ORIGINAL PAPER

Selective separation of lead from aqueous solution with a novel Pb(II) surface ion-imprinted sol-gel sorbent

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Abstract A novel Pb(II) ion-imprinted mesoporous sorbent (IIMS) was synthesized by a surface imprinting technique combined with a sol-gel process and characterized by FT-IR and N_2 adsorption-desorption. Compared to the non-imprinted mesoporous sorbent (NIMS), the IIMS had a higher adsorption capacity and selectivity for Pb(II). The maximum static adsorption capacities of the IIMS and NIMS for Pb(II) were 221 and 173 mg g^{-1}, respectively. The relative selectivity coefficients of the sorbent for Pb(II) in the presence of Cd(II), Cu(II) and Zn(II) were 3.7, 1.9 and 3.4, respectively. Furthermore, the IIMS possessed a fast kinetics for Pb(II) sorption from aqueous solution with saturation time of <20 min, and could be used repeatedly. The detection limit (3σ) of this method was 0.23 ng mL^{-1} and relative standard deviation of 11 replicate determinations was 3.7 %. The IIMS has been applied to selectively separate and determine Pb(II) in real water samples with satisfactory results.

Keywords Pb(II) ion-imprinted mesoporous sorbent · Selective solid-phase extraction · Preconcentration · Surface imprinting technique · Sol-gel process

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Introduction

Lead is one of the most toxic heavy elements for animals and humans, even at low concentrations [1–3]. Unlike organic compounds, lead is non-biodegradable but accumulates through its association with inorganic and organic matter, e.g. by adsorption processes, formation of complexes, or chemical combinations. Therefore, removal and determination of lead from environment have become one of the primary aims for scientific workers [4–6]. However, the concentrations of lead in environmental are usually too low to be determined directly by conventional techniques owing to insufficient sensitivity and matrix interference. Thus, an effective preconcentration and separation procedure is usually necessary prior to determination [7].

Nowadays, metal ion-imprinting polymers (mIIPs), employing metal coordination between template and functional monomer, are widely investigated as highly selective sorbent [8–15]. A particularly promising application of MIIPs is the solid-phase extractive preconcentration of analytes at low concentration or the separation from other coexisting ions or a complex matrix [16].

Surface imprinting technique (SIT) is one of the important molecular imprinting methods. Imprinted polymers prepared by this technique show many advantages including high selectivity, more accessible sites, mass transfer and binding kinetics quickly [17, 18]. Dai et al [19] developed a novel method for template-selective recognition sites on mesoporous sorbents by combining a SIT with a sol-gel process. The sol-gel materials exhibit several advantages, such as large surface areas, excellent metal ion transfer kinetics, high metal adsorption capacity and high selectivity. Yan and Fan et al [20, 21] have also described the synthesis ion-imprinted functionalized silica gel sorbent by SIT and have been successfully used for selective solid-phase extraction of Cd and Hg. However, there is no report on

the synthesis Pb(II) ion-imprinted functionalized silica gel sorbent by SIT.

In the present work, a novel Pb(II) ion-imprinted mesoporous sorbent (IIMS) was synthesized by combining a surface molecular imprinting technique with a sol-gel process for selective separation and preconcentration of Pb (II). The sorption and desorption characteristics of the ion-imprinted sorbent were investigated. The separation and preconcentration of Pb(II) from real water samples were also discussed using batch procedures.

Experimental

Materials and reagents

Tetraethylorthosilicate (TEOS) was obtained from Aldrich Chem. Co. (Germany). 3-Mercaptopropyltrimethoxysilane (MPS) was supplied from Wuhan University Chemical Factory (China). Cetyltrimethylammonium bromide (CTAB) and $Pb(NO_3)_2$ were purchased from Beijing Chemical Co. (China). The certified reference materials used in this work are water GBW 08619 (obtained from National Institute of Standards and Technology, Beijing, China). All metal stock solutions (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of metals (spectral purity) in HNO_3 and further diluted daily prior to use. Doubly deionized water (DDW) was used throughout this work. All other reagents used were of at least analytical grade.

