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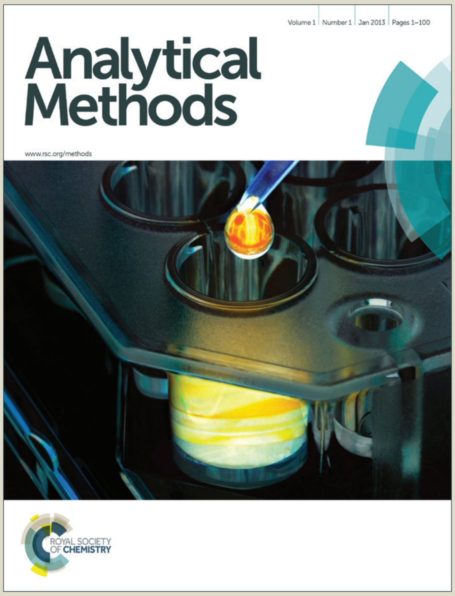
Accepted Manuscript



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Poly-γ-glutamic acid modified magnetic nanoparticles for fast solid phase extraction of trace amounts of Cu (II) and Pb (II)

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Abbreviations: γ-PGA, poly-γ-glutamic acid; SPE, solid-phase extraction; MNPs, magnetic nanoparticles; SCMNPs, silica-coated magnetic nanoparticles; γ-PGA-SCMNPs, γ-PGA-modified silica-coated magnetic nanoparticles.

Abstract:

In the present study, poly-γ-glutamic acid (γ-PGA) was applied to functionalize the silica-coated magnetic nanoparticles for solid-phase extraction of Cu (II) and Pb (II). Firstly, the silica-coated magnetic nanoparticles were modified with γ-PGA using the sol-gel method. Fourier Transform Infrared (FT-IR) spectrum analysis confirmed that the γ-PGA was bound onto the magnetic nanoparticles, and the Transmission electron microscope (TEM) image showed that as-prepared nanoparticles were typical core-shell structure with an average size of 12.5 nm. Secondly, the γ-PGA modified magnetic nanoparticles were used in solid-phase extraction of Cu (II) and Pb (II). Various parameters including pH, eluent concentration, eluent volume, extraction time, sample volume, and potentially interfering ions were investigated to establish the optimal experimental conditions. Under the optimal conditions, the limits of detection (LOD) for Cu (II) and Pb (II) were 0.46 and 1.43 μg L^{-1} respectively, and the enrichment factors reached 166 and 133, as well as the low relative standard deviations (RSDs, n=7, c =50 μg L^{-1}) of 2.48% and 7.42% for Cu and Pb, respectively. Moreover, as-synthesized sorbent was efficient for extraction of Cu (II) and Pb (II) from different practical water samples. This study provided a fast, simple and selective heavy metal analysis method using solid phase extraction coupled with flame atomic absorption spectrometry.

Keywords: Heavy metal; Magnetic nanoparticles; Poly-γ-glutamic acid; Solid phase extraction

1. Introduction

With the rapid development of industry, heavy metal contamination causes severe risks to human and ecosystem.[1] Heavy metal ions such as lead and copper are hazardous to flora and fauna, and excessive levels of copper could induce gastrointestinal distress and even liver and kidney damage on humans under long-term exposure,[2] meanwhile, lead can cause severe damage to the nervous, cardiovascular, renal, and reproductive systems of human even at relatively low concentration.[1] Hence, development of effective methods for removal and determination of heavy metal in environmental sample is of particular significance. Several advanced instruments such as inductively coupled plasma optical emission spectrometry (ICP-OES),[3] inductively coupled plasma mass spectrometry (ICP-MS),[4] graphite furnace atomic absorption spectrometry (GFAAS),[5] and flame atomic absorption spectrometry (FAAS)[6] have been applied for determination of the trace metals in biological and environmental samples. Even though the advanced techniques such as ICP-MS are more accurate than FAAS, FAAS is still the routine instrument in many laboratories due to its fast detection procedure, simplicity and low cost.[7]

Due to the extremely low concentrations of target analytes and matrix interferences of the samples, the direct determination of heavy metal sample by FAAS is often a difficult task. To solve these problems, a separation and enrichment step is required before determination. Several methods have been applied for separation and preconcentration of trace heavy metal ions, such as cloud point extraction,[8] biosorption,[9] dispersive liquid–liquid microextraction,[5] and solid-phase extraction (SPE).[10] Among these techniques, SPE is more popular for its simplicity, high enrichment factor, and low reagent consumption.

