Full Paper

Using the Hydroxymethyl-Modified Nanoporous Silica as a PVC Membrane Electrode Modifier to Determination of Lead Ions

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Abstract- A PVC membrane electrode to determination of lead ions based on hydroxymethyl -modified SBA-15 nanoporous silica as a carrier was prepared. The electrode exhibits a Nernstian response for Pb^{2+} over a concentration range (1.0×10^{-1} to 1.0×10^{-4} mol L^{-1}) with a slope of 28.9 ± 0.2 mV per decade. The limit of detection of the sensor is 5.5×10^{-5} mol L^{-1}. The sensor has a relatively fast response time (~10s) and a useful working pH range of 3.5–8.0. Interference of some divalent cations was also evaluated. It was used as an indicator electrode in potentiometric titration of Pb^{2+} with EDTA and in direct determination of lead ion in wastewater and pepper samples. The results indicate that this electrode is sensitive for determination of Pb^{2+}.

1. INTRODUCTION

The increasing use of ion sensors in the field of environmental, agricultural, industrial and medicinal analysis is putting more and more pressure on analytical chemists to develop new sensors for the fast, accurate, reproducible, and selective determination of various species. On the other hands, since the discovery of mesoporous materials, there has been much interest and research into mesoporous silicate materials. The nanoporous silica materials such as MCM-41 [1], LUS-1 [2] and SBA-15 [3] are suitable for application in catalysis [4], micro extraction [5] and modified carbon paste electrodes [6] due to their high specific surface area, narrow pore size distribution and high concentration of surface hydroxyl groups. Chemical functionalization of the inorganic framework of porous materials through the covalent coupling of an organic moiety is a promising approach for preparing porous surfaces having pecific properties allowing many applications in chemistry [7-9]. In analytical chemistry such materials can be applied in improvement of selectivity and sensitivity in the preparation of electrodes for electro analysis of chemistry species.

Lead in the environment arises from both natural and anthropogenic sources. Exposure can occur through drinking water, food, air, soil and dust from old paint containing lead. In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. High levels of exposure may result in toxicity in humans which in turn cause problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tract, joints, reproductive system, and acute or chronic damage to the nervous system. Some studies suggest that there may be a loss of up to 2 IQ points for the rise in blood lead levels from 10 to 20µg/dl in young children [10].

As it mentioned, large-scale nano-structured materials have attracted significant interest in development of chemical sensors [11-14]. Carbon paste electrodes modified with functional SBA-15 have been more widely used to quantify trace metal ions [15-21], but there are not many reports about their application in the PVC membrane sensor. Therefore, in this work, hydroxymethyl-modified SBA-15 was used as a selective sensing material in the PVC membrane for the first time. The proposed sensor was successfully applied for direct determination of the lead ions in environmental samples without any separation or purification.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The glass cell, where the Pb^{2+} ion-selective electrode was placed, consisted of two Ag/AgCl reference electrodes (Azar electrode, Iran) as the internal and external reference electrodes. Both electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ±0.1 mV precision.

The FT-IR spectra of samples were recorded on an EQINOX 50 Bruker instrument. N_2 adsorption-desorption measurements were performed on BELSORP-miniII at -196 °C, with samples degassed at 100 °C before measurement. Structural parameters (specific surface area, pore diameter and pore size distribution) were calculated using Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods by means of BELSORP-miniII analysis software.

2.2. Reagents and Materials

Reagent grade dibutyl phthalate (DBP)**,** nitrobenzene (NB), high relative molecular weight polyvinyl chloride (PVC), sodium tetraphenyl borate (NaTPB), oleic acid (OA) and tetrahydrofurane (THF) were purchased from Merck and used as received. Nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available, and used without any further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout.

Tetraethyl orthosilicate (TEOS, Merck), poly (ethylene glycol)-block poly (propylene glycol)-block-poly (ethylene glycol) (P123, Aldrich), tris(hyrdroxymethyl)aminomethane (HMAM,Merck) , 3-(chloropropyl)-trimethoxysilane (CPMS, Merck), triethylamine (TEA, Merck), hydrochloric acid (Merck), and ethanol (Merck) were used as received from suppliers.

