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Preparation of xylenol orange functionalized silica gel as a selective solid phase extractor and its application for preconcentration—separation of mercury from waters

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Abstract

A new selective solid phase extractor was prepared from silica gel modified with xylenol orange (SGMXO). The solid phase extractor is stable in $6 \, mol \, L^{-1}$ HCl, common organic solvents, and pH 1.0–9.0 buffer solutions. In the batch experiments, Hg(II) can be adsorbed on SGMXO at pH 1.0 with 90.0% retention, whereas the retention of other common coexisting metal ions such as Cd(II), Pb(II), Cu(II), Ni(II), Co(II), Mn(II), Zn(II), and Fe(III) is less than 4.1%.. The adsorption equilibration for Hg(II) was achieved within 3 min. At optimum conditions, the adsorption capacity of the extractor is $18.26 \, \mu mol \, g^{-1}$ of dry modified silica gel, and the preconcentration factor is as high as 333. The recovery is still higher than 95% for the preconcentration of $10 \, ng \, mL^{-1}$ Hg(II). The new solid phase extractor has been used for the preconcentration of low level of Hg(II) in surface water, tap water in chemistry laboratory and student's dormitory and a simulated sea water samples, recoveries of 98.2–100.6% were obtained. It is showed that low level of Hg(II) can be effectively preconcentrated by this new selective solid phase extractor.
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1. Introduction

Although atomic absorption spectrometry (AAS) [1,2] and inductively coupled plasma atomic emission spectrometry (ICP-AES) [3–6] are among the most widely used methods for trace metal determination, they are usually insufficient due to the matrix interferences and the very low concentration of metal ions. Therefore, a separation/pre-concentration step is required.

The traditional separation and pre-concentration methods for metal ions include liquid–liquid extraction, coprecipitation, and ion exchange, etc. These methods often require large amount of high purity organic solvents, some of which are harmful to health and cause environmental problems. Nowadays, several methods have been used for pretreatment of the samples, solid phase extraction (SPE) [7–12] is one of them. Its advantage is visible [13], which include: (i) higher enrichment factors; (ii) safety

with respect to hazardous samples; (iii) minimal costs due to low consumption of reagents. So, SPE has been widely used for the isolation and concentration of target analytes, and the clean-up of samples (removal of matrix interferences) in pharmaceutical, clinical, environmental and food chemistry [14].

The choice of sorbent is therefore a key point in SPE, because it can control the analytical parameters such as selectivity, affinity and capacity [15,16]. Preparation of new selective extractor is an important trend of solid phase extraction [13]. Reagents can be modified on organic or inorganic support as solid phase extractors. Silica gel presents the advantages of no swelling, fast kinetics, mechanical, thermal and chemical stability under various conditions [17]. Therefore, it is a widely used support for various solid phase extractors. Recently, some chelating agents have been modified on silica gel as solid phase extractors for the pre-concentration of some metal ions. Safavi et al. [18] used glycerol modified silica gel to enrich Co(II) in aqueous solutions before determination. Soliman et al. [19] and Khan et al. [20] modified silica gel chemically by 2-thiophenecarboxaldehyde and 1,5-diphenylcarbazide, respectively, then they used these

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extractors for the pre-concentration of Hg(II) in aqueous solution. Rojas et al. [21] used silica gel modified with 1,5-bis(di-2-pyridyl) methylene tiocarbohydrazide as an extractor to enrich Pd(II) before its on-line determination. Madrakian et al. [22] modified silica gel with 2,4,6-trimorpholino-1,3,5-triazin as an extractor for separation and preconcentration of Ag(I) in natural water. Moraes et al. [23] and Silva et al. [24] used 1,3-diamine propane-3-propyl and 3-(1-imidazolyl)propyl for modified silica gel pre-concentration of Cu(II) in biological materials and water samples. Wu et al. [25] used polyamidoamine modified silica gel to enrich and separate Pd(II) prior to FAAS determination. Zougagh et al. [26] used the column packed with methylthiosalicylate modified silica gel for preconcentration of Pb(II) in water prior to its determination.

So far as we know, several sorbents have been used for solid phase extraction of Hg(II) [27,28]. They are produced by immobilization of complexing or chelating compounds on different solid surface through physical loading or chemical bonding. Generally speaking, chemical bonding is more stable than physical loading. In the present work, xylenol orange was chemically

modified on silica gel as a new selective solid phase extractor. The utility of the new sorbent for separation/pre-concentration of low level of Hg(II) were studied and evaluated. The results showed that inorganic mercury can be selectively extracted by the new solid phase extractor in acidic aqueous solutions in presence of common coexisting metal ions. This new extractor has been used for separation and pre-concentration of trace amount of mercury from environmental waters.