The development of new sorbents is the key factor in SPE. Various adsorbents have been used as solid-phase extractants, such as nanoporous silica,[11] activated carbon,[12] molecularly imprinted polymer[13] and nanometer-sized materials.[14] Among these materials, nanometer-sized materials, especially nanoparticles, have gained much attention due to their unique properties.[15] Nanoparticles, ranged from 1 nm to 100 nm in size, can offer a high surface area-to-volume ratio to adsorb metal ions with high extraction capacity and efficiency. Magnetic nanoparticles have been applied in many fields such as targeted drug delivery,[16] magnetic resonance imaging,[17] separation and preconcentration of target component.[18] Superparamagnetic nanoparticles can be easily magnetized in an external magnetic field, and dispersed after removal of the magnetic field. Accordingly, target analytes adsorbed by the superparamagnetic particles can be separated from a matrix by altering the outer magnetic field. Thus, magnetic nanoparticles are suitable as SPE adsorbents. However, bare magnetic nanoparticles are inclined to aggregate to affect the dispersion stability, which will reduce the extraction efficiency.[19] Hence, the modification of magnetic nanoparticles surface is considered as the key factor to improve their dispersion stability and extraction efficiency.

Poly-γ-glutamic acid (γ-PGA) is a microbial polymer consisting of D- and L-glutamic acid monomers, and it has been developed for various potential applications, such as hydrogel, bioflocculant, drug carrier, cosmetic and food additives.[20] The structure of γ-PGA was showed in Fig.1. In our previous reports, the

B. licheniformis WX-02 was isolated to synthesize γ-PGA, and multiple production technologies have been developed.[21, 22] To the best of our knowledge, the application of γ-PGA as SPE adsorbent has not been reported. Herein, γ-PGA was used to modify magnetic nanoparticles as an SPE adsorbent for separation and enrichment of trace Cu (II) and Pb (II), the concentrated samples were then determined by FAAS. The research objective of this work is to establish a fast and sensitive SPE procedure to determine the trace amount of heavy metal ions in environmental samples.

2. Experimental

2.1 Apparatus

The heavy metal ions were determined on a Perkin Elmer AAnalyst 700 flame atomic absorption spectrometer (Perkin Elmer, Waltham, USA). The γ-PGA modified magnetic nanoparticles were characterized by NEXUS 870 FI-IR (Thermo, Madison, USA) and a Hitachi H-7000 FA electron microscope (Hitachi, Tokyo, Japan). A KQ3200E ultrasonicator with the ultrasonic frequency of 40 KHz (KunShan Ultrasonic Instruments Co., Ltd. KunShan, China) was used to disperse the nanoparticles in solution. A HJ-5 Multi-Purpose Stirrer (Hua Li Experimental Instruments Co., Ltd. Jin Tan, China) was used to mechanical stirred the magnetic nanoparticles during the synthesis.

2.2 Reagents and standard solutions

All reagents used in this study were of specpure or at least analytical reagent grade. The stock solutions (1g L^{-1}) for Cu (II) and Pb (II) were provided by National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials (Beijing, China). Iron (III) chloride, Iron (II) sulfate and tetraethoxysilane (TEOS) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). (3-aminopropyl) triethoxysilane (APTES) was supplied by Wuhan University Chemical Factory (Wuhan, China). Toluene was bought from Shanghai Experiment Reagent Co., Ltd (Shanghai, China), and the high purity γ-PGA (purity>92%, molecular weight>1000 kD) was prepared by our laboratory.

