2+} was used respectively for sample loading. When sample solution volume was not more than 10.0 ml, adsorption rate of Pb^{2+} were more than 95%. Different volume (5.0-40.0 ml) HCl solution was used as eluent, and elution recovery of Pb^{2+} could reach more than 95%. So 10.0 ml sample solution and 10.0 ml eluent solution were selected in the further experiments.

3.6 Interference of Co-existing Ions

The effects of anions and co-existing metal ions were tested when 10 ml sample solution with 0.2 μg mL^{-1} Pb^{2+} was determined. More than 5 μg mL^{-1} of co-existing metal ions (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, Mn^{2+}, Cu^{2+}, Cr^{3+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Fe^{3+}) and 100 μg mL^{-1} of anions (PO_{4}^{3-}, SO_{4}^{2-}, NO_{3}^{-}, ClO_{4}^{-}, Cl^{-}) (added as sodium salts) did not interfere with the enrichment and determination.

3.7 Saturated Adsorption Capacity

Under the above selected conditions, 40.0 μg mL^{-1} Pb^{2+} solution (pH=5.0) passed through micro-column with flow rate of 1.8 mL min^{-1}. The saturated adsorption capacity of PAMAM-n.0TMSG (n=1,2,3,4) for Pb^{2+} were 14.42, 16.19, 20.79 and 25.32 mg g^{-1}, which indicated that the increase of grafting generation of PAMAM was helpful for increase of functional group amount and adsorption capacity of adsorbent.

3.8 Low Concentration Enrichment

Pb^{2+} solutions with 2 μg Pb^{2+} and different volume (10mL, 100mL, 1000mL, 1500mL, 2000mL) were respectively enriched according to the procedure and then Pb^{2+} was eluted with 10.0 ml eluent and determined. 2.0 μg Pb^{2+} in 1000 mL solution could be quantitatively preconcentrated with PAMAM-1.0SSASG or PAMAM-2.0SSASG and eluted with 10 mL eluent and a factor of 100 was obtained. The enrichment factor with PAMAM-n0SSASG (n=1,2,3,4) as adsorbents respectively was 100,100,150 and 200.

3.9 Analytical Performances

The characteristic data for the analytical performance of microcolumn enrichment system with PAMAM-4.0TMSG as adsorbent and GFAAS detection of Pb^{2+} are investigated. With the proposed method, the relative standard deviation (R.S.D.) was 1.4% for 0.2 μg mL^{-1} of Pb^{2+}. The limit of detection (LOD) was 2.9 ng mL^{-1}, calculated as the concentration of Pb^{2+} required to yield a net peak-height absorbance that was equal to three times the standard deviation of the background signal (3σ) of the blank solution. Regression equation (five standards, n=5, C in μg mL^{-1}) was A=3.0952*C+0.1090 in Pb^{2+} concentration range of 0.05-0.3 μg mL^{-1} with a correlation coefficient R= 0.9990.
3.10 Water Sample Analysis

TABLE 1 DETERMINATION OF Pb²⁺ IN WATER SAMPLES AND ADDITION–RECOVERY TESTS

| Sample   | Added (µg mL⁻¹) | Found a (µg mL⁻¹) | RSD (%) | Recovery (%) |
|----------|----------------|-------------------|---------|--------------|
| tap water| 0              | unfound           | 2.0     | --           |
|          | 0.005          | 0.0052            | 1.6     | 104.0        |
|          | 0.010          | 0.0099            | 2.8     | 99.0         |
|          | 0.020          | 0.0201            | 4.5     | 100.5        |
| sea water| 0.020          | 0.0031            | 1.7     |              |
|          | 0.005          | 0.0083            | 1.3     | 104.0        |
|          | 0.010          | 0.00134           | 0.8     | 103.0        |
|          | 0.020          | 0.00230           | 2.6     | 99.5         |

a Mean (n=6)

The proposed column enrichment method was applied for the preconcentration and determination of Pb²⁺ in tap water and sea water samples (100 mL). The standard addition method was applied for evaluation of the method in analysis of water samples. The analytical results are given in Table 1. As it can be seen, the recoveries of Pb²⁺ are in the range of 98.0–105.0% with R.S.D not more than 5.0%. The results indicate that the proposed method is reliable.

