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Synthesis of different types of salamthio molecularly imprinted polymers for separation and preconcentration of lead

Hamid Hashemi-Moghaddam[a,*], Mahbobe Asadian-Amiri[a], Siyamak Bagheriyan[b]

[a]*Department of Chemistry, Damghan Branch, Islamic Azad University, P.O. Box 36716-39998, Damghan, Iran, Tel. +98 23 35225058; Fax: +98 23 35225044; emails: h.hashemimoghadam@damghaniau.ac.ir (H. Hashemi-Moghaddam), amahbobas@yahoo.com (M. Asadian-Amiri)*
[b]*Department of Geology, Shahriyar Branch, Islamic Azad University, Shahriyar, Iran, email: siyamakbagherian@yahoo.com*

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ABSTRACT

A molecularly imprinted polymer (MIP) was synthesized via non-covalent, bulk, thermal radical polymerization using methacrylic acid (functional monomer), ethylene glycol dimethacrylate (cross-linker), 2,2´-azobisisobutironitril (initiator), acidic and basic lead salamthio complex (templates), and methanol (porogenic solvent). A control polymer (non-imprinted polymer, NIP) was prepared under well-defined conditions without the use of template for comparison. Acidic and basic MIP and NIP were subjected to extraction experiments. Various parameters, including pH, time, concentration of sample, and type of eluent for elution of lead from polymer, were optimized. In addition, the interfering effect of MIP on lead absorption was investigated. Results obtained for acidic, basic, and NIP showed that acidic lead salamthio complex has significantly better adsorption capacity and faster adsorption kinetic, and can elute lead more efficiently than basic lead salamthio MIP. The amount of lead was measured in the lipstick and tap water after preconcentration by the synthesized MIPs, and then compared with the results obtained using GFAAS. The proposed method showed high performance for preconcentration of lead.

Keywords: Molecularly imprinted polymer; Solid-phase extraction; Lead; Salamthio

1. Introduction

Among the heavy metals, lead has attracted increasing concern owing to its high-environmental persistence, severe toxicity, and wide distribution. Lead is the second most hazardous substance after arsenic according to the Agency for Toxic Substances and Disease Registry. Therefore, the biogeochemical behavior of lead has been extensively studied, particularly in the perspective of risk assessment and remediation of polluted sites [1].

Flame atomic absorption spectrometry (FAAS) is a good technique for determination of lead in several types of samples. Inductive coupled mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) have produced low-detection limits. However, the use of ICP-MS and GFAAS often involves high cost and complex sample preparation, thereby limiting their widespread application to routine analysis. FAAS is still being used because it offers fast analysis time, low cost, relative simplicity, and

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*Corresponding author.

low-sample volume requirements. However, determination of lead at low concentrations is often difficult because of insufficient sensitivity of methods and matrix interferences during real sample analysis.

For this reason, a preliminary separation and preconcentration step is often required to enhance the sensitivity of an analytical method.

The most widely used techniques for preconcentration and separation of lead are liquid–liquid extraction [2], co-precipitation [3], and ion exchange [4], and solid-phase extraction (SPE) [5].

SPE is utilized for preconcentration of heavy metals owing to its flexibility, economical and environmentally friendliness, absence of emulsion, speed and simplicity, suitability for sampling in the field, safety, and ease of automation [6]. However, the main problem associated with SPE is the low selectivity for lead [7]. The need of more selective system for separation of lead has increased the development of new extractants and adsorbents.

In the context of selective recognition sites, two types are particularly important: immunosorbents, which have been applied to various types of matrices, and molecularly imprinted polymers (MIPs), whose application in SPE is now being actively investigated [8–11]. The selectivity of MIPs is attributed to the presence of the target analyte (template) in the polymerization mixture during synthesis of the MIP.

Imprinting of organic molecules is a well-established technology; however, few attempts have been made for imprinting of ions such as trace elements. In such cases, the synthesized sorbent is called an ionic-imprinted polymer (IIP). IIPs are synthesized mostly for recognizing lanthanides, actinides, and noble metals. Recently, a variety of IIPs have been prepared as selective sorbents for SPE of heavy metals and transition elements, such as copper [12], cadmium [13], cobalt [14], selenium [15], nickel [16], and silver [17].

