Novel Pb(II) ion-imprinted materials based on bis-pyrazolyl functionalized mesoporous silica for the selective removal of Pb(II) in water samples

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Abstract: Three highly efficient adsorbents Pb-IIMS-SBA-15, Pb-IIMS-MCM-41 and Pb-IIMS-FDU-12 for Pb(II) were prepared by grafting the functional monomer 4-(di (1H-pyrazol-1-yl) methyl) phenol (DPP) on corresponding mesoporous silicas with Pb(II) as temple. All these three Pb(II) ion-imprinted mesoporous silica (Pb-IIMS) were characterized by Fourier transform-infrared spectroscopy (FT-IR), solid-state ²⁹Si and ¹³C NMR spectra, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), N₂ adsorption–desorption analysis and small angle X-ray diffraction (XRD). The adsorption experiments revealed three Pb-IIMS all possessed considerable adsorption performance for Pb(II), their adsorption profiles obeyed pseudo-second-order kinetics and Langmuir isotherm model. Compared with their corresponding non-imprinted materials, three Pb-IIMS displayed satisfactory selectivity to Pb(II) over seven competing metal ions. Among them, Pb-IIMS-MCM-41 particularly owned outstanding adsorption performance and selectivity, the maximum adsorption capacity as high as 344.8 mg g⁻¹, as well as excellent reusability through twelve adsorption-desorption cycles. Additionally,

Pb-IIMS-MCM-41 was employed as packing material to construct a solid-phase extraction column for detection of Pb(II), which exhibited detection limit of $0.015 \mu\text{g L}^{-1}$, then method was successfully applied to the removal and determination of trace Pb(II) in practical water samples.

Keywords: Pb(II), ion-imprinted mesoporous silica, bis-pyrazolyl functional monomer, selective adsorption, solid-phase extraction column

1. Introduction

Heavy metals, due to their non-biodegradability and accumulation in environment and living body, become more noticeable for human beings [1,2]. Lead (Pb(II)) is one of most toxic and plentiful heavy metals with important environmental and toxicological significances [3]. Hence, determination or removal of Pb(II) is highly demanded for the sustainability of environment. At present, a lot of methods and technologies, such as ion-exchange method [4], chemical precipitation [5], and adsorption [6,7] are applied to remove Pb(II) ions. However, most of these methods have the same disadvantage on their selectivity. Thus, it is strong required to develop more effective methods for selectively removal of Pb(II).

Ion imprinted polymers (IIPs), which are developed to mimic the binding cavities of biological compounds for an improved recognition of the template ions, are attractive solid sorbent for selective separation of metal ions [8]. The synthesis of IIPs generally includes the preparation of a monomer-metal complex and its further copolymerization with a cross-linker to eventually obtain 3-D recognition sites inside the polymeric network [9]. So far, various functional monomer such as methylacrylic acid (MAA) [10,11], 4-vinyl pyridine (4-VP) [12,13], chitosan [14-16], organic silane [17-19] and amine [20,21] have been employed for the preparation of the Pb(II) complexes. And the IIPs with amine functionalities were found to be the most effective ones for the adsorption and separation of Pb(II) [20,21]. However, owing to their tendency to oxidation, organic amines have poor chemical stability.

Consequently, an alternative ligand system is desired to further develop stable and effective IIPs for the adsorption and separation of Pb(II).

Recently, the utilization of mesoporous silica materials as solid support for **adsorption of toxic substances [22-24] such as the separation and preconcentration of** heavy metals have gained considerable attention, due to their high surface area, good chemical and mechanical stability, fast adsorption rate as well as tunable profile [25-27]. Furthermore, it was found that the mesoporous silica materials could exhibit increased separation efficiency for heavy metals with functional monomers attached [28-33]. He et al. reported a Pb(II) ion-imprinted SBA-15 type mesoporous silica material, by using amino carboxylic acid as functional group, for selective removal of Pb(II) [31]. Liu et al. synthesized a highly selective mesoporous adsorbent with fast kinetics for adsorption of Pb(II) by grafting functional monomer chitosan onto SBA-15 [14]. Meng et al. described the preparation of an ion-imprinted SBA-15 material modified by functional monomer of 4-VP for effective removal of Ce^{3+} ion [32].

With this context and our former experience on modification of mesoporous silica materials [34-36], we herein report the preparation of a series of highly selective Pb(II) ion-imprinted mesoporous silica materials (Pb-IIMS) for separation of Pb(II). In this work, DPP, which processed a *N, N*-bidentate group was selected as functional group to interact with the template ion Pb(II), therefore preparing a monomer/metal complex. This complex was then grafted to three kinds of mesoporous silica materials SBA-15, MCM-41 and FDU-12, respectively, synthesizing Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12. Furthermore, the morphologies and structures of the as-prepared Pb-IIMS were fully characterized by various analytic tools. In addition, static and dynamic adsorptions and a set of operational parameters such as pH, the stripping agent of Pb(II), selectivity, effects of interfering ions and reusability were systematically investigated by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Finally, the method of Pb-IIMS-MCM-41 filled solid-phase extraction (SPE) column coupled with inductively coupled plasma-atomic mass spectrometry (ICP-MS) was developed for removal and determination of trace Pb(II)

in real water samples, which further confirmed the practical applicability of Pb-IIMS-MCM-41.

