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Synthesize of Ion Imprinted Polymer for Selective Extraction of lead (II) from Environmental Water Samples

Mahboobeh Manoochehri*, Homayon Ahmad Panahi, Meghdad Karimi
Department of Chemistry, Islamic Azad University, Tehran Central Branch, Tehran, Iran.

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Abstract

A new Pb(II) imprinted mercapto functionalized Montmorillonite was synthesize by an easy one step reaction by combining a surface imprinting technique for selective phase extraction of Pb(II) prior to its determinations by flame atomic absorption spectroscopy. The modified sorbent was characterized by FTIR and studied for preconcentration and determination of Pb(II) in natural water samples. The optimum pH value for sorption of lead (II) was 5.5. A recovery of 100% was obtained for lead (II), with 0.5 M nitric acid as eluting agent. The kinetic study reveals good accessibility of the chelating sites in the imprinted sorbent for uptake of selected ion. The sorption capacity was obtained at 27 mg·g^{-1} at optimum condition and 20 °C.

Keywords: *Preconcentration, Surface imprinting technique, Solid-phase extraction*.

Introduction

Heavy metal pollution has become a more serious environmental problem in the last several decades as a result of its toxicity and insusceptibility to the environment, and therefore rapid and sensitive methods must be accessible for determination of toxic metals in actual samples [1, 2]. Lead is one of the most widespread heavy metals in the environment, in view of its extensive use in storage batteries, solders, cable sheaths, pigments, anti-knock products and radiation shields and due to corrosion of household plumbing systems and erosion of natural deposits. The consumption of lead-contaminated drinking water causes delay in physical or mental development, slight deficit in learning abilities of children, high blood pressure and kidney problems in adults [3].

Preconcentration is usually required for the determination of trace metals in various samples by flam atomic absorption spectroscopy (FAAS) because of complex matrices of samples and low concentrations of some metals, which are near or below

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*** Corresponding author:** *Dr. Mahboobeh Manoochehri, Department of Chemistry, Islamic Azad University, Tehran Central Branch, Tehran, Iran. Email: mmanooch@yahoo.com.*

the limit of detection of the instrument [4]. For this purpose, numerous separation and preconcentration procedures have been developed for trace metal ion determination in various matrices. These methods include ion exchange [5], solvent extraction [6], cloud-point extraction [7], co precipitation [8] and solid phase extractions [9-11]. Solid phase extraction (SPE) is a well-established sample pretreatment technique in pharmaceutical, biomedical and environmental field because it demands less organic solvent and can remove interferences and preconcentrates the objective simultaneously.

Montmorillonite is an interesting support for the immobilization of charged complexes. There are solvent and matrix cooperative effects arising from the clay interlayer environment and from the clay surface that would be interesting to the catalytic point of view. Montmorillonite is a clay mineral belonging to the group of the smectites. Chemically speaking, it is a hydrated aluminosilicate of idealized formulation $Al_2Si_4O_{10}(OH)_2$ (mineral pyrophyllite) and its crystalline structure are generated by the encapsulation of a gibbsite layer (polymorph of $Al(OH)_3$) with two silica layers.

There is a continued interest in the development of modified solid supports that can provide good stability and high sorption capacity for metal ions [12, 13]. The purpose of present study is to indicate the feasibility of using surface-grafted lead (II) – imprinted polymer as a solid-phase extractant for preconcentration of trace lead in biological fluids and environmental water samples. Trace lead can be retained on the surface of imprinted polymer and then desorbed with 0.5 M nitric acid prior to determinations by FAAS. This proposed novel method has advantages of good accuracy and precision, high recovery and preconcentration factor.

Experimental

Instruments

The pH measurements were made with Metrohm model 744 (Switzerland) pH meter. IR spectra were recorded on a FT-IR spectrophotometer Jasco/FT-IR-410 by KBr pellet method. A Shimadzu AA-670/G atomic absorption spectrophotometer equipped with single element lamps and an air/acetylene burner was used for the determination of trace element. There are no cationic interferences, but several anionic ones. At high concentrations (relative to lead), phosphate, carbonate, iodide, fluoride, and acetate anions can all depress the lead signal. These interferences can be alleviated by the addition of 0.1 M EDTA. The authors in this paper tried to avoid all the interferences effect in Pb(II) measurement by FAAS.

