Extraction and preconcentration of Pb(II) from water and soil samples using modified activated carbon

Fatemeh Sabermahani*, Nosrat Madadi Mahani

Department of Chemistry, Payame Noor University, P.O. BOX 19395-4697 Tehran, Iran

Abstract

In this work, a new extractant was prepared by immobilizing ligand 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, (5-Br-PADAP), on the activated carbon and, then, applied to extraction of Pb(II) prior to determination by flame atomic absorption spectrometry. It was confirmed by FT- IR analysis. The metal ion was retained on the 0.05 g of the sorbent in the pH range 6-8, and then eluted with 5 mL of 0.5 mol L-1 nitric acid. Seven replicate determinations of a 1.0 µg mL-1 of lead solution in the final solution gave relative standard deviation of ±3.3%. The maximum equilibrium capacity of the new sorbent from Langmuir model was 18.2 mg g-1. The linearity was maintained in the concentration range of 0.1-10.0 ng mL-1 for the concentrated solution. The limit of detection based on three times the standard deviation of the blank ($3\sigma bl/m$), was found to be 0.83 ng mL-1 in original solution. Common coexisting ions did not interfere with the separation and determination of the lead. The prepared sorbent was applied to the preconcentration of Pb(II) in water and soil samples with satisfactory results.

Keywords: Lead; 5-Br-PADAP; modified carbon active.

Introduction

In recent years, water and soil pollution caused by heavy metals is one of the major environmental problems. Among heavy metals, Pb(II) is considered to be non-biodegrade like organic pollutants, and attracted more attention due to its toxicity, persistent in nature particularly, even at low concentrations [1–3]. The World Health Organization (WHO) recommended a limit of 10 µg L^{-1} of lead in drinking water [4], which requires a very sensitive measurement technique. The most common analytical methods for the lead trace determination are flame atomic absorption spectrometry (FAAS) [5-9], electrothermal atomic absorption spectrometry (ET-AAS) [10-13], inductively coupled plasma atomic emission spectrometry (ICP-AES) [14], and inductively coupled plasma-mass spectrometry (ICP-MS) [15,16]. FAAS is still being used because it combines a fast analysis time, a relative simplicity and a cheaper cost. Nevertheless, the detection of metal trace elements in aqueous samples is difficult due to various factors, particularly their low concentration and the matrix effects [17]. Solid phase extraction (SPE) technique has become increasingly popular in compared with other techniques such as liquid-liquid extraction, it is so because of its advantages of high enrichment factor,

*Corresponding author: Fatemeh Sabermahani
Tel: +98 (341) 3341468; Fax: +98 (341) 3353667
E-mail: fatemehsaber2003@yahoo.com

high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in The choice of sorbent is a key point in SPE, because. The choice of sorbent is a key point in SPE, because it can control the analytical parameters such as selectivity, affinity and capacity. Preparation of new material for selective solid phase extraction of analytics is an important trend of solid phase extraction. Reagents can be modified on organic or inorganic support as solid phase extractant. Activated carbon is one of the most extensive adsorbents of the removal of metal ions from aqueous solution. However, without any surface treatment, activated carbon does not adsorb metal ions quantitatively.

In this work, the activated carbon was modified with (5-Br-PADAP) and applied to extraction of Pb(II) in water and soil samples prior to determination by flame atomic absorption spectrometry.

Experimental

Apparatus and Reagents

An atomic absorption spectrometer model VARIAN AA 240 equipped with deuterium lamp background corrector was used for determination of lead in air-acetylene flame. The instrumental settings of the spectrometer were as follows: wavelength, 217.0 nm; slit width 1.0 nm; lamp current, 5 mA; acetylene flow 2.0 L min^{-1}. Funnel-tipped glass tube (ten columns, 10 cm long and 0.5 cm in diameter) equipped to stopcock was used as the column for preconcentration purposes. The flow rate of solution was controlled by using a stopcock in end of the column. A 691 Metrohm pH meter was employed for pH measurements.