2. Experimental

2.1. Reagents and methods

All chemical reagents and materials were obtained from commercial sources and used without further purification. Deionized water was obtained from Milli-Q Plus water purification system.

NMR spectra were measured using Bruker spectrometers operating at 400 MHz (^1H) and 100 MHz (^{13}C) in CDCl_3 . Solid-state ^{13}C and ^{29}Si CP MAS NMR spectra were performed at 100.6 MHz using a Bruker AV-400 spectrometer. Fourier transform infrared (FT-IR) spectra in KBr were analyzed on a Nicolet AVATAR-360 IR. Small angle X-ray diffraction (XRD) measurements were measured with a Bruker D4 powder X-ray scattering using Cu K α radiation (45 kV, 650 mA). Transmission electron microscopy (TEM) images were conducted with a JEOL JEM 2010 electron microscope at 200 kV. Energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were recorded using a Phenom Prox at an acceleration voltage of 4.8kV to 15kV. Nitrogen adsorption isotherms were measured at 77 K after being outgassed at 383 K overnight on a Quantachrome Nova 4000 analyzer. Pore size distributions and specific surface areas (SBET) were calculated using the BJH model and the BET method, respectively.

2.2. Preparation of Pb(II) ion-imprinted mesoporous silica

2.2.1. Synthesis of 4-(di (1H-pyrazol-1-yl) methyl) phenol (DPP)

The synthesis method for preparation of DPP was modified according to the reference [37]. Pale yellow powder, Yield 51%. ^1H NMR (400 MHz, CD_3OD , ppm): δ 6.39-6.40 (m, 2H), 6.80-6.82 (d, 2H), 6.91-6.93 (d, 2H), 7.62-7.63 (m, 4H), 7.78(s, 1H).

2.2.2. Preparation of lead complex

First, 2 mmol of DPP (480 mg) were dissolved in 50 mL of methanol in a 250 mL Erlenmeyer flasks. Subsequently, 1 mmol of $\text{Pb}(\text{NO}_3)_2$ (331 mg) as an imprinted metal ion (template) was added slowly to a glass flask and the resultant mixture was stirred for 5 h at room temperature. After filtering and drying, the light yellow powder was obtained (770 mg, 95%). ^1H NMR (400 MHz, CD_3OD , ppm): δ 6.39-6.4 (m, 2H), 6.8-6.82 (d, 2H), 6.91-6.93 (d, 2H), 7.62-7.63 (m, 4H), 7.78(s, 1H). ^{13}C -NMR (400 MHz, CDCl_3 , ppm): δ 77.11, 106.05, 115.20, 126.44, 128.43, 130.04, 140.30, 158.30.

2.2.3. Synthesis of Pb(II) ion imprinted and non-ion imprinted mesoporous silicas

Pb(II) ion-imprinted mesoporous silicas were obtained by following the procedure: 1 mmol of lead complex (811 mg) was dissolved in 80 mL tetrahydrofuran with stirring, and 1 mmol dehydrated K_2CO_3 (138 mg) was added to the solution. After 2 hours, 1 mmol (247 mg) 3-(triethoxysilyl)-propyl-isocyanate (TEPIC) was added into the solution drop by drop. The whole mixture was refluxed at 65 °C for 12 hours, the solvent was dried under vacuum. The resultant solid dissolved in 20 mL toluene, followed by adding 973 mg of SBA-15, MCM-41, FDU-12, then reflux for 48 h at 110 °C, respectively. After filtration, resulting solid was repeatedly washed with dichloromethane, distilled water, ethanol and ethyl acetate, then dried under vacuum. Each 5 mg of obtained materials washed by 10 mL, 3 mol L^{-1} HCl to elute the template lead. After drying, Pb(II) ion-imprinted mesoporous silicas (Pb-IIMS) were gained, namely Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12.

The corresponding non-imprinted mesoporous silicas (NIMS) DPP@SBA-15, DPP@MCM-41, DPP@FDU-12 were synthesized by using DPP as monomer, the following procedure was the same as that of IIMS without eluting.

2.3. Adsorption experiment

To investigate the effect of pH, 5 mg Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 were added to 20 mL sample solutions containing 5 mg L^{-1} of Pb(II)

ion at pH range 2.0-8.0, respectively, pH values were adjusted by 1 mol L⁻¹ HNO₃ and 1 mol L⁻¹ NaOH. The mixture was continuously bath oscillated for 30 min at 25 °C, and then placed stably for 30 min, centrifugation, filtration, the concentration of Pb(II) in upper solutions were measured by (ICP-AES). To choose the optimal pH, we studied the extraction efficiency. As comparison, we also researched the influence of pH on non-ion imprinted polymers. The extraction efficiency was calculated with the following equation:

$$\text{Extraction efficiency (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

Where C_o and C_e are the concentrations of lead ion at original and equilibrium state in the solution.

For desorption of Pb(II) functionalized mesoporous silica, a series of selected elution solutions, such as HNO₃, HCl at different concentrations, were considered.

To investigate the adsorption capacity of three kinds of Pb-IIMS and the corresponding NIMS, 5 mg of each adsorption dispersed in 20 mL aqueous solutions containing different contents of Pb(II) (5-70 ppm) at their optimal pH values, respectively. Then the mixture was continuously bath oscillated for 30 min at 25 °C, and then placed stably for 30 min, centrifugation, filtration, the concentration of the Pb(II) in upper solutions were measured by ICP-AES.