2. Experimental

2.1. Reagents and apparatus

Analytical reagent-grade chemicals were employed for preparation of all solutions. Doubly distilled water was used for the preparation of the reagent solutions. Standard solutions of $1.000 \, mg \, mL^{-1}$ of Cd(II), Ni(II), Co(II), Mn(II), Pb(II), Zn(II), Cu(II), Fe(III) and Hg(II) were prepared by dissolving the corresponding metal salts in $0.03 \, mol \, L^{-1}$ of nitric acid, hydrochloric acid or sulfuric acid.
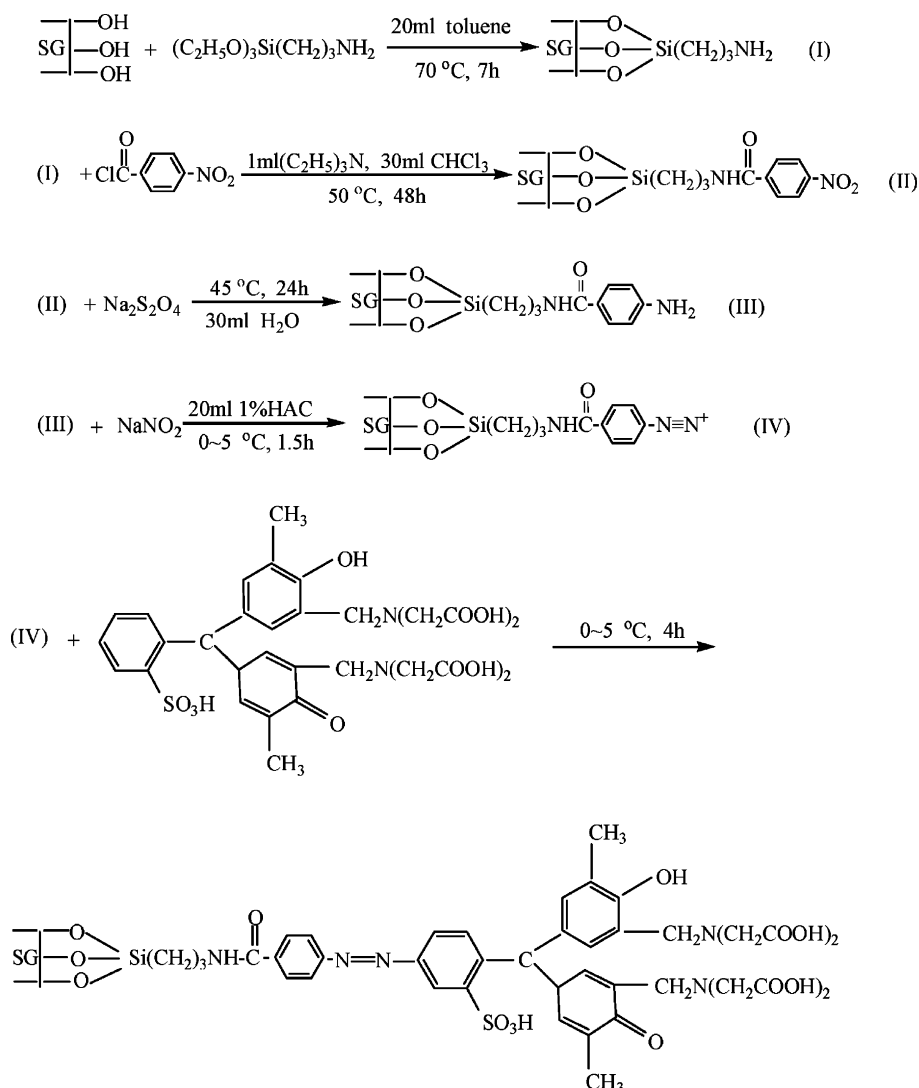
Scheme 1. The route for preparation of silica gel modified with xylenol orange.

