



Analytical Methods

Synthesis and characterisation of nano structure lead (II) ion-imprinted polymer as a new sorbent for selective extraction and preconcentration of ultra trace amounts of lead ions from vegetables, rice, and fish samples

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ABSTRACT

This paper describes the preparation of new Pb(II)-imprinted polymeric particles using 2-vinylpyridine as a functional monomer, ethylene glycol dimethacrylate as the cross-linker, 2,2'-azobisisobutyronitrile as the initiator, diphenylcarbazone as the ligand, acetonitrile as the solvent, and Pb(NO₃)₂ as the template ion, through bulk polymerisation technique. The imprinted lead ions were removed from the polymeric matrix using 5 mL of HCl (2 mol.L⁻¹) as the eluting solvent. The lead ion concentration was determined by flame atomic absorption spectrometry. Optimum pH for maximum sorption was obtained at 6.0. Sorption and desorption of Pb(II) ions on the IIP particles were quite fast and achieved fully over 5 min.

In the proposed method, the maximum sorbent capacity of the ion-imprinted polymer was calculated to be 75.4 mg g⁻¹. The preconcentration factor, relative standard deviation, and limit of detection of the method were found to be 245, 2.1%, and 0.42 ng mL⁻¹, respectively. 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. This ion-imprinted polymer is an efficient solid phase for extraction and preconcentration of lead ions in complex matrixes. For proving that the proposed method is reliable, a wide range of food samples with different and complex matrixes was used.

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1. Introduction

Trace levels of heavy metals are widely spread in environment owing to soil erosion, industrial, and agricultural processes (Tuzen, Soylak, & Parlar, 2005). Nowadays, the pollution by heavy metals deriving from various environmental sources has attracted much more attention (Melek, Tuzen, & Soylak, 2006). Lead, cadmium, nickel, and mercury are heavy metals with unquestionable toxicity (Davis, Wu, Zhanq, Hou, & Jones, 2006; Grahek, Macefat, & Luli, 2006; Korn et al., 2006). These metals as the main sources of contamination are found in water and food. Lead is one of the most hazardous elements for human health, because it can cause adverse effect on metabolic processes of human beings (Gama, Lima, & Lemos, 2006), and lead has been proved to be a carcinogenic agent. So many countries and international organizations have set a permissible level for lead. For example, the World Health Organization (WHO) has made a maximum allowable limit of 10 µg L⁻¹ for lead in

drinking water (World Health Organization, 1996). Consequently, the development of reliable methods for the removal and determination of lead in biological and water samples is of particular significance. Therefore, separation and pre-concentration procedures are commonly used for trace element determinations in water, vegetables, fish, rice, and food samples. The analytical methods of lead usually involves in using flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) (Biasino, Domínguez, & Alvarado, 2007; Liang & Sang, 2008; Manzoori, Amjadi, & Abulhassani, 2009; Marchisio, Sales, Cerutti, Marchevski, & Martinez, 2005; Portugal, Ferreira, dos Santos, & Ferreira, 2007; Soylak, Elci, Akkaya, & Dogan, 2002; Soylak, Narin, Bezerra, & Ferreira, 2005). These instruments have sufficient sensitivity; however some of them are very expensive, and not available for a common analytical laboratory. Atomic fluorescence spectrometry is a relatively new and sensitive method for elemental analysis, and has been successfully used for the determination of cadmium, zinc,