The adsorption capacity was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where q_e (adsorption capacity, mg g⁻¹) is amount of Pb(II) adsorbed by Pb-IIMS, C_o and C_e are original and equilibrated concentration of Pb(II) in solutions separately, m (g) is the weight of IIMS, V (L) is the volume of Pb(II) ion solution.

In a meanwhile, kinetic studies for Pb(II) were conducted to determine the adsorption rate of Pb(II) from water samples as follows: 5 mg of each sorbent were dispersed in 20 mL solution containing the same initial Pb(II) concentration of 90 ppm. Each of the mixture was continuously bath oscillated at 25 °C for 10, 20, 30, 40 or 50 min. After each time period, solutions were filtered and analyzed by ICP-AES to determine the concentration of Pb(II) in the final solution.

2.4. Selectivity studies

To study of specific and selective adsorption to Pb(II), the adsorption performance of our three ion-imprinted materials and their corresponding non-imprinted materials were conducted in a mixed ion solution containing Cd(II), Co(II), Cu(II), Pb(II), Hg(II), Mg(II), Mn(II), Zn(II) as competitive ions, the amount of IIMS and NIMS are all 5 mg, the initial concentrations of these ions are all 20 ppm. Then the mixture was continuously bath oscillated for 30 min at 25 °C, and then placed stably for 30 min, centrifugation, filtration. The ICP-AES is used to measure the concentration of Cd(II), Co(II), Cu(II), Pb(II), Hg(II), Mg(II), Mn(II), Zn(II) before and after adsorption. Distribution coefficient K_d (mL g^{-1}), selectivity coefficient (α), relative selectivity coefficient (β) were calculated based on the following equations:

$$K_d = \frac{(C_o - C_e)V}{C_e m} \quad (3)$$

$$\alpha = \frac{K_{d1}}{K_{d2}} \quad (4)$$

$$\beta = \frac{\alpha_1}{\alpha_2} \quad (5)$$

where C_o (mg g^{-1}) and C_e (mg g^{-1}) represents the original and equilibrated concentration of Pb(II); m (g) is the weight of IIMS, V (L) is the volume of Pb(II) ion solution; K_{d1} and K_{d2} are the distribution coefficient of Pb(II) and the competitive ions, respectively; α_1 and α_2 denote the selectivity coefficient of ion-imprinted materials and non-ion-imprinted materials, respectively.

To investigate the inference of various cations in natural samples, the tests were carried out by using the same amount of Li(I), Na(I), K(I), Mg(II), Mn(II), Co(II), Cd(II), Ba(II), Hg(II), Cr(III), Cu(II), Cl^- , SO_4^{2-} , CH_3COO^- , NH_4^+ as concomitant ions added to 20 mL of solution containing 0.5 ppm Pb(II). The aqueous mixtures of X/Pb(II) mixed with 5 mg Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 and their corresponding NIMS respectively, the mixture was continuously bath oscillated for 30 min at 25 °C, and then placed stably for 30 min, centrifugation, filtration, the concentration of Pb(II) in the final solution were determined by ICP-AES. We used extraction efficiencies of adsorbents towards Pb(II) to illustrate

anti-interference of our adsorbents in the condition of the presence of interfering ions.

2.5 Reusability studies of Pb-IIMS-MCM-41

The adsorption-deposition experiments were conducted to show the reusability of Pb-IIMS-MCM-41. First, 5 mg Pb-IIMS-MCM-41 were dispersed in 20 mL of 5ppm Pb(II) standard solution (pH 6.0), consecutively bath oscillated for 30 min at 25 °C. The adsorbed Pb(II) on 5 mg Pb-IIMS-MCM-41 was desorbed by 10 mL, 3 mol L⁻¹ HCl, then bath oscillated for 30 min at 25 °C, the released Pb(II) in the supernatant were determined by ICP-AES. By using the identical adsorbent to accomplish twelve cycles of adsorption-deposition experiments, the reusability assessment of Pb-IIMS-MCM-41 were obtained.

2.6 The application of Pb-IIMS-MCM-41 packed SPE column

The SPE cartridge was prepared by packing 200 mg Pb-IIMS-MCM-41 in a column (12.8 mm, i.d.), which were preconditioned with 3 mol/L HCl (5 mL) and deionized water (5 mL) at a flow rate of 1.0 mL min⁻¹. The prepared water sample solutions (5 mL) were passed through cartridges at a flow rate of 0.2 mL min⁻¹, respectively. The cartridges were washed with deionized water (5 mL), after that, the absorbed Pb²⁺ was eluted with 2.5 mL of 3 mol/L HCl at a flow rate of 0.5 mL min⁻¹. Ultimately, the obtained extractions were determined by ICP-MS.

Tap water and river water sample were collected from laboratory, Huangpu River (Shanghai, China), respectively, then centrifuged and filtered to remove the suspended particles. The resultant filtrates spiked with two concentrations of Pb(II) standards (5 µg L⁻¹, 10 µg L⁻¹), the resultant mixture were adjusted to pH 6.0 using 1mol L⁻¹ HNO₃ and 1 mol L⁻¹ NaOH, and three repeated experiments have been done for each concentration, respectively.