2.3 Preparation of the sorbent

2.3.1 Synthesis of bare magnetic nanoparticles (MNPs)

The MNPs were synthesized using the modified chemical co-precipitation method.[23] Briefly, $FeCl_3{\cdot}6H_2O$ (4.2 g) and $FeCl_2{\cdot}4H_2O$ (2.16 g) were dissolved in 200 mL deionized water under nitrogen gas with vigorous stirring (400 rpm) at 85°C for 5 min. Then, 40 mL of 30% $NH_3{\cdot}H_2O$ was added into the reaction solution rapidly, with a color change from orange to black immediately, stirred for 30 min. Afterward, the magnetic nanoparticles were collected by magnetic separation, and washed with deionized water for 3 times. Finally, the magnetic Fe_3O_4 particles were dispersed in

200 mL deionized water.

2.3.2 Preparation of silica-coated magnetic nanoparticles (SCMNPs)

The Silica coated magnetic nanoparticles were synthesized by the sol–gel reaction using tetraethyl orthosilicate (TEOS).[24] Firstly, Fe_3O_4 particles were washed 3 times with ethanol, and dispersed in 200 mL of ethanol. Afterward, 1.35 mL of TEOS and 8.5 mL of 30% ammonium hydroxide were added into the dispersion solution, stirred (200 rpm) at 40°C for 24 hour. The products were washed with dry toluene for 3 times for further use.

2.3.3 Preparation of γ-PGA-modified silica-coated magnetic nanoparticles (γ-PGA-SCMNPs)

Firstly, the SCMNPs were modified with APTES according to a previous reported method.[25] 1.6 g SCMNPs were dispersed in 200 mL dry toluene, added with 1.5 mL APTES, and stirred (200 rpm) at room temperature for 24 hour to obtain amino-functionalized silica-coated magnetic nanoparticles. The products were washed for 3 times with ethanol and deionized water respectively.

To prepare γ-PGA-modified magnetic nanoparticles, 1.7 g amino-functionalized magnetic nanoparticles (NH_2-SCMNPs) were dispersed in 100 mL deionized water. Then, 100 mL γ-PGA solution (20 mg mL^{-1}) was poured into the dispersion, stirred

(400 rpm) vigorously for 1 hour at room temperature. The final products were washed 3 times with deionized water and freeze-dried. SCMNPs modified with APTES in order to make the particles positively charged, Then, negatively charged γ-PGA solution were assembled on NH_2-SCMNPs through electrostatic interactions. Fig. 2 shows the synthesis procedure for γ-PGA-SCMNPs.

2.4 Adsorption experiments

2.4.1 General procedure

100 mL diluted sample solution and 50 mg γ-PGA-SCMNPs were added into a 250 mL flask, and ultrasonicated for 2 min to facilitate the adsorption of metal ions. Afterwards, the magnetic adsorbents were separated by an external magnetic field, and the supernatants were decanted directly. The magnet was removed, and the elution (0.05 mol L^{-1} HCl) was added, ultrasonicated for 2 min. After desorption, the nanoparticles were magnetically separated and the eluent was determined by FAAS. High purity deionized water was employed as the blank solution and was subjected to the same procedure.

2.4.2 Sample preparation

Two practical samples including tap water and lake water were measured in this study. Tap water samples were obtained from laboratory, and lake water samples were collected from South Lake of Wuhan, China. The samples were acidified to pH 1 with HNO_3 and stored in polyethylene container for further use. Before determination, all the samples were adjusted to pH 7 according to optimized experiment conditions.

