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Modification of Carbon Paste Electrodes using Pyridine Functionalized SBA-15 and Multi-walled Carbon Nanotubes (MWCNTs) for Determination of Lead Ions in Real Aqueous Solutions

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Abstract: *For determination of trace amounts of lead(II) ions, a carbon paste electrode was modified with functionalized SBA-15 and Multi-Walled Carbon Nanotubes. The electrode composition was graphite powder 59%, Paraffin 23%, modified SBA-15 14%, MWCNTs 4% (W/W). The linear range for lead(II) was* 6.5×10^{-8} *to* 2.0×10^{-3} *and the limit of detection was obtained* 5.5×10^{-8} *mol* L^{-1}*. The lifetime of the electrode was 4 months and a fast response time was observed. The electrode was used for determination of trace amounts of lead in real samples.*

Keywords: Carbon paste electrode; Lead; Modified SBA-15; MWCNTs; Potentiometry

1. INTRODUCTION

Nowadays, the importance of controlling the level of environmental pollutants in natural and potable water samples cause to develop of novel methods for determination of heavy metals. Due to lead toxicity and uncontrolled dispersion in the environment many uses of this element currently are being phased out. For example lead was added to petrol in the form of tetra-ethyl lead ($PbEt_4$) as an anti-knocking function but in developed countries this kind of petrol is currently being phased out for environmental reasons [1]. Humans have been using this heavy metal for thousands years, poisoning themselves in the process due to accumulation, exposure and direct contact. Lead may cause irreversible neurological damage as well as renal disease, cardiovascular effects, and reproductive toxicity [2]. Therefore, new methods for determination and separation of Pb^{2+} ions in environment are so important.

Carbon pastes are useful materials for the fabrication of various electrometric-analytical electrodes. In comparison with ion-selective electrodes based on polymeric membranes, carbon paste electrodes are inexpensive and possess advantages of much lower Ohmic resistance, very stable response and easy renewal of its surface [3-4]. A chemical modifier can preconcentrate metallic ions on the electrode surface by either complexation or electrostatic attraction, so can lead to more sensitive electroanalytical procedures with lower detection limit values [5]. Recently, carbon nanotubes (CNTs) and nanoporous silicas such as SBA-15, MCM-48 and MCM-41 have been used in carbon paste electrodes due to their interesting physicochemical properties, such as Highly ordered structure, high mechanical strength, high electrical and thermal conductivity and also high surface area (200-1500 m^2 g^{-1}) [6]. This would impart high diffusion rates of selected target analytes to a large number of accessible binding sites, which constitutes definite key factor in increasing sensitivity. And also when this modifier applied in connection to electrochemistry, these properties could be advantageously exploited in electroanalysis by inducing high selectivity (either by specific binding or by preferential recognition) [7]. This paper describes the construction of a carbon paste electrode modified with Pyridine functionalized nanoporous silica py-SBA-15 (which is a selective modifier for preconcenteration of Pb^{2+}) materials, with substantial improvement in selectivity and detection limit toward Lead (II) ions. The modified electrode was successfully used in determination of lead content of wastewater samples.

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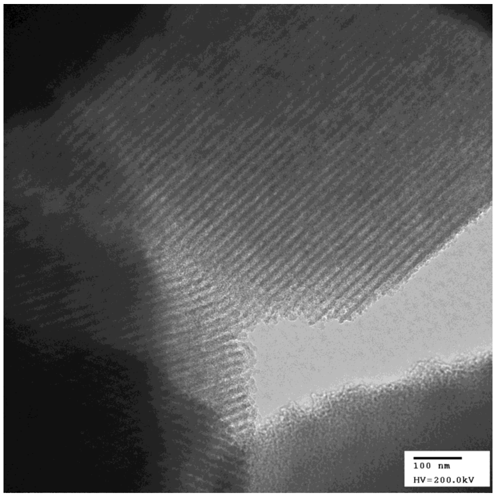

Figure 1. TEM micrographs of nanoporous SBA-15

2. EXPERIMENTAL

2.1. Regents and solutions

All reagents were analytical grade and purchased from Merck or Fluka and used without further purification. The multi-walled carbon nanotubes (MWCNTs) with 10–40 nm diameters, 1–25 μm length and 5–10 nm core diameter purchased from Research Institute of the Petroleum Industry (Iran). Paraffin oil, lead nitrate and pluronic P123 were provided from Aldrich Company. All solutions were made using deionized water, provided from a Milli-Q (Millipore, Bedford, MA, USA) purification system.