Reagents and solutions

Acetic acid, sodium acetate, sodium hydrogen phosphate, sodium dihydrogen phosphate, lead nitrate, metric acid, sodium nitrite, 3-mercptotrimethoxysilane were products of

Merck (Darmstadt, Germany). All the solutions were prepared in deionized water using analytical grade reagents. The stock solution (1000 mg L^{-1}) of Pb(II) was prepared by dissolving appropriate amount of lead nitrate in deionized water. 5 mL of 0.01M acetic acetate buffer (pH 3-6.5) or 0.01M phosphate buffer (pH 7-8.5) were used to adjust the pH of the solutions, wherever suitable. Montmorillonite-K10 was obtained from Fluka.

Method

Synthesis of ion imprinted sorbent

The Montmorillonite surfaces were activated by refluxing 8 g of Montmorillonite (80–120 mesh) with 60 ml of 6 mol L^{-1} hydrochloric acid under stirring for 8 h, then the activated Montmorillonite was filtered and washed with doubly distilled water to neutral and dried under vacuum at 70 °C for 8 h. The Pb(II)-imprinted Montmorillonite sorbent shown in Figure 1. At this level, 2.782 g of $Pb(NO_3)_2$ was dissolved in 80 ml of methanol under stirring and heating, then 4 ml of 3-mercaptopropyltrimethoxysilane (3-MTMS) was added into the mixture. The solution was stirred and refluxed for 1 h, to which 6 g of activated silica gel was added. After 24 h of stirring and refluxing the mixture, the product was recovered by filtration, washed with ethanol to remove the remnant 3-MTMS, and stirred in 50 mL of 6 mol L^{-1} hydrochloric acid for 2 h to remove Pb(II) from the polymer. The final product was filtered, washed with doubly distilled water to neutral and dried under vacuum at 80 °C for 12 h.

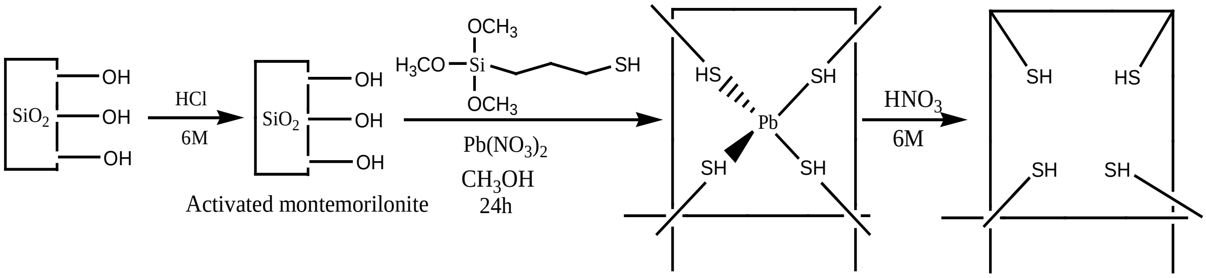

Figure 1. Procedure of synthesize MM-3-MMTMS.

Batch method

A sample solution (50 mL) containing (0.5 mg. L^{-1}) of Pb (II) was taken in a glass stoppered bottle, after adjusting its pH to the optimum value. The 0.05g of ion imprinted Montmorillonite sorbent was added to the bottle and the mixture was shaken for optimum time and temperature. The resin was filtered and sorbet metal ions was eluted with 0.5M HNO_3 (5ml). The concentration of metal ions in elute was determined by FAAS. The wavelength of 317 nm was used for Pb determination.

Effect of time

Ion imprinted Montmorillonite sorbent (0.05 g) was shaken with 50mL of solution containing 80 μg·mL^{-1} of Pb(II) for different length of time (5, 15, 30, 45, 60, 90 and 120min) under optimum pH. After filtration of the sorbent, the concentration of copper ions in solution was determined with FAAS using the recommended batch method.

Total Sorption Capacity

At this point, 0.05 g of imprinted Montmorillonite sorbent was stirred for 4 h with 50 ml solution containing 10-100 μg·mL−1 of Pb(II) at optimum pH and 20, 30 and 40 ^{o}C. The metal ion concentration in the supernatant liquid was estimated by FAAS. The sorption capacity of the sorbent for the metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption.