In this study, 2-((E)-(2-mercaptophenylimino) methyl)phenol (salamthio) was synthesized, and then acidic and basic lead salamthio complex were prepared.

The lead adsorption conditions of the acidic and basic lead salamthio MIPs were then investigated. Finally, lead was preconcentrated in real samples. Results show good repeatability of acidic lead salamthio MIP for lead ion adsorption.

2. Experimental

2.1. Reagents

Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), salicylaldehyde, aminothiophenol, methanol, lead nitrate, acetic acid, methanol, sulfuric acid, and the nitrate salts of all cations were obtained from Merck. 2,2´-Azobisisobutyronitrile (AIBN) was obtained from Aldrich.

All chemicals and reagents were of analytical grade and used without any further purification. All solutions were prepared using double-distilled water. Stock solution of lead nitrate (1×10^{-5} M) was prepared by dissolving an appropriate amount of lead nitrate in double-distilled water. All pH values were adjusted with HNO_3 or NaOH.

2.2. Apparatus

Fourier Transform infrared (FT-IR) spectra of non-imprinted polymer (NIP) and MIPs were obtained using a 6,700 Thermo Nicolet FT-IR spectrometer. IR spectra were recorded in the range 400–4,000 cm^{-1}. A Varian atomic absorption spectrometer (Model AA-240) equipped with a deuterium background correcting system was used for the determination of lead concentration. A Varian standard premixed air–acetylene burner and a Varian hollow cathode lamp were also used. The instrumental conditions for the determination of lead are as follows: wavelength, 217.0 nm; slit, 1.0 nm; and lamp current, 5 mA.

In addition, lead was determined by GFAAS using a Varian model Spectra AA-240 atomic absorption spectrometer coupled to GTA-120 electrothermal atomizer and a programmable sample dispenser (Varian Techtron PTY. Ltd, Australia). The optimized heating programs for lead analysis of lead were in accordance with the instrument manufacturer. Lead was analyzed by mixing one volume of digest (usually 3 μl) with an equal volume of 1% (w/v) ammonium dihydrogen phosphate modifier.

2.3. Preparation of the ligand (H2L)

The ligand was synthesized using a general condensation reaction. Briefly, 0.050 mol (6.10 g) of salicylaldehyde was dissolved in 50 mL of ethanol. 2-Aminothiophenol (0.050 mol, 6.25 g) was added to the solution, and the mixture was stirred for 4 h. The solvent was evaporated in vacuum and the resulting solid was recrystallized in ethanol. The yellow crystals were filtered and dried in air [18].

2.4. Synthesis of acidic and basic lead salamthio complex

The lead salamthio complex was prepared in two pH values. The synthesized ligand was dissolved in water–methanol 50% v/v, and pH of solutions was adjusted to 5 and 10. Then, Pb(II) was added to the solutions. The lead salamthio complexes are yellow–orange in acidic medium and brown in basic medium. Structures of acidic and basic lead salamthio complex are shown in Fig. 1. Regardless of the type of sites of salamthio (O,S), it acts as a monodendate ligand through sulfur with lead in natural or acidic medium; therefore, the O–H site is inactive in case of lead [19,20].

2.5. Preparation of MIPs and the corresponding NIP

MIPs and NIP were prepared in parallel and with identical compositions (except that template is to be omitted from the NIP). The procedure for the polymer synthesis is as follows: the template comprising 5.25 mL of 2% methanolic solution of acidic and basic Pb-Salamthio complexes, as well as the functional monomer (MAA; 2 mmol, or 0.17 mL), cross-linker (EGDMA; 10 mmol, or 1.89 mL), and initiator (AIBN; 0.25 mmol, or 0.042 g) in methanol (20 mL), were added to a three-necked round-bottom flask. The mixture was sparged with nitrogen for 10 min to remove dissolved oxygen, which can inhibit free-radical polymerization. The polymerization was allowed to continue in a water bath at 60˚C for 18 h. After polymerization, a hard polymer monolith was obtained, which was crushed and pulverized with a mortar and pestle. To remove lead, the remaining particles were treated with 2 M HNO_3 for 72 h for three times, and then the polymers were washed with methanol. Finally, the particles were dried under vacuum in a desiccator and used for the extraction studies.