2.2. Preparation and modification of nano porous SBA-15

SBA-15 nanoporous silica was synthesized according to the previous reported procedure [8]. The TEM micrograph of SBA-15 is shown in Fig.1. For modification, in a typical reaction 1 g of SBA-15 was suspended in 50 ml of toluene, afterward 5.0 ml of 3-Aminopropyl trimethyloxy silane was added to the mixture, and the mixture was refluxed for 24 hours. The white solid was removed from the solvent by filtration and washed with ethanol. Afterward, this solid was suspended in 50 ml of toluene and then 2cc of 4-Pyridine carbaldehyde was added and refluxed for 24 hours. This white brownish solid was removed from the mixture by filtration. The particles were washed by toluene and Ethanol and dried at 70 °C in vacuum. A schematic model for synthesis is shown in Fig. 2. Functionalization by Pyridine Group was confirmed by IR spectroscopy and elemental analysis. IR spectroscopy data are given below: IR (KBr, cm^{-1}): 2905 (CH, aliphatic), 2930 (CH, aliphatic), 1561 (C=N), 1548 (C=C), 1080 (Si-O-Si). The loading of pyridine was obtained 1.5 mmol g^{-1} by using of elemental analysis.

2.3. Instruments

The glass cell, where the Pb^{2+} carbon paste electrode was placed, consisted of an R684 model Analion Ag/AgCl double junction reference electrode was used as a reference electrode. A Corning ion analyzer 250pH/mV meter was used for the potential measurements.

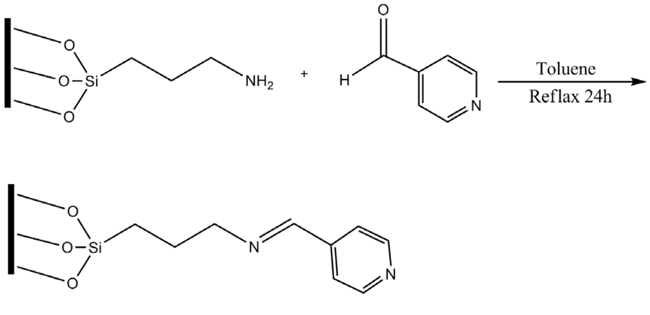

Figure 2. A schematic model for synthesis of functionalized SBA-15

The pH meter was a digital WTW Metrohm 827 Ion analyzer (Switzerland) equipped with a combined glass-calomel electrode. All measurements were made at 25±1°C.

2.4. Preparation of modified carbon paste electrode

A mixture contains 59% of graphite powder, 23% of Paraffin, 14% of modified SBA-15, 4% (W/W) of MWCNTs were thoroughly mixed and packed in the end of a disposable 1 mL polypropylene syringe. The electrical contact with the electrode was established by inserting a copper wire in it. The electrode surface was pressing against a filter paper to obtain an appropriate packing of the carbon paste and a smooth surface.

2.5. Conditioning the carbon paste electrode

The electrode surface was conditioned in a solution containing 1.0×10^{-4} mol L^{-1} $Pb(NO_3)_2$ and 1.0×10^{-3} mol L^{-1} $NaNO_3$ for 24 hours. The pH of solution was adjusted by adding 0.01-6 mol L^{-1} of buffer solutions of acetate. Then it was rinsed with deionized water.

2.6. Emf measurements

The electrochemical cell can be represented as follows:

Ag, AgCl (s), KCl (3 mol L^{-1}) || test solution | modified carbon paste electrode

All measurements were done versus Ag, AgCl(s) reference electrode. In all of the solutions $NaNO_3$ in concentration of 0.1 mol L^{-1} was used as supporting electrolyte and the pH was adjusted to 6 by acetate buffer with concentration of 0.01 mol L^{-1}. (The pH was changed in section “Influences of pH”).

3. RESULTS AND DISCUSSION

The selectivity of carbon paste electrode to an ion depends on the selectivity of the chelating agent to metal ions. Since the lone pair electrons of pyridine group are contributed in the ring resonance, in higher pHs pyridine group can react selectively with soft ions like Pb^{2+}. In addition, the pore size of SBA-15 is suitable for Pb^{2+} radius size to form complex with pyridine group. Therefore, modified SBA-15 with pyridine has a selective interaction with Pb^{2+} ion.