2.3. Synthesis of Ionophore

The modification steps of the SBA-15 are shown in Fig. 1 and synthesis procedure is as follows:

2.3.1. Synthesis of SBA-15

The nanoporous SBA-15 was synthesized based on our previous reports [5, 22]. In a typical synthesis, pluronic P123 (2 g) was dissolved in deionized water (2 mL) and HCl (30 g, 2 mol L^{-1}) was added consequently. Then, the TEOS (4 g) was added drop wise while the reaction mixture was being stirred at 35 °C. After adding the TEOS, the resultant mixture was stirred at 35 °C for 24 h. In the next step, the resultant mixture was transferred to a Teflon-lined autoclave. The reactor was sealed and maintained at 100 °C for 48 h. The white solid was filtered off after allowing the reactor to being cold. Then the product was washed several times with deionized water. The template was removed using Soxhlet extractor and ethanol as solvent. Finally, the product was dried and calcined at 600 °C for 6 h.
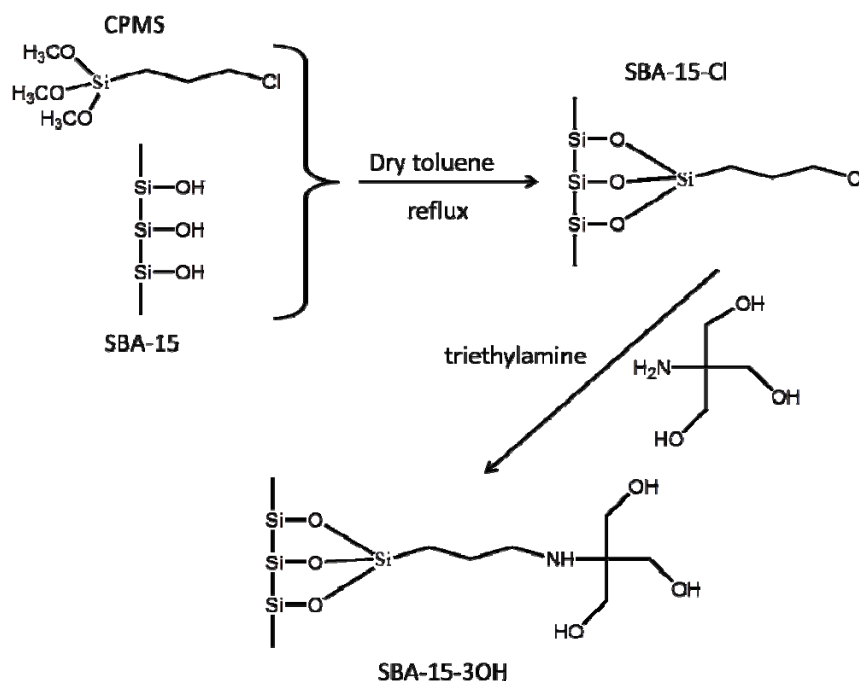
Fig. 1. Schematic representation of modification steps

2.3.2. Synthesis of SBA-15-Cl

The synthesis procedure for modification of the SBA-15 with chloropropyl moiety is as follows, the synthesized SBA-15 (1 g) and dry toluene (100 mL) were placed in a two-neck round-bottom flask. The mixture was stirred with heating to achieve a homogenous dispersion. Afterward, CPMS (1 mL, about 5 mmol) was added and then the reaction mixture refluxed for 24 h. Then, the solid was filtered and washed several times with fresh dry toluene in order to remove unreacted CPMS. Finally, the product was dried at 100 °C overnight.

2.3.3. Synthesis of SBA-15-3OH

The SBA-15-Cl material was placed in a round-bottom flask. Then, the solution of HMAM in distilled water was added to the reaction vessel. The stoichiometric amount of TEA was added to the reaction mixture and it was heated under reflux condition for 24 h. Then, the solid was filtered and washed several times with deionized water and finally dried at 100 °C overnight.