All reagents were of analytical grade. Deionized and distilled water was used in all experiments. The stock solution 1000.0 $\mu g\ mL^{-1}$ of Pb (II) was prepared by dissolving an appropriate amount of $Pb(NO_3)_2$, (99.99%, Merck, Darmstad, Germany), in distilled water and diluting to 100.0 mL. The standard working solutions were diluted daily prior to use. A 0.01% (w/v) solution of the ligand was prepared by dissolving 0.01 g of 5-Br-PADAP (99.999%, Aldrich, Milwaukee, WI, USA) in ethanol and diluting to 100.0 mL. Activated carbon powder (gas chromatographic grade, 40-60 mesh, Merck, Darmstad, Germany), was used as sorbent. It was treated with concentrated HCl, washed with distilled water and dried at 110 °C.

Preparation of the sorbent

For the synthesis of the sorbent, 2 g of activated carbon powder was added to 100.0 mL of the solution containing 0.01% 5-Br-PADAP and the mixture was shaken at room temperature for 3 h. The reagent coated activated carbon was filtered, washed with dis-tilled water and dried at room temperature.

The modified activated carbon was confirmed by FT-IR analysis. When Comparing the IR spectrum of bare activated carbon (Figure 1) with that of the modified activated carbon (Figure 2), many new peaks appeared in the spectrum. The infrared spectrum of the ligand showed CH stretching vibration at 2950-3000 cm^{-1}. Aromatic rings show a characteristic series of peaks in the 1622-1573 cm^{-1} range of the infrared spectra. Moreover, the stretching vibrations were observed at 1476 and 1498 cm^{-1} due to N=N and stretching vibrations and C-O bands at 1160-1200 cm^{-1} they also show strong absorptions in the 700-800 cm^{-1} range due to C-H out-of-plane bending.

However, the IR-spectrum of modified carbon active adsorbent with ligand is dominated by the peaks corresponding to the carbon active matrix, it is so because carbons are black materials which can

absorb almost all of the radiation in the visible spectrum, and the peaks obtained were usually a sum of the interactions of different types of groups and some assignments of the band corresponding to ligand. e.g. at 1622(C=C), 1467(N=N) and 1221 (C=O) and C-C. Consequently, the above experimental results suggest that carbon active is successfully modified by the 5-Br-PADAP ligand.
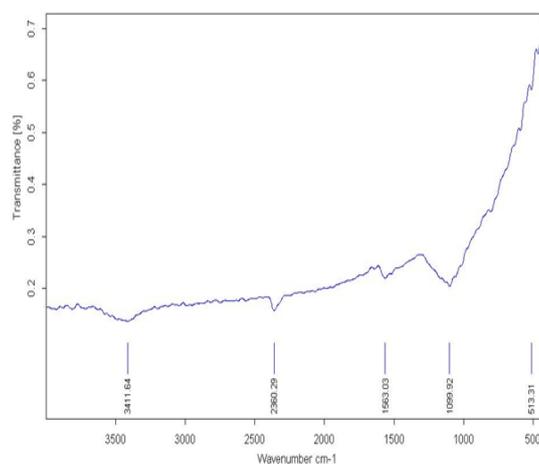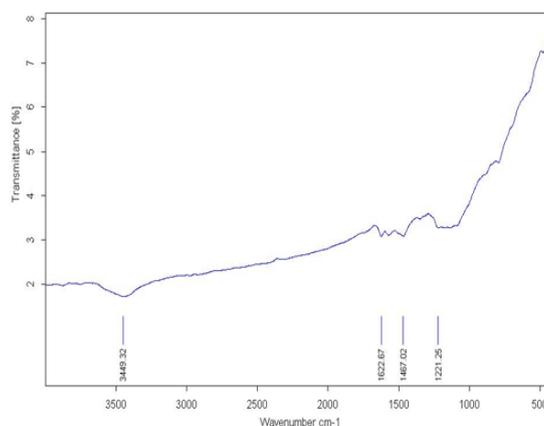