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the speciation of mercury, and arsenic (Frentiu, Darvasi, Senila, Ponta, & Cordos, 2008; Frentiu et al., 2010; Lu, Liu, Dong, & Li, 2010; Wietecha, Koscielniak, Lech, & Kielar (2005); Yang, Kang, Zhang, Li, & Gao, 2004). Atomic fluorescence spectrometry has also reported for the determination of lead (Li & Liu, 2007; Shen, Dong, & Shen, 2000). In this experiment, it is utilised because of its merits such as simplicity, easy to operate, low cost, and high sensitivity. Moreover, it is often difficult to determine lead directly at very low concentrations because of the matrix interferences occurring in real samples. Hence a preliminary separation and preconcentration step are often needed. Up to now, many sample preconcentration methods have been developed for the enrichment of lead in water samples, for example, knotted reactor (Souza et al., 2007), combination of flow injection and cloud point extraction (Silva & dos Santos Roldan, 2009), solid phase extraction (Karve & Rajgor, 2007; Li, Yang, Tang, & Pan, 2003), cloud point extraction (Silva & Roldan, 2009, capillary microextraction (Zheng & Hu, 2007), solid phase microextraction (Gorecki & Pawliszyn, 1996), and liquid phase microextraction (Xia, Li, Wu, Hu, & Chen, 2008). Solid phase extraction, mainly using ionic exchange resins, functionalised chelating resins or C_{18} adsorbent material, is mostly used to pre-concentrate the trace elements and to remove the salt matrix (Romani, Pineiro, Barrera, & Esteban, 2008; Romani, Pineiro, Barrera, & Esteban, 2009), and this technique has become quite popular because it offers many practical and operating advantages over other pre-concentration methods such as higher preconcentration factor, simple operation, rapid phase separation, lower cost and less time, and the ability to combine with different modern detection techniques (Romani et al., 2008, 2009). However, interfering compounds might be co-extracted with the target analytes on conventional sorbents (Romani, Pineiro, Barrera, & Esteban, 2008). Hence, to overcome this lack of selectivity, the use of molecular imprinted polymers (MIPs) has been proposed (Romani et al., 2008). These rigid and stable materials are prepared by formation of specific recognition sites in a polymeric matrix (Zambrzycka, Roszko, Leśniewska, Wilczewska, & Godlewska-Zytkiewicz, 2011). Molecular imprinting is an attractive method for the preparation of a selective sorbent. Due to the interaction between monomers and templates, the imprinted materials possess a predetermined arrangement of ligands and tailored binding pockets, which show affinity for the template molecule over other structurally related compounds (Xie, Liu, Wu, Guo, & Li, 2012)). Besides the fast synthesis of MIPs, the less expensive synthesis and materials also provide a high degree of molecular recognition (Romani et al., 2008). Synthesised sorbents in the presence of ions instead of molecules as the template generate ionic imprinted polymers (IIPs) which can offer all the benefits derived from MIPs and a high capacity for recognising ions (Romani, Pineiro, Barrera, & Esteban, 2009). The concept of ion-imprinting is understood as a process whereby cross-linking functional monomers align in a predetermined orientation according to their stereochemical interactions with the template metal ions (Tsoi, Ho, & Leung, 2012). Ion-imprinted polymers (IIPs) are similar to molecular imprinting polymer, but they can recognise metal ions after imprinting and retain all of virtue of molecular imprinting polymer. In the ion imprinted process, the selectivity of polymeric adsorbent is based on the specificity of the ligand, coordination geometry, coordination number of the ions, charge, and size (Fan, Li, Li, & Sun, 2012).

In this study, a novel nano structure Pb(II) ion-imprinted polymer has been synthesised for faster extraction of Pb(II) ions from various matrixes. Characterisation of this polymer was evaluated by fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermogravimetric (TG), and differential thermal analysis (DTA). The effect of several variables on the separation and determination of Pb(II) was investigated and optimised by using the one variable at a time method. These variables included pH of

solution, sorption and desorption rate, the kind, concentration and volume of eluent, breakthrough volume, the effect of coexisting ions on the extraction recovery. Finally, this sorbent was used for preconcentration and determination of Pb(II) ions in different real samples.

2. Materials and methods

2.1. Apparatus

AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer with a deuterium background corrector was used for determination of Pb(II) ions (Divrikli, Akdogan, Soylak, & Elci, 2007; Narin, Surme, Bercin, & Soylak, 2007). A lead hollow cathode lamp (HCl) was used as the light source operated at 5 mA. The wavelength was set at 283.3 nm resonance line and the spectral band pass at 0.5 nm. All measurements were carried out in an air/acetylene flame. A digital pH meter, WTW Metrohm 827 Ion analyzer (Herisau, Switzerland), equipped with a combined glass calomel electrode was used for the pH adjustments at 25 ± 1 °C temperature. Fourier Transform Infrared (FT-IR) spectra ($4000\text{--}200\text{ cm}^{-1}$) in KBr were recorded using Bruker IFS66/S FT-IR spectrometer. Heidolph heater stirrer model MR 3001 (Germany) was employed for heating and stirring of the solutions. Scanning electron microscopy (SEM) was performed by gently distributing the powder sample onto the stainless steel stubs, using SEM (Philips, XL30, Almelo, the Netherlands) instrument. The thermal properties of samples were determined, using a Bahr-Thermoanalyse GmbH (Germany) with employing, heating and cooling rates of $10\text{ }^{\circ}\text{C min}^{-1}$ and using a condenser as the coolant. The samples have been weighed as a thin film and carefully packed into a clean aluminum pan ($11.5\text{--}12.5\text{ mg}$) and sealed by crimping an aluminum lid onto the pan (Shimadzu universal crimper). An Al_2O_3 empty pan sealed with a cover pan was used as a reference sample. A scanning range of $10\text{--}800\text{ }^{\circ}\text{C}$ was used for samples at $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen gas.

