

# Ion imprinted activated carbon solid-phase extraction coupled to flame atomic absorption spectrometry for selective determination of lead ions in environmental samples

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**Abstract**—A simple lead ion imprinted sorbent was synthesized by coupling activated carbon with a known metal chelating compound, iminodiacetic acid. The ion imprinted sorbent has been characterized using Fourier transform infrared spectroscopy, elemental analysis and thermogravimetric analysis and subjected for the extraction and determination of trace Pb(II) in environmental water samples. The optimum pH value for sorption of the lead ion was 6.5. The sorption capacity of lead imprinted sorbent was 42.2 mg g<sup>-1</sup>. The chelating imprinted sorbent can be reused for five cycles of sorption-desorption without any significant change in sorption capacity. Compared with non-imprinted polymer particles, the lead ion imprinted sorbent showed high adsorption capacity, significant selectivity, good site accessibility for Pb(II). The equilibrium adsorption data of Pb(II) by modified resin were analyzed by Langmuir, Freundlich, Temkin and Redlich-Peterson models.

**Keywords:** Solid Phase Extraction, Polymer Grafting, Lead (II), Preconcentration, Isotherm Study

## INTRODUCTION

Determination of trace metals is very important in environmental samples, including natural waters, food and high purity materials. However, the direct determination of metal ions at trace levels is limited due to their low concentrations and matrix interferences. It is a necessity to preconcentrate the trace elements before their analysis to enhance the concentration of the analyte ions to be determined [1-4]. For this purpose, several methods, such as ion exchange [5,6], solvent extraction [7,8], coprecipitation [9-12], and chemical, solid phase extraction [13] and bio-sorption [14], have been proposed.

There are general approaches to metal preconcentration using activated carbon from aqueous solutions by simply adjusting the pH to an adequate value and by using chelating agent [15,16]. Chelating resin sorption is one of the most effective multi-element preconcentration methods because it can provide more flexible working conditions together with good stability, selectivity, high concentrating ability, high capacity for metal ions and simple operation [17,18].

On the other hand, solid-phase extraction (SPE) is the most common technique used for separation and enrichment of various inorganic and organic analytes [19], because of its high enrichment factor, low cost, rapid phase separation, high recovery, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [20,21].

Lead is a toxic metal that accumulates in the vital organs of humans and animals. Its cumulative poisoning effects include serious brain

damage, kidney malfunctioning, hematological damage, and anemia. In natural water its typical concentration lies between 2 and 10 ng mL<sup>-1</sup>. Flame atomic absorption spectrometry (FAAS) can be used to determine it at low concentration levels in diverse matrices, but preconcentration becomes a necessity many times [22].

The purpose of this work is preconcentration of Pb<sup>2+</sup> on activated carbon modified with iminodiacetic acid to improve the adsorption capacity and surface properties. The new adsorbent has a high sorption capacity for the solid phase extraction of Pb(II) present in the environmental liquid samples. The influences of the some analytical parameters including pH and contact time and other important parameters were studied in batch modes.

## EXPERIMENTAL

### 1. Instruments

The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Flame atomic absorption spectrometer Varian, (Palo Alto, CA, USA) AA240, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 L·min<sup>-1</sup>, respectively) was used for concentration measurements of metal ions. Elemental analysis was carried out on a Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer. Infrared spectra were recorded on a Jasco Fourier transform infrared spectrometer (FT-IR-410, Jasco Inc., Easton, Maryland).

### 2. Reagents and Solutions

NaOH, HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>, K<sub>2</sub>SO<sub>4</sub>, NaCl, CH<sub>3</sub>COOH, CH<sub>3</sub>COONa, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, KNO<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, NaNO<sub>3</sub>, Ag(NO<sub>3</sub>), Mg(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, Anhydrous 1,4-Dioxane, carbon active (particle size <100 μm) and iminodiacetic acid were products of Merck (Darmstadt,