2.4. Electrode Preparation

The general procedure to prepare the PVC membrane was as followed: Different amounts of the ionophore along with appropriate amounts of additive were weighed. Then, 30 mg PVC and known amounts of plasticizer were added to the mixture. The mixture was dissolved in 2 mL of tetrahydrofuran (THF), and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated

slowly until an oily concentrated mixture was obtained. A pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with an internal filling solution (1.0×10^{-3} mol L^{-1} Pb(NO$_3$)$_2$). The electrode was finally conditioned for 48 h by soaking in a 1.0×10^{-3} mol L^{-1} Pb(NO$_3$)$_2$ solution.

2.5. Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements; Ag–AgCl, KC1 (satd.) | internal solution, 1.0×10^{-3} mol L^{-1} Pb(NO$_3$)$_2$ | PVC membrane | sample solution | Ag–AgCl, KC1 (satd.)

A Corning ion analyzer 250 pH/mV meters was used for the potential measurements at 25.0±0.1 °C. Activities were calculated according to the Debye- Huckel procedure.

3. RESULTS AND DISCUSSION

3.1. Hydroxymethyl Modified Nanoporous Silica

The FT-IR was used to monitor the different steps of modification. The spectra of SBA-15, SBA-15-Cl and SBA-15-3OH are given in Fig. 2.
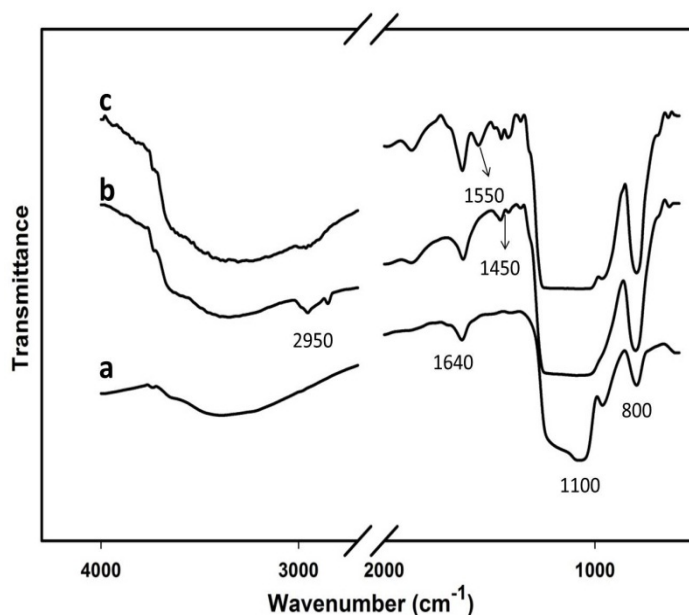

Fig. 2. The FT-IR spectra of a) SBA-15, b) SBA-15-Cl, c) SBA-15-3OH

All materials have similar peaks around 800 and 1100 cm^{-1} which are attributed to the Si-O-Si framework stretching vibrations. Also, there is a band observed around 1640 cm^{-1}

which comes from vibrations of physically adsorbed water molecules. The first modification step is confirmed by comparison of FT-IR spectrum of SBA-15 and SBA-15-Cl. Herein, the main evidence of successful incorporation of chloropropyl into the SBA-15 is the observation of C-H vibrations around 2950 cm^{-1} which are related to $-CH_2-$ groups in chloropropyl moiety. The observed band around 1450 cm^{-1} which is raised from vibrations of C-H bands is another evidence of successful reaction. The next synthesis step was observed by comparison between FT-IR spectra of SBA-Cl and SBA-3OH. The only evidence that seems enough for conformation of successful attachment of HMAM to the SBA-Cl material is the presence of a band around 1550 cm^{-1} which is due to the scissor bending of N-H groups.

