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ORIGINAL ARTICLE

A novel lead imprinted polymer as the selective solid phase for extraction and trace detection of lead ions by flame atomic absorption spectrophotometry: Synthesis, characterization and analytical application

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Abstract A novel ion imprinted polymer as the selective solid phase combined with flame atomic absorption spectrometry (FAAS) was applied for preconcentration and determination of lead in real samples. In the first step, Pb(II)-IIP was synthesized by copolymerization of 2-vinyl pyridine as the functional monomer, ethylene glycol dimethacrylate as the cross-linker, 2,2-azobisisobutyronitrile as the initiator that imprinted with Pb(II) as the template ion, 2-amino pyridine as the ligand. Subsequently, the imprinted Pb(II) was completely removed by leaching the dried and powdered imprinted polymer with HCl (2 mol L^{-1}). This polymer was characterized by Fourier Transform Infrared (FT-IR) spectrometer. The effect of different variables on the extraction efficiency such as type and volume of eluent for extraction, solution's pH for adsorption, sorption and desorption times was evaluated. Under the optimum conditions: type of eluent, HCl (2 mol L^{-1}); volume of eluent, 5 mL; solution's pH for sorption, 5; sorption time, 90 min; desorption time, 125 min and breakthrough volume of 750 mL were obtained. Preconcentration factor of the method was about 150. The limit of detection was obtained 0.75 μg L^{-1} and a dynamic linear range (DLR) of 3–150 μg L^{-1} was found. The maximum sorption retention capacity of Pb(II) ions on the imprinted polymer was 85.6 mg g^{-1}. The prepared ion-imprinted polymer particles have an increased selectivity toward Pb(II) ions over a range of competing metal ions with the same charge and similar ionic radius. Performance of the present method was evaluated for extraction and determination of Pb(II) in water

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samples at microgram per liter concentration and satisfactory results were obtained (RSD = 2.7%).

1. Introduction

Lead is one of the most toxic heavy metal elements for animals and human beings (Carletto et al., 2011). It is known that heavy metal ion contamination represents a significant threat to the ecosystem and especially to people due to the severe toxicological effects on living organisms (Soylak et al., 2005; Yaman, 2006). Soil and water pollution by toxic heavy metals are a major environmental concern. Through the food chain system of soil–plant–animal–human, Pb(II) is transferred into animals and human beings, causing severe contamination (Nagihan et al., 2010; Liu et al., 2003; Krishnamurthy, 1992). Unlike organic compounds, lead is non-biodegradable, and accumulates through its association with inorganic and organic matter, e.g., by adsorption processes, formation of complexes, or chemical combinations (Anthemidis, 2008; Boonamnuayvitaya et al., 2004). Consequently, the development of reliable methods for the removal and determination of lead in biological and water samples is of particular significance. The most widely used techniques for separation and preconcentration of trace concentrations of lead include liquid–liquid extraction (Yadav and Khopkar, 1971; Manzoori et al., 2009; Bai et al., 2010), cloud point extraction (Silva and Roldan, 2009; Luconi et al., 2000; Ghaedi and Tavallali, 2009; Chen et al., 2005; Surme et al., 2007), and solid–phase extraction (Xie et al., 2005; Zachariadis et al., 2002; Ensafi and Zendegi, 2008; Shamsipur et al., 2000). Since the first report on lead removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in different applications throughout the world (Lee et al., 1998; Li et al., 2003). But activated carbon requires ligands to improve its removal performance for heavy metals. Although other adsorbents such as chitosan (Huang et al., 1996), zeolites (Inglezakis et al., 2003; Godelitsas and Armbruster, 2003), clay, and even industrial wastes (Babel and Kurniawan, 2003) are widely adopted in applications today, their adsorption capacity and selective removal of lead are still poor.

Molecular imprinting has become an established technique for preparing robust molecular recognition elements for a wide variety of target molecules (Masque et al., 2000; Mullett et al., 2001). Molecularly imprinting polymers (MIPs) have been investigated as highly selective sorbents for solid phase extraction to concentrate and clean up samples prior to analysis. A particularly promising application of ion imprinted polymer (IIP) (similar to MIP) is the solid phase extractive preconcentration and/or separation from other coexisting ions or complex matrices (Rao et al., 2006; Shamsipur et al., 2007; Moullec et al., 2007; Mayes and Whitcombe, 2005). Thus, ion-imprinted polymer as solid–phase extraction (IIP-SPE) is a fast developing area for the application of IIP technology. Many studies have been established for preconcentration of Pb(II) from real samples using IIP (Pan et al., 2006; Payehghadr et al., 2008; Zhu et al., 2009). For example, Kozlowski et al. (2008) introduced -cyclodextrin polymer as a selective ion carrier for separation of Pb(II) ions from dilute aqueous solutions by transport across polymer inclusion membranes. Also, other studies were carried out, in which nano-TiO_2 matrix (Chunxiang et al., 2009) and imidazole azo crown ethers (Ulewicza et al., 2009) were synthesized by IIP technique for preconcentration and trace analysis of Pb(II). Important disadvantages of these techniques are low maximum sorption capacity, high relative standard deviation, and limit of detection.