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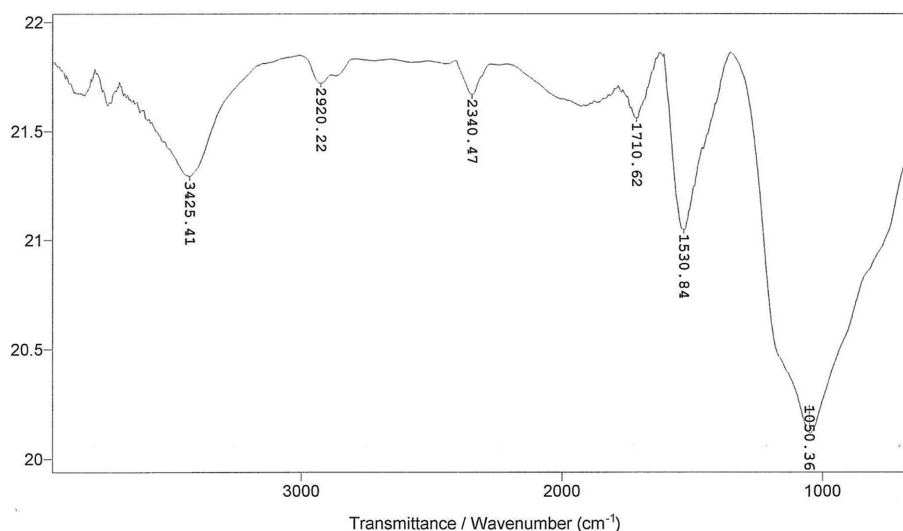


Fig. 1. The FT-IR spectrum of LIA.

Germany).

All the reagents were of analytical grade and used without any further purification.

The stock solution ( $1,000 \text{ mg L}^{-1}$ ) of Pb(II), was prepared by dissolving appropriate amounts of  $\text{Pb}(\text{NO}_3)_2$  in deionized water. To adjust the pH of the solution, 0.01 M acetate or phosphate buffer was used.

### 3. Synthesis of Lead Ion Imprinted Activated Carbon (LIA)

#### 3-1. Modification of Activated Carbon with Cyanoric Chloride

The 20% (v/v)  $\text{HNO}_3$  was used for cleaning the activated carbon particles. The surface was hydrolyzed and oxidated by immersion in water and filtration several times, and then washed with deionized water until the pH became neutral and dried in room temperature. The washed activated carbon particles (5 g) were reacted with 250 mL solution of 2% (w/v) cyanoric chloride in mixture of 1, 4 dioxane and xylene (1 : 1) under shaking for 10 h then filtered and dried in ambient condition. The modified activated carbon particles were soaked in 40 mL petroleum ether for 24 h and dried under vacuum.

#### 3-2. Synthesis of LIA

Iminodiacetic acid (0.5 g) and lead(II) nitrate (0.62 g) were solved in 50 mL of 0.1 M sodium acetate buffer (pH 5), and 1 g modified activated carbon was added into the mixture and shaken for 24 h. The solution was filtered and washed with 50 mL of 0.1 M  $\text{CH}_3\text{COONa}$ , 50 mL of 0.1 M  $\text{NaCl}$  and 80 mL  $\text{H}_2\text{O}$ . Additional washing was performed with 100 mL of 0.5 M  $\text{HNO}_3$  under stirring for 2 h (three times), and then with ultra pure water until pH was no longer acidic, for removal of template lead ions.

Ultimately, the LIA was dried under vacuum and stored in  $4^\circ\text{C}$ . The LIA was characterized by FT-IR, elemental analysis, thermogravimetric analysis.

#### 3-3. Batch Method

A series of solutions (100 mL) containing  $0.5 \text{ mg L}^{-1}$  of Pb(II) were taken. The range of pH solutions was adjusted between 3-9 with acetate or phosphate buffer solution. The 0.1 g of LIA was poured to each solution and shaken for 4 h. The sorbent was separated by filtration and the adsorbed metal ions were eluted with 0.5 M  $\text{HNO}_3$  (10 mL). The filtrate was analyzed for the residual lead (II) con-

centration by atomic absorption spectrophotometer.

#### 3-4. Isotherm Studies

A series of diluted solutions of Pb(II) ( $10\text{--}100 \text{ mg L}^{-1}$ ) were placed in a beakers, and then a fix amount of LIA (0.1 g) was added in optimum pH and shaken in water bath for 4 h at  $20^\circ\text{C}$ . The final concentration of Pb(II) in the solution was determined by FAAS. The data obtained of adsorption tests were used to calculate the capacity of Pb(II) at equilibrium on LIA,  $q_e$  ( $\text{mg g}^{-1}$ ) by the following equation:

$$q_e = (C_0 - C_e) V / W \quad (1)$$

where  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the concentrations of Pb(II),  $V$  (L) is the volume of the solution and  $W$  (g) is the mass of the LIA used.