Figure 1. IR spectrum of bare activated carbon

Figure 2. IR spectrum of modified activated carbon

General procedure

A small amount of glass wool was placed in the end of the columns to prevent the loss of our sorbent during sample loading. Then, the columns were packed with 50.0 mg of the carbon active coated with ligand and conditioned with distilled water. An aliquot of the sample solution containing Pb(II) was taken and pH of them was adjusted to 7 with diluted nitric acid or sodium hydroxide. The total volume of the solution was made up to about 30 mL with distilled water. It was then passed through the column with flow rate of 3.0 mL min^{-1}. The flow rate of solution was controlled by using a stopcock in end of the column. The retained lead ions were eluted from the solid phase with 5.0 mL of 0.5 mol L^{-1} HNO$_3$ solution. This solution was aspirated into an air-acetylene flame for the determination of Pb.

Results and discussion

Effect of pH

The pH of the sample solution plays an important role in retention of metal ions. Thus, the effect of pH on the recovery of Pb(II) was examined. The pH value of the sample solution was adjusted in a range 3-9 with diluted HNO_3 or NaOH.

The obtained solutions were passed through the column at a flow rate 3.0 mL min^{-1}. The lead ions were then eluted by an appropriate eluent. As can be seen in Figure 3, quantitative recovery was found in the pH range 6-8 for lead. pH= 7 was selected for further studies.
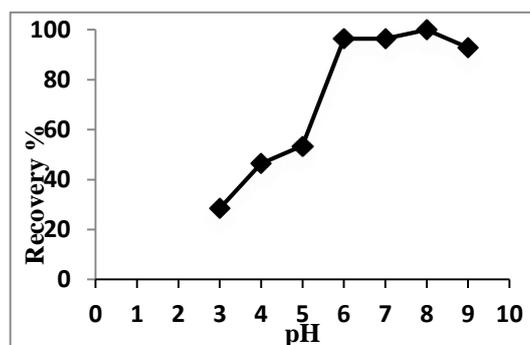

Figure 3. Effect of pH on recovery of lead
Conditions: Pb, 5.0 µg;; flow rate, 3.0 mL min^{-1}; sorbent, 50.0 mg; elution solution, 5.0 mL 0.5 mol L^{-1} HNO_3

Effect of eluent

In order to choose the most effective eluent for desorbing of the retained Pb (II) from the column, different acids such as HNO_3, H_2SO_4 and HCl were tested. It was observed that all of them can desorb Pb from the column. Among the tested acids, the nitric acid provided the highest recovery compared to the other acids. It seems that oxidation capability of HNO_3 is the reason for high recovery, as the concentration of hydronium ion in acids such as HCl and HNO_3 is the same. Thus, HNO_3 was selected due to the fact that its concentration was varied between 0.05-2 mol L^{-1}. It was observed that 0.5 mol L^{-1} HNO_3 was sufficient for desorption of Pb. HNO_3 volume was optimized, also. According the experiment, 5.0 mL 0.5 mol L^{-1} HNO_3 was best eluent for desorption of lead.

Effect of flow rate of sample

The retention of an element on a sorbent

Also depends on the flow rate of the sample solution. Thus, the effect of flow rate on the retention and recovery of lead ions was investigated under optimum conditions. The solution containing Pb was passed through the column with the flow rates adjusted in a range 0.5-3 mL min^{-1}. It was observed that, at flow rates greater than 3.0 mL min^{-1}, there was a decrease in the recovery Pb. The reason for this decrease is probably insufficient contact of the metal ions and the sorbent to reach equilibrium. Therefore, a flow rate of 3.0 mL min^{-1} was selected for subsequent experiments.

