Selective Separation and Analysis of Pb(II) Using a New Surface Imprinted Multi-Walled Carbon Nanotubes Combined with AAS

Haisheng Zhang¹, Weiping Zhou², Hongqing Wang¹*, Yuyuan Wang¹, Fangfang He¹, Zhiqiang Cheng¹, Honglin Li¹, Jinhui Tang¹

¹School of Chemistry and Chemical Engineering, University of South China, Hengyang, China; ²College of Mathematics and Physical, University of South China, Hengyang, China.
Email: hqwang2009cn@yahoo.com.cn

Received March 2nd, 2012; revised March 20th, 2012; accepted April 10th, 2012

ABSTRACT

A new surface ion-imprinted Multi-walled carbon nanotubes (MCNTs), which was 6,6’-((1E,1’E)-(pyridine-2,6-diylbis(azanylyl))bis(methanylylidene))bis(2-allyl-phenol) and Pb(II) complex as functional monomer and template ion was presented for extracting and enrichment traces of Pb(II) ion. Parameters affecting the recovery of Pb(II) have been investigated in detail. The novel IMCNTs display high affinity, specificity, and selectivity for Pb(II) with a maximum uptake capacity of 115.5 mg·g⁻¹ at pH 4.0. Meanwhile, only 11 mins was enough for extracting 98.5% Pb(II) for the IMCNTs. No significant loss in adsorption capacity is observed when the IMCNTs are reused for eleven times. Separation and preconcentration with IMCNTs particles results in a limit of detection of 0.47 μg·L⁻¹ (3σ) and RSD (n = 8) of 1.16% by using atomic absorption spectrophotometer (AAS).

Keywords: Lead Determination; Ion Imprinted Particles; Carbon Nanotube; Selective Recognition

1. Introduction

Soil and water pollution, caused by toxic heavy metals, is a major environmental concern [1]. Among toxic heavy elements, lead is one of the commonest for animals and humans, even at lower concentrations [2,3]. Unlike organic compounds, lead is non-biodegradable and accumulative through its interaction with inorganic and organic materials, including adsorption, formation of complexes and chemical combinations etc. [4]. Consequently, the development of reliable methods for the removal and determination of lead from environment is of particular significance [5,6]. However, for conventional techniques, determining lead is very difficult due to its low concentrations in environmental samples and matrix interference. Thus, an effective enrichment and separation process is usually necessary prior to determination.

In recent years, Surface imprinting technique (SIT) has become a powerful method for high selectivity adsorption of target metal ions [7]. It is flexible, economical, environment-friendly, highly selective, speedy, simple, rich in accessible sites, safe, easily automatic, and quick in mass transfer and binding kinetics [8-10]. The particularly promising applications of SIT are trace enrichment and trace separation [8-12]. SIT is mainly based on the utilization of inorganic and organic solid sorbents which possess a stable and insoluble porous matrix having suitable active groups (typically organic groups) to interact with metal ions. Silica gel [13,14] and MCNTs [15] are ideal supports for organic groups. There are some reports about the enrichment and separation of Pb(II), using SIT with silica gel as the support [2,3,6]. However, there is few report on the synthesis of IMCNTs for Pb(II) extraction.

The classical preparation procedure of ion-imprinted polymer is collecting template molecule, functional monomer and cross-linker together to compounding. But the template molecule with functional monomer often isn’t monogamous combination in ion-imprinted polymer. The coordination effect between metal ion and ligand is forceful, combination quickly, steady, convenient [16]. So, the coordination effect between metal ion and ligand is a top choice in SIT progress. The kinds of o-Hydroxyphenol Schiff base chemical compound have very well coordination capability with metal ions [17,18]. In order to increase relative selectivity of absorbent for Pb(II), a novel complex of 6,6’-((1E,1’E)-(pyridine-2,6-diylbis (azanylyl))bis(methanylylidene))bis(2-allylphenol)w(PD

*Corresponding author.