## RESULTS AND DISCUSSION

### 1. Characterization of LIA

Activated carbon is a unique material because of the way it is filled with porosity. The modified carbon has macroporosity with particle size of less than  $100 \mu\text{m}$ . The LIA was characterized by FT-IR and elemental analysis as shown in Fig. 1. The IR spectra of LIA are compared with activated carbon. There are two bands at  $1,636$  and  $3,434 \text{ cm}^{-1}$  in activated carbon related to  $\text{C}=\text{O}$  and  $\text{O-H}$ , respectively. The additional bands at  $2,920$ ,  $1,050$ ,  $1,530$ ,  $1,710 \text{ cm}^{-1}$  in LIA attributed to  $\text{CH}$  aliphatic,  $\text{C-N}$ ,  $\text{CH}_2$ ,  $\text{COOH}$ , respectively, confirmed the modification was done successfully.

Elemental analysis demonstrates 83.856% carbon, 1.53% hydrogen and 1.87% nitrogen in the LIA. The presence of nitrogen in the LIA consistently approved the modification of activated carbon.

### 2. Pb (II) Adsorption

The maximum adsorption of Pb(II) was obtained at pH 6.5 (Fig. 2). At acidic pH the ion pair of nitrogen and oxygen groups in the iminoacetic acid was protonated and so there was less interaction with  $\text{Pb}^{2+}$ . At alkaline pH, Pb(II) tend to form the  $\text{Pb}(\text{OH})_2$ . Therefore the best pH sorption is near to neutral pH. The kinetic sorption of Pb(II) at optimum pH was investigated and presented in Fig. 3. The sorption rate of Pb(II) was quite rapid such that less than 5 min shaking was required for 90% saturation sorption and remained more

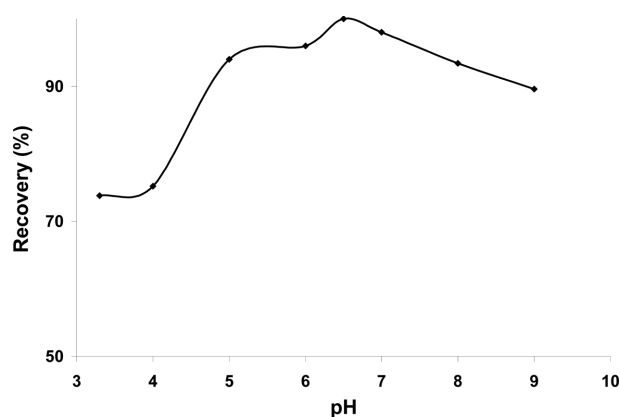


Fig. 2. Effect of pH sorption of Pb(II) onto LIA. Volume of each 100 mL containing  $0.5 \mu\text{g mL}^{-1}$  of Pb(II). The 0.1 g of LIA was added to each solution.

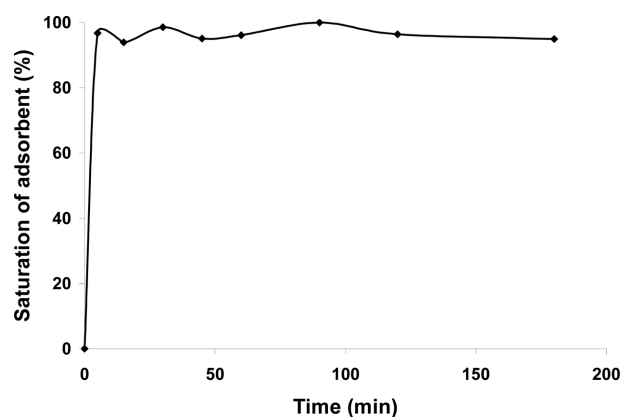


Fig. 3. Kinetics of Pb(II) sorption on LIA. Volume of each 100 mL containing  $60 \mu\text{g mL}^{-1}$  of Pb(II). The 0.1 g of LIA was added to each solution and the mixture was shaken for different length of time at pH 6.5.

or less constant at around it even after 60 minutes. The sorbent was readily regenerated with 1 M nitric acid and used repeatedly with sorption capacity after five cycles changing less than 10%. The sorption capacity of the resin stored for more than six months under ambient conditions was unchanged.