2.6. Batch procedure

MIPs were immersed in 100-ml polyethylene bottles containing the buffer solution and the metal ion solution, and then shaken at 25˚C. The bottles were previously cleaned with detergent, DDI water, dilute nitric acid, and DDI water in sequence. At a pre-fixed time, an aliquot of the supernatant was separated and lead ions were determined by FAAS. The adsorbed Pb (II) was eluted with 4 M H_2SO_4, and desorbed Pb(II) was measured with FAAS. The adsorption capacity, distribution ratio, selectivity factor of Pb(I) with respect to Ni(II), Cu(II), Co(II), Fe(II), Zn(II), Pb(II), Cd (II), Al(III), or Hg(II), and relative selectivity factor were calculated using the following equations:

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

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{W} \tag{2}$$

where C_0 and C_e represent the initial and equilibrium concentration of lead in the aqueous phase (μmol L^{-1}), respectively, W is the weight of the polymer (g), and V is the volume of the aqueous phase (L). Percent extraction, E, was calculated using the following equation:

$$E = \frac{C_0 - C_e}{C_e} \times 100 \tag{3}$$

where D is the distribution ratio (ml g^{-1}), α is the selectivity factor, and α_r the relative selectivity factor, which were calculated using the following equations:

$$D = \frac{Q}{C_e} \tag{4}$$

$$\alpha = \frac{D_{Pb}}{D_M} \tag{5}$$

$$\alpha_r = \frac{\alpha_i}{\alpha_n} \tag{6}$$

D_{Pb} and D_M represent the distribution ratios of Pb(II) and M (i.e. Ni(II), Cu(II), Co(II), Fe(II), Zn(II), Ag(I), Cd(II), Al(III), or Hg(II)); α_i and α_n represent the selectivity factor of MIP and NIP, respectively.

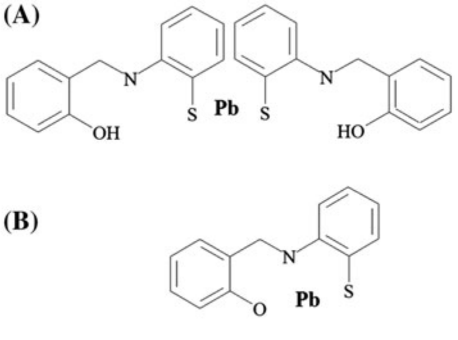

Fig. 1. Structures of (A) acidic lead salamthio and (B) basic lead salamthio complexes.

3. Results and discussion

The aim of this work was to evaluate the feasibility of using a MIP for direct SPE of lead in real samples. The effect of type of complex (acidic or basic) on lead adsorption was also investigated. Three polymers were prepared and tested by batch rebinding study.

Two MIPs were prepared in the presence of acidic and basic lead salamthio complex, and a control polymer (NIP) was prepared under identical conditions in the absence of guest molecule.

3.1. FT-IR spectra

Synthesized salamthio ligand, acidic and basic lead salamthio complexes, acidic and basic salamthio MIPs complexes, and control polymer were characterized by FT-IR. The FT-IR spectra of salamthio ligand and the lead salamthio complexes in acidic and basic media are shown in Fig. 2.

The free Schiff base ligand (H2L) showed a strong band in the region 1,614 cm^{-1}, which is the characteristic frequency of the azomethine *v* (C=N) group. The strong peak in 3,000–3,500 cm^{-1} is attributed to S–H and O–H groups of the synthesized ligand. In addition, the peak in 1,350 cm^{-1} is attributed to aromatic C–C.

The peak for O–H and S–H in 3,500 cm^{-1} disappeared after complexation. The intensities of the main peaks had decreased because of the difference in the ratio of ligand to metal in acidic (2:1) and basic (1:1) salamthio complexes.

In case of MIPs and NIP, both have similar IR spectra (Fig. 3), indicating the similarity in the backbone structure.