3.1. Influences of electrode composition

Considering the important influence of composition on electrode responses, different amounts of graphite powder, paraffin oil,

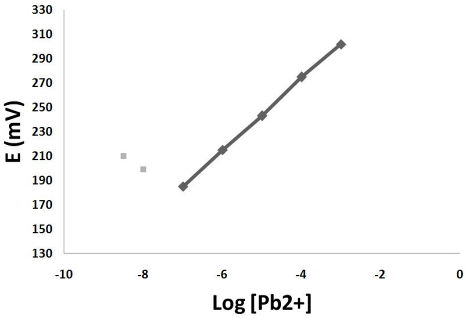

Figure 3. The calibration curve for Lead(II) ion, buffer pH = 5.5, Supporting electrolyte 0.1M $NaNO_3$

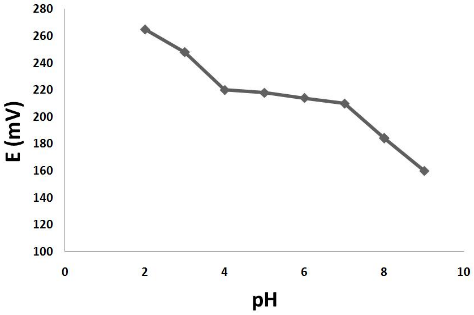

Figure 4. Influence of pH on electrode response to Lead(II) , Supporting electrolyte 0.1M $NaNO_3$

modified SBA-15 and MWCNTs were thoroughly mixed and the responses were studied and listed in table 1. In the first attempt no modified SBA-15 and MWCNTs were used, then in the different electrodes, some amounts of modified SBA-15 were added and the optimum amount was obtained. SBA-15 has a silica structure and is not electrically conductive, so using a large amount of it can decreases response slope. Since MWCNTs can increase electrical conductivity, some amounts of them were added to the electrode and the results were improved. The composition for the best electrode (No.8) was obtained Graphite powder 59%, Paraffin 23%, modified SBA-15 14%, MWCNTs 4% (W/W).

3.2. Calibration curve

For quantitative determination of lead ions, a calibration curve in the linear range of 6.5×10^{-8} to 2.0×10^{-3} mol L^{-1} was drown versus measurements of Emf. Results were shown in Fig. 3. By extrapolating the linear parts of the ion selective calibration curve, the detection limit of the electrode was calculated to be 5.5×10^{-8} mol L^{-1} [9]. The wide response range of the electrode and the low detection limit are all due to the special composition of the electrode.

3.3. Influences of pH

In this step the influence of pH on the electrode responses was studied. A solution containing 5×10^{-4} mol L^{-1} of $Pb(NO_3)_2$ and 0.1 mol L^{-1} $NaNO_3$ as supporting electrolyte was prepared. The pH was adjusted in the range of 2-9 by adding low amounts of HNO_3 or KOH to the solution. The results showed in Fig. 4 that in the wide range of 4-7 a linear response was achieved.

In pHs lower than 4, the interaction of H^+ ions with lone pair electron of pyridine could disturb the electrode responses and in pHs higher than 7, formation of hydroxyl species of lead could affect the responses.

Considering the fact that most of natural water samples polluted by lead ions are a bit acidic, and the wide linear response of the electrode in the pH range of 4-7, no pH adjustment is required in determination of lead ions in the most of real water samples.

3.4. Study of Response time

The response time of an ion selective electrode is defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values, after successive immersions in a series of solutions, each having a 10-fold concentration difference. To study this factor, concentration of lead(II) ion was changed from 6.5×10^{-8} to 2.0×10^{-3} mol L^{-1}. The results showed that the response time for the proposed electrode is 40s.

The low response time of the electrode is an important advantage of this method for determination of lead(II) ions. With this electrode after a simple sample preparation, the concentration of lead(II) ions could be quantitatively measured in less than 1 min.

Table 1. Optimization of the electrode composition, pH=5.5, Supporting electrolyte 0.1M $NaNO_3$.