3. Results and discussion

3.1 Characterization of γ-PGA-modified SCMNPs

3.1.1 FT-IR spectrum

The FT-IR analysis was performed to validate the immobilization of γ-PGA on SCMNPs. The FT-IR spectra for NH_2-SCMNPs, γ-PGA-SCMNPs and γ-PGA are shown in Fig. 3. The bands at 588 and 582 cm^{-1} in the spectra of NH_2-SCMNPs and γ-PGA-SCMNPs were the characteristic absorption of Fe–O bond, confirming the presence of magnetite nanoparticles. The characteristic peaks of the Si–O–Si stretching vibration appeared around 1060 cm^{-1}, which indicated the covalent anchoring of silane polymer onto the surface of magnetite particles. Moreover, the absorption bands at 3440 and 1630 cm^{-1} can be ascribed to the N–H stretching vibration and NH_2 stretching, indicating that the coupling agent APTES had been introduced onto the Fe_3O_4 MNPs surface. Three characteristic peaks of pure γ-PGA included C=O stretch of free carboxylic acids at 1637 cm^{-1}, asymmetric COO^- stretch at 1560 cm^{-1} and a broad band due to peak-overlap of N–H/C–N deformation and symmetric COO^- at $1400 cm^{-1}$, could be seen in the FT-IR spectra of γ-PGA and γ-PGA-SCMNPs, indicating that γ-PGA has been successfully bonded to the surface of SCMNPs.

3.1.2 Analysis of the morphology and particle size

TEM image of γ-PGA-SCMNPs showed that the new synthesized MNPs were circular nanoparticles (Fig. 4), featured with a core-shell structure. Based on the TEM, the diameters of 100 γ-PGA-SCMNPs particles were recorded by SmileView 2.0 software, and the diameters distributions were in the range from 7.7 to 18.4 nm with an average size of 12.5 nm.

3.2 Adsorption selectivity of γ-PGA-SCMNPs

To evaluate the adsorption selectivity of γ-PGA-SCMNPs, the adsorption rate of Cu (II), Pb (II), Cd (II) and Cr (III) was investigated. The results were showed in Fig.5. As can be seen, the adsorption rate of Cu (II) and Pb(II) was almost 100%, which was much higher than that of Cd (II) and Cr (III), indicating that the sorbent has high adsorption selectivity toward Cu (II) and Pb (II).

3.3 Metal binding studies of γ-PGA

To confirm the effect of γ-PGA on the extraction process, γ-PGA-SCMNPs and NH_2-SCMNPs were employed as SPE absorbents for extraction of trace amounts of Cu (II) and Pb (II) under the condition recommend by general procedure. The recovery of Cu (II) and Pb (II) was 91.44% and 93.1% for γ-PGA-SCMNPs, while for NH_2-SCMNPs, the recovery of Cu (II) and Pb (II) was 59.83% and 31.5%, respectively. The results indicating that the γ-PGA could improve the metal binding capability of the nanoparticles obviously. For the metal binding mechanism of γ-PGA, Cu (II) complexation with γ-PGA has been studied by Hikichi et al.[26] The authors used NMR studies to determine the interactions of Cu (II) with γ-PGA. NMR spectra showed that Cu (II) interacted with the carboxylic acid groups as well as forming a short lived bond with N of the amide linkages. While for Pb (II), the metal ions probably only interacted with carboxylic groups of linear γ-PGA chains.[27] Moreover, metal interactions with γ-PGA have significant effects on γ-PGA conformation. It has been reported that the metal-γ-PGA interactions lead γ-PGA to form the helical conformation at higher pH because of metal binding to COO^- side-chains,[28] and helix conformation has less functional groups for metal binding than that of the random coil conformation. Thus, metal interactions cause significant changes in the γ-PGA helix-coil transitions which may have pronounced impact on overall metal sorption.

3.4 Effect of pH

To obtain the optimal pH for adsorption of target analytes, effects of different pH values (2-9) on the recovery of Cu (II) and Pb (II) were investigated. The pH value of 100 mL metal solution (100 μg L^{-1}) was adjusted to 2, 3, 4, 5, 6, 7, 8 and 9, respectively. As shown in Fig.6, no recovery was determined at pH 2 for Cu (II) or Pb (II). The carboxyl groups of γ-PGA remained in the nonionized form when the pH was lower than the pK_a of γ-PGA (4.09). Thus, it was difficult for metal adsorption. Moreover, γ-PGA tends to form intramolecular hydrogen bonds at a low pH with a more compact α-helix conformation, which might reduce the number of functional groups available for metal binding.[29] The recovery of Cu (II) and Pb (II) increased with the improving pH from 2 to 4, which might be due to the ionization of carboxyl groups and the conformational change from α-helix to random coil.[29] When the pH exceeded 4, the recovery of Cu (II) was above 90%. On the other hand, Pb (II) was intensively adsorbed from pH 4 to 7, while the recovery decreased as the increased pH from 7 to 9. Under the conditions of pH >pK_a of Pb (7.7), Pb (II) can form a significant number of hydrolysis species such as $[Pb_3(OH)_5]^{+1}$ and $[Pb_4(OH)_4]^{+4}$, reducing the ion exchange between carboxylic groups and Pb (II). Thus, the appropriate pH for extraction of Cu (II) was ranged from 4 to 9, with pH 4-7 for Pb (II). In this work, pH 7 was selected for all subsequent experiments.