Instrumentation

A TAS-986 atomic absorption spectrometer (Bejing Puxi General Instrument Ltd., China) with deuterium background correction was used for the determination of Pb(II) and other metals. Lead absorbance measurements were made at 283.3 nm using spectral bandwidth of 0.5 nm. FT-IR spectra (4000-400 cm^{-1}) in KBr were recorded using a Nicolet-6700 spectrometer (Thermo Elemental, USA). N_2 adsorption–desorption analysis was performed on each sorbent by ASAP 2010 system (Micromeritics, USA). Surface areas were obtained using the Brunauer–Emmentt–Teller (BET) method [22]. The pore size calculated using the Barrett–Joyner–Halenda (BJH) formula [23]. A model pH-10C digital pH meter (Xiaoshan Instrument Factory, Zhejiang, China) was used for the pH adjustments.

Preparation of Pb(II) ion-imprinted mesoporous sorbent

The fabrication of IIMS consisted of following steps: Firstly, the mesoporous sorbent (MS) was prepared according to the literature [19]. Secondly, 1.0 g of $Pb(NO_3)_2$ was dissolved in 120 mL of methanol under stirring and

heating. After the $Pb(NO_3)_2$ had completely dissolved, 4.0 mL of MPS was added. The solution was stirred and refluxed for 1 h, 2.0 g of MS was added, and then continued to stir and reflux for 20 h. Thirdly, the product was recovered via vacuum filtration. The filter cake was washed with ethanol, and stirred in 50 mL HNO_3 (1 mol L^{-1}) for 6 h. Lastly, the final product, IIMS, was recovered by filtration, washed with DDW up to the eluent pH=4~5 and dried under vacuum at 80°C for 12 h. For comparison, the non-imprinted mesoporous sorbent (NIMS) was also prepared using the same procedure, but without the addition of $Pb(NO_3)_2$.

Sorption-desorption experiments

A portion of standard solution containing Pb(II) or other ions was transferred into a 25 mL beaker and pH was adjusted with buffer solution to the desired value. 50 mg IIMS or NIMS was respectively added to above solution, which was stirred for 30 min. Then, the mixtures were filtrated. The concentration of Pb(II) or other metal ions in the filtrate was measured by flame atomic absorption spectrometer (FAAS). The adsorbed sorbent was eluted with 5 mL HNO_3 (0.5 mol L^{-1}) for 30 min and the desorbed Pb(II) was measured with FAAS. The extraction percentage, the distribution ratio, the selectivity coefficient and the relative selectivity coefficient were calculated as the following equations:

$$\begin{pmatrix} E\% = \frac{C_0 - C_e}{C_0} \times 100 & D = \frac{C_0 - C_e}{C_e} \times \frac{V}{W} \\ k = \frac{D_{Pb}}{D_{Me}} & k' = \frac{k_{\text{imprinted}}}{k_{\text{non-imprinted}}} \end{pmatrix}$$

where C_0 and C_e are initial and final concentration of metal ions (μg mL^{-1}), V is the volume of metal ion solution (mL), W is the mass of the sorbent (g), $E\%$ is the extraction percentage, D is the distribution ratio (mL g^{-1}), k is the selectivity coefficient, k' is the relative selectivity coefficient, D_{Pb} and D_{Me} are the distribution ratios for Pb (II) and Cd(II), Cu(II) or Zn(II), respectively.

Recycling test

A 0.1 g portion of IIMS was equilibrated with 25 mL of the buffered solutions (pH 6.0 acetic acid/sodium acetate buffer) containing 10 μg of Pb(II). After the mixtures were mechanically shaken for 30 min at room temperature, the sorbent was isolated by filtration, washed in sequence with DDW and 1 mol L^{-1} HNO_3, and then dried under vacuum at 80°C for 12 h before next recycling.