The textural properties of final product was investigated using N_2 adsorption-desorption isotherms and consecutive calculation of specific surface area, pore size distribution and pore diameter based on sorption isotherms by means of BET and BJH equations. The adsorption-desorption isotherms of SBA-15-3OH are given in Fig. 3.
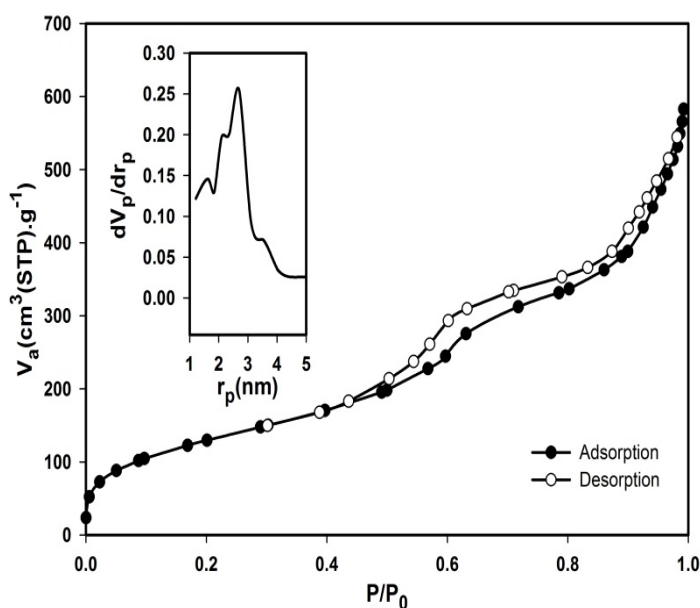
Fig. 3. The N_2 adsorption-desorption isotherms of SBA-15-3OH (inset: BJH pore size distribution of SBA-15-3OH)

The isotherms show a type IV standard isotherm. Although it can be obvious that it almost deformed after two steps of modification, it still shows the hysteresis loop indicating that the pores are available and not blocked during the modifications. The inset diagram shows the BJH pore size distribution. It can be seen that it has shoulders as well as main peak which indicates that incorporation of functional moieties into the SBA-15 influenced the pore structure of final product. The BET specific surface area and BJH pore diameter of SBA-15-3OH are 474 m^2/g and 5.4 nm, respectively. The mentioned properties are lower than pure

SBA-15 which is normal after two steps of functionalization but still considerable for further applications.

3.2. Membrane Composition Effect on the Potential Response of the Sensor

Because the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane ingredients, the influence of membrane composition on the potential responses of the Pb^{2+} sensor was inspected [23,24]. In this study, different membrane compositions, as shown in Table 1, were tested. As can be seen, the membrane with the composition of 30% PVC, 7% SBA-15-3OH, 2% NaTPB and 61 % DBP (no. 12) was the optimum one in the development of this sensor. This membrane composition was selected after many considerations.

The Pb^{2+} ion extraction into the liquid membrane is a result of the high concentration of the ligand in the membrane. From Table 1, it was obvious that in the absence of ionophore and with the presence of other components (no. 2), the response of the recommended electrode was low (slope of 5.55 ± 0.3 mV per decade).

The second factor which helps the extraction of the Pb^{2+} ion is plasticizer. After the evaluation of two solvent mediators (NB and DBP), it was observed that the DBP displays the better sensitivity than NB, because NB presented higher dielectric constant values than DBP, leading to the extraction of the polar interfering ions, which may have negative effects on the selectivity behavior of the sensor.

The presence of lipophilic anions in a cation-selective membrane was also considered. Actually, the presence of such anions in a cation-selective membrane, which is based on a neutral carrier, decreases the ohmic resistance and improves the response behaviour and selectivity. Furthermore, when the extraction capability is poor, it increases the membrane electrode sensitivity [25-27]. Here, a NaTPB addition of 2% as an additive led to the slope increase of the potential sensor response from the sub-Nernstian value of 26.5 ± 0.3 mV per decade (no. 11) to the Nernstian value of 28.9 ± 0.2 mV per decade (no. 12).

3.3. pH Effect on the Electrode Response

The influence of the pH of the test solution on the potential response of Pb^{2+} sensor investigated at 1.0×10^{-3} M Pb^{2+} concentration, in the pH value of 2.0 up to 11.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment). In agreement with the resulting data (Fig. 4), the potential remained constant despite the pH change in the range of 3.5 to 8.0, indicating the applicability of this electrode in this specific pH range.