The reagents used in detecting metal ions were as follows: 5.0×10^{-3} mol L^{-1} of 4-(2-pyridylazo) resorcinol (PAR), 5.0×10^{-3} mol L^{-1} of 1-(2-pyridylazo)-2-naphthol (PAN), 1.0×10^{-2} mol L^{-1} of 1,10-phenanthroline, and 0.8 mol L^{-1} of HClO$_4$. A series of buffer solutions (0.2 mol L^{-1}) of pH 1.0–9.0 were used for pH adjustment: pH 1.0–2.0 (HCl–KCl), pH 3.0–6.0 (NaAc–HAc), pH 6.0–8.0 (KH$_2$PO$_4$–Na$_2$HPO$_4$), pH 6.0–9.0 (KH$_2$PO$_4$–NaOH). A 110–125 mm diameter particles of silica gel (Qingdao Haiyang Chemical Factory), Aminopropyltriethoxysilane (Lancs Research Chemicals LTD), Xylenol Orange (ShangHai SSS Reagent Co., Ltd.); a glass tube of Ø 3 mm × 20 mm was washed with 6 mol L^{-1} HCl, 95% ethanol, and doubly distilled water, and then used as a chromatographic column.

A 722 spectrophotometer (Xiamen, China) was used for the determination of absorbance at a given wavelength. A digital pH meter pHS-3C (Hangzhou, China) was used for the pH measurements.

2.2. Preparation of xylenol orange modified silica gel

In order to remove any adsorbed metal ions and increase the content of –OH, silica gel (SG) was activated by dipping in 6 mol L^{-1} of hydrochloric acid for two days, then filtered and washed repeatedly with distilled water until no detectable Cl$^-$ can be found in the filtrate. Such treated silica gel was dried in an oven at 110 °C to remove any adsorbed water on the surface. The preparation process of xylenol orange modified silica gel was showed in Scheme 1. The steps (I)–(IV) were performed according to methods described in literature [29]. A 10 g of dried silica gel was mixed with 10 mL aminopropyltriethoxysilane in anhydrous acetone incubated in a sealed flask at 70 °C, the reaction was completed within 7 h, and the product aminopropyl silica gel (APSG) was filtered, washed with dry acetone and dried under vacuum. The dried APSG was benzoylated in a sealed flask at 50 °C with 30 mL of a solution in chloroform containing 1 g of p-nitrobenzoyl chloride and 1 mL of triethylamine. The reaction was completed within 48 h. The product was filtered, washed with chloroform to remove excess reagents, and then dried under vacuum. Incubating the silica gel with 20 mL of 5% sodium dithionite in a sealed flask at 45 °C for 24 h, the –NO$_2$ group was reduced into –NH$_2$. This arninophenyl derivative was then diazotized for 1.5 h at 0–5 °C with 20 mL of 2% (w/v) NaNO$_2$ in 1% acetic acid. After filtering and washing with cold distilled water, the silica gel was mixed with 50 mL of aqueous solution containing 1 g of xylenol orange. The reaction was finished in about 4 h, and color of the system was changed into deep orange. The resulting solid phase was filtered, washed with ethanol and water until the filtrate showed no characteristic color of xylenol orange. The solid was then dried at 80 °C for 6 h to obtain the xylenol orange modified silica gel. According to the adsorption capacity of Hg(II) on the SGMXO, bonding of XO on silica gel is 18.26 μmol.

2.3. Batch experiments

Xylenol orange modified silica gel was stirred in a suitable amount of metal ion solution for a fixed period of time at room temperature. The supernatants were taken for the un-extracted metal ions measurements by spectrophotometry. This method was used to study the effects of pH and stirring time on the retention of metal ions on the xylenol orange modified silica gel, and to measure the maximum adsorption capacity of Hg(II) on the modified silica gel.

2.4. Column experiments

For the column experiment, SGMXO was packed in a glass column, a solution containing metal ions was adjusted to a suitable pH and passed though the column at a certain flow rate. Metal ion retained on the column was eluted with 0.8 mol L^{-1} of HClO$_4$ at a lower flow rate and its concentration was determined by spectrophotometry.

2.5. Constants

The adsorption capacity, extraction percentage, distribution ratio and selectivity coefficient were calculated, respectively, by the following equations:

$$Q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$E\ (\%) = \frac{C_0 - C_e}{C_e} \times 100 \tag{2}$$

$$D = \frac{Q}{C_e} \tag{3}$$

$$\alpha_{Hg/M} = \frac{D_{Hg}}{D_M} \tag{4}$$

where Q represents the adsorption capacity (mg g^{-1}), C_0 and C_e are the initial and equilibrium concentrations of metal ions (μg mL^{-1}), W the mass of SGMXO (g), and V is the volume of metal ion solution (L); $E(\%)$ stands for the extraction percentage, and D is the distribution ratio (mL g^{-1}); $\alpha_{Hg/M}$ denote the selectivity coefficient of Hg(II) with respect to other common coexisting metals, indicating the selectivity factor of SGMXO.