In the proposed method, ion imprinted polymer technique followed by FAAS was applied for trace monitoring of Pb(II) in water samples. Pb(II)-IIP was synthesized by copolymerization of 2-vinylpyridine (2-VP), ethylene glycol dimethacrylate (EGDMA), 2,2-azobisisobutyronitrile (AIBN) imprinted with $Pb(NO_3)_2$ as the template ion, and 2-aminopyridine as the ligand molecule. Elution of Pb(II) from IIP was performed by HCl (2 mol L^{-1}) at 40 °C. Effects of several factors such as type, concentration, and volume of eluent for extraction, solution's pH, and sorption and desorption times were investigated and optimized. Finally, the proposed method was successfully applied for extraction and determination of Pb(II) ions in water and standard reference material, which showed low detection limit and high maximum binding capacity.

2. Experimental

2.1. Reagents and standard solutions

Ethylene glycol dimethacrylate (EGDMA), 2-vinylpyridine (2-VP), $Pb(NO_3)_2$, 2-aminopyridine, 2,2′-Azo bisisobutyronitrile (AIBN), methanol, acetonitril, toluene, nitric acid, hydrochloric acid, thio urine, and sodium hydroxide with the highest purity were available from the Merck (Darmstadt, Germany). Ultra pure water was prepared using a Milli-Q system from Millipore (Bedford, MA, USA). An ore polymetallic gold zidarovo-PMZrZ (206 BG 326) from Bulgaria was prepared as the standard reference material.

The water samples were obtained from distilled, tap (Tehran, Iran) and sea (Caspian sea (Iran)) water. The water samples were collected in polyethylene bottles and stored in dark at 4 °C and analyzed within 48 h after collection without any previous treatments.

2.2. Preparation of standard solutions

A stock standard solution of the Pb(II) as template was prepared in ultra pure water with HCl (1%). Working standard solutions were daily prepared by appropriate dilution with ultra pure water. All of the solutions were stored in the fridge (4 °C) and brought to ambient temperature just prior to use. Standard reference material (50 mg) was digested with 6 mL of HCl (37%) and 2 mL of HNO_3 (65%) in a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W, and then venting for 8 min. The residue from digestion was then diluted with ultra pure water to 750 mL, as well as, a blank digestion (Tuzen et al., 2008).

2.3. Apparatus

Concentration of Pb(II) ions was determined by an AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer (FAAS) in an air-acetylene flame, according to the user's manual provided by the manufacturer. A lead hollow cathode lamp was used as the radiation source at 283.3 nm. All pH measurements were made at 25 ± 1 °C with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. A vacuum pump was obtained from Leybold (Germany) and adjustable vacuum gauge and controller were obtained from Analytichem International (Harber City, CA). Fourier Transform Infrared (FT-IR) spectra (4000–400 cm^{-1}) in KBr were recorded using a Bruker IFS66/S FT-IR spectrometer. Heidolph heater stirrer model MR 3001 (Germany) was employed for heating and stirring of the solutions.

2.4. Preparation of lead imprinted polymer and non imprinted polymer

The following procedure was used for synthesizing the polymer: 1 mmol of 2-aminopyridine (ligand) and 0.5 mmol of Pb(II) as the template ion were separately dissolved in 5 mL of methanol. Then lead solution was added slowly to the ligand solution and stirred for 5 h in the room temperature. A white complex was obtained that was filtered and eluted with ultra pure water. The complex was dissolved in 20 mL of ACN/toluene (1:1) in the 100 mL glass flask at the ambient temperature. Then, 2 mmol of 2-vinylprydine (functional monomer) was added to this solution and stirred for 5 h to become sure of the complete interaction. Fifteen mmol EGDMA and 0.1 mmol AIBN were added to 20 mL of pre-polymerization solution, which was purged with nitrogen for 10 min and the flask was sealed under nitrogen. The polymerization reaction was performed in an oil bath at 65 °C for 24 h in the presence of nitrogen. Then, white color polymer was crushed, ground, and sieved to obtain particles with diameters in the range of 50–80 μm. Fine particles were removed by suspending polymer beads in acetone and decantation of acetone for several times. Removal of template was performed by HCl (2 mol L^{-1}) for several times until the washing solution was free of Pb(II) ions, and then was repeatedly washed with ultra pure water until achieving neutral pH. Finally, the particles were dried under vacuum in a desiccator and used for the extraction studies. The synthesis of Pb(II)-IIP is showed schematically in Fig. 1. Non-imprinted polymer (NIP), as a reference, was prepared using the same process in the absence of template (lead ions).