3 Results and discussion

3.1 Preparation

The stepwise preparation of Pb-IIMS was illustrated in Scheme 1. The DPP was

synthesized by the reaction between pyrazole and *p*-hydroxybenzaldehyde in THF, then DPP chelated with Pb(II) to obtained the lead complex. The resultant complex cross-linked with three kinds of mesoporous silica SBA-15, MCM-41, FDU-12 by using TEPIC, respectively. The cross-linking reaction occurred between phenolic hydroxyl groups of DPP and isocyanate of TEPIC, afterwards grafted on mesoporous silica through Si-OH of mesoporous. Subsequent removal of chelated Pb(II) by HCl solution to obtain the Pb(II) ion-imprinted mesoporous silica adsorbents Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12.

Scheme 1

3.2 Characterization

Fig. 1 displays the FT-IR spectra of DPP and Pb-IIMS. All Pb-IIMS can be seen the stretching vibration of near 3423 and 1629 cm^{-1} attribute to variety vibration and inplane bending vibration of surface Si-OH. The adsorption bands near 1084, 807, 463 cm^{-1} were attributed to the stretching and bending vibration of Si-O-Si on mesoporous silicas. In addition, the adsorption band near 2940 cm^{-1} was assigned to C-H stretching vibration of organic groups [38-41]. These spectra preliminary confirmed that Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 were prepared.

Fig. 1

Fig. 2 exhibits solid-state ^{29}Si and ^{13}C NMR spectra of Pb-IIMS. As seen from Fig. 2(a), the typical peaks at about -109.0, -100.7 ppm can be attributed to Q^4 [$\text{Si}(\text{OSi})_4$, siloxane], Q^3 [$\text{Si}(\text{OH})(\text{OSi})_3$, single silanol] which are highly comprehensible to two types of the framework crosslinking on mesoporous silica. The peak at -57.3, -16.3 ppm are assigned to T^3 [$\text{SiR}(\text{OSi})_3$] organosilicon, and D^2 ethyl silane of silylating agents, respectively [42-44]. Fig. 2(b) shows the characteristic band of C=O at 201.4 ppm, and the peak near 59.9, 42.6, 23.6 ppm belonged to carbon atom of silica chain;

the characteristic carbon peaks of benzene were found at 122.0, 129.0, 118.9, 161.7 ppm; methyne carbon was near 77.6 ppm. These results confirm that the functional monomer DPP is covalently anchored to the surface of mesoporous silica.

Fig. 2

SEM results (Fig. 3) show the Pb-IIMS particles are packing regularly, moreover, the surface of Pb-IIMS become tough which is likely to the formation of functionalization on the surface of mesoporous silicas. TEM images (Fig. 4) demonstrated that Pb-IIMS-SBA-15, Pb-IIMS-MCM-41 are a clear arrangement of hexagonal pores with channel-like structures running parallel, and Pb-IIMS-FDU-12 with spherical mesopores arranged in cubic structure, which provide the evidence that IIMS materials well preserved the structures of SBA-15, MCM-41, FDU-12 after functionalization [45-47].

Fig. 3

Fig. 4

The elements on the surface of Pb-IIMS were studied by energy dispersive X-ray (EDX). As shown in Fig. 5, we can clearly observe the presence of C, N, O and Si, which further demonstrate the functional monomer successfully modified on mesoporous silicas. Compared with Pb-IIMS-SBA-15 and Pb-IIMS-FDU-12, Pb-IIMS-MCM-41 possessed higher percentage of nitrogen indicating that more functional monomers were grafted on MCM-41. The absence of Pb(II) in EDX spectrum confirm complete elution of Pb(II) from IIMS.

The nitrogen adsorption-desorption isotherm and distribution of pore size are shown in Fig. 6, indicating isotherms of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41 and Pb-IIMS-FDU-12 were typical type IV with H1 [31], H1 [48] and H2 [49] hysteresis loop. Compared with SBA-15, MCM-41 and FDU-12, the volumes of our prepared adsorbents reduced and hysteresis loops shifted to lower relative pressure after

loading, which suggested that the pore size of mesoporous had decreased. Moreover, the decrease of the pore size after modification can be clearly seen from the pore size distribution curves. These changes were indicative that the functional monomer had successfully grafted on the channel of SBA-15, MCM-41, FDU-12.

Fig. 5

Fig. 6

The small angle XRD results are shown in Fig. 7, which exhibited well-recorded peaks in the range of $2\theta=0.7-2.0^\circ$, $2\theta=2.08^\circ$, $2\theta=0.6-1.5^\circ$ for Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 respectively, which could be indexed to (100), (110) and (200) reflections of SBA-15 [50,51], (100) reflection of MCM-41 [52], (311) and (400) reflections of FDU-12 [47]. These details suggested that the structure of SBA-15, MCM-41, FDU-12 were well preserved, which well supported the results of SEM and TEM. Compared with original mesoporous, there was obvious reduce in diffraction peak of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 testified Pb(II) ion-imprinted polymers have coated inside mesoporous channels, since the sticking of organic functional monomer to mesoporous channels can decrease the scattering power of mesoporous silicate wall [53].