2.6. Determination of metal ions

Concentrations of various metal ions were measured by visible spectrophotometry as described in literature [30]. The experimental condition for these measurement are listed in Table 1.

3. Results and discussion

3.1. Analysis of the IR and Raman spectrum of SGMXO

IR absorption bands found for SG at 3458, 1635 and 1104 cm^{-1} are assigned to the stretching vibration for –OH, bending vibration for –OH and absorption band for –Si–O–, respectively. The bands at 970, 803 and 473 cm^{-1} are assigned to the absorption bands for the background of silica gel. Comparison of the IR spectrum between SG and SGMXO reveals

Table 1
The experimental conditions for metal ion measurements

Developing reagent	Metal ion	pH	Buffer solution	Measuring wavelength (nm)
PAR	Cd(II)	9.0	Sodium borate	500
PAR	NiII)	9.3	Sodium borate	494
PAR	Co(II)	8.0	Sodium borate	510
PAR	Mn(II)	10.0	Sodium borate	500
PAR	Pb(II)	10.0	Sodium borate	517
PAR	Zn(II)	8.67	Sodium borate	495
PAR	Cu(II)	9.3	Sodium borate	510
1,10-Phenanthroline	Fe(III)	4.6	NaAc–HAc	510
PAN	Hg(II)	9.3	Sodium borate	550

two new bands at 1550 and 1530 cm^{-1}, which are the bending vibration for C–N–H.

Raman absorption spectrum of SG is weak. The observed Raman absorption bands for SGMXO at 2925.74, 1603.81, 1445.20, 1348.68 and 1108.98 cm^{-1} are assigned to the dissymmetry stretching vibration for –CH$_2$, the stretching vibration for –C=C–, the stretching vibration for –N=N–, the bending vibration for –C–H in –CH$_3$, the bending vibration for –Si–O–Si–, respectively.

3.2. The stability of SGMXO

Add 0.2 g of SGMXO in some organic solvents (ethanol, acetone, chloroform), 6.0 mol L^{-1} of HCl and aqueous solutions with pH 1.0–9.0, respectively. The systems were stirred for 30 min, and the supernatants were found to be colorless. The solid was filtered, washed with water, then added into 20 mL solution containing 100 μg Hg(II), and stirred for 30 min, the Hg(II) in the supernatant was determined by spectrophotometry. There is no difference in extraction percentage between before and after chemical treatment. SGMXO is thus fairly stable in these media. Such a behavior strongly supports the fact that xylenol orange is chemically modified on the silica gel.

3.3. Effect of pH on the adsorption of metal ions

The pH value is one of the important factors controlling the extraction of metal ions from aqueous solutions. In order to obtain optimum extraction, the adsorption of metal ions on SGMXO in solutions with different pHs was examined by a batch mode experiment. For this purpose, 0.2 g of SGMXO was added into 20 mL of solution containing 100 μg metal ions at different pHs. The suspended systems were stirred for 30 min, then the unextracted metal ions in the supernatants were determined by spectrophotometry. It is noted from Fig. 1 that the retention for most of the metal ions various significantly with change in the pH. About 90.0% of Hg(II) is adsorbed on SGMXO at pH 1.0, whereas the adsorption of other metal ions, such as Fe(III), Pb(II), Cd(II), Co(II), Ni(II), Mn(II), Cu(II) and Zn(II), is less than 4.1% under the same experimental conditions. With the increase of pH, the absorption of some metal ions such as Cu(II), Zn(II) and Fe(III) creased. Therefore, pH 1.0 was chosen for the separation and preconcentration of Hg(II) in the following studies.
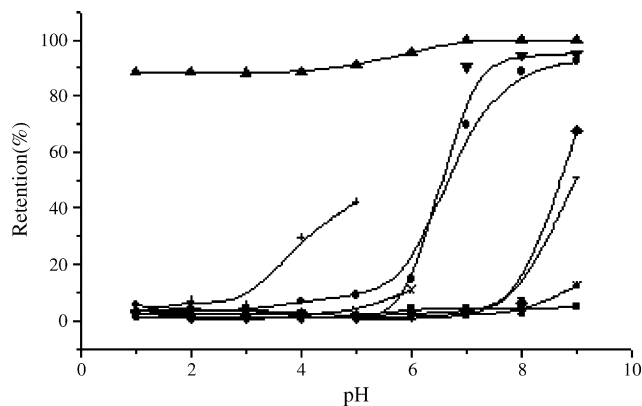

Fig. 1. Effect of pH on the adsorption of metal ions: 0.2 g of SGMXO; 100 μg metal ions per 20 mL solution; stirring time 30 min. (■) Cd; (●) Cu; (▲), Hg; (▼) Zn; (◆) Mn; (+) Fe; (×) Pb; (*) Ni; (–) Co.