2.5. Complex sorption–desorption studies

Sorption and desorption of Pb(II) from aqueous solutions were carried out in batch experiments. In sorption step, the dry imprinted polymer (50 mg) without template was immersed in 25 mL of the sample solution containing 1 μg mL^{-1} concentration of Pb(II). Then, pH was adjusted at 5 by drop wise addition of 2 mol L^{-1} of sodium hydroxide or hydrochloric acid solution. The sorbed lead ions in polymer were desorbed from the IIP by elution with 5 mL of HCl (2 mol L^{-1}). After extraction, the polymer was dried and used for another extraction. The final lead concentration in the aqueous phase was determined by FAAS. Lead extraction percentage was calculated from the following equation:

$$\%\text{Extraction} = \frac{C_a - C_b}{C_a} \times 100$$

where C_a and C_b are the concentrations of lead ion before and dividing the concentration of lead after extraction to 5 in the sample solution, respectively.

3. Results and discussion

In the proposed method, a novel ion imprinted polymer as the selective solid phase extraction combined with flame atomic absorption spectrometry (FAAS) was employed for preconcentration and determination of trace lead in real samples. The effect of different parameters on the extraction efficiency was optimized using one variable at a time method.

3.1. Characterization of the synthesized lead imprinted polymer by FT-IR

To ascertain the presence of lead ion and ligand in the synthesized IIP, the IR spectra of 2-aminopyridine (ligand), non imprinted polymer (NIP), leached, and unleached ion imprinted polymer (IIP) were recorded by KBr pellet method (Fig. 2a–d). As it is obvious, important absorption is present in the region of 3438.9 cm^{-1}, which belongs to stretching vibration of NH_2 that exists in the leached, unleached IIP and ligand, which is absent in the spectra of NIP. The band frequencies of NH_2 (binding site of ligand) in unleached and leached IIP were 3420.7 cm^{-1} (D) and 3438.9 cm^{-1} (C), respectively. The shifted band frequency to lower vibration in unleached IIP proves the interaction between lead ions and NH_2 groups in the ligand. After removal of the template from the IIP, the ligand remained in the polymer beads. Vibration absorption at about 1730 cm^{-1} appeared in the IIP and NIP polymer, because of the double-bound of C=O and the synthesis of the polymer. Also, another band in polymer is 2957.6 cm^{-1} that belongs to stretch vibration single bond of C–H.

3.2. Effect of solution's pH on sorption

For the metal, ionic complexation with ligand is highly dependent on the pH equilibrium of the medium, because the pH value of the solution is an important parameter for adsorbing metal ions. The effect of pH on the sorption of Pb(II) ions was investigated by varying the solution pH from 1.0 to 8.0. Twenty-five mL of the standard solution of Pb(II) with concentration of 1 μg mL^{-1} was loaded on 50 mg of polymer under the desired range of pH. After the extraction step, desorption solution was introduced into FAAS for determination of Pb(II). According to Fig. 3, extraction efficiency of the analyte increases significantly by increasing the pH of the sample solution, which is due to the increase of bonding between ligand and ion. In lower pH values, nitrogen atoms may be protonated; so negligible amounts of lead ions are absorbed to the polymer. Higher values of pH were

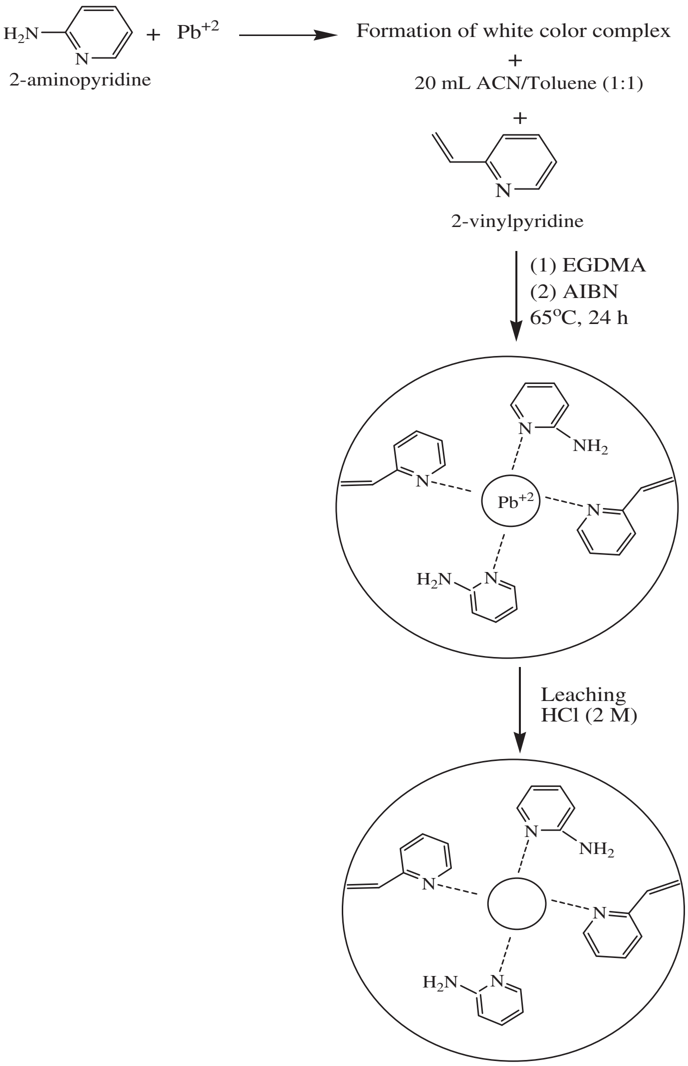

Figure 1 Preparation of Pb(II)-imprinted polymer material.