Copyright © 2012 SciRes.
Selective Separation and Analysis of Pb(II) Using a New Surface Imprinted Multi-Walled Carbon Nanotubes Combined with AAS

ABMBAPOL) with Pb(II) was synthesized as functional monomer and template molecule of ion-imprinted polymer in this study. Meanwhile, a new surface-grafted Pb(II)-imprinted carbon nanotubes sorbent was presented. Parameters affecting the separation and pre-concentration of Pb(II) from aqueous solution were also discussed. Finally, a new method for determining traces of Pb(II) was developed.

2. Materials and Methods

2.1. Reagents and Chemicals

Analytical and spectral grade chemicals and doubly distilled water (DDW) were used throughout the experiments. 0.1 M HNO₃ or 0.1 M NH₃·H₂O were utilized for adjusting pH of solutions. Standard solutions (1.0 mg·mL⁻¹) of Pb(II), Cd(II), Cu(II) and Ni(II), containing 1.0% HNO₃, were prepared by dissolving corresponding amounts of nitrate salts in DDW.

3-Allylsalicylaldehyde, 2,6-Diaminopyridine, Acrolein, and 2,2’-azobisisobutyronitrile (AIBN) (98%) were offered by Aladdin. 3-Aminopropyltrimethoxysilane (APS) and ethylene glycol dimethacrylate (EGDMA) were purchased from Golden Dragon Industrial (HK) Co., Ltd. MCNTs was supplied by Shenzhen Nanotech Port Co. Ltd. Lead standard liquid (GBW08619) was supplied by National Institute of Metrology. Other chemicals were purchased from J&K scientific LTD.

2.2. Apparatus

Scanning Electron Microscope (SEM, JEOL JSM 6700 F) was used to study the morphology and shape of the MCNTs. A Perkin-Elmer Lambda 45 AAS spectrometer was used for determining concentrations of metal ions. IR Spectra (4000 - 400 cm⁻¹) in KBr pellets were recorded using IR Prestige-21 from Shimadzu. 1H-NMR spectra were taken on a Varian XL-300 Spectrometer with TMS as the internal reference and CD₃COCD₃ as the solvents. A pHs-3 C digital pH meter was used for measuring pH.

2.3. Preparation of Samples

Natural water samples were taken locally. River water came from Xiangjiang River, Hengyang, China. The Tap water was collected from our laboratory. The waste water was obtained from lead-zinc mine of Songbai, Hengyang, China. Before filled with the water samples, polyethylene bottles were cleaned with detergent, water, diluted nitric acid and DDW in sequence. All water samples were filtered through a 0.45 μm membrane filter and adjusted to pH 4 with the diluted HNO₃ and NH₃·H₂O.

2.4. Preparation of IMCNTs and Non-IMCNTs

2.4.1. Synthesis of 6,6’-((1E,1′E)-(pyridine-2,6-diylbis(azanylyl))bis(methanylylidene))bis-(2-allylphenol)

The functional monomer was prepared as the literature [19]. Firstly, 100 mL methanol (MeOH) and 3-Allylsalicylaldehyde (2.97 g) were added to a three-neck flask one after another. Then, 2,6-Diaminopyridine (1.00 g) in 60 mL MeOH was added dropwise to the above solution under stirring at room temperature. After being continuously stirred for 2 h at room temperature, many yellow solids were obtained by filter. Recrystallization of the yellow compound with CH₂Cl₂ and n-hexane (2:1), gave 2.38 g yellow crystals.

Yield: 2.38 g (60%), mp: 162.1°C - 162.8°C, 1H-NMR: (CD₃COCD₃, d ppm), δ: 3.48 (d, 4H, CH₂), 5.04 - 5.14 (m, 4H, CH₂), 6.04 - 6.09 (m, 2H, CH), 6.96 - 8.08 (m, 9H, Ar), 9.70 (s, 2H, CH). FT-IR (KBr, cm⁻¹) γ: 3633.89 (O-H); 3045.60 (C-H of Ar-C-H); 2938.10, 2870.67(C-H); 1683.74 (C=N); 1662.32 (C=C); 1608.04 (C=N, pyridine); 1487.56, 1450.21 (Ar-C=C).