Sampling procedure

Real samples of river water and lake water were collected from the Songhua River and Songhua Lake (Jilin, China).

The wastewater samples were provided by the chemical plant locally. The polyethylene bottles filled with the water samples were cleaned with detergent, water, diluted nitric acid and water in sequence. The samples were immediately filtered through a cellulose filter membrane (pore size 0.45 μm), and were acidified to pH 2.0 for storage. Prior to determination, the samples were adjusted to the optimal pH range according to optimized experiment conditions.

Results and discussion

Characterization of sorbent

IR spectra of sorbent

In order to ascertain the presence of –SH in the matrix, FT-IR spectra were obtained from MS, NIMS and IIMS (Fig. 1). The features around 798 and 1077 cm^{-1} indicate Si-O and Si-O-Si stretching vibrations, respectively. The –OH bond stretching band of the MS were observed at 3200–3600 cm^{-1}. After grafting of the thiol functionality, a very weak –SH stretching peak can be seen at 2552 cm^{-1} for NIMS and IIMS.

Surface properties

The surface properties of these sorbents were summarized in Table 1. The surface areas and pore diameter of IIMS and NIMS were less than that of MS as a result of the grafting of the organic functional group. Both IIMS and NIMS have very similar surface areas and porous diameters.
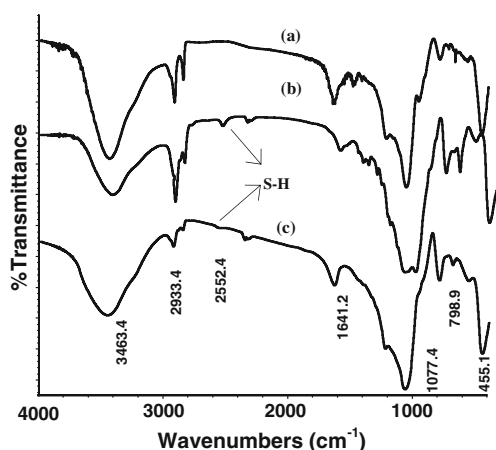
Table 1 Surface properties of sorbents

Sorbent	$S_{BET}(m^2 \cdot g^{-1})$	$d_{average}$ (nm)	$V_{total}(cm^3 \cdot g^{-1})$
MS	838	2.60	0.345
IIMS	638	2.03	0.360
NIMS	648	2.03	0.380

Adsorption behaviour of sorbents

Adsorption capacity of the sorbents for Pb(II)

Adsorption of Pb(II) from aqueous solution was investigated in batch experiments. Figure 2 shows the initial concentration of metal ions dependence of the adsorbed amount of Pb(II) onto the IIMS. The adsorption values increased with increase the initial concentrations of Pb(II) till the plateau values were obtained. The maximum adsorption capacity of IIMS for Pb(II) was 221 mg g^{-1}, which was higher than those of the NIMS (173 mg g^{-1}) and other sorbents [15, 24, 25]. The Langmuir adsorption model could be applied in this affinity system and the linear equation was y=0.05109 x+0.00462 (R^2=0.9752).

Binding kinetics of the imprinted sorbent for Pb(II)

The time dependence of Pb(II) extracted on IIMS was shown in Fig. 3. As seen here, a time of about 5 min was required for reaching 96% equilibrium adsorption. It is clear that the IIMS possessed a fast kinetics for the removal of Pb(II) from aqueous solution with the saturation time less than 20 min. This phenomenon can be explained that a lot of the thiol groups existed on the surface of the IIMS, so the target ions would easily reach the adsorption sites and then were trapped by the sorbent.
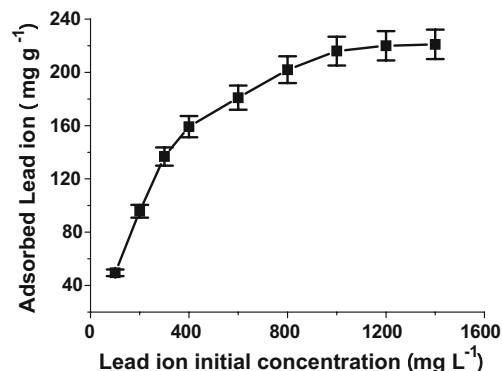