not investigated because of the possibility of precipitation of lead ions. Hence, the pH was adjusted to 5 in all subsequent studies.

3.3. Effect of type, concentration, and volume of eluent

In ion imprinted techniques, complete removal of template from IIP is a very crucial step to guarantee the absence of memory effect. In order to choose a proper eluent for the retained lead complex, after its extraction from water, the complex was stripped with different solvents with various concentrations. For elution of Pb(II) from IIP, the dry imprinted polymer (50 mg) was immersed in 10 mL of the desired solvents, and the solutions were stirred for 3 h. Then resulted solution was filtered and lead ions were measured by FAAS. According to the results in Fig. 4, HCl (2 mol L^{-1}) has better recovery in comparison with other solvents. After selection of the best eluent, the influence of eluent volume on the extraction efficiency of the Pb(II) was studied in the range of 1–10 mL and the results are shown in Fig. 4. It is obvious that 5 mL of HCl (2 mol L^{-1}) can extract lead ions from the polymer beads.

3.4. Optimization of sorption and desorption times of the analyte on IIP

In the IIP extraction technique, sorption time is required for quantitative extraction of the analyte from aqueous sample into solid phase. To choose the best time for extraction, 50 mg of the polymer was added into 25 mL of standard solution containing 1 μg $mL^{-1}$of Pb(II). The pH of the solution was adjusted to 5 and all of the extraction steps were followed. After extraction, the amount of Pb(II) was evaluated by FAAS. The results showed that higher quantities of Pb(II) can be obtained within 90 min (Fig. 5).

Desorption time was examined in the range of 25–180 min, while other parameters were fixed. Fig. 5 shows the percentage of recovery in different times, in which the maximum recovery was obtained in 125 min.

3.5. Effect of breakthrough volume

To study the break-through volume of sample solution, 50 mg of IIP was suspended in different sample volumes (50, 100, 250, 500, 750 and 1000 mL), each of them containing 0.1 mg