2.4.2. Synthesis of MCNTs Functionalized by Amino-Group

MCNTs were first hydroxylated according to literature [20]. Then, they were functionalized with amino to prepare MCNTs-NH₂ as described in literature [21]. The typical process was as following. Under stirring, 4 ml of 3-aminopropyltriethoxysilane was added to the mixture of MCNTs-OH (4.01 g) and dry-toluene (100 ml). After the reactions proceeded for 24 h at room temperature, the MCNTs-NH₂ was obtained by centrifugation, followed by redispersion in methanol and centrifugation for three times.

2.4.3. Synthesis of Vinyl-Group-Functionalized MCNTs

Under stirring, 4 mL acrolein (dissolved in 10 mL MeOH) was added dropwise to a solution of MCNTs-NH₂ (1.90 g) and MeOH (90 mL). After reacting for 3 h at room temperature, the reaction solution was centrifugated, resulting in the solid nanoparticles Vinyl-Group-Functionalized MCNTs (MCNTs-CH=CH₂, 1.99 g) which was then washed with MeOH/DDW/DMF (1:1:1 in volume).

2.4.4. Synthesis of IMCNTs and Non-IMCNTs [22]

The synthesis process of IMCNTs, whose surface was grafted by Pb(II)-imprinted group, is presented as Scheme 1. Firstly, 0.76 g (CH₃COO)₂Pb·3H₂O was dissolved in 25 mL MeOH. Then, this solution was slowly added to a glass reactor containing the functional monomer (PDABMBAPOL, 1.59 g) in DMF (25 mL) under...
Selective Separation and Analysis of Pb(II) Using a New Surface Imprinted Multi-Walled Carbon Nanotubes Combined with AAS

stirring. After the mixture was stirred for 3 h at room temperature, MCNTs-CH=CH₂ (2.01 g), AIBN (0.10 g) and EGDMA (4 mL) were added. Then, nitrogen was bubbled in to drive away oxygen in the reactor for 25 mins. After being kept stirred for 24 h at 60°C under nitrogen atmosphere, the mixture was naturally cooled down to room temperature and filtered. The products obtained were washed with MeOH/DDW/DMF (1:1:1 in volume), and then treated with 6 M HCl solution for 12 h to remove Pb(II) imprinted in IMCNTs. The final products were cleaned with DDW several times until acid-free, and then dried under vacuum at 70°C for 48 h. Non-IMCNTs were prepared similarly in the absence of (CH₃COO)₂Pb·3H₂O.

2.5. Enrichment of Pb(II)

2.5.1. Batch Process

The pH values of Pb(II) standard and sample solution were adjusted to the desired with 0.1 mol·L⁻¹ HNO₃ or 0.1 mol·L⁻¹ NH₃·H₂O, and the volume was adjusted as desired with DDW. After that, 30 mg of IMCNTs or Non-IMCNTs were added, and the mixed solution was shaken vigorously for 30 mins. Thereafter, the solution was centrifuged, and the concentrations of the metal ions in the filtrate were directly determined by AAS. The adsorbing IMCNTs were eluted with 10 mL HCl (6 M) solution, and the concentrations of the metal ions in the eluent were also determined by AAS. Unless otherwise stated, each measured value is mean to three replicates. Pb(II)-IMCNTs-elute was used to denote these MCNTs eluted.

2.5.2. Parameters

The amount of Pb(II) adsorbed on the MCNTs (Q), the distribution ratio (Kᵅ), the selectivity coefficient (k) and the relative selectivity coefficient (k') were calculated using the following equations, respectively:

\[ Q = \frac{(C₀ - Cₜ)}{W} V \]  
(1)

\[ Kᵅ = \frac{(C₀ - Cₜ) V}{Cᵢ W} \]  
(2)

\[ k = \frac{K_d-Pb}{K_d-X} \]  
(3)

\[ k' = \frac{k_{IMCNTs}}{k_{NIMCNTs}} \]  
(4)