Effect of amount of the sorbent

The amount of sorbent is another important parameter that affects the recovery. For this purpose, different amounts of the sorbent were examined by using 5.0 mL of elution solution. 50.0 mg sorbent gave the highest recovery using 5.0 mL of elution solution. So in order to achieve higher recovery, subsequent extraction experiments were carried out using 50.0 mg of the sorbent.

Breakthrough volume

The measurement of breakthrough volume is important in solid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample. The volume of the first aqueous phase, containing a fixed amount of analyte (5.0 µg Pb), was varied in the range of 50-600 mL, under the optimum conditions, and was passed through a column for preconcentration. As can be seen in Figure 4, quantitative recovery (>95%) was found to 500.0 mL. At higher sample volumes, the recovery decreased gradually. Since the final elution volume was 5.0 mL, preconcentration factor of 100 was obtained.
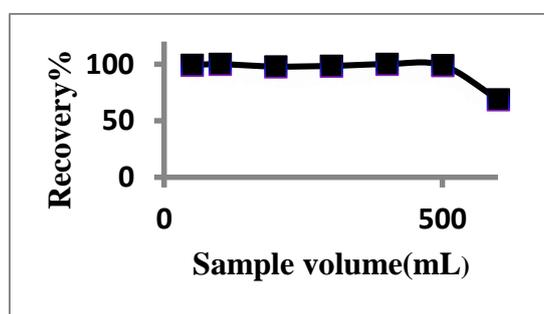

Figure 4. Effect of sample volume on recovery of lead
Conditions: Pb, 5.0 µg;; flow rate, 3.0 mL min^{-1}; sorbent, 50.0 mg; elution solution, 5.0 mL
0.5 mol L^{-1} HNO$_3$

Sorption capacity

Sorption capacity was determined by batch method. Several solutions with difference concentrations of lead were made and mixed with a specific mass of sorbent and shaken for 15 min. Then the solutions were filtered and concentration of the analyte was determined by FAAS. The sorption data have been analyzed according to the linear form of the Langmuir isotherm, as represented in Eq. (1).

$$C_e \ / \ q_e \ = \ (1/Qb) \ + \ (1/ \ Q) \ C_e$$
(1)

b is Langmuir constant which is a measure of energy of adsorption and *Q* is adsorption capacity expressed in mg/g. Langmuir isotherm and its equation is given in Figure 5.
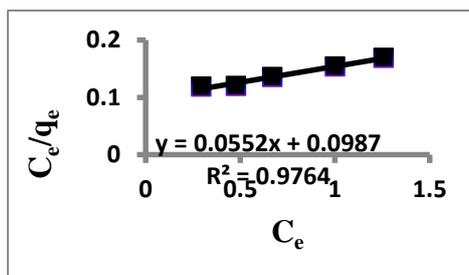
Figure 5. Langmuir isotherm for lead

The adsorption capacity was found to be 18.2 mg g^{-1} sorbent.

Analytical features

Calibration curve for the determination of lead was prepared according to the proposed procedure under the optimum conditions. The linearity was maintained in the concentration range of 0.1-10.0 µg mL^{-1} in the final solution. The equation of the line is A=0.035C+0.005 with the regression coefficient 0.992 where A is the absorbance and C is concentration of the metal ion (µg mL^{-1}) in the final solution.

The limit of detection (LOD) based on three times the standard deviation of the blank (n=8)($3\sigma_{bl}/m$), on a sample volume 500.0 mL was found to be was 0.83 ng mL^{-1}. Seven replicate determinations a mixture of 1.0 µg mL^{-1} of lead in the final solution, gives a relative standard deviation (RSD%) of ±3.3%. With using 500.0 mL of the first aqueous solution, preconcentration factor of 100 was obtained.

Effect of interference ions

The effect of some foreign ions which interfere with the determination of trace of lead was examined. The results are given in Table 1. The tolerance limit was set as the concentration of the ion required to cause ±3% error. The experiments Table 1 indicated that within ±3% error range, interfering effects from most of inorganic cation and some anions were not observed. This suggests that the new solid phase extractant has good selectivity and can be used for determination of Pb in various samples.