The absorptions attributed to carboxyl OH stretch (~3,500 cm^{-1}), carbonyl group stretch (~1,730 cm^{-1}),

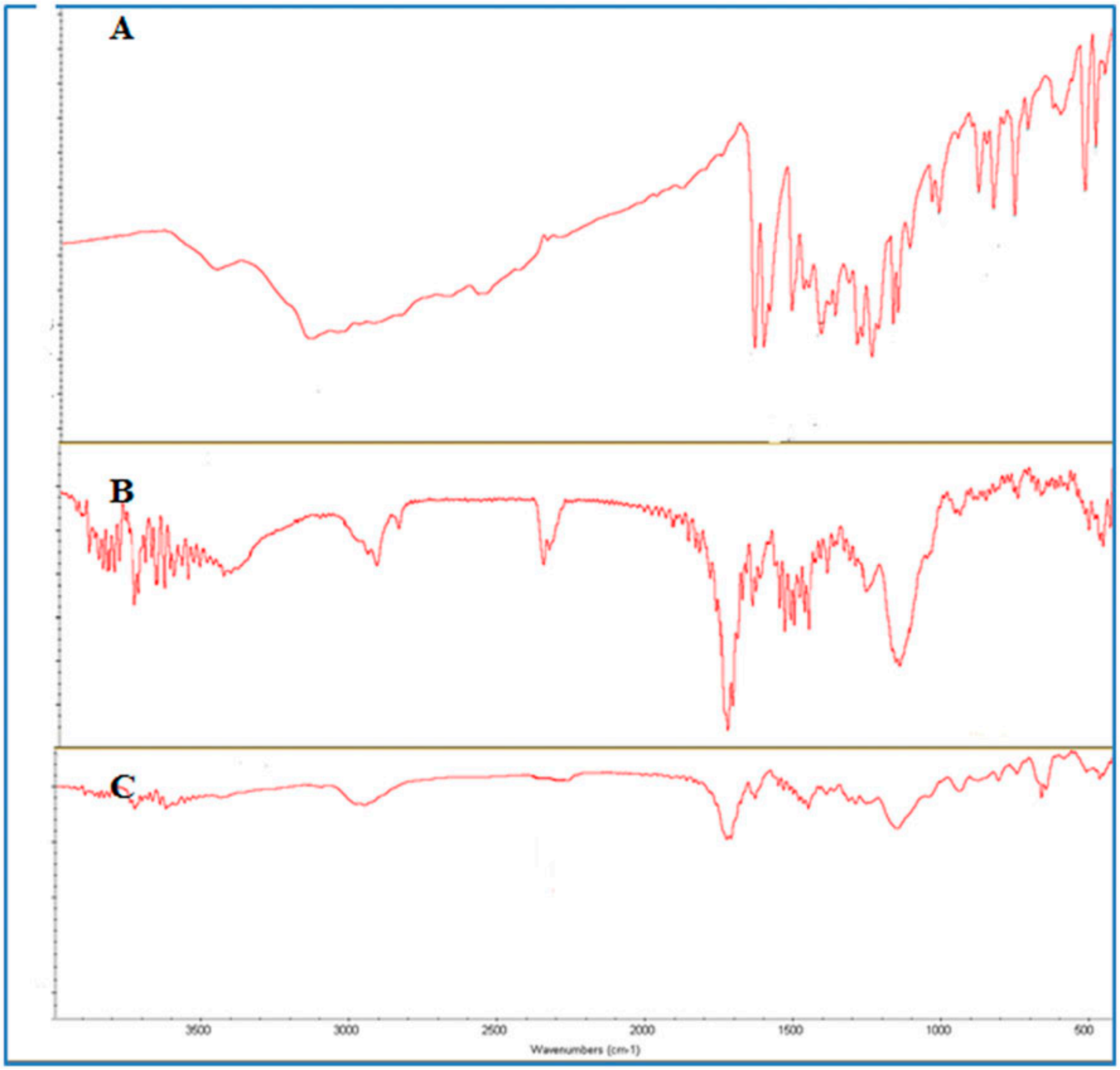

Fig. 2. FT-IR spectra in the 400–4,000 cm^{-1} range by KBr pellet method: (A) synthesized salamthio ligand, (B) acidic lead salamthio complex, and (C) basic lead salamthio complex.