Scheme 1. Preparation of IMCNTS and Non-IMCNTS.
where $C_0$ and $C_e$ are the initial and equilibrium concentrations of metal ions (mg·mL$^{-1}$), respectively. $W$ is the mass of Pb(II)-ion-imprinted or non-imprinted carbon nanotube (g) and $V$ is the volume of metal ion solution (mL). $X$ is the interfering ion. $K_{d,Pb}$ and $K_{d,X}$ represent the distribution ratios of Pb(II) and Cd(II), Cu(II), Ni(II). $k_{MCNTs}$ and $k_{IMCNTs}$ represent the selectivity factor of imprinted sorbent and non-imprinted sorbent, respectively.

3. Results and Discussion

3.1. Characterization

FT-IR spectra was used to confirm functional groups on the IMCNTs (Figure 1). Compared with the original MCNTs, the IMCNTs, whether adsorbing Pb(II) or not, or being eluted, presented -C=N- bond locating around 1681.75 - 1724.29 cm$^{-1}$, and -OH bond around 3650 cm$^{-1}$ [15,18,23,24]. These phenomena demonstrated that the functional groups had been grafted onto the surface of IMCNTs. With Non-IMCNTs and Pb(II)-IMCNTs-elute (curve b and d), there were almost no difference between their FT-IR spectra, demonstrating Pb(II) was removed from the IMCNTs completely. However, for Pb(II)-IMCNTs saturated, it wasn’t the case. The characteristic absorption peak of -C=N- groups shifted from 1681.75 cm$^{-1}$ (curve b, d) to 1724.29 cm$^{-1}$ (curve c), suggesting the Pb (II) ions had been imprinted on IMCNTs. In curves b, c and d, the absorption peak at 3650 cm$^{-1}$, was attributed to $\gamma$ O-H. This suggested that -OH had not been coordinated with Pb(II).

The surface morphologies of MCNTs and Pb(II)-imprinted functionalized MCNTs were shown in Figure 2. Apparently, the surface of MCNTs was smooth. On the contrary, the IMCNTs appear porous, rough, irregular and agglomerative.

3.2. Effect of pH

The effect of pH on Pb(II) uptake was investigated using batch process. Because of the hydrolysis of Pb(II) ion in strong alkali solution, all the experiments were carried out under pH lower than 7.0. Figure 3 showed that the adsorption of lead was strongly affected by pH of the solution. The enrichment efficiency of lead was very low at pH below 2, because the protonation made the bonding capability of adsorbent decrease. From pH 2.0 to 4.0, the adsorption efficiency increased sharply with increasing pH. The recoveries of Pb(II) were 95.6% - 97.5% with in the pH range of 4.0 - 6.0. Here, pH 4.0 was a relatively optimal condition for adsorbing Pb(II), and subsequent experiments were made at pH 4.0.

3.3. Kinetic Experiment

Uptake kinetics of Pb(II) on the IMCNTs were investigated using batch process. After adjusted pH to 4.0, Pb(II) aqueous solution (25 mL, 10 μg·mL$^{-1}$) was mixed with 30 mg IMCNTs. During the process of absorbing, Pb(II)
concentration in the suspension was determined every 3 min. Figure 4 showed that only 11 mins. was enough for extracting 98.5% Pb(II) of the solution and plateau values were gradually attained within 17 mins, owing to the high complexation rate between Pb(II) ions and functional ligand of IMCNTs.

3.4. Static Adsorption Capacity

Adsorption capacity of the IMCNTs and Non-IMCNTs was investigated using batch experiments. The concentration of Pb(II) ion in the initial solution ranged from 20 to 180 μg·mL\(^{-1}\). Figure 5 showed that the adsorption amount increased with increasing the initial concentration of Pb(II). When the initial concentration of Pb(II) was large enough, a plateau began. The maximum Pb(II) adsorption capacity of the IMCNTs was 115.5 mg·g\(^{-1}\), much higher than that of Non-IMCNTs (84.4 mg·g\(^{-1}\)).