Table 1. Effect of diverse salts and metal ions

Ion	Tolerance limit (mg)
HCO_3^-	100
NO_3^-	500
Cl^- , SO_4^{2-}	250
CH_3COO^-	500
F^-	1000
Ca^{2+}, K^+	1000
Zn^{2+}, Mg^{2+}, Mn^{2+}	500
Cd^{2+}, Fe^{2+}	5
Cr^{3+}	10
Cu^{2+}	8

Conditions: Pb, 5.0 µg; pH ~7; flow rate, 3 mL min^{-1}; sorbent, 50.0 mg; elution solution, 5.0 mL of 0.5 mol L^{-1} HNO$_3$

Analysis of real samples

Various soil samples were dried in 80 °C for 72 h. 1.00 g of each sample was weighted exactly into a teflon vessel, separately, and dissolved in concentrated nitric acid, sulfuric acid and flouridric acid (12:4:1) by heating on a heater. Then were transferred to beaker and heated to dissolving. The solutions were cooled, diluted and

filtered. The filtered solution was diluted to 100.0 mL with distilled water in a calibration flask. 25.0 mL of the pretreated sample solution was taken individually and lead was determined by the proposed procedure. The results are given in Table 2.

Table 2. Determination of lead in the Soil samples

Sample	lead (μg g^{-1})		Recovery (%)
	Spiked	Found[a]	
Soil-1	0.0	9.14±0.28	-----
	5.0	13.98±0.43	96.8
	10.0	18.92±0.65	97.8
Soil-2	0.0	4.00±0.15	-----
	5.0	8.92±0.36	98.4
	10.0	14.02±0.43	100.2

Sample: 1.00 g; Conditions: pH ~7; flow rate, 3.0 mL min^{-1}; sorbent, 50.0 mg;
Elution solution, 5.0 mL of 0.5 mol L^{-1} HNO$_3$
[a]Average of three determinations, ± S.D.

The proposed preconcentration procedure has been also applied to determine lead in water different samples including a tap water from Kerman and river water from Mahan in Kerman. The water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. 50.0 mL of the water samples was transferred to a beaker, and pH was adjusted to about 7 and then the proposed procedure was applied to these samples. The results are given in Table 3.

Table 3. Determination of lead in the water samples

Sample	lead (ng mL^{-1})		Recovery (%)
	Spiked	Found[a]	
Tap water[b]	0.0	0.71±0.01	----
	5.0	5.60±0.07	97.8
	10.0	10.90±0.22	101.9
River water[b]	0.0	0.86±0.02	----
(Mahan)	5.0	5.70±0.12	96.8
	10.0	11.10±0.27	102.4

Sample volume: 50.0 mL; Conditions: pH ~7; flow rate, 3.0 mL min^{-1}; sorbent, 50 mg;
Elution solution, 5.0 mL of 0.5 mol L^{-1} HNO$_3$
[a]Average of three determinations, ± S.D.
[b]Kerman, Iran

Conclusion

The present work proves the capability and effectiveness of carbon active modified with 5-Br-PADAP ligand for separation and preconcentration of lead from water and soil samples. The preparation of the sorbent is simple, rapid and low cost. The use of 50.0 mg of the modified carbon active allows the enrichment of Pb(II) by a factor 100, and the modified material can be reused ten times. The applied method provides good precision with low relative standard deviation and high accuracy obtained with the quantitative recoveries of and spiked materials (Tables 2 and 3). Thus, it may be concluded that the method in an effective approach in preconcentration and selective separation of lead from the complex matrices. Comparative data from some recent papers on solid phase extraction of lead for the figure of merits are summarized in Table 4. The analytical performance of the present method is Comparable with other methods.