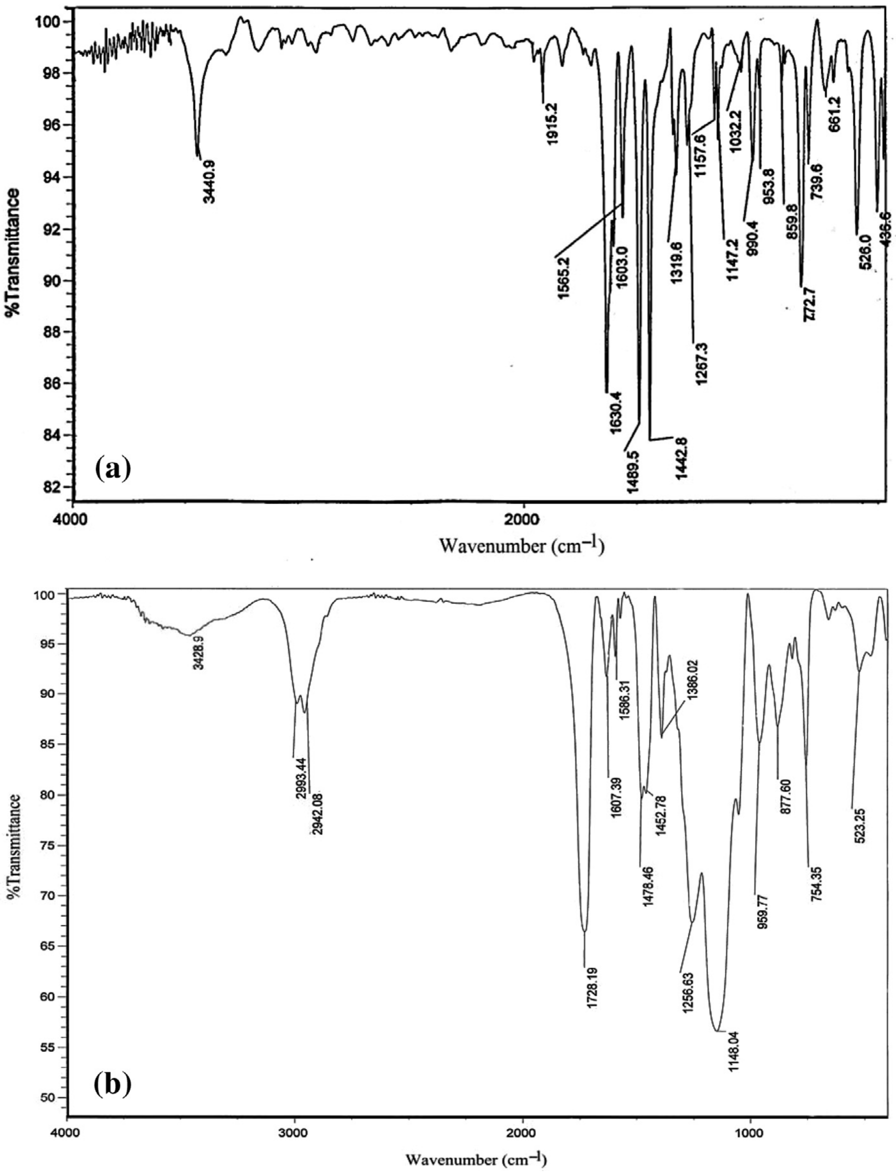

Figure 2 The IR spectra of ligand (a), non imprinted polymer (b), leached (c) and unleached (d) Pb(II)-imprinted polymer.

of Pb(II). All the solutions were extracted under the optimum condition for the proposed method. Fig. 6 illustrates the effect of break-through volume on the percentage of recovery. According to the results, as the volume increased up to 750 mL, the sample solution recovery was constant, but in higher volumes, the recovery decreased. Thus, 750 mL was determined as the maximum sample volume, in which quantitative extraction of Pb(II) is possible.

3.6. Comparison of IIP and NIP

To investigate the different sized cavity of NIP and IIP, a comparison on selective adsorption of analyte was accomplished. Fifty mg of IIP and NIP beads was separately treated with 25 mL of 1 μg mL^{-1} of Pb(II) aqueous solutions, and the recommended procedure was followed under the optimum condition for sorption and desorption steps. The results showed that extraction recovery was 98.7% and 38.9% for IIP and NIP, respectively. Therefore, IIP is more selective for Pb(II), compared with NIP, which is defined as cavity selectivity.

3.7. Maximum sorption capacity

To evaluate this factor, 100 mL of a solution containing 10 mg lead ion was applied for the extraction procedure and the sorption capacity was calculated (50 mg of IIP in the optimum conditions). Based on three replicate measurements, the sorption capacity of the ion imprinted polymer was calculated to be 85.6 mg g^{-1} (RSD = 3.2%). In order to evaluate the maximum sorption capacity, the difference between concentration of the solution before and after solid phase extraction was calculated.

3.8. Selectivity studies

The imprinted polymers were also characterized by a uniform distribution of chelating sites. In ion-imprinted polymers, the