Table 1. The optimization of the membrane ingredients

| Membrane No.	Composition (%)			Slope (mV per decade)
	Plasticizer (%wt.)	Ionophore (%wt.)	Additive (%wt.)	
1	DBP, 70	----	-----	0.30±0.5
2	DBP, 69	----	1 (NaTPB)	5.55±0.3
3	DBP, 67	3	-----	11.32±0.4
4	DBP, 65	5	-----	19.92±0.3
5	DBP, 64	5	1 (NaTPB)	21.62±0.2
6	DBP, 63	5	2 (NaTPB)	25.84 ± 0.3
7	DBP, 63	5	2 (OA)	14.21±0.4
8	DBP, 60	5	5 (OA)	18.12±0.3
9	NB, 65	5	-----	13.02±0.5
10	DBP, 60	7	3 (OA)	16.42±0.4
11	DBP, 63	7	-----	26.50±0.3
12	DBP, 61	7	2 (NaTPB)	28.99±0.2
13	NB, 63	7	-----	11.10±0.3
14	DBP, 61	9	-----	20.23 ± 0.5

On the contrary, relatively noteworthy fluctuations in the potential *vs*. pH behavior took place below and above the formerly stated pH limits. In detail, the fluctuations above the pH value of 8.0 might be justified by the formation of the soluble and insoluble Pb^{2+} ion hydroxy complexes in the solution. On the other hand, the fluctuations below the pH value of 3.5 were attributed to the partial protonation of the employed ionophore.
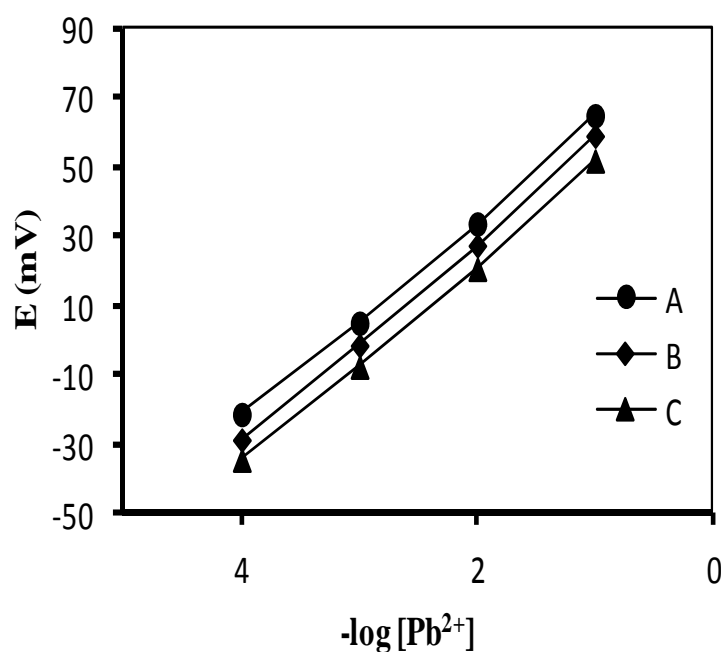
3.4. Internal Solution

The concentration of the internal solution ($Pb(NO_3)_2$) of the electrode was changed from 1.0×10^{-2} M to 1.0×10^{-4} M and the potential response of the Pb^{2+} selective electrode was obtained (Fig. 5). It was found that the variation of concentration of the internal solution does

not cause any significant differences in potential response, except for an expected change in the intercept of the resulting Nernstian plot. A 1.0×10^{-3} M concentration $Pb(NO_3)_2$ solution is quite appropriate for smooth functioning of the electrode system.
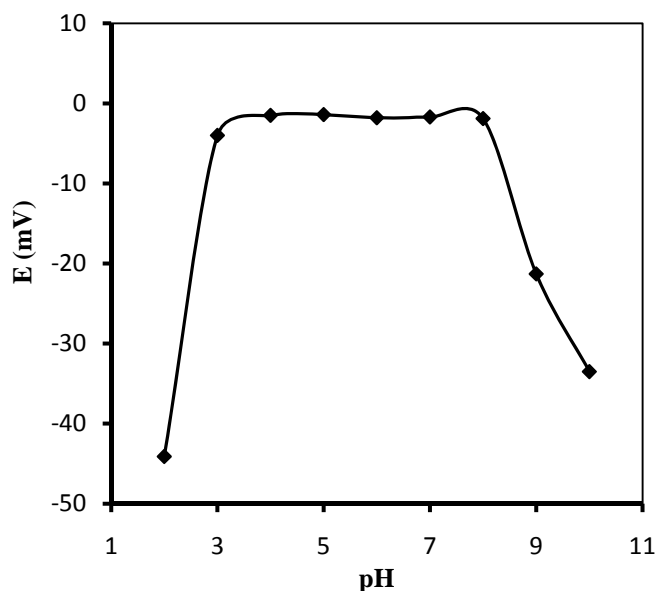
Fig. 4. The effect of the pH of the test solution (1.0×10^{-3} M Pb^{2+}) on the potential response of the lead sensor