Results and discussion

Characterization of resin

The comparison of FTIR spectra of ion imprinted Montmorillonite with that of parent Montmorillonite indicate two additional bands at 2340 and 2940 cm^{-1} which appear to originate due to the groups S-H and aliphatic CH, respectively.

Pb(II) sorption by ion imprinted Montmorillonite

The degree of metal sorption at different pH values was determined by batch equilibration. The optimum pH range for sorption of Pb(II) is shown Figure 2. The maximum recovery was 100% at pH 5. The sorption as a function of contact time for all the metal ions is shown in Figure 3. Less than 5min shaking was required for 95% sorption. The profile of lead uptake on this sorbent reflects good accessibility of the chelating sites in the imprinted Montmorillonite sorbent. The saturated adsorption capacity of the resin is shown in Figure 4. This figure indicates the effect of initial concentration of the Pb(II) in the solution and temperature on sorption capacity of Pb(II) by imprinted Montmorillonite sorbent. The adsorption capacity in initial concentration of 100 μg·mL^{-1} of Pb(II) at optimum pH and 20 ^{o}C was obtained at 27 mg·g^{-1}.

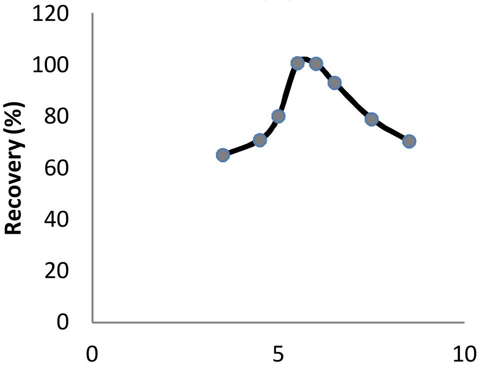

Figure 2. Metal sorption as a function of pH.

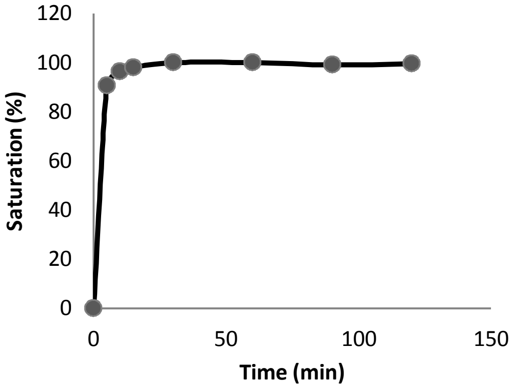

Figure 3. Kinetics of Pb(II) sorption on imprinted Montmorillonite sorbent.

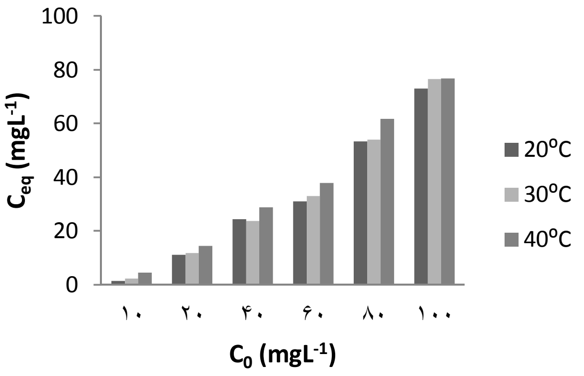

Figure 4. Effect of initial concentration of the Cu in the solution and temperature on capacity sorption of Pb(II) onto imprinted Montmorillonite sorbent.

Effect of Foreign Ions

To evaluate the selectivity of the preconcentration system, the effect of some metal ions (10 mg·L^{-1}) on the sorption behavior of Pb(II) ion (concentration 20 mg·L^{-1}) was investigated. The result is shown in Table 1. This Table indicates that the most effective ions on adsorption of Pb(II) on imprinted Montmorillonite sorbent are Co(II), Ni(II). The adsorption of Pb(II) on the imprinted Montmorillonite sorbent in presence of all mentioned ions (with each ion having the concentration of 20 mg·L^{-1}) shows that the Pb(II) can be determined quantitatively in the .environmental samples

Table 1. Effect of Foreign Ions.