Fig. 7

3.3. Adsorption performances

3.3.1. Effect of pH

The pH values of solutions are the most important parameter affecting the adsorption capacity of adsorbents, as pH influences protonation of coordination sites of heavy metal ions grafted on mesoporous silica. The relationship between extraction efficiency of Pb(II) and various pH values of solutions were presented in Fig. 8. It

was clear that the effect of solution pH on adsorption capacity is significant. This graph displayed a maximum extraction efficiency of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 near pH 6.0. The extraction efficiency kept increasing from pH 2.0 to 6.0, and then the increase of pH had no obvious effect on extraction efficiency of sorbents. So the optimal pH values of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 were determined to be pH 6.0. This phenomenon may due to the degree of protonation of bis-pyrazolyl group gradually decrease with increasing of pH values, resulting in Pb-IIMS more easily adsorbed Pb(II) in the solution [14,19].

Fig. 8

3.3.2. Choice of elution

Series of acidic elution solutions such as HNO₃, HCl, at different concentrations and their mixture with thiourea as an auxiliary ligand [54] were used to explore the elution efficiency of Pb(II) ions from ion-imprinted materials. As Table 1 shown, optimal quantitative percentage of recovery of Pb(II) could be obtained with 10 mL of HCl (3 mol L⁻¹). The percentage of recoveries of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 are 95.9%, 96.7% and 93.9%, partly.

Table 1 Effect of diverse types and concentrations of stripping agents. ^a

Stripping agent	Concentration (mol L ⁻¹)	R ^b (%)±S ^c (%)		
		Pb-IIMS-SBA-15	Pb-IIMS-MCM-41	Pb-IIMS-FDU-12
HNO ₃	1	87.5±0.9	91.1±0.5	84.7±1.5
HCl	1	92.7±1.0	92.5±0.9	89.9±1.3
HNO ₃	3	90.6±1.5	93.1±0.7	90.1±0.7
HCl	3	95.9±0.5	96.7±0.7	93.9±1.0
HNO ₃ +thiourea	1/1	85.3±0.5	89.4±1.1	84.3±0.4
HCl+thiourea	1/1	90.1±0.6	90.8±1.6	88.4±0.9

^a The volumes of stripping agents are all 10 mL.

^b Recovery

^c Standard deviation

3.3.3. Adsorption and kinetic studies

The adsorption isotherms of IIMS and NIMS towards Pb(II) ions at 25 °C were shown in Fig. 9. It could be observed that the adsorption capacity of Pb(II) increased fast with increasing initial concentrations of Pb(II), until the Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, and Pb-IIMS-FDU-12 reached saturation adsorption capacity (193.2, 283.7 and 155.2 mg g⁻¹, respectively) when the concentrations of Pb(II) were near 50, 70 and 40 ppm, respectively. Compared with their corresponding NIMS, the adsorption capacity of IIMS were higher, indicating the recognition sites of Pb(II) modified on IIMS with higher affinity. Furthermore, the Pb-IIMS-MCM-41 possessed better binding ability than that of Pb-IIMS-SBA-15, Pb-IIMS-FDU-12, which was well corresponding to results of EDX that Pb-IIMS-MCM-41 was modified more functional monomer.

The adsorption isotherm experiments can contribute to understand the adsorption characters of Pb-IIMS. The Langmuir and Freundlich models were employed to study the adsorbate-adsorbent interactions. Langmuir model, which assumed that the adsorption sites grafted on the surface of adsorbent are homogeneous, causing the monolayer adsorption of adsorbate [55,56]. The Langmuir equation was expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m} \quad (6)$$

where q_e (mg g⁻¹) and C_e (mg L⁻¹) are the adsorption capacity and concentration of Pb(II) in solution, q_m (mg g⁻¹) is the maximum adsorption capacity of adsorbent, b (L mg⁻¹) is the Langmuir constant.

The Freundlich model describes the multilayer adsorption and the heterogeneous system [57]. The equation of Freundlich was defined as:

$$q_e = K_f C_e^{1/n} \quad (7)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (8)$$

Where K_f ((mg g⁻¹) (L mol⁻¹)^{1/n}) and n are the constants of Freundlich, which correlate adsorption capacity and adsorption intensity, respectively.

The constants of Langmuir and Freundlich models were summarized in Table 2. For Pb-IIMS-SBA-15, Pb-IIMS-MCM-41 and Pb-IIMS-FDU-12, the correlation coefficients got from Langmuir model ($R^2 = 0.9932, 0.9928, 0.9699$) were higher than that of Freundlich model ($R^2 = 0.6674, 0.4609, 0.2758$), indicating that Langmuir model showed better fit and the adsorption of IIMS for Pb(II) take place at a monolayer coverage of adsorbents surface. The maximum adsorption capacity of Pb-IIMS-MCM-41 obtained from Langmuir model is 344.8 mg g⁻¹, which is higher than previously reported Pb(II) ion-imprinted adsorbents. (Listed in Table 3).

Fig. 9

The influence of contact time between adsorbents and Pb(II) were carried out to judge adsorption kinetics, results were displayed in Fig. 9. (c). It can be seen that the adsorption capacity of adsorbents increased sharply during the initial stage. Adsorption of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12 reached equilibrium within 40, 20, 40 min, respectively. Excitedly, Pb-IIMS-MCM-41 presented not only faster adsorption rate to Pb(II) than that of other two adsorbents, but higher equilibrium adsorption capacity within 20 min.