4. Summary

PAMAM-n.0TMSG (n=1,2,3,4) adsorbents with PAMAM and thiomalic acid as functional groups have been synthesized and characterized with FTIR, SEM and TG, then enrichment conditions for Pb²⁺ was investigated. PAMAM-n.0TMSG showed good adsorption capability. The proposed column enrichment-GFAAS method was successfully applied for detection of Pb²⁺ in tap water and sea water samples.

5. Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 51262005), Guangxi Colleges and Universities Key Laboratory of Food Safety and Detection, and the project of high level innovation team and outstanding scholar in Guangxi colleges and universities (No.49 2014).

References

1. T. Madrakian, M.A. Zolfigol, M. Solgi, Solid-phase extraction method for preconcentration of trace amounts of some metal ions in environmental samples using silica gel modified by 2,4,6-trimorpholino-1,3,5-triazin, J. Hazard. Mater. 160 (2008) 468-472.
2. M. L. Chen, Y. Sun, C. B. Huo, C. Liu, J. H. Wang, Akaganeite decorated graphene oxide composite for arsenic adsorption/removal and its proconcentration at ultra-trace level, Chemosphere 130 (2015) 52-58.
3. Y. Wang, S. Gao, X. Zang, J. Li, J. Ma, Graphene-based solid-phase extraction combined with flame atomic absorption spectrometry for a sensitive determination of trace amounts of lead in environmental water and vegetable samples, Anal. Chim. Acta 716 (2012) 112-118.
4. K. Johari, N. Saman, H. Mat, Adsorption enhancement of elemental mercury onto sulphur-functionalized silica gel adsorbents, Environ. Technol. 35 (2014) 629-636.

5. Y. Zhai, Y. Liu, X. Chang, S. Chen, X. Huang, Selective solid-phase extraction of trace cadmium(II) with an ionic imprinted polymer prepared from a dual-ligand monomer, Anal. Chim. Acta 593 (2007) 123-128.

6. H.T. Fan, X.T. Sun, W.X. Li, Sol–gel derived ion-imprinted silica-supported organic–inorganic hybrid sorbent for selective removal of lead(II) from aqueous solution, J. Sol-Gel Sci. Technol. 72 (2014) 144-155.

7. M. Rashid, F. Khan, Lutfullah, Removal of Pb(II) ions from aqueous solutions using hybrid organic–inorganic composite material: Zr(IV) iodosulphosalicylate, J. Water. Process Eng. 3 (2014) 53-61.

8. R. Qu, Y. Niu, C. Sun, C. Ji, C. Wang, G. Cheng, Syntheses, characterization, and adsorption properties for metal ions of silica-gel functionalized by ester- and amino-terminated dendrimer-like polyamidoamine polymer, Microporous Mesoporous Mater. 97 (2006) 58-65.

9. Y. Niu, R. Qu, C. Sun, C. Wang, H. Chen, C. Ji, Y. Zhang, X. Shao, F. Bu, Adsorption of Pb(II) from aqueous solution by silica-gel supported hyperbranched polyamidoamine dendrimers, J. Hazard. Mater. 244-245 (2013) 276-286.

10. X. Z. Wu, P. Liu, Q.S. Pu, Q.Y. Sun, Z. X. Su, Preparation of dendrimer-like polyamidoamine immobilized silica gel and its application to online preconcentration and separation palladium prior to FAAS determination, Talanta 62 (2004) 918-923.

11. Y. Niu, R. Qu, H. Chen, L. Mu, X. Liu, T. Wang, Y. Zhang, C. Sun, Synthesis of silica gel supported salicylaldehyde modified PAMAM dendrimers for the effective removal of Hg(II) from aqueous solution, J. Hazard. Mater. 278 (2014) 267-278.