3.4. Absorption of metal ions on the un-modified silica gel

In order to compare the absorption of metal ions on silica gel and the modified silica gel, 0.2 g of silica gel was added into 20 mL solution containing 100 μg metal ions at pH 1.0. The system was stirred for 30 min, and the un-extracted metal ions in the supernatant were determined by spectrophotometry. Experimental data were collected in Table 2. It can be seen that no selective absorption of metal ions has been observed for the un-modified silica gel, and the role played by silica gel itself is weak in the absorption of metal ions.

Table 2
Absorption of metal ions on silica gel and SGMXO at pH 1.0

Metal ion	Added (μg)	The absorption on SGMXO (μg)	The absorption on SG (μg)
Co(II)	100	0.68	12.37
Cd(II)	100	3.4	1.7
Cu(II)	100	2.69	2.97
Pb(II)	100	3.53	8.27
Fe(III)	100	4.05	2.78
Hg(II)	100	89.91	2.38
Ni(II)	100	0.33	2.38
Mn(II)	100	3.22	4.79
Zn(II)	100	2.38	0.8

Table 3
The distribution ratio selectivity coefficient of Hg(II) with respect to other metal ions

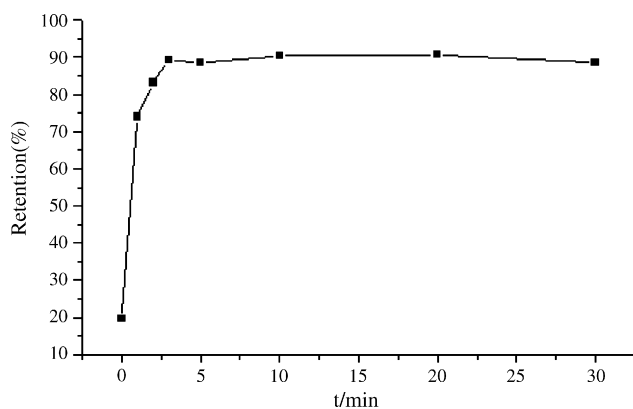|	Metal ions								
	Zn(II)	Cd(II)	Pb(II)	Fe(III)	Ni(II)	Mn(II)	Co(II)	Cu(II)	Hg(II)
D	2.44	3.52	3.66	4.22	0.33	3.33	0.68	2.76	891.08
$\alpha_{Hg/M}$	365.20	253.15	243.46	211.16	2700.24	267.59	1301.41	322.85	–

Fig. 2. Effect of stirring time on the retention of Hg(II): 0.2 g of SGMXO; 100 μg of Hg(II) per 20 mL solution; pH 1.0.

3.5. Selectivity of SGMXO

At the chosen pH, we calculated the distribution ratio and selectivity coefficient of Hg(II) by Eqs. (3) and (4) from the concentration data for single metal ions in the supernatant determined in batch mode experiments. As can be seen from Table 3, the values of distribution ratio of SGMXO sorbent for Hg(II) is as large as 891.08, which is several hundreds of times higher than that for the common coexisting metals. This result indicates that the SGMXO sorbent has excellent selectivity for Hg(II), and could be used to enrich the Hg(II) selectively in the presence of Pb(II), Cd(II), Cu(II) and Zn(II).

3.6. Effect of stirring time on retention of Hg(II)

The stirring time taken for the adsorption of the metal ion by the modified silica gel and the attainment of the equilibrium conditions is of considerable importance. Effect of stirring time on the retention of Hg(II) by SGMXO was studied by the batch experiments. As can be seen from Fig. 2, 3 min of the stirring time is necessary for the retention equilibrium of Hg(II). This confirmed the fact that modification of silica gel surface with organic complexing agents results in metal ion extractors, which need only a few minutes to complete extraction processes [31]. This is one of the advantages of using silica gel support for immobilization of chelating compounds.