3.5 Effect of elution

As shown in Fig.6, the Cu (II) and Pb (II) were almost not adsorbed on γ-PGA-SCMNPs at pH 2, indicating that heavy metal ions reserved on γ-PGA could be desorbed under acid conditions. Compared to HCl, HNO_3 was a strong oxidizing agent, which might shorten the lifespan of γ-PGA. Thus, HCl was employed as the desorption reagent. The influence of HCl concentration on the recovery of Cu (II) and Pb (II) was investigated. The results showed that 0.05 mol L^{-1} HCl solution was sufficient for 95% recovery. Also, the effect of elution volume on quantitative elution of the tested ion was investigated. The results indicated that the metal ions could be eluted completely with 3 mL of 0.05 mol L^{-1} HCl.

3.6 Effect of ultrasonic time

Ultrasonic times (1–10 min) for adsorption and elution were also investigated. The results indicated that quantitative recovery of Cu (II) and Pb (II) could be achieved when the ultrasonication time was greater than 2 min for adsorption and elution. Therefore, 2 min was selected as the adsorption and desorption time. As discussed above, the adsorption mechanism of γ-PGA-SCMNPs was probably ion exchange, which was the main reason for the fast adsorption and elution. Moreover, analysis time of magnetic solid phase extraction (MSPE) is faster than that of traditional SPE methods.[30] In conclusion, the given method has rapid adsorption and desorption time, which showed great efficiency for future practical applications.

3.7 Effect of sample volume and the enrichment factor

To achieve a higher enrichment factor, a large volume of sample solution is required. To study the effect of sample volume, the sample solutions of 100, 200, 300, 400, 500 and 600 mL containing 10 mg of target analytes were determined according to the general procedure. The results showed that quantitative recovery for Cu (II) was obtained when sample volumes were less than 500 mL, and less than 400 mL for Pb (II). The decreased recovery might be caused by the reduced metal ion concentration in the solution when sample volume increased. Since the final elution volume was 3 mL, the enrichment factor of Cu (II) and Pb (II) was reached 166 and 133, respectively. Compared with the reported results given in Table 1, the enrichment factors obtained by our method are higher.

3.8 Effect of potentially interfering ions

Under the optimal experimental conditions described above, the interference effects of different ions on extraction of Cu (II) and Pb (II) were studied. The tolerance limit was defined as the concentration of ions that reduced the recovery of Cu (II) and Pb (II) to less than 90%. The results showed that the recovery of the target analyte was remained above 90% even in the presence of the following ions: 2 mg mL^{-1} Na^+ and K^+, 1 mg mL^{-1} Ca^{2+} and Mg^{2+}, 50 µg mL^{-1} Zn^{2+}, 3 mg mL^{-1} Cl^-, and 2 mg mL^{-1} SO_4^{2-} and NO_3^-. It could be seen that this method had a good tolerance to the interference of tested ions. Hence, our method was effective for the separation of heavy metal ions from complex matrices.

3.9 Adsorption capacity study and sorbent regeneration

The adsorption capacity of the adsorbent is an important factor. In this work, the adsorption capacity was determined by a recommended method.[31] Briefly, 20 mg γ-PGA-SCMNPs and 100 mL Cu (II) or Pb (II) solution with different concentrations was equilibrated for 2 min, and the concentrations of metal ions were increased till the sorbents reached the “saturation”. The static adsorption capacities of γ-PGA-SCMNPs were found to be 5.22 and 0.11 mg g^{-1} for Cu (II) and Pb (II).