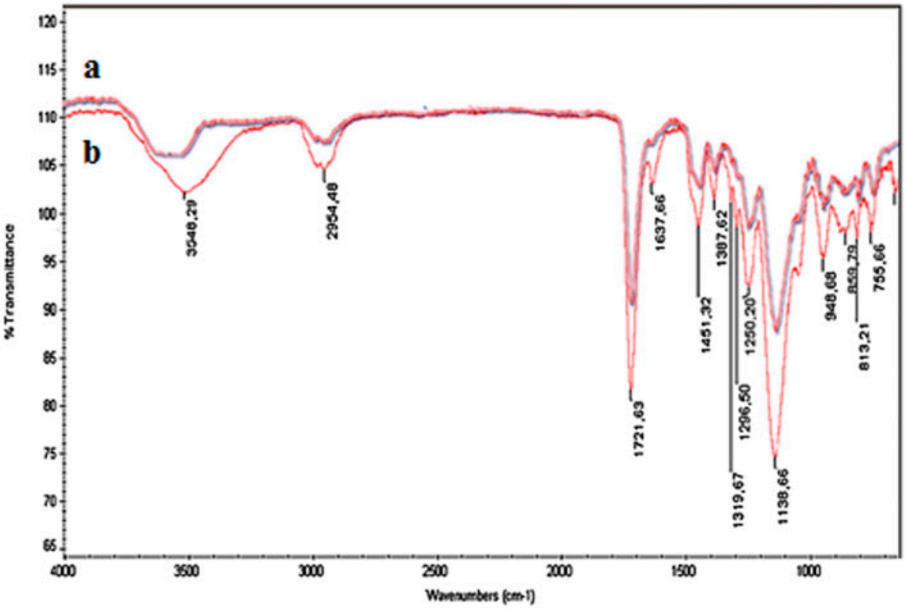

Fig. 3. FT-IR spectra of synthesized NIP (blue line) and MIP (red line).

C–O stretch (~1,260 cm^{-1}), and C–H vibrations (~756, ~1,390, ~1,460, and ~2,956 cm^{-1}) were observed in the IR spectra in Fig. 3. In addition to backbone similarity, the following important results were also acquired:

This feature clearly indicates that absorbance peaks attributed to C–H stretching of methylene group (~2989.15 cm^{-1}), carbonyl group stretching (~1,731 cm^{-1}), C–O stretching (~1,254 cm^{-1}), and C–H bending of CH_2 (~1,460 cm^{-1}) for the MIP are relatively stronger than those for NIP. Thus, the presence of imprint molecule (Pb–salamthio complex) increases the incorporation of ethylene glycol dimethacrylate in the preparation of polymer.

3.2. Choice of eluent

A chelating agent and various concentrations of different acids were tested to choose the most efficient eluent. The data given in Table 1 show that 4 M sulfuric acid can provide the best elution of lead from the acidic salamthio MIP. The volume of all eluents was 10 mL. In basic salamthio complex, none of the eluents could completely elute the Pb, which may be because of formation of small and compressed holes in polymer under basic condition.

3.3. Optimization of adsorption and elution conditions of the complex

3.3.1. Kinetics of Pb(II) sorption

Six portions of standard or sample solutions (100 mL) containing lead nitrate (0.5 mg) were transferred into 250-mL beakers. Then, exactly 0.2 g of acidic or basic salamthio MIP adsorbent was added to each beaker, and the mixtures were shaken vigorously for 5, 10, 30, 60, 90, 120, 150, 180, and 210 min to facilitate adsorption of the lead onto the MIP particles. After the solutions were centrifuged, the amount of

Table 1
Effect of type and amount of eluent on extraction efficiency

	Recovery (%)	
Eluent	Acidic	Basic
H_2SO_4 (2 M)	93.4	7.8
H_2SO_4 (4 M)	95.2	14.6
CH_3COOH (2 M)	91.7	4.4
$C_5H_{10}NS_2Na$ (0.01 M) diethyldithiocarbamate	30.5	5.2

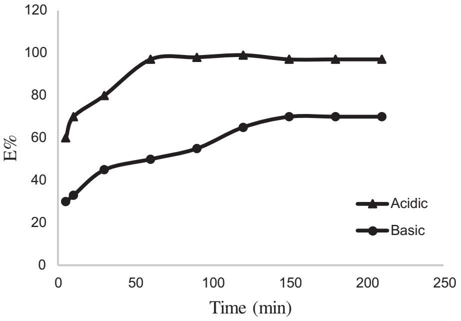

Fig. 4. Kinetics of Pb(II) sorption on synthesized polymers by acidic and basic ligands. Other conditions: 0.2 g of polymer and 5 mg L^{-1} Pb(II) at pH 6.0 and 25°C.

non-adsorbed lead in the filtrate solutions was directly determined by GFAAS. Fig. 4 shows that approximately 60 and 150 min were required for maximum adsorption of lead for acid and basic salamthio MIPs, respectively. The sorption rate of basic salamthio MIP was significantly slower than that of the acidic salamthio MIP, which could be attributed to the smaller holes in basic salamthio ligand (Fig. 1).