### 3. Adsorption Isotherms

The linearized form of Langmuir, Freundlich, Temkin and Redlich-Peterson isotherms was considered for Pb(II) sorption by LIA (see Table 1). The  $q_{\text{max}}$  is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface and obtained  $42.2 \text{ mg g}^{-1}$ . The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor,  $R_L$ , defined as:

$$R_L = 1 / (1 + K_L \cdot C_0) \quad (2)$$

The table shows the values of  $R_L$  (0.03) are in the range of 0-1, which indicates the favorable uptake of the Pb(II).

The Freundlich equation is an empirical equation employed to describe heterogeneous systems. A plot of  $\ln q_e$  versus  $\ln C_e$  enables the constant  $K_F$  and exponent  $n$  to be determined.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of LIA is increased.

$B = RT/b$  and  $b$ ,  $R$  and  $T$  are the Temkin constant related to heat of sorption, the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and the absolute temperature (K).

The Redlich-Peterson isotherm contains three parameters and incorporates the features of both the Langmuir (at  $g=1$ ) and the Freundlich (at  $g=0$ ) isotherms. The  $g$  values were close to unity, indicating that the isotherms were approaching the Langmuir form rather than Freundlich isotherm.

### 4. Selectivity of the Imprinted Sorbent

The ions of Zn(II) and Cd(II) were chosen as the competitive

Table 1. Isotherm parameters obtained by using linear method at  $20^\circ\text{C}$

| Langmuir isotherm model                               |   |  |                          |        |
|---|---|--|--------------------------|--------|
| Linear form   | $q_{max}$ (mg g <sup>-1</sup> )   | $K_L$ (L mg <sup>-1</sup> )<br>Langmuir constant | $R_L$                    | $R^2$  |
| $C_e/q_e=(1/q_{max} \cdot K_L)+(C_e/q_{max})$         | 42.2  | 0.31   | 0.03                     | 0.9894 |
| Freundlich isotherm model                             |   |  |                          |        |
| Linear form   | $K_F$ (mg g <sup>-1</sup> ) (L mg <sup>-1</sup> ) <sup>1/n</sup><br>Freundlich constant | n<br>heterogeneity factor                        |                          | $R^2$  |
| $\ln q_e=\ln K_F+1/n \ln C_e$                         | 14.3  | 3.69   |                          | 0.9812 |
| Temkin isotherm model                                 |   |  |                          |        |
| Linear form   | A (L g <sup>-1</sup> )<br>Temkin constant   | B  | b (J mol <sup>-1</sup> ) | $R^2$  |
| $q_e=B \ln A+B \ln C_e$                               | 14.2  | 6.0228   | 404.7                    | 0.9793 |
| Redlich-Peterson isotherm model                       |   |  |                          |        |
| Linear form   | g   | B (L mg <sup>-1</sup> ) <sup>g</sup>             | A (L g <sup>-1</sup> )   | $R^2$  |
| $\ln\left(A\frac{C_e}{q_e}-1\right)=g\ln(C_e)+\ln(B)$ | 0.9277  | 1.54   | 44                       | 0.9973 |

**Table 2. Competitive loading of Pb(II) and two other transition ions by the Pb-imprinted and non-imprinted sorbent**

| Sorbent       | K      |        |        | $K'_{Pb/Zn}$ | $K'_{Pb/Cd}$ | $K''_{Pb/Zn}$ | $K''_{Pb/Cd}$ |
|---------------|--------|--------|--------|--------------|--------------|---------------|---------------|
|               | Pb(II) | Zn(II) | Cd(II) |              |              |               |               |
| Imprinted     | 1.27   | 0.52   | 0.52   | 2.5          | 2.5          | 2.1           | 1.6           |
| Non-imprinted | 1.00   | 0.82   | 0.61   | 1.2          | 1.6          |               |               |