Regeneration is another important factor for evaluating the performance of the adsorption material. γ-PGA-SCMNPs were repeatedly employed for preconcentration of Cu (II), and the γ-PGA-SCMNPs were washed three times with deionized water after each cycle. The results showed that γ-PGA-SCMNPs can be re-used up to 10 times without loss of analytical performance, indicating that γ-PGA-SCMNPs were stable for long-term applications.

3.10 Analytical performance

Under the optimal experimental conditions, the analytical performance of this method was also investigated. The detection limit of the method, which defined by the IUPAC as three times the standard deviation of blank (N=20), was found to be 0.46 and 1.43μg L^{-1} for Cu (II) and Pb (II), respectively. The relative standard deviations

(RSDs, n=7, c=50 μg L^{-1}) reached 2.48% and 7.42% for Cu (II) and Pb (II), respectively. The results showed that the given method possessed relatively higher sensitivity with low RSDs.

3.11 Analytical applications

To evaluate the accuracy of the developed method, the sorbent was applied to the extraction of Cu (II) and Pb (II) in lake water and tap water. The accuracy was investigated by an analysis of the samples added with known amounts of Cu (II) and Pb (II) ions. The results are given in Table 2. As can be seen, recoveries for the target analytes ranged from 93% to 109%, indicating that γ-PGA-SCMNPs were suitable for selective solid phase extraction and preconcentration of trace Cu (II) and Pb (II) from practical samples.

3.12 Comparison with other methods

A comparison of the given method with other SPE methods was given in Table 1. Compared to other methods, the given method showed higher enrichment factor and faster analysis process, as well as the low LOD, which could be attributed to the large surface area, rapid dynamics of extraction, and high extraction efficiencies of the γ-PGA-SCMNPs.

4. Conclusion

In this study, the novel γ-PGA-modified magnetic nanoparticles, γ-PGA-SCMNPs were prepared and applied for solid phase extraction of trace amounts of Cu (II) and Pb (II). Compared with common SPE absorbents, γ-PGA-SCMNPs showed higher enrichment factor and lower LODs, indicating that γ-PGA-SCMNPs were effective SPE absorbents. Furthermore, it was easy to separate the sorbent from aqueous solution by a permanent magnet, which required a very short analytical time. In conclusion, our developed method is simple, fast and selective for the solid phase extraction of trace Cu (II) and Pb (II) in environmental water samples.

Acknowledgements

This work was supported by rural areas of the national science and technology plan in the 12th five-year plan of China (No.2013AA102801-52). This work was also supported by the National Natural Science Foundation of China (Grant No.31170046) and Wuhan Municipal Key Technologies R & D Program of China (2013020602010301).

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Figure captions

Fig.1 Structure of γ-PGA

Fig.2 Synthesis procedure of the γ-PGA-SCMNPs

Fig.3 FT-IR spectra of γ-PGA (A), γ-PGA-SCMNPs (B) and NH_2-SCMNPs (C)

Fig.4 TEM image of γ-PGA-SCMNPs

Fig.5 Adsorption rate of some heavy metal ions (experimental condition: concentration of metal ion=1 mg L^{-1}, sample volume=5 mL, adsorption time=2 min)

Fig.6 Effect of pH on the recovery of Cu (II) and Pb (II) on γ-PGA-SCMNPs (other conditions: sample volume=100 mL, adsorption time=2 min, desorption time=2 min, eluent=3 mL of 0.05 mol L^{-1} HCl)

Table 1

Comparison of analytical performance of γ-PGA-SCMNPs with other absorbents used in SPE-FAAS method.