Electrode No.	Graphite powder (%)	Paraffin (%)	Modified SBA-15(%)	MWCNTs (%)	Slope (mV)	Linear range (mol L−1)	R^2
1	75	25	0	0	14.8±2.7	-	0.913
2	70	25	5	0	19.1±1.4	1.0×10^{-6} to1.0×10^{-2}	0.942
3	65	25	10	0	22.5±1.3	9.0×10^{-7} to1.0×10^{-2}	0.956
4	60	25	15	0	25.4±1.3	4.0×10^{-7} to 5.0×10^{-3}	0.961
5	60	25	13	0	25.9±1.2	3.0×10^{-7} to 5.0×10^{-3}	0.965
6	63	23	14	0	27.3±1.2	1.5×10^{-7} to 2.0×10^{-3}	0.976
7	61	23	14	2	28.5±1.1	1.0×10^{-7} to 2.0×10^{-3}	0.986
8	59	23	14	4	29.8±1.0	6.5×10^{-8} to 2.0×10^{-3}	0.995
9	57	23	14	6	28.1±1.1	1.0×10^{-7} to 2.0×10^{-3}	0.983

3.5. Influence of interference ions

The IUPAC has recommended a method for studying Influence of interference ions in ion selective electrodes which is called Matched potential method (MPM) [10]. In this method the specific activity of the primary ion is added to a reference solution and the potential should be measured. For this goal, a reference solution with concentration of 5.0×10^{-8} mol L^{-1} was chosen. Then interfering ions were successively added to an identical reference solution, until the measured potential matched to obtained value before adding the primary ions. Then matched potential selectivity coefficient, $k_{Pb,X}^{MPM}$ is calculated from the resulting primary ion to the interfering ion activity ratio, $k_{Pb,X}^{MPM} = \Delta_{a_x}^{a_{Hg}}$ [11]. The interference of Na^+, K^+, Cs^+, Ca^{2+}, Mg^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+}, Ag^+ and Zn^{2+} was investigated and showed that they have no significant effect on the response to Pb^{2+}. The $k_{Pb,X}^{MPM}$ values for the interferences are shown in Table 2.

The high selectivity of the electrode to Pb^{2+} ions is due to the special interaction of modified SBA-15 with Pb^{2+} ions. Considering no interference of most cations on the electrode response, the electrode could be considered as a successive tool for determination of Pb^{2+} ions in real water samples.

3.6. Lifetime

The lifetime of an electrode is the period of time that the electrode shows no changes in the efficiency of the measurements. To study this factor, the electrode was calibrated periodically with standard lead solutions. Then the electrode was conditioned and calibrated in the next month. The lifetime of the electrode was evaluated to be 4 month. This long lifetime period may be due to stability of modified SBA-15 and multi-walled carbon nanotubes.

3.7. Sample preparation

The application of the electrode responses was studied by measurement of lead content in real samples. The samples were obtained from tap water (Tehran, Iran), Karaj River and Mand River. The pH of all samples solutions were adjusted to 6 by acetate 0.01 mol L^{-1} and the supporting electrolyte was $NaNO_3$. Different amounts of lead were spiked to the solutions and the results are listed in table 3. The results showed that the electrode has a good response to lead ions in real water samples.

Table 2. Matched potential selectivity coefficient for interfering cations.

interfering ions (X)	$k_{Pb,X}^{MPM}$
Na^+	1.3×10^{-4}
K^+	6.8×10^{-4}
Cs^+	10×10^{-3}
Ca^{2+}	4.1×10^{-4}
Mg^{2+}	3.9×10^{-4}
Cd^{2+}	2.1×10^{-3}
Ni^{2+}	5.5×10^{-3}
Cu^{2+}	1.9×10^{-3}
Cr^{3+}	4.8×10^{-3}
Fe^{3+}	2.2×10^{-3}
Ag^+	1.8×10^{-3}
Zn^{2+}	5.3×10^{-3}

4. CONCLUSION

The special composition of this modified carbon paste electrode is the key role of its special characteristics, since the modified SAB-15 is selective to lead ions; high selectivity is obtained. By using MWCNTs, a wide linear range is achieved which due to increasing the conductivity. The long lifetime of the electrode is because of stability of all ingredients of electrode specially modified SBA-15. In addition, no pH adjustment is required in most real water samples. The short period of the response time and simplicity of preparation makes the electrode a unique sensor for determination of trace amounts lead in real samples.

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Table 3. Data of Real sample analysis

	Real sample mol L^{-1}	Added/ mol L^{-1}	Found/ mol L^{-1}	Recovery, %
tap water	ND*	5.0×10^{-4}	4.9×10^{-4}	98.5
		1.0×10^{-5}	9.9×10^{-6}	99.3
Karaj River	1.5×10^{-7}	5.0×10^{-4}	5.1×10^{-4}	102.0
		1.0×10^{-5}	1.0×10^{-5}	100.0
Mand River	3.4×10^{-7}	5.0×10^{-4}	4.9×10^{-4}	99.0
		1.0×10^{-5}	9.8×10^{-6}	98.0

*Not determined