Table 2 Langmuir and Freundlich isotherm constants of IIMS for the adsorption of Pb(II)

Langmuir isotherm constants			
Adsorbent	q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2
Pb-IIMS-SBA-15	211.4	2.3107	0.9932
Pb-IIMS-MCM-41	344.8	2.3499	0.9928
Pb-IIMS-FDU-12	178.5	0.7763	0.9699
Freundlich isotherm constants			
Adsorbent	$K_f((\text{mg g}^{-1})(\text{Lmol}^{-1})^{1/n})$	N	R^2
Pb-IIMS-SBA-15	128.8	5.441	0.6674

Pb-IIMS-MCM-41	172.3	3.833	0.4609
Pb-IIMS-FDU-12	93.2	6.707	0.2758

Table 3 Comparison of maximum adsorption capacity between Pb-IIMS-MCM-41 and the reported adsorbents towards Pb(II)

Adsorbent	q_m (mg g ⁻¹ , Pb(II))	Reference
Chitosan grafted on SBA-15	38.01	58
Chitosan modified on SBA-15	42.55	14
iminodiacetic acid on support matrix of SBA-15	160	31
Hexadecyltrimethyl ammoniumbromide functionalized on MCM-41	57.74	29
Chitosan beads	72.89	59
4-VP and acrylate-moded spirulina platensis magnetic ion-imprinted polymer	136.6	60
triethylene-tetramine grafted magnetic chitosan	370.63	61
Amino siloxane oligomer-linked graphene oxide	312.5	62
Pb-IIMS-MCM-41	344.8	this work

To investigate the mechanism of adsorption of Pb(II), the adsorption kinetics were further analyzed by using different kinetic models containing the pseudo-first-order (eq. 9) and pseudo-second –order (eq. 10) [63].

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (9)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where q_e and q_t (mg g⁻¹) are the amounts of adsorbed Pb(II) per mass of sorbent at equilibrium conditions and at time t , respectively. k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate constant of pseudo-first-order and pseudo-second –order, respectively. The kinetic constants and correlation coefficients are calculated and summed up in Table 4. The correlation coefficients of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, and Pb-IIMS-FDU-12 obtained from pseudo-second-order ($R^2=0.9691$, 0.9992 , and 0.9735) greater than that of pseudo-first-order ($R^2=0.9567$, 0.7090 , and 0.7829). Hence, the adsorption processes of IIMS for Pb(II) follow the pseudo-second-order model better, which can be accessed as chemical reaction between adsorbents and Pb(II) ion [64]. The adsorption rate could be dominated by chemical adsorption

through election exchange between adsorbent and Pb(II) [65].

According to above analysis, the reasons of considerable adsorption performance results could be explained from the following aspects. First, the traditional adsorbents show poor site accessibility, may owe to adsorption sites are embedded with high density of cross-linked polymer matrix [14]. Second, metal ion-imprint mesoporous silica solves the disadvantage of traditional adsorbents [31], abundant Si-OH on the surface of mesoporous silica could provide more modification sites to graft more functional monomers. Third, our gained bidentate functional group containing N can easily react to Pb(II). Consequently, a large number of adsorption sites grafted on the surface of IIMS could own high adsorption capacity and fast adsorption rate.

Table 4 Kinetics parameters of pseudo-fiirst and pseudo-second order for adsorbents.

Adsorbent	pseudo-first-order				pseudo-second-order		
	exptl q_e (mg g^{-1})	K_1 (min^{-1})	q_e (mg g^{-1})	R^2	K_2 (min^{-1})	q_e (mg g^{-1})	R^2
Pb-IIMS-SBA-15	193.2	0.1026	298.2	0.9567	1.09×10^{-3}	204.1	0.9691
Pb-IIMS-MCM-41	283.7	0.0540	38.98	0.7090	5.59×10^{-3}	285.7	0.9992
Pb-IIMS-FDU-12	155.2	0.0438	107.1	0.7829	2.60×10^{-4}	200.0	0.9735

3.4 Selectivity studies

3.4.1 Selective adsorption experiments

Adsorption selectivity and anti-influence were both studied, as selectivity is the essence to assess the adsorption performance of IIMS to Pb(II). Adsorption selectivity examinations toward Pb(II) were carried out in presence of Cd(II), Co(II), Cu(II), Hg(II), Mg(II), Mn(II), and Zn(II) at optimal conditions of three kinds of adsorbents, the concentrations were same as Pb(II) (10 mg L^{-1}). The selectivity coefficient (α) and relative selectivity coefficient (β) are summarized in Table 5. As can be seen from the Fig. 10, Pb-IIMS-SBA-15, Pb-IIMS-MCM-41 and Pb-IIMS-FDU-12 presented commendable adsorption selectivity for Pb(II) containing competitive metal ions. More concretely, Table 5 clearly shows that selectivity coefficients of Pb-IIMS-MCM-41 for Pb(II) with respect to competitive metal ions were higher than

that of the other two adsorbents. Moreover, the selectivity coefficients of Pb-IIMS-MCM-41 for Pb(II)/Cd(II), Pb(II)/Mg(II) and Pb(II)/Zn(II) were 132.68, 576.61 and 104.25 respectively, while selectivity coefficients of DPP@MCM-41 are only 7.13, 6.95 and 5.86. It could be concluded that the ion-imprinting dramatically increase the selectivity to the template ion due to the formation of 3-D recognition sites inside the Pb-IIMS [11,58]. Meanwhile, Pb-IIMS-MCM-41 shown the best selectivity which can be explained as follow. From the results of EDX, Pb-IIMS-MCM-41 possessed the highest percentage of nitrogen indicating that more functional monomers were grafted on MCM-41, so we can conclude that the most recognition sites for Pb(II) formed on Pb-IIMS-MCM-41 which results in the best selectivity.