Fig. 1 FT-IR spectra (**a**) mesoporous sorbent, (**b**) Pb(II)-imprinted mesoporous sorbent, and (**c**) non-imprinted mesoporous sorbent

Fig. 2 The effect of initial concentration on the adsorption capacity of Pb(II) ion-imprinted sorbents . 50 mg of imprinted sorbents; pH 6.0; V 25 mL; shaking time 30 min; temperature 25°C
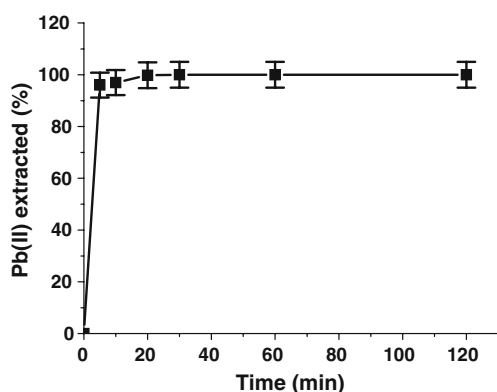
Fig. 3 Kinetics of Pb(II) sorption on Pb(II) ion-imprinted sorbent. Imprinted sorbents: 50 mg; $C_{Pb(II)}$: 10 μg mL^{-1}; V: 25 mL; Temperature: 25°C; pH: 6.0

Effect of pH on Pb(II) uptake

The effect of varying pH values on Pb(II) ion uptake of IIMS was investigated using the batch procedure with shaking for 30 min. It can be seen from Fig. 4, Pb(II) ions could be adsorbed quantitatively on IIMS with a pH range of 5–7. In this pH range, neither precipitation of the metal hydroxide nor the protonation of the thiol group was expected. In order to avoid precipitation at higher pH values, pH 6 was selected as the enrichment acidity for subsequent work.

Selectivity of the sorbents

Competitive loading of Pb(II)/Cd(II), Pb(II)/Cu(II) and Pb(II)/Zn(II) from their mixture aqueous solution was individual investigated by batch procedure. In their mixtures, each metal ion had the same concentration of 50 μg mL^{-1}. The results are listed in Table 2. The relative selectivity coefficient (k') values, which are greater than one for IIMS of Pb(II)/Cd(II), Pb(II)/Cu(II) and Pb(II)/Zn(II), are 3.7, 1.9 and 3.4, respectively. Therefore, competitive sorption of Pb(II)/Cd(II), Pb(II)/Cu(II) and Pb(II)/Zn(II) was apparent
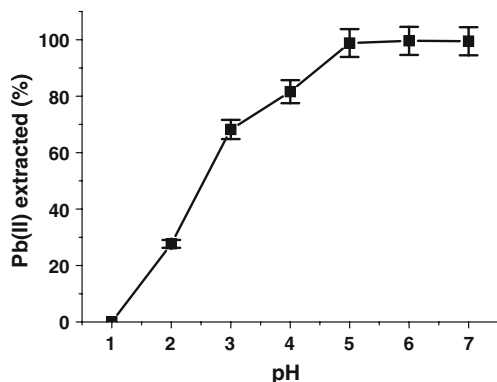

Fig. 4 Effect of pH on adsorption of Pb(II). Imprinted sorbents: 50 mg; $C_{Pb(II)}$: 10 μg mL^{-1}; V: 25 mL; Shaking time: 30 min; Temperature: 25°C

Table 2 Competitive sorption of Pb(II) and metal ions on IIMS and NIMS at pH 6.0

Metal ions	IIMS		NIMS		k'
	D (mLg^{-1})	k	D (mL g^{-1})	k	
Pb(II)	16790	-	3940	-	-
Cd(II)	512	33	443	8.9	3.7
Cu(II)	89	188	41	96	1.9
Zn(II)	908	19	706	5.6	3.4

from their mixture. This means that Pb(II) can be determined even in the presence of Cd(II), Cu(II) and Zn(II) interference.