Fig. 5. The effect of concentration of internal reference solution concentration on the electrode response; (A) 1.0×10^{-2} M, (B) 1.0×10^{-3} M, (C) 1.0×10^{-4} M of lead ion

3.5. Response Time

The response time of an electrode is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions-like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurements were performed, any previous usages or preconditioning of the electrode, and the testing temperature have an effort on the experimental response time of a sensor [28].

In this work, dynamic response time was obtained by changing the Pb^{2+} concentration in solution, over a concentration range 1.0×10^{-4} to 1.0×10^{-1} M. The actual potential versus time traces is shown in Fig. 6. As can be seen, in whole concentration range the electrode reaches its equilibrium response in a relatively short time (10 s).
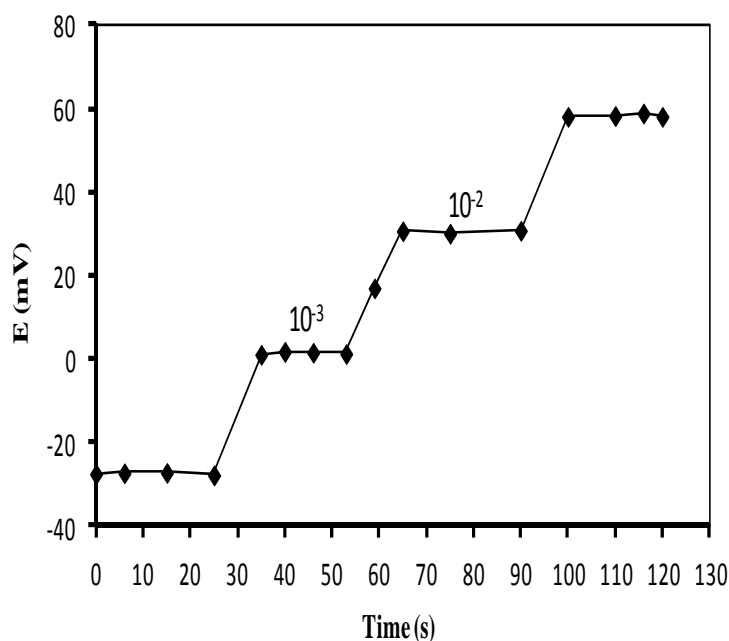
Fig. 6. Dynamic response of lead sensor for step changes in concentration of Pb^{2+}

3.6. Measuring Range

The measuring range of an ion-selective electrode includes the linear part of the calibration graph as shown in Fig. 7. For many electrodes the measuring range can extend from 1 molar down to 10^{-6} molar concentrations. The applicable measuring range of the proposed sensor is between 1×10^{-4} and 1×10^{-1} M.
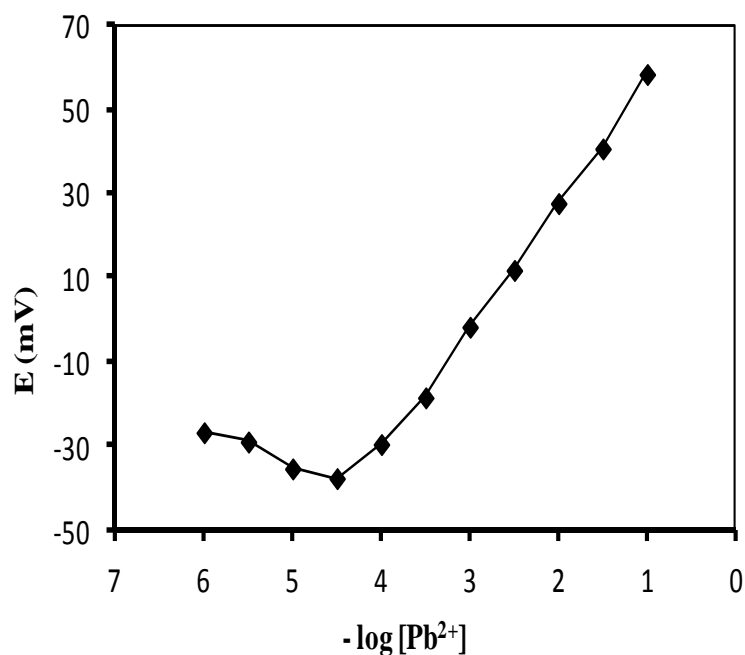
Fig. 7. The calibration curve of the Pb^{2+} membrane sensor based on SBA-15-3OH