3.5. Thermodynamics of Adsorption

The effect of temperature on the adsorption equilibrium of Pb(II) ion was analyzed for IMCNTs in the temperature range from 298.15 to 318.15 K. Thermodynamic parameters such as standard Gibbs free energy change (\(\Delta G^\circ\), kJ·mol\(^{-1}\)), enthalpy change (\(\Delta H^\circ\), kJ·mol\(^{-1}\)), and entropy change (\(\Delta S^\circ\), kJ·(mol·K)\(^{-1}\)) were calculated using the following equations:

\[
\Delta G^\circ = -RT \ln K \tag{5}
\]

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}
\]

\[
\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}
\]

where \(K\) is equilibrium constant (\(K = C_a/C_i\), \(C_a\) and \(C_i\) are the equilibrium concentration of Pb(II) on adsorbent and in the solution, respectively), \(T\) is absolute temperature (K), and \(R\) is the gas constant (\(R = 8.314\) J·(K·mol\(^{-1}\)).

The plot of \(\ln K\) against \(1/T\) is shown in Figure 6. According to Equation (7), the slope and intercept of the straight line in Figure 6 corresponds to \(-\Delta H^\circ/R\) and \(\Delta S^\circ/R\) respectively. Therefore, \(\Delta H^\circ\) and \(\Delta S^\circ\) were calculated to be 70.12 kJ·mol\(^{-1}\) and 0.27 kJ·(mol·K)\(^{-1}\), respectively. By Equation (5), \(\Delta G^\circ\) at various temperature was calculated as –10.37 kJ·mol\(^{-1}\) (298.15 K), –11.72 kJ·mol\(^{-1}\) (303.15 K), –13.07 kJ·mol\(^{-1}\) (308.15 K), –14.42 kJ·mol\(^{-1}\) (313.15 K), and –15.77 kJ·mol\(^{-1}\) (318.15 K). The positive \(\Delta H^\circ\) indicates the endothermic character of the adsorption process, however, the negative \(\Delta G^\circ\) reveals the adsorption spontaneous nature of Pb(II). The positive \(\Delta S^\circ\) represents a chaos increase in the adsorption process.
3.6. Cycling and Reproducibility of Pb(II)-IMCNTs

Pb(II)-IMCNTs, were subjected to adsorption-desorption cycles in a batch process to test their reproducibility and cycling behavior. 6 M HCl (10 mL) acted as a desorption agent. The recycled Pb(II)-IMCNTs presented a recovery not less than 95% at the 10th cycle, suggesting an adsorption capacity loss only by about 4%. Therefore, it can be concluded that the IMCNTs can be used repeatedly without compromising their adsorption capacities, noticeably.

3.7. Selectivity of the IMCNTs

The selectivity of an imprinted material for a given ion plays the key role in its practical use. This paper has estimated the selectivity of the imprinted MCNTs for Pb(II) relative to Cd(II), Cu(II) and Ni(II), separately. Each metal ion in its solution had the concentration of 10 μg·mL⁻¹. As shown in Table 1, with IMCNTs, the relative selectivity coefficients (k') of Pb(II)/Cd(II), Pb(II)/Cu(II) and Pb(II)/Ni(II), were 21.6, 5.5 and 22, respectively, greater than one, indicating IMCNTs displayed higher selectivity for Pb(II) relative to Cd(II), Cu(II) and Ni(II). Therefore, the above IMCNTs could be applied to selectively separating Pb(II) from the solution containing Cd(II), Cu(II) and Ni(II). Two possible factors contributed to the higher selectivity for Pb(II) in the presence of the above competitive ions. One was the holes size selectivity. The size of Pb(II) ion cut out for the cavity of the IMCNTs. The other was the coordination geometry selectivity. IMCNTs could provide ligand groups with preferred selectivity for Pb(II) ions.

3.8. Accuracy and Precision of the Analytical Method

The accuracy and precision of the analytical method were evaluated by repeating the experiment for eight times under the optimal experimental conditions. The results indicated that the precision of the method, evaluated as the relative standard deviation (RSD, n = 8), was 1.16%. The limit of detection (LOD), calculated based on the three times of the blank standard deviation of eight runs the blank solution, was 0.47 μg·L⁻¹. This indicated that the method had good precision for the analysis of trace Pb(II).