Fig. 10

Table 5 Selective adsorption performance of IIMS and NIMS

Metal ions	Selectivity coefficient (α)						Relative selectivity coefficient (β)		
	Pb-IIMS -SBA-15	Pb-IIMS -MCM-41	Pb-IIMS -FDU-12	DPP@ SBA-15	DPP@ MCM-41	DPP@ FDU-12	SBA- 15	MCM -41	FDU- 12
Cd(II)	61.12	132.68	8.89	3.61	7.13	2.58	16.93	18.61	3.45
Co(II)	19.79	38.76	5.23	2.60	4.53	2.05	7.60	8.56	2.55
Cu(II)	32.83	63.13	4.07	1.00	1.68	0.71	32.70	37.62	5.73
Hg(II)	21.21	44.77	3.79	0.81	1.08	0.41	26.19	41.54	9.37
Mg(II)	158.48	576.61	26.34	3.36	6.95	2.86	47.10	82.81	9.22
Mn(II)	22.10	63.07	7.15	2.5	7.98	2.45	8.82	7.90	2.92
Pb(II)	1	1	1	1	1	1	1	1	1
Zn(II)	59.54	104.25	13.18	3.74	5.86	4.40	15.91	17.78	2.99

3.4.2 Effect of the Interfering Ions

To evaluate the possibility of application of adsorbents, the influences of various ions exist in water such as Li(I), Na(I), K(I), Mg(II), Mn(II), Co(II), Cd(II), Cr(III), Cu(II), Cl^- , SO_4^{2-} , CH_3COO^- , NH_4^+ were studied. We used tolerable limit to defined the maximum concentration of foreign ions that could cause an error less than $\pm 5\%$ in the

absence of interference, the tolerable concentration ratio was used X/Pb(II) to indicate. The results are presented in Table 6. From the sheet, it can be seen that the foreign ions have no significant effects on detection of Pb(II) ion for NIMS at their optimal conditions, respectively.

Table 6 The tolerance ratio of various ions on the determination of Pb(II) ions

Interference ions (X)	Tolerable concentration ratio X/Pb(II)	Extraction %		
		Pb-IIMS-SBA-15	Pb-IIMS-MCM-41	Pb-IIMS-FDU-12
Li ⁺	1000	94.3	96.3	93.5
Na ⁺	1000	95.3	93.3	94.3
K ⁺	1000	91.4	94.1	92.8
Mg ²⁺	1000	97.1	93.8	95.2
Mn ²⁺	1000	96.4	92.5	95.8
Co ²⁺	1000	98.4	93.6	96.4
Cd ²⁺	1000	94.1	94.7	95.7
Ba ²⁺	1000	97.2	95.2	96.2
Hg ²⁺	50	92.8	93.7	93.5
Cr ³⁺	1000	96.1	94.9	94.3
Cu ²⁺	1000	96.5	95.6	95.1
Cl ⁻	1000	99.5	99.9	98.5
SO ₄ ²⁻	1000	98.6	96.0	95.6
CH ₃ COO ⁻	800	54.9	99.7	48.3
	600	99.6	99.8	74.8
	400	98.9	99.6	94.5
NH ₄ ⁺	1000	95.17	96.04	65.62
	700	97.91	98.38	96.75

3.5. Reusability of Pb-IIMS-MCM-41

Other than selectivity, reusability is an important factor as well in application of IIMS.

Considering adsorption capacity, adsorption kinetic, selectivity and anti-interference of three kinds of adsorbents, we chose Pb-IIMS-MCM-41 as optimal adsorbent to investigate the reusability. The stability and reusability of Pb-IIMS-MCM-41 was reused for five adsorption-desorption cycles by using 3 mol L⁻¹ HCl as desorption medium, the results are displayed in Fig. 11. In addition to a slight decrease in extraction efficiency during twelve cycles, the ion-imprinted mesoporous silica still keep over 95.0% extraction efficiency for Pb(II). Consequently, the obtained IIMS were demonstrated to be reused with excellent extraction efficiency.

Fig. 11

3.6. The application of Pb-IIMS-MCM-41 packed SPE column (Pb-IIMS-MCM-41-SPE)

3.6.1 Optimal conditions

As the outstanding selectivity and reusability, Pb-IIMS-MCM-41 were applied as filling material to prepare SPE column for the removal and determination of Pb(II) in tap and river water. The flow rates of loading sample and the elution are critical parameters dominating the adsorption amount, analytical time and SPE recoveries. To obtain the optimal extraction recoveries, the effect of flow rate of the standard Pb(II) solution (5 mL, 50 µg L⁻¹) on the adsorption of Pb(II) was studied in the range of 0.2-2.0 mL min⁻¹ at pH 6.0. Generally speaking, the Pb(II) could be adsorbed quantitatively by Pb-IIMS-MCM-41 with the efficiency above 95% during the flow rate of 0.2-0.7 mL min⁻¹. However, the adsorption efficiency decreased to below 95.0% at the sample flow rate above 0.7 mL min⁻¹, which may well due to the reduction of the contact time between Pb(II) and the packing material with increasing of flow rate. So, a flow rate of 0.5 mL min⁻¹ was chosen as optimal sample rate. On the other hand, elution (2.5 mL, 3 mol/L HCl) flow rates varying from 0.2 to 2 mL min⁻¹ were studied to find the optimal SPE recoveries. Finally, the flow rate of 0.5 mL min⁻¹ was carried out for elution.