3.7. Adsorption capacity of Hg(II) on SGMXO

The adsorption capacity of the sorbent is an important parameter to determine how much sorbent is required to quantitatively adsorb a specific amount of metal ion from solution [22]. For investigation of the adsorption capacity of Hg(II) at pH 1.0,
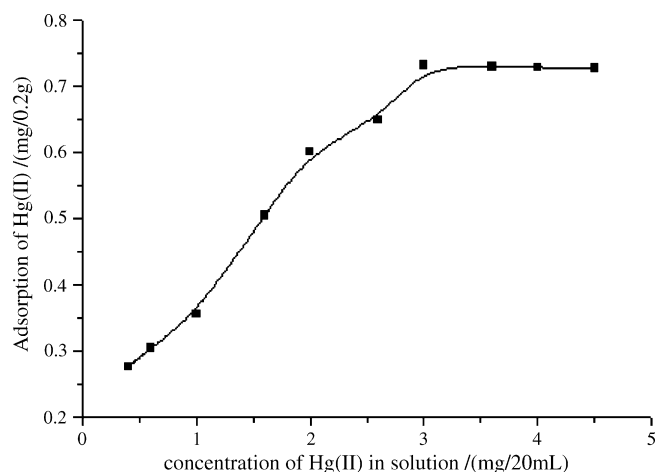

Fig. 3. Concentration dependence of the adsorption of Hg(II) on the SGMXO.

the same volumes of Hg(II) solutions with different concentrations was stirred with the same amount of SGMXO for 30 min, then the concentration of Hg(II) in solutions were determined. Change in the adsorption of Hg(II) by the modified silica gel was measured, and the results were shown in Fig. 3. The adsorption capacity of Hg(II) by SGMXO as calculated by Eq. (1) is found to be 18.26 μmol g^{-1} of dry modified silica gel at the optimum conditions. This is satisfactory for the trace analysis of Hg(II).

3.8. Effect of flow rate on retention of Hg(II)

In the column experiment, 0.2 g of SGMXO was conditioned with an appropriate solution and packed in a glass column, and then 20 mL of solution containing 100 μg of Hg(II) was passed
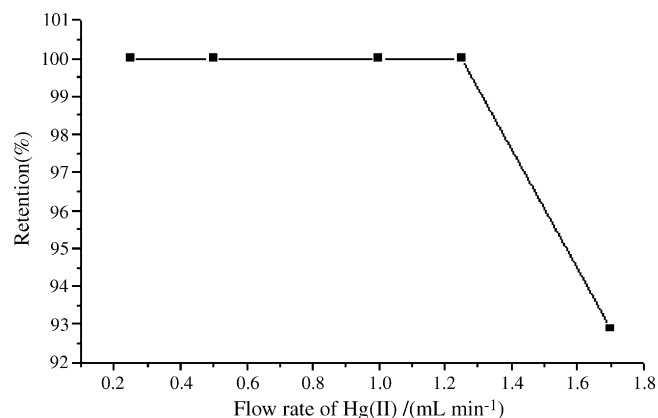

Fig. 4. Effect of flow rate for retention of Hg(II) 0.2 g SGMXO, 100 μg Hg(II)/20 mL at pH 1.0.
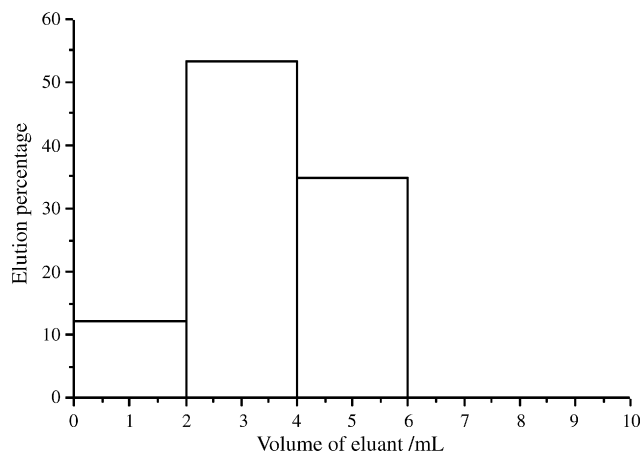
Fig. 5. Elution curve of Hg(II).