2.2. Materials and reagents

2-vinyl pyridine and diphenylcarbazone with high purity were purchased from Merck (Darmstadt, Germany). Ethylene glycol dimethacrylate (EGDMA) was obtained from Fluka (Buchs, Switzerland). 2,2'-Azobisisobutyronitrile (AIBN) was obtained from Acros Organics (Morris Plains, NJ, USA). NaOH, HCl, HNO_3 , acetic acid and methanol were purchased from Merck. All the other reagents used were of analytical grade and purchased from Merck. Ultrapure 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 used as the certified reference material.

2.3. Preparation of standard solutions

Reference material was digested with 6 mL of HCl (37% (v/v)) and 2 mL of HNO_3 (65% (v/v)) 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 ultrapure water (Tuzen, Saygi, & Soylak, 2008).

Standard Stock solutions (1000 mg L^{-1}) of Pb(II), Ni(II), Mn(II), Fe(II), Ca(II), Zn(II), Cu(II), Cd(II), Al(III), and Ag(I) were prepared in 2% (v/v) HNO_3 . The used standard solutions were prepared by appropriate dilution of the stock solution with double distilled water. All of these solutions were stored in ambient temperature.

2.4. Real sample pretreatment

Ten fish samples were collected from two different sites of Moosa creek randomly. Moosa creek is located in Northwest of Persian

Gulf, and has several subsidiary creeks. Among them, Jafare creek was chosen as a polluted site and Behad creek as a reference site which is far from petrochemical industries. Sampling was carried out in August 2010. The fish samples (*platycephalusindicus*) were stored in plastic bags with ice and transported back to the laboratory. They were kept at -20°C before being used. A part of the muscle tissue was taken out quickly and was dried in an oven at 70°C for 48 h. After grinding the dry tissue, 0.5 g of each sample was digested with 5 mL of concentrated HNO_3 in Teflon beakers for 4 h at 100°C . To deproteinate the sample, resulted mixture was filtered into 500 mL Erlenmeyer flask and then diluted with double distilled water up to 500 mL. The Resulted mixture was filtered into 500 mL Erlenmeyer flask and then diluted with double distilled water up to 500 mL.

Three types of vegetables were chosen for analysis in August 2010. These were parsley, basil and mint which were collected from five local supermarkets in five different areas in Tehran, Iran, randomly. Five samples of parsley which were collected from five supermarkets were combined for further analysis. The same procedure was carried out for basil and mint separately. Parsley, basil and mint samples were air-dried followed by drying at 105°C for 2 h and then powdered. 0.5 g of basil, parsley and mint samples were taken in Teflon flasks, and 5.0 mL of concentrated nitric acid and 5.0 mL of 30% (v/v) hydrofluoric acid were added. After stood

for 8 h, the samples were digested in a microwave system for 10 min at 106°C . The clear solutions obtained were transferred to a 500.0 mL beaker; and the pH was adjusted to 6.0.

For determination of lead in rice samples, five samples were collected from five supermarkets in five different areas in Tehran, Iran, in August 2010 and then the samples were combined for the next procedure. 5 g of rice sample was used. Wet digestion of sample was performed by using the mixture of HNO_3 and HCl . 30 mL of concentrated HNO_3 was used for 5.0 g of sample. The mixture was heated on the hot plate. The mixture was gently boiled until 3–6 mL of digestion solution remains. Then, 25 mL of concentrated HCl was added. The resulted solution was heated and boiled again until 10–15 mL of solution remains. After cooling, the residue was filtered through blue band filter paper. Then the sample was diluted to 500 mL with distilled water; and the pH was adjusted to 6.0.

2.5. Synthesis of a nano structure ion-imprinted polymer

The $\text{Pb}(\text{II})$ -imprinted particles were prepared by bulk polymerisation technique. In the first step, 4 mmol of 2-VP (functional monomer) and 1 mmol of diphenylcarbazone (ligand) were dissolved in 35 mL of acetonitril in a 100 mL glass flask. Subsequently, as the second step, 0.5 mmol of $\text{Pb}(\text{NO}_3)_2$ as an imprinted metal ion