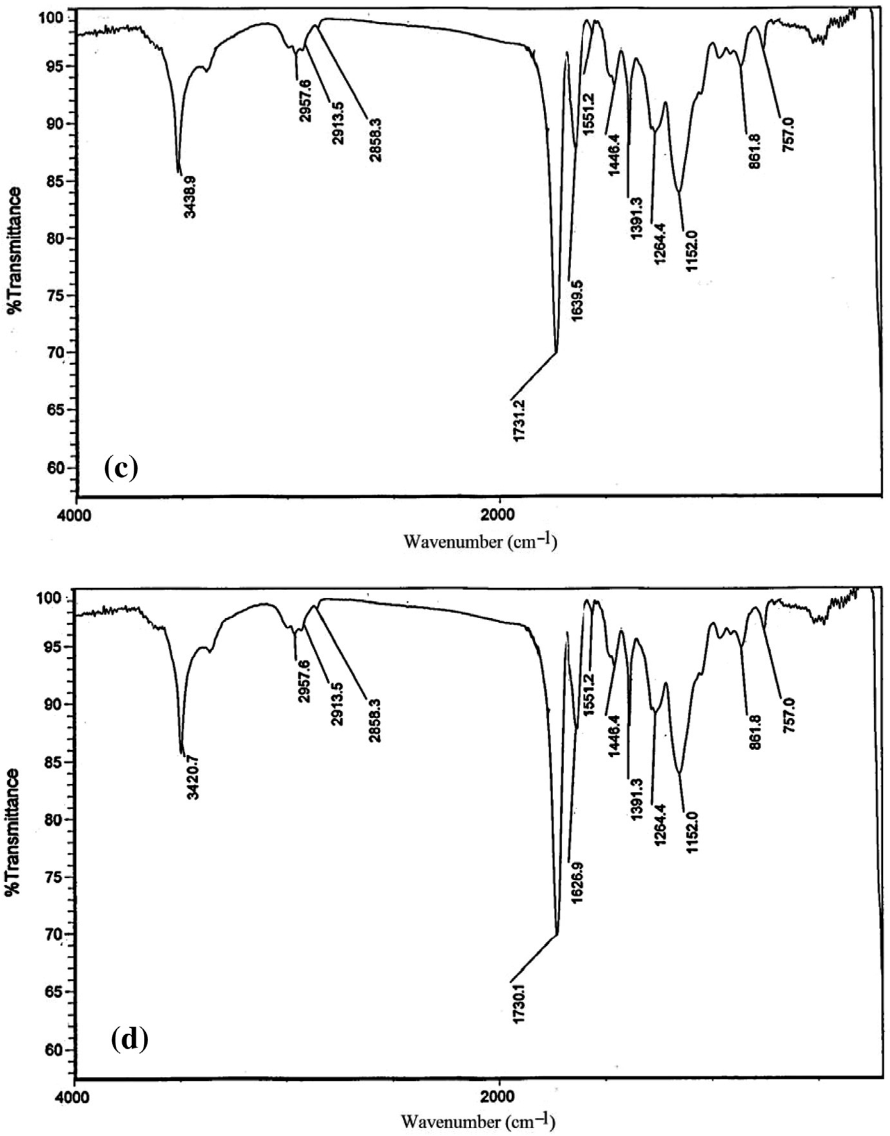

Fig. 2 (*continued*)

cavities created after removal of template were complementary to the imprint ion in size and coordination geometries. For investigating the selectivity of IIP, some binary mixtures containing Pb^{2+}/Li^{+}, Pb^{2+}/Na^{+}, Pb^{2+}/K^{+}, Pb^{2+}/Ca^{2+}, Pb^{2+}/Mg^{2+}, Pb^{2+}/Ni^{2+}, and Pb^{2+}/Co^{2+} were selected and passed through the IIP column. First, 10 μg L^{-1} of lead solutions with 4000 times of interference ion of Li, Na, and K was prepared. In the presence of Li^{+}, K^{+} and Na^{+} with different sizes and charges, IIP had high interaction with Pb(II) in comparison with these ions. Also the selectivity in the presence of other ions with similar ionic radii (Pb(II) = 71 pm, Co(II) = 72 pm, Ni(II) = 69 pm, Mg(II) = 86 pm, and Ca(II) = 74 pm) was studied. At 10 μg L^{-1} lead solutions with 1000 times of interference ion, the competitive adsorption capacity of Pb(II)-imprinted polymer for Pb(II) ions was higher than that for other metals, as shown in Table 1. The results clearly revealed that the synthesized Pb-IIP has high selectivity for lead ion even in the presence of high concentrations of similar ions.

3.9. Evaluation of the method performance

Under the optimal conditions, the dynamic linear range (DLR), correlation of determination (r^2), limit of detection (LOD), relative standard deviation (RSD), the preconcentration factor (PF), and recovery were calculated and summarized in Table 2.

The analyte calibration curve showed a good linearity with the correlation of determination of 0.9998. The LOD was calculated based on $3S_b/m$; where S_b is the standard deviation of the blank signal and m is the slope of the calibration curve after extraction, which was obtained to be 0.75 μg L^{-1}.

The preconcentration factor was calculated as the ratio of the initial volume of the analyte in the original solution to its final volume into the extraction solution. In the proposed method, PF was determined to be approximately 150, because the analyte was extacted from 750 mL of the original solution into 5 mL of extraction solution (HCl 2 mol L^{-1}).

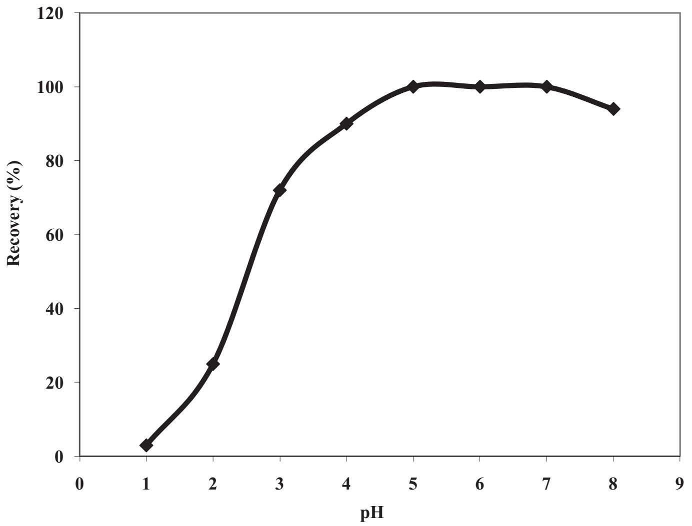

Figure 3 Effect of solution's pH on sorption (condition: IIP = 50 mg, aqueous sample = 25 mL, Pb(II) = 1 μg mL^{-1}, temperature = room temperature, eluent = 5 mL of HCl (2 mol L^{-1}), sorption time = 90 min, desorption time = 125 min).