Table 5
Effect of the common metal ions on the recovery of Hg(II)

Interfered ions	Recovery of Hg(II) (%)
Cd(II)	97
Ni(II)	98
Co(II)	98
Mn(II)	100.5
Pb(II)	99
Zn(II)	100.1
Cu(II)	101.7
Fe(III)	98.3

through the column. The flow rate of solution is an important factor affecting the retention of Hg(II), it is necessary to choose an appropriate flow rate that ensures a higher mercury species uptake. Hence, the influence of flow rate on species retention was studied in the range from 0.2 to 1.7 mL min^{-1}. As indicated by Fig. 4, 100% of Hg(II) was absorbed by SGMXO when the flow rate is less than 1.3 mL min^{-1}. However, when the flow rate is up to 1.7 mL min^{-1}, the retention of Hg(II) is only 92.9%. It is well known that when the flow rate is too fast, Hg(II) cannot sufficiently be adsorbed by SGMXO in the column. Therefore, we choose 0.7 mL min^{-1} as flow rate in our experiments.

3.9. Elution curve for Hg(II)

A 20 mL of solution containing 20 μg of Hg(II) at pH 1.0 was passed through the column with a flow rate of 0.7 mL min^{-1}. Hg(II) retained in the column was eluted by 0.8 mol L^{-1} of HClO$_4$ with a rate of 0.3 mL min^{-1}. 6.0 mL of the eluent was collected in three aliquots, the Hg(II) concentration in the eluent was determined and the total recovery of 100% Hg(II) was obtain(Fig. 5), so, a flow rate of 0.3 mL min^{-1} for the eluant and 6.0 mL of the eluent were selected for our studies.

3.10. Pre-concentration and recoveries of Hg(II)

The results for preconcentration and recovery of Hg(II) using the column method are shown in Table 4. Solutions containing 20 μg of Hg(II) but in different volumes were made up and passed through the column .The Hg(II) retained in the column

Table 4
Preconcentration and recoveries of Hg(II)

Volume (mL)	Hg(II) in elution (μg)	Recovery (%)	Preconcentration factor
20	20.0	100	3.3
50	20.0	100	8.3
250	19.8	99.6	42
500	19.7	98.4	83
1000	19.7	97.0	167
2000	19.5	95.6	333

was eluted and its content determined. It is found that the recovery reaches 95.6% and the preconcentration factor of 333 was observed even when the concentration of Hg(II) is as low as 10 ng mL^{-1}. Therefore, it is possible to enrich low level of Hg(II) from aqueous solutions by SGMXO.

3.11. Effect of common coexisting metal ions on the recovery of Hg(II)

To assess the possibility of analytical applications for the proposed procedure, the effects of some foreign ions, which interfere with the determination of Hg(II) and often accompany with Hg(II) in various real samples, were examined under the optimized conditions. For this purpose, 20 μg of each metal ion, such as Cd(II), Ni(II), Co(II), Mn(II), Pb(II), Zn(II), Cu(II) and Fe(III), was mixed with 20 μg of Hg(II) in 20 mL of solution at pH 1.0. These mixtures were passed through the column, then the Hg(II) retained in the column was eluted with 6 mL of HClO$_4$, and the Hg(II) content in the eluent was determined. The recovery data of Hg(II) were given in Table 5. It is clear that metal ions often co-existed with Hg(II) in various real samples did not interfere with the recoveries and the determination of Hg(II). The new solid phase extractor has good selectivity for recovery of Hg(II), and this further confirmed the conclusion obtained from the data in Table 3.

In addition, each of the 20 mL solutions containing 20 μg of Hg(II), Cd(II), Ni(II), Co(II), Mn(II), Pb(II), Zn(II), Cu(II) or Fe(III), was passed through the column and eluted by 0.8 mol L^{-1} of HClO$_4$. The recovery of Hg(II) is calculated to be 107%. It is found that presence of foreign metal ions whose content is eight times of Hg(II) did not interfere with the determination of Hg(II).

3.12. Analysis of water samples

Water samples used in the present work include surface water in campus of Henan normal university, tap water in our chemistry laboratory and in the student's dormitory, and a simulate sea water sample consisting of 19.10 g kg^{-1} of Cl$^-$, 2.66 g kg^{-1} of SO$_4{}^{2-}$, 10.62 g kg^{-1} of Na$^+$, 0.4 g kg^{-1} of Ca^{2+}, 0.38 g kg^{-1} of K$^+$, 1.28 g kg^{-1} of Mg^{2+} [32].