**Table 3. Effect of other ions on sorption**

| Interfering | Amount of adsorbed Pb(II) (mg · L <sup>-1</sup> ) | Loss adsorption (%) | Extraction percentage (%) | Distribution ratio |
|-------------|---|---------------------|---------------------------|--------------------|
| —           | 18.3  | 0                   | 91.5                      | 10.76              |
| Cd(II)      | 16.4  | 10.38               | 82                        | 4.56               |
| Mn(II)      | 15.9  | 13.11               | 79.5                      | 3.88               |
| Zn(II)      | 16.5  | 9.84                | 82.5                      | 4.71               |
| Ag(I)       | 16.2  | 11.48               | 81                        | 4.26               |
| Mg(II)      | 18.3  | 0                   | 91.5                      | 10.76              |
| Fe (II)     | 18.3  | 0                   | 91.5                      | 10.76              |
| Ni(II)      | 14  | 23.50               | 70                        | 2.33               |
| Cu(II)      | 15.5  | 15.30               | 77.5                      | 3.44               |
| Na(I)       | 18.3  | 0                   | 91.5                      | 10.76              |
| K(I)        | 18.3  | 0                   | 91.5                      | 10.76              |
| Fe(III)     | 17.9  | 2.19                | 89.5                      | 8.52               |
| Cu(II)      | 16.5  | 9.84                | 82.5                      | 4.71               |
| Hg(II)      | 16.4  | 10.38               | 82                        | 4.56               |

species with Pb(II) for sorption. Distribution coefficient (K), selectivity coefficient of the sorbent ( $k'$ ) and the relative selectivity coefficient ( $k''$ ) are shown in Table 2. These factors were calculated as [23,24]:

$$K = \frac{C_0 - C_e}{C_e} \times \frac{V}{W} \quad (3)$$

where  $C_0$  and  $C_e$  (mg L<sup>-1</sup>) are initial and equilibrium concentrations of Pb(II), respectively, V (L) is the volume of the solution and W (g) is the mass of LIA used.

$$K' = \frac{K_A}{K_B} \quad (4)$$

where  $K_A$  and  $K_B$  are distribution coefficient of template (Pb(II)) and competitive substance adsorbed by sorbent, respectively.

$$K'' = \frac{K'_{\text{impr int ed}}}{K'_{\text{non-impr int ed}}} \quad (5)$$

Table 2 shows that K values for Zn(II) and Cd(II) in the imprinted sorbent are less than in the non-imprinted sorbent. On the other side K value for Pb-imprinted sorbent is higher than the non-imprinted one. The  $k'$  (Pb/Cd) and  $k'$  (Pb/Zn) values of the imprinted sorbent were greater than that of non-imprinted sorbent, which indicated that the imprinted sorbent had high selectivity for Pb(II) over the two other transition ions. Table 2 also shows that the  $K''$  values were greater than unity. It means that the imprinted sorbent had higher selectivity than the non-imprinted sorbent toward Pb(II) ions.

### 5. Effect of Foreign Ions

To evaluate the selectivity of the preconcentration system, the

effect of some metal ions in concentration of each 20 mg · L<sup>-1</sup> on the sorption behavior of Pb(II) ion (20 mg L<sup>-1</sup>) was studied. The extraction percentage (E %) and the distribution ratios (D) were calculated from the following equations:

$$Q = (C_0 - C_e) V / W \quad (6)$$

$$E = [(C_0 - C_e) / C_0] \times 100 \quad (7)$$

$$D = Q / C_e \quad (8)$$

where Q represents the adsorption capacity (mg g<sup>-1</sup>),  $C_0$  and  $C_e$  represent the initial and equilibrium concentration of Pb(II) (μg mL<sup>-1</sup>), W is the mass of LIA (g), V is the volume of metal ions solution (L), E % is the extraction percentage and D is the distribution ratio (mL g<sup>-1</sup>). The result is listed in Table 3. This table indicates the most effective ion on sorption of Pb(II) on LIA is Ni(II). The adsorption of Pb(II) on the LIA in presence of all mentioned ions confirms that the Pb(II) can be determined quantitatively in the environmental samples.