Analytes	Absorbent	LOD (μg L^{-1})	Enrichment factor	Adsorption time (min)	Reference
Cu, Pb	γ-PGA-SCMNPs	0.46-1.43	133-166	2	This work
Cu, Zn	DAPD-SCMNPs	0.14-0.22	125	2	[32]
Mn, Co, Ni, Cu, Cd, Pb	Column packed with Amberlite XAD-2010 resin	0.08-0.26	100	50	[33]
Cd, Ni	TiO_2 nanotubes	0.25-1	66.7	160	[34]
Cu, Ni, Cd, Pb, Cr, Co	PAN impregnated Ambersorb 563 resin	0.67	125	50	[35]
Cu, Cd, Pb, Zn, Ni, Co	Multiwalled carbon nanotubes	0.3	80	80	[36]
Cu, Cd, Pb, Zn, Mn, Fe, Cr, Ni, Co	Chromosorb 108	0.16	80	80	[37]

LOD: limit of detection

DAPD-SCMNPs: 2,6-diaminopyridine modified magnetic nanoparticles

PAN: 1-(2-pyridylazo) 2-naphtol

Table 2

Analytical results of Cu and Pb in tap water and South Lake water (mean ± S.D., n = 3).

Sample	Element	Added/μg L^{-1}	Found/μg L^{-1}	Recovery
Tap water	Cu	0	1.27±0.23	
		40	50.31±2.09	109.42%
	Pb	0	0.01±0.01	
		50	48.58±1.12	97.02%
South Lake	Cu	0	1.73±0.11	
		40	51.48±0.82	106.68%
	Pb	0	0.04±0.04	
		50	46.95±1.67	93.47%