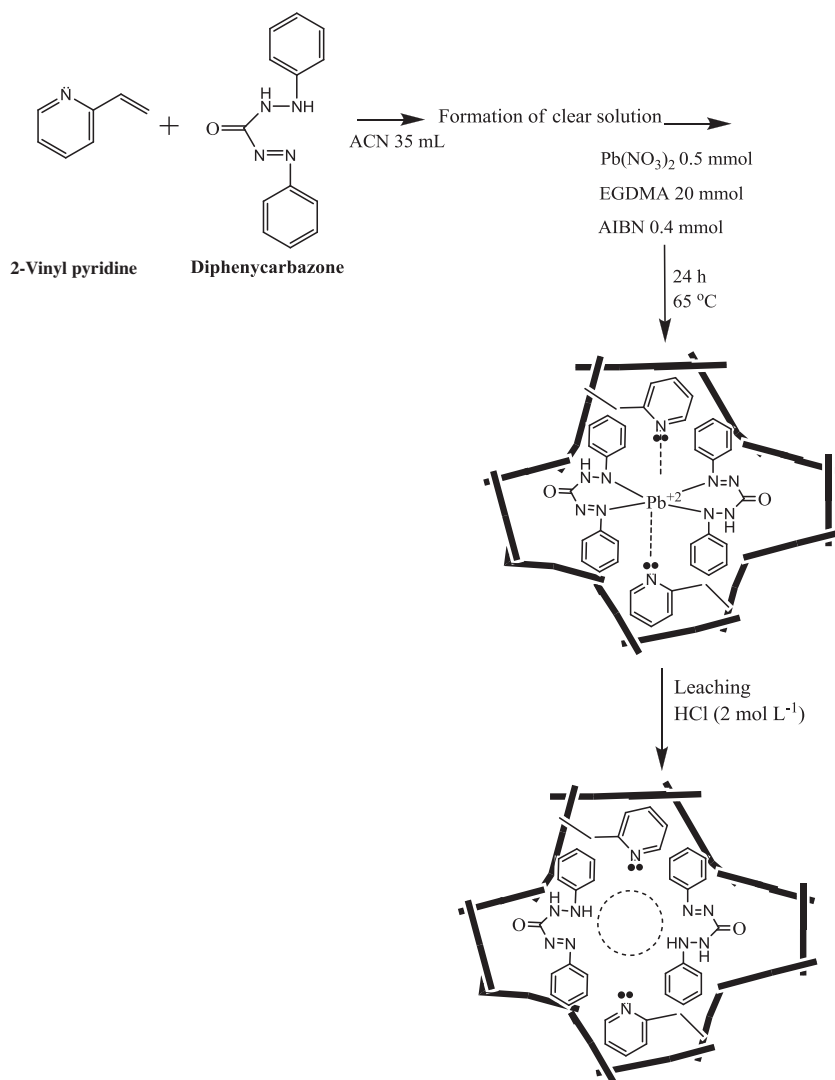


Fig. 1. Schematic illustration of imprinting process for the preparation of nano structure lead imprinted polymer by bulk polymerisation technique.

(template) was added slowly to a glass flask and the resulted mixture was stirred for 5 h at room temperature. In the third step, 20 mmol of EGDMA and 0.4 mmol of AIBN were added as cross-linker and initiator. The oxygen of the sample solution was removed by bubbling nitrogen through the sample for 10.0 min. Polymerisation was performed in an oil bath at 65 °C for 24 h in the presence of nitrogen under magnetic stirring at 400 rpm. The prepared polymer was washed several times with 1:4 (v/v) methanol/water to remove the unreacted materials and then with HCl (2 mol.L⁻¹) for leaching the imprinted metal ions until the washing solution was free from Pb(II) ions. Finally, it was washed with double distilled water until reached a neutral pH. The resulting fine powder was dried under vacuum in a desiccator before sorption and desorption studies. Diphenylcarbazone as the ligand was retained in the polymer structure due to conditions that were used in the elution of the polymer. Furthermore, during the synthesis of the polymer, the ligand was trapped in the structure of the IIP due to π - π interactions between molecules present in the polymer and furthermore, the elution conditions were completely soft for the removal of lead ions from ion-imprinted polymer structure. In the same way, the non imprinted polymer (NIP) was also prepared without ions of lead. (Fig. 1 provides the images of synthesised IIP after each step).