### 6. Application of Method

LIA was used to preconcentrate and determine Pb(II) ions in water from tap water and Amin Abad well, Tehran, Iran. The pH of water sample was adjusted to the optimum pH. Solid phase extraction with LIA coupled with FAAS was applied to determine the Pb(II) in the water sample. The water sample was spiked with Pb(II) before subjecting it to extraction. The results in Table 4 demonstrate the applicability of the procedure for lead determination with reasonable recovery. Comparative information from a number of researches on preconcentration of Pb(II) by various methods for the figure of merits is also given in Table 5. This newly developed method has

**Table 4. Pb(II) determination in environmental water sample**

| The tap water                  |                                |              |                         | The well water                 |                                |              |                         |
|--------------------------------|--------------------------------|--------------|-------------------------|--------------------------------|--------------------------------|--------------|-------------------------|
| Added ( $\mu\text{g L}^{-1}$ ) | Found ( $\mu\text{g L}^{-1}$ ) | Recovery (%) | Preconcentration factor | Added ( $\mu\text{g L}^{-1}$ ) | Found ( $\mu\text{g L}^{-1}$ ) | Recovery (%) | Preconcentration factor |
| 0                              | —                              | —            | 10                      | 0                              | 13.3 $\pm$ 0.9                 | —            | 10                      |
| 10                             | 9.4 $\pm$ 0.5                  | 93.9         | 10                      | 5                              | 15.8 $\pm$ 0.7                 | 86.4         | 10                      |

Average of three determinations

**Table 5. Comparison of recovery, preconcentration and capacities with some literatures**

| Type of sorbent  | Recovery (%) | Preconcentration factor | Capacity ( $\text{mg g}^{-1}$ ) | Reference |
|--|--------------|-------------------------|---------------------------------|-----------|
| Poly[1-(N,N-bis-carboxymethyl)amino-3-allylglycerol-codimethylacrylamide] copolymer onto siliceous support | 97           | 10                      | 15.06                           | 26        |
| Amberlite XAD-2- SAL/IDA   | 95           | 10                      | 67                              | 27        |
| Amberlite XAD-2 functionalized with o-aminophenol  | 91           | 40                      | 3.32                            | 28        |
| Gallic acid-modified silica gel  | 96           | 25                      | 12.6                            | 29        |
| Sugarcane bagasse chemically modified with succinic anhydride  | —            | —                       | 83.3                            | 30        |
| Chitosan modified ordered mesoporous silica  | 95           | —                       | 22.9                            | 31        |
| Thioureasulfonamide resin  | 97           | 20                      | 0.5                             | 32        |
| Dibenzylthiocarbamate chelates on Dowex Optipore V-493   | 96           | 4-8                     | 8.6                             | 33        |
| Amberlite XAD-7 with xylenol orange  | 91           | 4-10                    | 16.9                            | 34        |
| Ion imprinted activated carbon   | 93.9         | 10                      | 42                              | Our work  |

been successfully applied to the analysis of trace lead ions in natural water sample.

### 7. Analytical Performance of the Proposed System

Fifth replicate determinations of 0.2  $\text{mg L}^{-1}$  lead solutions gave a relative standard deviation of 4.6%. The limit of detection corresponding to three times the blank standard deviation was found to be 2.2  $\mu\text{g L}^{-1}$ . The limit of quantification corresponding to ten times the blank standard deviation was found to be 7.3  $\mu\text{g L}^{-1}$ . The regression equation after preconcentration was  $A=0.0332 C_{pb}+5\times 10^{-4}$  ( $R^2=0.9973$ ), and the regression equation was  $A=0.0042 C_{pb}+9\times 10^{-5}$  ( $R^2=0.9985$ ). The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 7.9. The theoretical preconcentration factor, calculated as the ratio of the sample to the eluent volume, was 10.

### CONCLUSION

A method for the fabrication of selective Pb-imprinted sorbent base on activated carbon was described. The sorption rate of Pb(II) on LIA was quite rapid. The LIA has a good potential for enrichment of trace amount of Pb(II) from liquid samples. The LIA also presents the advantage of reasonable adsorption capacity and good chemical stability. The Langmuir isotherm model was found to be the most compatible model for analyzing adsorption capacity of LIA. The highest adsorption capacity obtained using the Langmuir isotherm model was 42  $\text{mg g}^{-1}$  at 20 °C. The  $R_L$  value showed that the LIA was favorable for the adsorption of Pb(II). Preconcentration by LIA combined with FAAS can be applied to the extraction and determination of traces of Pb(II) ions in the environmental water samples.

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