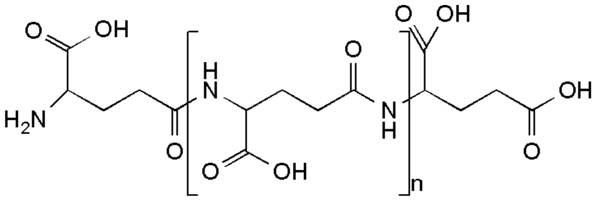

Fig.1 Structure of γ-PGA

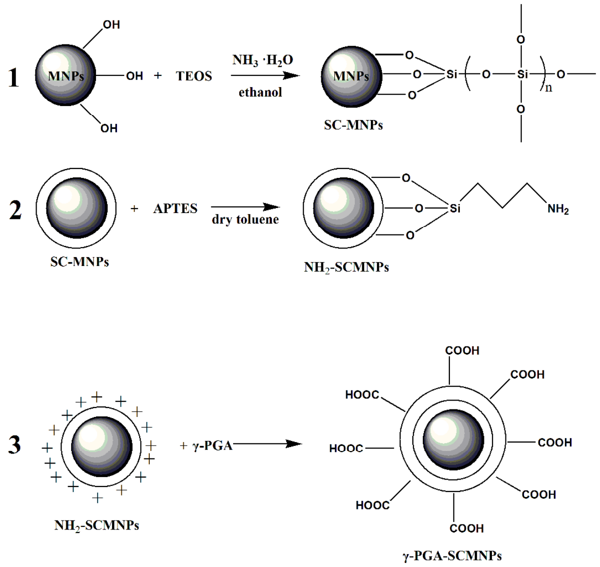

Fig.2 Synthesis procedure of the γ-PGA-SCMNPs

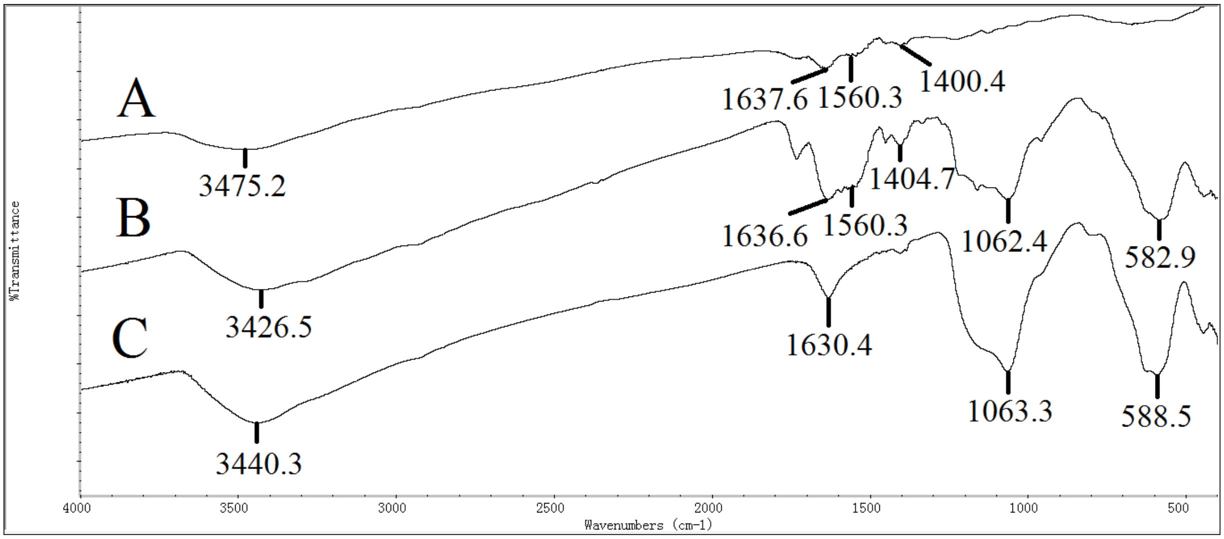

Fig.3 FT-IR spectra of γ-PGA (A), γ-PGA-SCMNPs (B) and NH_2-SCMNPs (C).

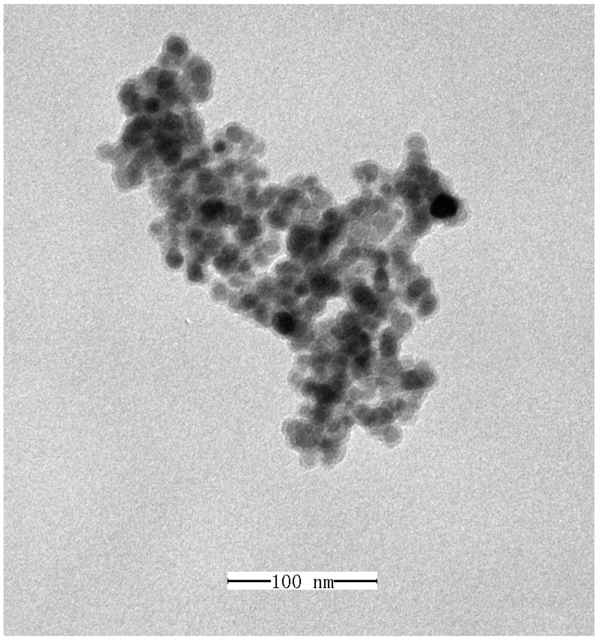

Fig.4 TEM image of γ-PGA-SCMNPs

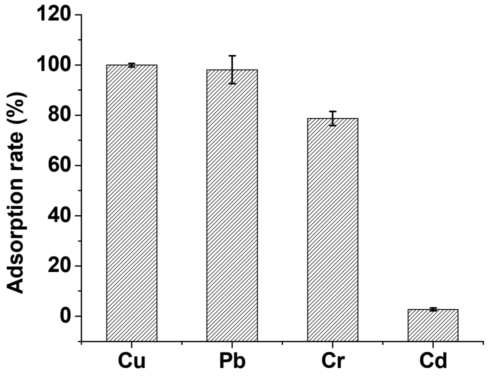

Fig.5 Adsorption rate of some heavy metal ions

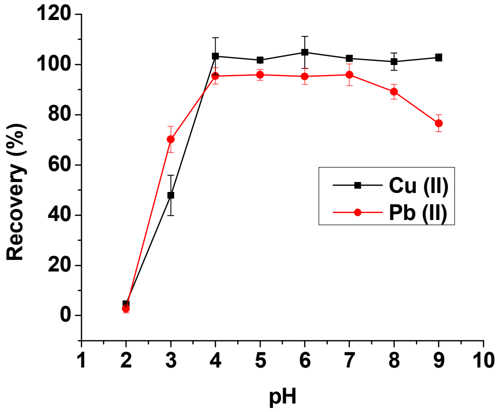

Fig.6 Effect of pH on the recovery of Cu (II) and Pb (II) on γ-PGA-SCMNPs.