2.6. Characterisation of IIP

The resulting imprinted particles were characterised by IR spectroscopy, scanning electron microscopy, thermogravimetric, and differential thermal analysis. The IR spectra of unleached and leached ion-imprinted polymer (IIP) were recorded by using KBr pellet method. In the IR spectra, the absorptions due to C=O (1729 cm⁻¹), C-O (1260 cm⁻¹), C-N (1151 cm⁻¹), C=N (1637 cm⁻¹), N-H (3442 cm⁻¹) and C-H bands (755, 1456 and 2956 cm⁻¹) were observed. The N-H and C=N bands at 3442.01 and 1637 cm⁻¹ in unleached IIP were shifted to 3442.8 and 1644.06 cm⁻¹ in leached IIP. This amount of reduction in band frequencies indicates that the lead ions have been coordinated with non-bonding electron pairs of nitrogen in N-H and C=N groups in diphenylcarbazone, and as a result, it demonstrates the presence of Pb ions in unleached IIP structure. Moreover, the presence of C=N and N-H bands in the IR spectra of these materials indicated that diphenylcarbazone had been sufficiently immobilised in the polymer matrix. Different colors of the non-imprinted polymers prepared in the absence (poly (EGDMA), white) and presence (poly (EGDMA-diphenylcarbazone), yellow) of diphenylcarbazone clearly indicated the presence of ligand in the polymer matrix.

While, the brown color of the imprinted polymer (poly (EGDMA-diphenylcarbazone/Pb(II))) is an obvious indication for the presence of the template ion as a Pb²⁺-diphenylcarbazone complex in the polymeric matrix. Moreover, a further change in color from brown to yellow is a clear result of desorption of the Pb(II) ions from the IIP particles upon its washing with a HCl (2 mol.L⁻¹) solution. Thermal stability of the leached and unleached polymer particles was evaluated by thermo gravimetric analysis. Fig. 1S shows that thermogravimetry (TG) and differential thermal analysis (DTA) plots for (a) unleached and (b) leached ion-imprinted polymer. In DTA plots of lead imprinted polymer, exothermic peaks were observed at 353, 374, 452 and 591 °C (for unleached) and 352, 376 and 618 °C (for leached). As it is shown in TG plots for ion imprinted particles, weight loss for Pb(II)-IIP was about 97%, and this amount of reduction in weight was related to the presence of Pb(II) ions in polymer bead. While decrease in weight for leached imprinted polymer up to 100%, is due to absence of lead ions in polymer. These observations indicate that the formation of Pb²⁺-imprinted polymer and elution of Pb(II) ions from the polymer was performed successfully. The morphology of the Pb(II)-IIP was assessed by scanning electron microscopy, and the SEM patterns are shown in Fig. 2. The SEM pattern showed particles with the size of about 38 nm. As a result, Pb²⁺-IIP can be used as a nano-size selective solid phase for very fast extraction of ultra trace amounts of Pb(II).

2.7. Extraction procedure

Batch experiments were used for investigation of factors in sorption and desorption steps. Extraction of Pb(II) ions from modeling solutions and real samples is followed by two steps: sorption and desorption. In sorption step, the pH of sample solution was adjusted to 6.0 by drop wise addition of 2 M-sodium hydroxide or hydrochloric acid solutions. Then, 50 mg of dried polymer was suspended in aqueous solution containing 1 μ g mL⁻¹ concentration of Pb(II) and stirred for 5 min with a magnetic stirrer. In desorption step, elution of Pb(II) ions from IIP bead was performed by 5 mL of HCl (2 mol.L⁻¹). After 5 min, the concentration of lead ion in this solution was determined by flame atomic absorption spectrometry (FAAS). Extraction percent of lead was calculated by the following equation:

$$\text{Extraction \%} = \frac{C_A - C_B}{C_A} \times 100$$

C_A and C_B are the concentrations of lead ion before and after extraction in the solution.

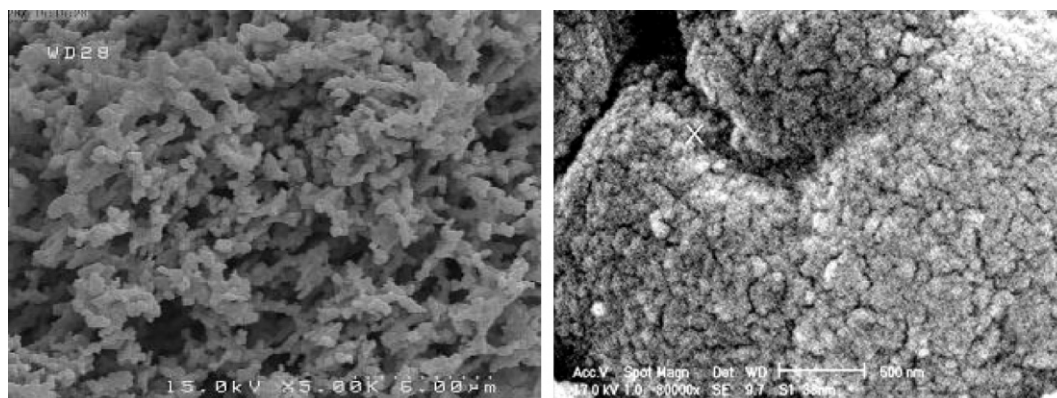


Fig. 2. The SEM micrograph of Pb(II)-ion-imprinted polymer in different magnetisations.