3.3.2. Effect of pH

The effect of pH on Pb(II) uptake was investigated using the batch procedure. Six portions of standard or sample solutions (100 mL) containing lead nitrate (0.5 mg) were transferred into beakers, and pH was adjusted in range of 3–8 with 0.001 mol L^{-1} HNO_3 or NaOH. Then, exactly 0.2 g of acidic or basic salamthio MIP adsorbent was added to each beaker, and the mixtures were shaken vigorously for 150 min to facilitate adsorption of lead onto the MIP particles. The sorption quantity of lead increases with the increase in pH, and it reach maximum at pH 5 and 7 for acidic and basic salamthio MIPs, respectively. This result could be due to strong complexing ability of the S–H group with lead in the basic salamthio MIP, given that both of lead and sulfur easily form a soft–soft complex.

3.4. Adsorption capacity of MIPs for Pb(II)

Adsorption of Pb(II) from aqueous solution was investigated in batch experiments. As shown in Fig. 5, the amount of Pb(II) adsorbed per unit mass of MIP increased with the increase in initial concentration of Pb(II). To reach saturation, the initial Pb(II) concentration was increased until plateau values (adsorption capacity values) were obtained. The average maximum adsorption capacities of acidic and basic salamthio MIPs were 29 and 93 μmol g^{-1}, respectively, possibly because of the complexity and ease of transfer of lead to hole and formation of complex in basic medium (Fig. 6).

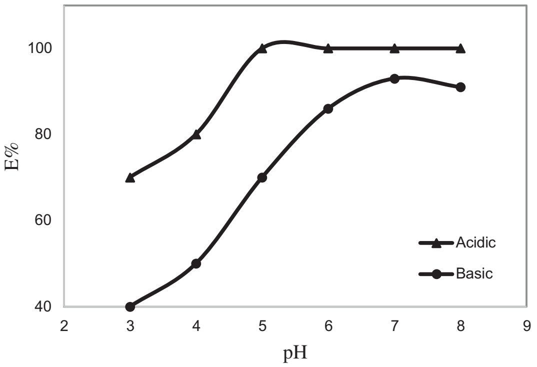

Fig. 5. Effect of pH on Pb(II) uptake, by synthesized polymers by acidic and basic ligands.

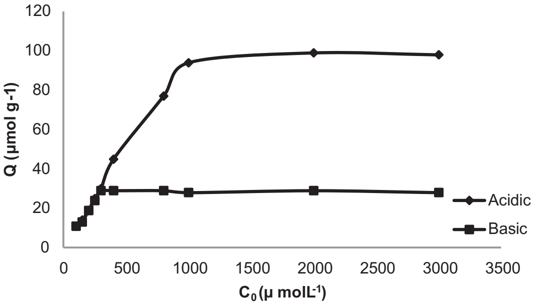

Fig. 6. Effect of Pb(II) initial concentration on adsorption quantity of MIPs. Other conditions: 0.2 g of polymer, pH 6.0, shaking time of 24 min, and temperature of 25°C.

3.5. Interference effects

Competitive adsorption of Zn(II)/Pb(II), Cu(II)/Pb (II), Ni(II)/Pb(II), Co(II)/Pb(II), Fe(II)/Pb(II), Ag(I)/Pb (II), Cd(II)/Pb(II), Al(III)/Pb(II), and Hg(II)/Pb(II) from their binary mixture was also investigated in batch procedure. Although these ions possess similar chemical properties, the competitive adsorption capacity of the acidic salamthio MIP for Pb(II) is higher than that of the basic salamthio MIP. The *D* values of the synthesized MIPs increases for Pb(II), whereas *D* decreases significantly for Ni(II), Cu(II), Co(II), Fe(II), Zn(II), Ag(I), Cd(II), Al(III), and Hg(II) (Table 2). Results show that the acidic salamthio complex has significantly higher selectivity than the basic salamthio MIP. This result is possibly because of the type of complex and the formation of soft–soft complex