A solution containing 500 mL of different water sample was adjusted to pH 1.0 and passed though the column. 6 mL of eluent was collected and the content of Hg(II) in the eluent determined. Because of the very low concentration, Hg(II) in waters can-

Table 6
The recoveries of Hg(II) in different samples ($n = 4$)

Sample	Determination	Amount of SGMXO (g)	Added (µg)	Found (µg)	Recovery (%)	R.S.D. (%)
Surface water	–	0.2	50	49.85	99.7	1.1
Tap water in chemistry laboratory	–	0.2	50	49.69	99.38	1.8
Dormitory tap water	–	0.2	50	50.32	100.6	1.6
A simulate sea water sample	–	0.2	50	49.1	98.2	1.1

Table 7
Comparison of SGMXO with some reported sorbents for Hg(II) absorption

Sorbent	Capacity (mmol g^{-1})	Equilibrating time (minutes)	Co-existing ion	Reference
2-Thiophenecarboxaldhyde	2.0	2	Ca(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II)	[19]
1,5-Diphenylcarbazide functionalized sol–gel material	0.028	30	Se(IV), Cd(II), Ni(II), Pb(II)	[20]
Chlorella vulgaris immobilized silica gel	3.29×10^{-5}	–	CH$_3$Hg$^+$	[28]
Hg(II)-imprinted diazoaminobenzene-vinylpyridine copolymers	0.205	60	Zn(II), Cu(II), Cd(II), CH$_3$HgCl, CH$_3$CH$_2$HgCl	[33]
TAN-functionalized AC	0.011	10	Na, K, Mg(II), Ca(II), Ba(II), Co(II), Ni(II), Mn(II), Cu(II), Zn(II), Cd(II), Pb(II), Al(III), V(V), As(V),Cr(VI)	[34]
Xylenol orange modified silica gel	0.018	3	Cd(II), Ni(II), Co(II), Mn(II), Pb(II), Zn(II), Cu(II), Fe(III),	This work

not be detected by the present method. So, we added a known amount of Hg(II) in different samples. Following the procedure used above, 500 mL of water sample containing 50 µg of Hg(II) at pH 1.0 was passed through the column and then eluted, the content of Hg(II) in the eluent was measured by spectrophotometry. The recovery data of Hg(II) in different samples are included in Table 6, the high recoveries of Hg(II) confirmed the validity of this new solid phase extractor. It is also noted from Table 6 that even the samples have complex matrix, Hg(II) still can be enriched and separate selectively by SGMXO.

3.13. The regenerability of SGMXO

The self made chromatographic column can be reused for 50 times and the recovery of Hg(II) is higher than 95%, the experimental can still be reproduced after SGMXO is kept in a desiccator for five months, demonstrating the regenerability and stability of SGMXO.

4. The possible mechanism for selective absorption of Hg(II) by SGMXO

At pH 1.0, SGMXO can absorb Hg(II) selectively from eight kinds of metal ions. The possible reason is that at pH 1.0, the buffer solution is rich in Cl$^-$, the Hg(II) are present as chloroanionic HgCl$_3^-$ and HgCl$_4^{2-}$ complexes, and the –CH$_2$N(CH$_2$COOH)$_2$ in xylenol orange was changed into –CH$_2$N$^+$(CH$_2$COOH)$_2$. At this working pH, it is suggested that the chloroanionic complexes of Hg(II) were retained via their electrostatic attraction interactions with –CH$_2$N$^+$ (CH$_2$COOH)$_2$ in xylenol orange. This mechanism was supported by the following experiment. We used HClO$_4$ to adjust the solution to pH 1.0, because of no Cl$^-$ in solution, Hg(II) can not exist as HgCl$_3^-$ and HgCl$_4^{2-}$ complexes, the absorption percentage by SGMXO

is only 3.32%. If HCl–KCl was used to adjust the solution to pH 1.0, the absorption percentage of Hg(II) by the un-modified silica gel is as low as 2.38% because of no SGMXO$^+$. With the increase of pH, the protonation of –CH$_2$N(CH$_2$COOH)$_2$ become weak and its chelation with Hg(II) become strong. Hence, the increased absorption percentage was observed.

5. Comparison with alternative sorbents

Table 7 shows the sorbents reported in the literature for the adsorption of Hg(II). Although they can be used for the effective adsorption of Hg(II), there is scope for further improvement. The modified silica described in this work showed fast exchange kinetics, regenerability and high selectivity.

6. Conclusions

A new solid phase extractor, xylenol orange functionalized silica gel has been prepared and properly characterized. This solid phase extractor has the following advantages: (i) can be used for selective separation and preconcentrate of Hg(II) from eight kinds of metal ions; (ii) can be used to remove the interference of complex matrix; (iii) the separation/preconcentration produce is simple, rapid and of low analytical cost; (iv) has high preconcentration factor and can be reused for many times.

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