3. Results and discussion

3.1. Sorption step

3.1.1. Effect of solution's pH

Among the tested variables, pH was found to be the most critical parameter for adsorption of metals on the ion-imprinted polymer. To evaluate the effect of pH on the extraction efficiency, the pH of 25 mL of sample solutions containing 1 mg.L⁻¹ of lead ions was adjusted in the range of 2–8. The Pb²⁺ adsorption of Pb²⁺-imprinted polymer increased from pH 2.0 to 6.0 but decreased slightly from pH 6.0 to 8.0. Therefore the maximum binding capacity was obtained at pH 6.0. The retained lead ions were then eluted with 5 mL of HCl (2 mol.L⁻¹). Lead ions concentration in the eluting solvent was determined by FAAS. The data graphed as a function of pH for ion-imprinted polymer (IIP) and non imprinted polymer (NIP) are shown in Fig. 3. The maximum quantitative recovery of imprinted polymer for lead ions was obtained at the pH of 6.0. By decreasing the pH value of the solution, the quantitative recovery of the sorbent was also decreased due to the electrostatic repulsion of the protonated active sites on the sorbent with the positively charged lead species. Due to hydrolysis of lead ions, pH above 8.0 was not tested.

3.1.2. Equilibrium sorption time

In a typical uptake kinetics test, 50 mg of the sorbent was added to 25 mL of 1 mg.L⁻¹ Pb(II) aqueous solution at pH 6.0. The resulting suspension was stirred in different times (i.e., from 2 to 10 min) under magnetic stirring. According to the results in Table 1, an optimum equilibration time of 5 min was obtained for quantitative extraction of the analyte from solution into the solid phase.

3.2. Desorption step

3.2.1. Effect of type, concentration and volume of eluent

Various solvents such as HNO₃, HCl, and acetic acid were tested to obtain the best eluent for the removal of Pb(II) ions. According to experiments, HCl showed the best recovery among other solvents. The effects of eluent's concentration and volume on the recovery of lead ions were also studied. As shown in Table 1S, quantitative recovery can be obtained with 5 mL of HCl (2 mol.L⁻¹). After the sorption of Pb(II) ions by the polymer, the Pb(II)-IIP particles were separated from the solution through filtration. Then, Pb(II)-IIP was first washed with distilled water in order to remove non-specifically retained matrices from the IIP. Then, Pb(II)-IIP was dried,

Table 1

Influence of adsorption and desorption times on the percent extraction of lead ion using IIP and NIP particles.

No.	Parameter	R ^a (%) ± S ^b	
		Ion-imprinted polymer	Non imprinted polymer
1	Sorption time (min)		
		78.0 ± 1.0	34.0 ± 1.0
		90.0 ± 1.0	41.0 ± 1.0
		99.0 ± 1.0	44.0 ± 1.0
		99.0 ± 1.0	45.0 ± 1.0
		99.0 ± 1.0	46.0 ± 1.0
2	Extraction time (min)		
		84.0 ± 1.0	32.0 ± 1.0
		94.0 ± 1.0	39.0 ± 1.0
		99.0 ± 1.0	40.0 ± 1.0
		99.0 ± 1.0	57.0 ± 1.0
		99.0 ± 1.0	64.0 ± 1.0

^a Recovery.

^b Standard deviation.

and the extracted lead ions were eluted by HCl through batch experiments.

3.2.2. Extraction time

In ion-imprinted polymer technique, after the sorption of analyte on IIP, a time interval is needed to break the bonding between ligand and metal ions. In order to investigate the optimum desorption time, various times were examined in the range of 2–10 min, while other parameters were kept in optimum condition. As shown in Table 1, extraction recovery was increased up to 5 min and it was constant in longer times. Therefore, 5 min can be the best quantitative time for the elution of metal ions from the imprinted polymer.

3.3. Effect of sample volume

In the analysis of real samples, the sample volume is one of the important parameters influencing the preconcentration factor. Therefore, the effect of sample volume on quantitative adsorption of Pb(II) ion was investigated. For this purpose, 50 mg of IIP was suspended in different sample volumes (25, 50, 100, 250, 500, 750 1000, 1250, 1400 and 1500 mL), and the total amount of loaded Pb(II) was kept constant in 0.1 mg. All solutions were extracted under the optimum condition by the proposed method. The results in Fig. 2S, demonstrated that the dilution effect was not significant for sample volumes up to 1250 mL for lead ions.