Table 4. Comparative data from some extraction methods of lead

Method Ref.	PF[a]	LOD ($\mu g\ L^{-1}$)	RSD%	Capacity ($mg\ g^{-1}$)	
SPE	100	4.5	1-2.2	0.3	[18]
SPE	100	0.45	4.8	6.42	[19]
SPE	30	6.1	4.7	19.9	[20]
SPE	80	0.6	3.0	6.8	[21]
SPE	20	0.28	1.6-3.2	------	[22]
SPE	300	0.15	<5	151	[23]
SPE	100	0.83	3.3	18.2	This work

[a]PF: Preconcentration Factor

References

[1] N. Chiron, R. Guilet, E. Deydier, *Water Res.*, **2003**, *37*, 3079-3086.

[2] M. Zabihi, A. Ahmadpour, A. Haghighi Asl, *J. Hazard.Mater.*, **2009**, *167*, 230-236.

[3] T.K. Naiya, A.K. Bhattacharya, S.K. Das, *J. Colloid Interf. Sci.*, **2009**, *333,* 14-26.

[4] C. Baird, *Environmental Chemistry,* **1999**, Second ed., W.H. Freeman Company.

[5] W.L. Dos Santos, C.M.M. Dos Santos, J.L.O. Costa, H.M.C. Andrade, S.L.C. Ferreira, *Microchem. J.,* **2004**, *77,* 123-129.

[6] E.L. Silva, P.S. Roldan, *J. Hazard. Mater.,* **2009**, *161,* 142-147.

[7] M. Soylak, M. Yuzen, I. Narin, *Qim. Nova,* **2006**, *29,* 203-207.

[8] S. Tokalioglu, V. Yilmaz, S. Kartal, A. Delibas, C. Soykan, *J. Hazard. Mater.,* **2009**, *169,* 593-598.

[9] M. Tuzen, E. Melek, M. Soylak, *J. Hazard. Mater.,* **2006**, *136,* 597-603.

[10] M. Martinis, P. Berton, J.C. Altamirano, U. Hakala, R.G. Wuilloud, *Talanta,* **2010**, *80,* 2034-2040.

[11] H. Jiang, B. Hu, *Microchim. Acta,* **2008**, *161,* 101-107.

[12] P. Liang, R. Liu, J. Cao, *Microchim. Acta,* **2008**, *160 (1-2),* 135-139.

[13] T. Minami, Y. Sohrin, J. Ueda, *Anal. Sci.,* **2005**, *21,* 1519-1522.

[14] Y. Liu, P. Liang, L. Guo, *Talanta,* **2005**, *68,* 25-30.

[15] J. Diedjibegovic, T. Larssen, A. Skrbo, A. Marganovic, M. Sober, *Food Chem.,* **2012**, *131,* 469-476.

[16] Z. Diang, X. Hu, *Adv. Mater. Res.,* **2012**, *356-360,* 3051-3054.

[17] J. Chen, S. Xiao, X. Wu, K. Fang, W. Liu, *Talanta,* **2005**, *67,* 992-996.

[18] N. Pourreza, R. Hoveizavi, *Anal. Chim. Acta,* **2005**, *549,* 124-128.

[19] V.N. Bulut, A. Gundogdu, C. Duran, H.B. Senturk, M. Soylak, L. Elci, M. Tufekci, *J. Hazard.Mater.,* **2007**, *146,* 155-163.

[20] E. Matoso, L.T. Kubota, S. Cardore, *Talanta,* **2003**, *60,* 1105-1111.

[21] M. Tuzen, M. Soylak, L. Elci, *Anal. Chim. Acta,* **2005**, *548,* 101-108.

[22] F.A. Aydin, M. Soylak, *J. Hazard. Mater.,* **2010**, *173,* 669-674.

[23] M. Javanbakht, H. Rudbaraki, M.R. Sohrabi, A.M. Attaran, A. Badiei, *Inter. J. Environ. Anal. Chem.,* **2010**, *90,* 1014-1024.