Table 2
Selectivity parameters of MIPs for Pb(II)

	D_i			α_i			α_r	
Metal ions	Acidic	Basic	D_{NIP}	Acidic	Basic	α_{NIP}	Acidic	Basic
Pb^{++}	1968.3	567.0	15					
Ni^{2+}	112.6	167.7	12	17.5	3.3	1.2	14.6	2.75
Cu^{2+}	87.5	201.3	15	22.5	2.8	1.0	22.5	2.8
Co^{2+}	45.5	187.8	10	43.2	3.0	1.5	28.8	2
Fe^{2+}	57.3	234.7	11	34.3	2.4	1.4	24.5	1.7
Zn^{2+}	67.8	456.6	14	29.0	1.2	1.1	26.3	1.1
Ag^{+}	26.4	145.7	18	74.5	3.9	0.8	93.1	4.87
Cd^{2+}	66.8	200.9	13	29.4	2.8	1.1	26.7	2.5
Al^{3+}	87.4	238.9	19	22.5	2.4	0.8	28.1	3
Hg^{2+}	77.5	229.7	17	25.4	2.5	0.9	10.1	2.8

Table 3
Analytical data of Pb(II) in the real samples

		Measured (ppm)		
		This method		
Sample	Pb added mg/L	Acidic salamthio	Basic salamthio	GFAAS
Tab water	0	ND	ND	ND
	2	1.87 ± 0.09	1.09 ± 0.27	1.76 ± 0.08
	4	3.74 ± 0.12	1.67 ± 0.21	3.86 ± 0.07
Lipstick	0	0.10 ± 0.04	0.05 ± 0.05	0.09 ± 0.02

ND: Not detected.

(Pb–S) in basic condition, where O–Pb–S could be formed, which has weaker selectivity.

3.6. Determination of Pb(II) ions in real sample

The applicability of the proposed method for real samples was investigated. Pb(II) in tap water (100 mL) and lipstick samples were examined.

For lipstick sample preparation, a weighed sample of 0.2 g lipstick was placed into a Teflon vessel and reacted with 8 mL of concentrated nitric acid, left at room temperature for 4 h, and then placed in an oven overnight at 85˚C. After digestion, the sample was allowed to cool to room temperature. After adding 5 mL of 30% hydrogen peroxide, the sample solutions were heated at 85˚C for another hour. The clear supernatant was transferred to a polypropylene tube and diluted to 50 mL, with deionized water. Then, lead content was separated and preconcentrated using the acidic and basic salamthio MIPs. Finally, lead concentration was determined by GFAAS. Lead content was expressed as part per million wet weight (mg kg^{-1} wet wt.).

The validity of the proposed method was confirmed by comparing the results obtained from the sample analysis with those obtained by GFAAS method without the preconcentration step (Table 3). Each analysis was replicated three times. The concentrations of Pb(II) determined by the proposed method were in good agreement with those obtained by the GFAAS method. These results show that the method is capable of determining Pb(II) concentration in various types of complicated samples.

4. Conclusions

Salamthio ligand was synthesized and acidic and basic lead salamthio complexes were formed in this study. The complexes were used as template for synthesis of MIPs. After confirmation of the structure of the complexes, the performance of acidic and basic salamthio MIPs as template were evaluated.

Lead adsorption kinetics, selectivity, and adsorption capacity of the acidic salamthio MIP were significantly better than that of the basic salamthio MIP, which could be attributed to the type of complex formed. The Pb(II) adsorption kinetics and desorption–adsorption capacity of the acidic salamthio MIP were significantly better than that in the basic salamthio MIP.

Soft ligands such as salamthio, 6-mercaptopurine [20], and dithizone [21] could form stable complexes with all of the soft metals; thus, most preconcentration methods suffer from lack of selectivity.

The proposed method takes advantage of the well-defined chemical, physical, and structural properties of templates used for controlled deposition of lead ion.

The proposed preconcentration method is suitable for repeated use without considerable loss of adsorption capacity and exhibits a desirable detection limit.

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