Interfering ions	-	K^+	Ag^+	Ni^{2+}	Co^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Ba^{2+}	Hg^{2+}	Al^{3+}	Mix
$C_{0\ Pb}{}^{2+}$ (mg.L^{-1})	**20**	**20**	**20**	**20**	**20**	**20**	**20**	**20**	**20**	**20**	**20**	**20**
$C_{eq\ Pb}{}^{2+}$ (mg.L^{-1})	**3.356**	**6.921**	**7.300**	**11.780**	**10.124**	**8.441**	**8.201**	**6.227**	**5.078**	**9.221**	**9.829**	**6.537**

Stability and reusability of the sorbent

The Pb(II) was sorbed and desorbed on 1 g of the ion imprinted Montmorillonite sorbent several times. It was found that sorption capacity of resin after 15 cycles of its equilibration with Pb(II), changes less than 10%. Therefore, repeated use of the resin is feasible. The resin cartridge after loading with samples can be readily regenerated with 0.5M HNO3. The sorption capacity of the resin stored for more than 6 months under ambient conditions has been found to be practically unchanged.

Comparison with other methods

Comparative information from a number of studies on preconcentration of Pb(II) by various methods for the figure of merits is given in Table 2. The sorption capacity and recovery of the present sorbent is superior in comparison to all the matrices shown in Table 2. This new developed method has been successfully applied to the analysis of trace copper ions in river water sample.

Table 2. Comparison with the other preconcentration procedures used the impregnated adsorbent for the determination of Pb (II).

Preconcentration system Studied	Eluent	PF	Resin capacity (mg g^{-1})	LOD (**μ**gL^{-1})	RSD (%)	Ref.
Activated Carbone/ 2-((aminoetylamino) methyl)phenol	1M HNO_3	100	16.20	0.16	<3.00	[14]
XAD-4/1,2-bis(O-aminophenylthio)ethane	1M HNO_3	150	416	3	<5.00	[15]
XAD-1180/1-(2-tiasolylazo)-2-naphtol	2M HNO_3	100	-	1.19	<5.10	[16]
XAD-1180/1-(2-pyridylazo)-2-naphtol	3M HNO_3	30	-	29	0.80	[17]
XAD-2/pyrogallol	4M HNO_3	25	6.71	0.025	4.11	[18]
XAD-2/2,3-dihydroxypyridine	1.5M HNO_3	300	65.7	13.88	14.06	[19]
XAD-7/p-xylenol	1M HCl	60	-	18.6	<10.00	[20]
XAD-2/chromotropic acid	2M HNO_3	200	38.59	4.06	2.14	[21]
XAD-4/dithiocarbamates	4M HNO_3	160	10.25	0.6	2.84	[22]
XAD-2/*o*-aminophenol	1-4M HNO_3	40	870	2.5	3.32	[23]
Imprinted Montmorillonite sorbent	0.5M HNO_3	10	27			This work

Application

Solid phase extraction with ion imprinted Montmorillonite sorbent coupled with FAAS determination was supplied to determine the Pb (II) in river water sample (Jajrod river, Tehran, Iran). The samples were collected in plastic containers with random sampling method and filter on site, acidify to pH 2 with HNO2. The batch method was applied for preconcentration of metal ions. The results are shown in Table 3. These results demonstrate the applicability of the procedure for Pb (II) determination in samples.

Table 3. Results obtained for metal determination in river water sample.

Analyte	Pb(II)
Sample (without spiking of Pb(II))	N.D.
Before preconcentration (after spiking Pb(II)) (mg L^{-1})	0.22
After preconcentration (mg L^{-1})	2.15
Preconcentration factor	10
Recovery (%)	69
Standard deviation	0.098
Relative standard deviation (%)	4.1

Conclusion

A new imprinted sorbent is prepared by grafting Montmorillonite onto 3-mercptotrimethoxysilane. The synthesis of the resin is simple and economical. The resin has a good potential for enrichment of trace amount of Cu (II) from large sample volumes. The resins also have high adsorption capacity, good reusability and high chemical stability. The sorption of the investigated metal ions increases by increasing the contact time. Preconcentration by this resin combined with FAAS can be applied to the determination of trace lead (II) ions in water and the mineral reference sample with satisfactory results.

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