3.9. Application of the Proposed Method

The accuracy of the method was evaluated by determining the amount of Pb²⁺ ions in the certified reference material and three environmental water samples (River water, Tap water, Waste water). For water samples, the standard addition method was adopted. From Table 2, it could be seen that the estimated values agreed well with the certified values. The recoveries of Pb(II) ions were in

### Table 1. Competitive sorption of Pb(II) and metal ions on IMCNTs and NIMCNTs at pH 4.0.

<table>
<thead>
<tr>
<th>Mixture of ions (10 μg·mL⁻¹, 250 mL)</th>
<th>Kₐ(IMCNTs) (mL·g⁻¹)</th>
<th>Kₐ(NIMCNTs) (mL·g⁻¹)</th>
<th>k(IMCNTs)</th>
<th>k(NIMCNTs)</th>
<th>k'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)/Cd(II)</td>
<td>1658.3/64</td>
<td>21.7/18.1</td>
<td>25.9</td>
<td>1.2</td>
<td>21.6</td>
</tr>
<tr>
<td>Pb(II)/Cu(II)</td>
<td>1647/71</td>
<td>33/7.9</td>
<td>23.2</td>
<td>4.2</td>
<td>5.5</td>
</tr>
<tr>
<td>Pb(II)/Ni(II)</td>
<td>1613/67</td>
<td>20.1/18.7</td>
<td>24.1</td>
<td>1.1</td>
<td>22</td>
</tr>
</tbody>
</table>

### Table 2. Determination of Pb(II) in environmental water samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb(II) added (μg·L⁻¹)</th>
<th>Pb(II) founded (μg·L⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>5.0</td>
<td>4.85 ± 0.02</td>
<td>97.0</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>9.75 ± 0.03</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0.59 ± 0.01</td>
<td>-</td>
</tr>
<tr>
<td>Tap water</td>
<td>5.0</td>
<td>4.98 ± 0.07</td>
<td>99.6</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>10.01 ± 0.11</td>
<td>100.1</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1.17 ± 0.02</td>
<td>-</td>
</tr>
<tr>
<td>Waste water</td>
<td>5.0</td>
<td>6.24 ± 0.08</td>
<td>101.1</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>11.08 ± 0.14</td>
<td>99.2</td>
</tr>
</tbody>
</table>

*Reference value. The certified sample solution was accurately diluted to 5 and 10 μg·L⁻¹, respectively; *Below the quantification limit.
the range of 97.0% - 103.0%. The comparisons of maximum adsorption capacity, analytical precision and accuracy of different SPE materials for Pb(II) was given in Tables 3. As could be seen, the present analytical method was comparable with that obtained by other reported different SPE materials in recent years. These results clearly demonstrated that the IMCNTs prepared were highly efficient, suitable and satisfactory for extracting and determining Pb(II) ions.

4. Conclusion

The newly IMCNTs was synthesized using a complex of PDABMBAPOL with Pb(II) as functional monomer and template ion. The IMCNTs exhibited high affinity, selectivity and fast kinetics for Pb(II) ions. Under optimal conditions, the maximum adsorption quantity of IMCNTs was 115.5 mg·g⁻¹ much higher than that of Non-IMCNTs (84.4 mg·g⁻¹). The presence of other metal ions such as Cd(II), Cu(II), or Ni(II) did not affect IMCNTs selectivity for Pb(II). Separation and pre-concentration by solid-phase extraction with IMCNTs particles results in a limit of detection of 0.47 μg·L⁻¹ (3σ) and RSD (n = 8) of 1.16% by using AAS. In addition, the IMCNTs prepared had high reproducibility and were efficient, sensitive and reliable for the enrichment and determination of trace lead.

5. Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 11175080) and by the Nature Science Fund of the Hunan Province (No. 10JJ6025).

REFERENCES