3.7. Detection Limit

In practice, detection limits for the most selective electrodes are in the range of 10^{-5}–10^{-6} mol L^{-1}. In this work the detection limit of the proposed membrane sensor was 5.5×10^{-5} mol L^{-1} which was calculated by extrapolating the two segments of the calibration curve (Fig. 7).

3.8. Selectivity

The potentiometric selectivity coefficients of the Pb^{2+} sensor were evaluated by the matched potential method (MPM) [29]. The resulting values of the selectivity coefficients are given in Table 2. As can be seen from Table 2, for the all mono and bivalent metal ions tested, the selectivity coefficients are about 10^{-4} or 10^{-3}, which seems to indicate negligible interferences in the performance of the electrode assembly.

3.9. Lifetime

The average lifetime of this sensors was investigated by monitoring the changes in sensor slope with time. The sensors were tested for 14 days, during which time the electrodes were used extensively (one hour per day). Fig. 8 shows the changes in the slope of a sensor with time. The proposed sensors can be used for 9 days. It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors.

Table 2. The selectivity coefficients of various interfering cations for the membrane

| Ion	K_{MPM}
Na^+	7.0×10^{-4}
K^+	1.7×10^{-4}
Ba^{2+}	6.0×10^{-4}
Ca^{+2}	1.5×10^{-4}
Co^{+2}	1.8×10^{-4}
Fe^{3+}	6.0×10^{-4}
Ni^{2+}	8.1×10^{-4}
Cu^{2+}	1.7×10^{-3}
Zn^{2+}	2.0×10^{-3}
Cd^{2+}	7.7×10^{-4}
Ag^+	2.2×10^{-3}
Hg^{2+}	3.1×10^{-3}
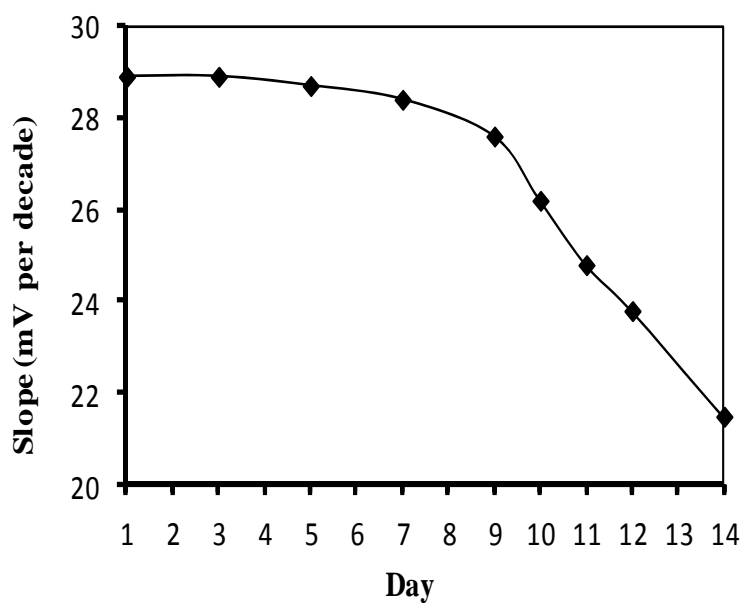
Fig. 8. The lifetime of the Pb^{2+} membrane sensor

3.10. Analytical Application

Ion-selective electrodes tend to be; low in cost, simple to use, easily automated for rapid sampling, with low interferences from the matrix, and can be applied to small volumes. These characteristics make them an ideal choice for both clinical and industrial measurements where speed, simplicity, and accuracy are essential.