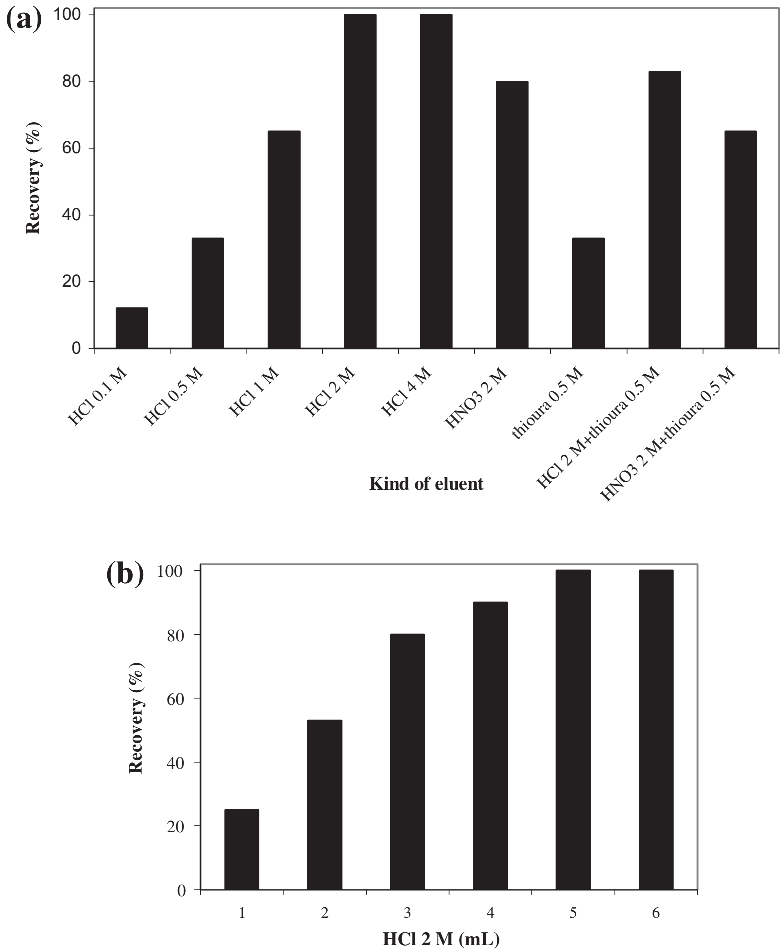

Figure 4 Effect of type, concentration and volume of eluent on extraction efficiency.

The presented method was evaluated by determining the Pb(II) ion concentration in water samples, which were collected from the Shahid Beheshti University (Tehran, Iran). Also, the reference materials were tested for efficiency of the proposed method. The concentration of Pb(II) ions in the sample solutions was measured after extraction by the proposed

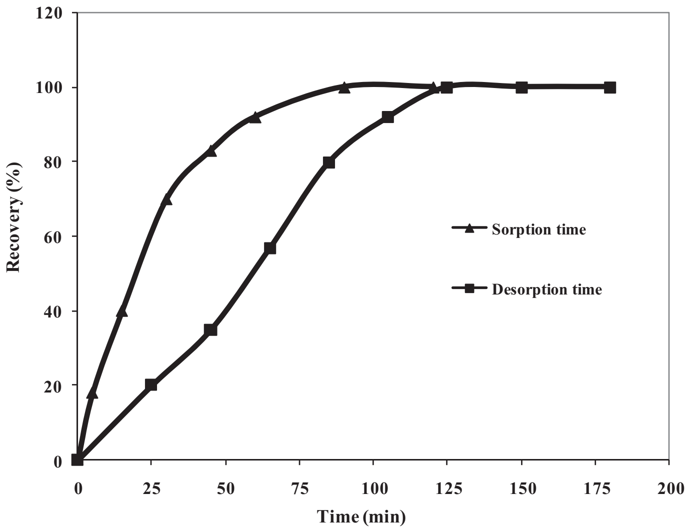

Figure 5 Effect of sorption and desorption times of the analyte on IIP (IIP = 50 mg, aqueous sample = 25 mL, concentration of Pb(II) = 1 μg mL^{-1}, temperature = room temperature, eluent = 5 mL of HCl (2 mol L^{-1})).

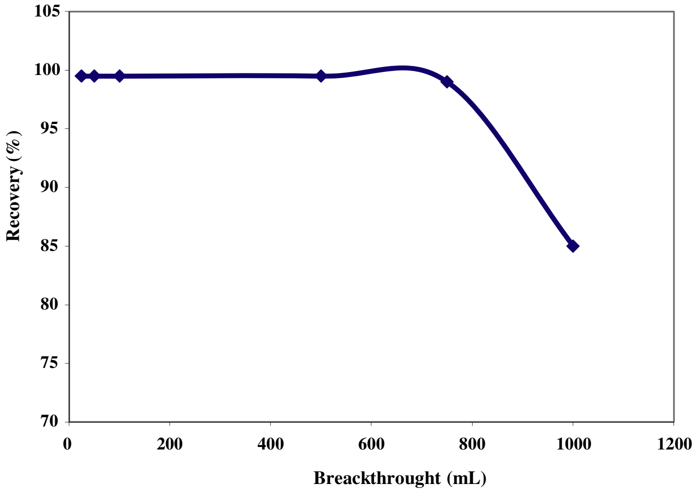

Figure 6 Effect of breakthrough volume on the extraction efficiency of Pb(II) ions (IIP = 50 mg, aqueous sample = 25 mL, concentration of Pb(II) = 0.1 μg mL^{-1}, temperature = room temperature, eluent = 5 mL of HCl (2 mol L^{-1})).