3.4. Sorption capacity

The sorption capacity as the maximum amount of metal ions sorbed per gram of the polymer is an important factor for evaluation of the synthesised IIP. To evaluate this factor, 500 mL of a solution containing 25 mg lead ion was applied to the extraction procedure and the sorption capacity was calculated. Based on three replicate measurements, the sorption capacities of the ion-imprinted polymer and non imprinted polymer were calculated to be 75.4 ± 0.05 and 5 ± 0.06 mg g⁻¹, respectively.

3.5. Effect of foreign ions

In order to investigate the effect of various cations existed in natural samples; elements that are known as alkaline, alkaline earth, and transition metals were added to 100 mL of solution containing 0.01 mg lead ions. The degree of tolerance for some alkaline, alkaline earth and transition metal ions is presented in

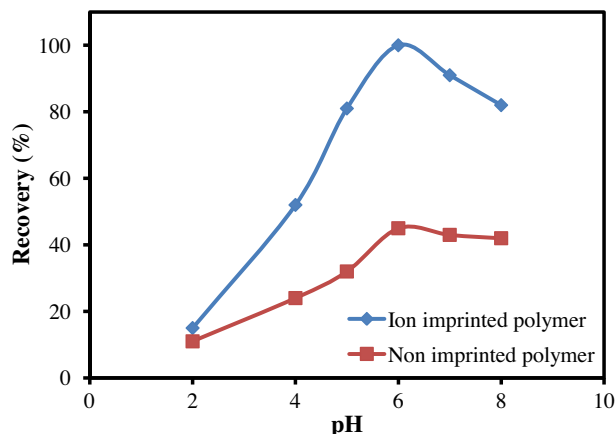


Fig. 3. Effect of sample pH on the recovery of Pb(II) ions on the Pb(II) ion-imprinted polymer and non imprinted polymer.

Table 2

The tolerance limit of the diverse ions on the determination of Lead. (condition: sample pH 6.0, sample volume = 100 ml, 100 $\mu\text{g.L}^{-1}$ of lead ion, sorption time = 5 min; eluent = 5 mL HCl (2 mol.L⁻¹), desorption time = 5 min); X, concentration of diverse ions.

Foreign ion	Tolerable concentration ratio X/Pb	Ion-imprinted polymer		Non imprinted polymer	
		R ^a (%) $\pm$ S ^b (template ion)	R ^a (%) $\pm$ S ^b (diverse ion)	R ^a (%) $\pm$ S ^b (template ion)	R ^a (%) $\pm$ S ^b (diverse ion)
K ⁺	10,000	99.0 $\pm$ 2.0	6.0 $\pm$ 2.0	42.0 $\pm$ 1.0	9.0 $\pm$ 2.0
Na ⁺	10,000	99.0 $\pm$ 2.0	5.0 $\pm$ 1.0	41.0 $\pm$ 1.0	10.0 $\pm$ 1.0
Ca ²⁺	1000	99.0 $\pm$ 1.2	8.0 $\pm$ 2.0	32.0 $\pm$ 1.0	12.0 $\pm$ 1.0
Al ³⁺	1000	99.0 $\pm$ 1.0	7.0 $\pm$ 2.0	41.0 $\pm$ 1.0	15.0 $\pm$ 2.0
Ag ⁺	1000	99.0 $\pm$ 1.0	8.0 $\pm$ 2.0	39.0 $\pm$ 2.0	13.0 $\pm$ 2.0
Cu ²⁺	1000	98.0 $\pm$ 0.7	9.0 $\pm$ 1.0	45.0 $\pm$ 1.0	14.0 $\pm$ 1.0
Fe ²⁺	1000	98.0 $\pm$ 1.4	6.0 $\pm$ 1.0	42.0 $\pm$ 1.0	16.0 $\pm$ 1.0
Cd ²⁺	1000	95.0 $\pm$ 2.0	6.0 $\pm$ 2.0	44.0 $\pm$ 2.0	18.0 $\pm$ 2.0
Ni ²⁺	1000	96.0 $\pm$ 1.0	7.0 $\pm$ 1.0	35.0 $\pm$ 2.0	17.0 $\pm$ 1.0
Mn ²⁺	1000	98.0 $\pm$ 1.0	8.0 $\pm$ 1.0	41.0 $\pm$ 2.0	16.0 $\pm$ 2.0
Zn ²⁺	1000	98.0 $\pm$ 1.0	9.0 $\pm$ 2.0	45.0 $\pm$ 1.0	20.0 $\pm$ 1.0

^a Recovery.