The effects of different foreign ions (which often accompany with Pb(II) in various real water samples) on adsorption of IIMS were studied using the batch procedure. The results showed that 3000 μg mL^{-1} of Na$^+$, K$^+$; 200 μg mL^{-1} of Ca^{2+}, Mg^{2+} and Mn^{2+}; 100 μg mL^{-1} of Ni^{2+} had no significant effects on the adsorption and desorption of 1 μg mL^{-1} of Pb(II). Additionally, 100−1000 fold anions (Cl$^-$, SO$_4^{2-}$, NO$_3^-$ and CO$_3^{2-}$) did not interfere with the determination of Pb(II). This indicates that the IIMS has good selectivity for the recovery of Pb(II). The reported tolerance limit is defined as the ion concentration causing a relative error<± 5 %.

Stability of the imprinted sorbent

To test the stability of the imprinted sorbent, 0.1 g of IIMS was subjected to several loading and elution batch operations. In this study, 1 mol L^{-1} HNO$_3$ was used as a desorption agent. The result of adsorption–desorption cycle of Pb(II) ion-imprinted sorbents showed that extraction

Table 3 Determination of Pb(II) in water samples ($n=3$)

Samples	Pb(II) added (μg L^{-1})	Pb(II) founded (μg L^{-1})	Recovery (%)
GBW 08619	5.0[a]	4.85±0.02[b]	97.0
	10.0[a]	9.65±0.03	96.5
River water	0.00	0.80±0.05	-
	1.00	1.76±0.03	96.0
	5.00	5.98±0.02	103.6
Lake water	0.00	BQL[c]	-
	1.00	1.04±0.04	104.0
	5.00	5.09±0.05	101.8
Waste water	0.00	3.89±0.06	-
	5.00	9.16±0.04	103.1

[a] Reference value. The certified sample solution was accurately diluted to 5 and 10 μg L^{-1}, respectively. [b] The value following "±" is the standard deviation. [c] Below quantification limit.

efficiencies were very high (up to 95%) till 5 cycles. Therefore, the Pb(II)-IIMS showed excellent reusability and stability towards Pb(II).

Analytical performance

The analytical values of merit of the present separation and preconcentration of trace amounts of Pb(II) using IIMS and its determination by FAAS were evaluated under optimal experimental conditions. The detection limit (3σ), defined as by IUPAC [26], was found to be 0.23 ng·mL^{-1} which lower than the published methods [15, 27]. The relative standard deviations (R.S.D.) was 3.7% ($n=11$, sample volume$=50$ mL), indicating that the method had good precision for the analysis of trace Pb(II) in solution samples.

Sample analysis

The method was applied to the determination of Pb(II) in water samples. A standard reference material containing 1.0 mg L^{-1} Pb(II) (GBW 08619, water) was accurately diluted to 5 and 10 µg L^{-1}, respectively. To a 50 mL water sample with pH adjusted to 6, 50 mg of Pb(II) ion-imprinted sorbent was added and stirred for 30 min. After filtration, the sorbent was washed twice with DDW. The loaded Pb(II) was eluted with 5 mL HNO$_3$ (0.5 mol L^{-1}) for 30 min. It was successfully applied to the preconcentration and selective separation of lead ion in water samples using standard addition method. The results displayed in Table 3 were quite quantitative, precise and accurate.

Conclusions

In this work, a new type of Pb(II) ion-imprinted sorbent was prepared by combining a surface molecular imprinting technique with a sol-gel process. Besides possessing mild imprinting reactive condition, low price, superior stability and reusability, the imprinted sorbent showed several good characteristics, such as high affinity, selectivity and accessibility for Pb(II). A selective and sensitive method was developed and successfully applied to the analysis of trace lead in certified, nature and wastewater samples with satisfactory results.

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