The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for the titration of 20.0 mL of 1.0×10^{-4} M of Pb^{2+} solution with EDTA 1.0×10^{-2} M. The resulting titration curve is shown in Fig. 9. As can be seen, the amount of Pb^{2+} ions in solution can be accurately determined with the electrode.

To assess the applicability of proposed electrode in real samples an attempt was made to determine lead ions in wastewater sample. The electrode was applied to the direct measurement of lead ion in Islamic Azad university of Shahre rey laboratory wastewater samples. Wastewater samples were filtered using a 0.45-µm pore size membrane filter to remove suspended particulate matter. Two aliquot (10 mL) of the waste water were diluted to 100 mL, and the samples were adjusted to pH of about 6 and their potentials were measured by direct potentiometry. Also, the real concentration of lead in wastewater samples, after filtration and dilution, were determined by flame atomic adsorption spectrometry (FAAS) method. The results are given in Table 3. As seen, the agreement is good and we conclude that the membrane electrode may have applications in the environmental monitoring of lead ions.
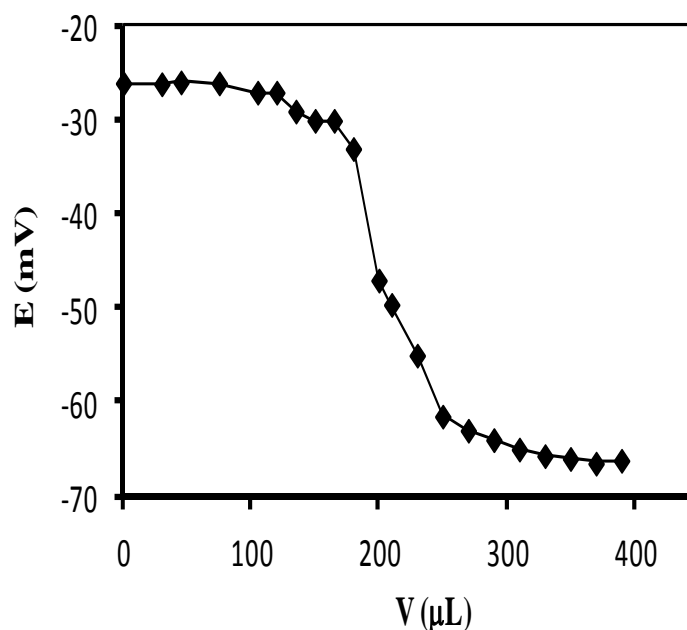
Fig. 9. Potentiometric titration curve of 20 mL 1.0×10^{-4} M Pb^{2+} with 1.0×10^{-2} M EDTA, using the proposed sensor as an indicator electrode

The proposed sensor was also applied to determination of lead in pepper samples. A 10 g black pepper was taken in a beaker and dissolved in concentrated nitric acid (20 mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 ml with water in a calibrated flask. An aliquot (20 mL) of the sample solution was taken and lead was determined by the calibration procedure. The results are given in Table 3. As seen the results obtained by the proposed method and FAAS are in satisfactory agreement.

Table 3. Determination of lead ions in real samples

Sample	Concentration of Pb^{2+} (ISE)	Concentration of Pb^{2+} (FAAS)
wastewater	221.6±3.1 (mg L^{-1})	223.4±2.4 (mg L^{-1})
Black pepper	404.9±4.2(µg g^{-1})	403.5±3.1 (µg g^{-1})

[a] % RSD based on three replicate analysis

4. CONCLUSIONS

The use of the hydroxymethyl-modified SBA-15 nanoporous silica for preparation of PVC membrane electrodes could be applied in the electroanalytical determination of Pb^{2+} for concentration in the mol L^{-1} level. Although a not so low detection limit is observed, but as a matter of fact, this sensor exhibited a fast response time and pH independent potential responses across the range of 3.5–8.0. Its selectivity towards the lead ions was not influenced by the presence of the common alkali, alkaline earth, or transition and heavy metal ions, since the interference of these substances was low. Reproducible results that agree with those from FAAS were obtained in relatively fast, low cost, low interference from the matrix and without need of time consuming sample preparation.

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