^b Standard deviation.

Table 2. From the tolerance data, it can be found that the foreign ions have no significant effects on preconcentration of lead ions at pH 6.0.

3.6. Statistical and calibration parameters

Under optimum conditions that have been described, the IIP-SPE showed a linear calibration curve within concentration ranging from 1 to 100 $\mu\text{g.L}^{-1}$. The least square equation at above dynamic linear range was as follows:

$$A = 0.01C_{\text{Pb}} (\mu\text{g.L}^{-1}) + 0.02, (R^2 = 0.998).$$

The limits of detection, defined as $C_{\text{LOD}} = 3S_b/m$, where S_b is the standard deviation of 7 replicate blank signals and m is the slope of the linear section of calibration curve after preconcentration, for a sample volume of 750 mL, was found to be 0.42 ng mL⁻¹ for lead ions. In order to calculate the blank value, 50 mg of the polymer was added to 750 mL of blank solution and the solution was stirred for 5 min. Then, the solution was filtered and the remaining polymer was added to 5 mL of HCl (2 mol.L⁻¹) as the elution solvent and again the solution was stirred for 5 min. Finally, the solution was filtered and determined by FAAS. The relative standard deviation for six separate batch experiments with 50 mg of sorbent for determination of 8 $\mu\text{g Pb(II)}$ in 100 mL of water was 2.1%.

3.7. Real sample analysis

The applicability of the sorbent for preconcentration of trace levels of Pb(II) was tested using fish, vegetables and rice samples. The mentioned samples were prepared according to the Section 2.4. For the preconcentration procedure, pH of 500 mL of real samples was adjusted to 6.0 and spiked with lead ions and was used in column method. The concentration of sorbed Pb(II) ions was determined based on a triplicate analysis (Table 3a). It was found that the quantitative extraction of lead ions was performed successfully by the sorbent even in the presence of various diverse ions.

3.8. Certified reference material analysis

Certified reference material (ore polymetallic gold zidarovo-PMZrZ (206 BG 326)) was used for the validation of the proposed method. As Table 3b shows, the measured mean value is not significantly different from the certified value (Linsinger, 2005). Therefore, Pb(II)-IIP particle can be used as a reliable solid-phase for extraction and determination of lead in environmental samples.

Table 3

(a) Analysis of lead in different real samples; (b) the comparison between measured values of the CRMs and the certified values.

Sample	C _{added} (μg kg ⁻¹)	C _{found} (μg kg ⁻¹)	Recovery %	RSD %
(a)				
Fish sample in Behad creek	–	44.5	–	
	10	53.2	97.6	3.6
Fish sample in Jafare creek	–	87.4	–	
	10	97.1	99.7	3.2
Parsley	–	8.2	–	
	10	18.1	99.4	2.7
Basil	–	7.8	–	
	10	17.6	98.8	3.7
Mint	–	3.2	–	
	10	13.3	100.7	2.9
Rice	–	–	–	
	10	37.2	97.9	4.4
Sample	Ore polymetallic gold zidarovo-PMZrZ (206 BG 326)			
(b)				
Element	Lead			
Certified value (C _{CRM})	5.47 ± 0.8 mg g ⁻¹			
Laboratory measurement (C _m)	5.30 ± 1.2 mg g ⁻¹			
u _{CRM}	0.8/2 = 0.4			
u _m	1.2/5 = 0.24			
Δ _m	5.3–5.47 = 0.17			
u _Δ	√(0.4 ² + 0.24 ²) = 0.46			
U _Δ = 2 u _Δ	0.92			
U _Δ ≥ Δ _m	The measured mean value is not significantly different from the certified value.			

3.9. Comparison of the synthesised IIP with literature

The proposed method was compared with other reported methods in literature. LOD and RSD are similar to the other synthesised IIPs. This method is clearly different from other reports in preconcentration factor (PF), maximum binding capacity, and extraction time.

4. Conclusion

The ion-imprinted polymer procedure is a useful technique for the preparation of sorbent for preconcentration of metal ions, such as lead from aqueous solutions. The prepared ion-imprinted polymer particles has an increased selectivity toward Pb(II) ion over a range of competing metal ions with the same charge and similar

ionic radius. Two of the most important characteristics of the prepared lead IIP are the fast sorption and desorption of Pb(II) ions. The Pb(II)-imprinted particles can be used repeatedly with no significant decrease in its binding affinities. Due to relatively high pre-concentration factor, trace metal ions at ng mL^{-1} levels in high-volume samples can be determined and separated by ion-imprinted polymers.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2012.11.042>.

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