3.6.2 Analytical performance and application in water samples

The analytical performances based on Pb-IIMS-MCM-41-SPE were investigated under the optimized conditions. An excellent linear relationship was presented in the range of 0.5-50 $\mu\text{g L}^{-1}$, with a linear equation of $y=0.9903x-0.0971$, ($R^2=0.9998$). The limit detection (LOD) of 0.015 $\mu\text{g L}^{-1}$ for Pb(II) was calculated as $3\text{SD}/m$, where SD is the standard deviation of nine replicate blank extraction divided by blank extraction and m is the slope of the calibration curve. The extraction precisions of Pb-IIMS-MCM-41-SPE at 10 and 50 $\mu\text{g L}^{-1}$ were assessed in the forms of relative standard deviation (RSD), which were achieved 3.5% and 1.9% respectively.

In addition, the Pb-IIMS-MCM-41-SPE was used for the determination of trace Pb(II) in tap and river water samples to access the applicability of the developed method. The recoveries were conducted with the standard addition method by spiking two different concentrations of Pb(II) (5 and 10 $\mu\text{g L}^{-1}$) with the pretreatment tap and river water, respectively, each sample was analyzed three replicates. As listed in Table 7, the analytical recoveries in the range of 98.3% - 101.4%, with the RSD varying from 2.0% to 1.2%. which can be inferred that Pb-IIMS-MCM-41 is a desired candidate for SPE adsorbent.

Table 7 Recoveries (%) and Relative standard deviations (RSD, %) of Pb-IIMS-MCM-41-SPE for Pb(II) obtained from water samples.

Sample	added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery $\pm$ RSD (%)
tap water	0	14.377 ± 0.382	-
	5	19.447 ± 0.577	$101.4\% \pm 1.3\%$
	10	24.203 ± 0.625	$98.3\% \pm 2.0\%$
Huangpu river water	0	30.705 ± 0.465	-
	5	35.663 ± 0.735	$99.2\% \pm 1.5\%$
	10	40.849 ± 0.628	$101.4\% \pm 1.2\%$

4. Conclusions

Pb(II) ion-imprinted mesoporous silica materials modified with bis-pyrazolyl group were successfully prepared. Adsorption experiments for Pb(II) indicated that these ion-imprinted materials possess good chemical stability, considerable adsorption

capacity, and do exhibit improved selectivity as compared to the corresponding non-imprinted materials. Pb(II) ion-imprinted material Pb-IIMS-MCM-41 performed excellent adsorption performance and outstanding reusability, and could be employed as filling adsorbent of solid-phase extraction column. These results demonstrated that Pb(II) ion-imprinted material Pb-IIMS-MCM-41 is promising solid-phase extraction adsorbent for removal, preconcentration and detection of Pb(II) in water.

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Graphical abstract

Scheme 1: Preparation procedures of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12.

Fig. 1. FT-IR spectra of Pb-IIMS.

Fig. 2. (a) Solid-state ^{29}Si NMR spectra of Pb-IIMS; (b) Solid-state ^{13}C NMR spectra of Pb-IIMS.

Fig. 3. SEM micrographs of Pb-IIMS-SBA-15 (a), Pb-IIMS-MCM-41 (b), Pb-IIMS-FDU-12 (c).

Fig. 4. TEM images of Pb-IIMS-SBA-15 (a1), (a2); Pb-IIMS-MCM-41 (b1), (b2); Pb-IIMS-FDU-12 (c1), (c2).

Fig. 5. EDX spectrum of Pb-IIMS

Fig. 6. N_2 adsorption-desorption isotherms and pore size distribution (inset) of Pb-IIMS-SBA-15 (a), Pb-IIMS-MCM-41 (b) and Pb-IIMS-FDU-12 (c)

Fig. 7. Small angle XRD of Pb-IIMS-SBA-15 (a), Pb-IIMS-MCM-41 (b), Pb-IIMS-FDU-12 (c).

Fig. 8. Effect of pH on the extraction efficiency of IIMS for Pb(II).

Fig. 9. Adsorption isotherms of IIMS (a) and NIMS (b) at different original concentrations of Pb(II). Influence of contact time on IIMS (c).

Fig. 10. Selectivity of Pb-IIMS-SBA-15, Pb-IIMS-MCM-41, Pb-IIMS-FDU-12, and their corresponding NIPs.

Fig. 11. Reusability of Pb-IIMS-MCM-41

Asorbance

- Pb-IIMS-SBA-15
- Pb-IIMS-MCM-41
- Pb-IIMS-FDU-12

(a) **(b)** **(c)**

(a) **(b)** **(c)**