Table 1 The figure of merit of the proposed method (X = C (μg L^{-1})).

Analyte	Regression equation	r^2	LOD (μg L^{-1})	DLR (μg L^{-1})	PF[a]	Recovery (%)	RSD (%)	Maximum extraction capacity (mg g^{-1})
Lead ion	$Y = 0.0039X + 0.002$	0.9998	0.75	3–150	150	97.3	2.7	85.6

[a] Preconcentration factor.

Table 2 Extraction of lead ion from binary mixtures. (X: Concentration of diverse ions).

R[a] (%) ± S [b] (diverse ion)	R[a] (%) ± S[b] (template ion)	Tolerable concentration ratio *X*/lead ion	Foreign ion
4.2 ± 1.5	99.0 ± 1.0	4000	K^+
3.8 ± 1.3	99.0 ± 1.0	4000	Na^+
3.2 ± 1.0	98.1 ± 0.5	1000	Mg^{2+}
2.9 ± 1.2	97.9 ± 0.5	1000	Ca^{2+}
3.1 ± 1.1	96.8 ± 1.0	1000	Co^{2+}
3.5 ± 1.0	94.9 ± 0.5	1000	Ni^{2+}

[a] Recovery.
[b] Standard deviation.

Table 3 Recovery and precision of the determination of lead in various water samples (a) and certified reference material (b).

Sample	C_{added} (μg L^{-1})	C_{found} (μg L^{-1})	Recovery (%)	RSD (%)
Distilled water	5.00	4.98	99.6	3.2
	10.00	9.98	99.8	3.3
Tap water	5.00	4.97	99.4	2.9
	10.00	9.96	99.6	3.1
Caspian sea water	–	16.2	–	
	50.0	65.8	99.3	4.5

Certified reference material	Certified value (mg g^{-1})	C_{found} (mg g^{-1})	Recovery (%)	RSD (%)
Ore polymetallic gold zidarovo-PMZrZ	5.00	4.94	98.7	3.4

Table 4 Comparison between this method and literatures. (Preconcentration factor was calculated for 750 mL of solution).

Method	LOD (ng mL^{-1})	RSD (%)	PF[a]	Maximum sorption capacity (mg g^{-1})	Extraction time	Reference
Pb(II)-IIP-FAAS	0.75	2.7	150	85.60	90 min	Proposed method
Surface grafted Pb(II)-IIP-ICP/OES	0.20	2	100	19.66	30 min	Zhu et al. (2009)
Polymeric resine-FAAS	0.15	10	25	19.40	45 min	Karaaslan et al. (2010)
IIP-ICP/OES/MS	0.18	8	100	–	–	Otero-Romania et al. (2009)
IIP-AAS	50.20	3.8	–	2.01	60 min	Esen et al. (2009)
Imprinted polymer-FAAS	15.00	1.5	–	36.56	50 min	Liu et al. (2011)

[a] Preconcentration factor.

method. Then, all were spiked with 5 μg L^{-1} of standard solution. The amount of the Pb(II) ions was subsequently extracted and determined by the FAAS (Table 3). Also, RSD was low in all the real samples and the recovery was suitable.

3.10. Comparison of proposed method with other researches

The proposed method was compared with other reported methods in the literature. According to Table 4, LOD and RSD obtained by this method are better or at least similar to the other synthesized IIP (Zhu et al., 2009; Karaaslan et al., 2010; Otero-Romania et al., 2009; Esen et al., 2009). Clear differences are in preconcentration factor and maximum sorption capacity. Most important reason for high rate sorption and preconcentration factor is using of special ligand in synthesize process.

4. Conclusion

In the proposed method, the Pb(II)-IIP was synthesized and selected as the specific solid phase for extraction and preconcentration of Pb(II) from real samples. The effects of various parameters on extraction efficiency were investigated and the amount of Pb(II) was determined by FAAS. The proposed method possesses some advantages, such as high sample clean-up efficiency, selectivity, affinity, low detection limit, preconcentration factor, and maximum binding capacity. As a conclusion, the performance of this procedure was excellent in extraction of trace amounts of Pb(II) from real samples. Furthermore, this method could be used in complex matrices. The method was applied for detection of low concentration of lead ions, and can be employed as the good sample pretreatment technique for determination of lead ions.

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