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Bulk optode sensors for batch and flow-through determinations of lead ion in water samples

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ABSTRACT

A sensitive optode consisting of highly lead-selective ionophore (Lead IV), proton-selective chromoionophore (ETH 5294) and lipophilic anionic sites (KT*p*ClPB) in plasticized polyvinyl chloride (PVC) membrane was fabricated. The optode membranes were used for determination of Pb^{2+} by absorption spectrophotometry in batch and flow-through systems. The influence parameters such as pH, type of buffer solution, response time and concentration of regenerating solution were optimized. The membrane responded to Pb^{2+} by changing its color from blue to pinkish purple in Tris buffer containing different concentration of Pb^{2+} at pH 7.0. The optode provided the response range of 3.16×10^{-8} to 5.00×10^{-5} mol L^{-1} Pb^{2+} with the detection limit of 2.49×10^{-8} mol L^{-1} in the batch system within the response time of 30 min. The dynamic range of 1.26×10^{-8} to 3.16×10^{-5} mol L^{-1} Pb^{2+} with detection limit of 8.97×10^{-9} mol L^{-1} were obtained in the flow-through system within the response time of 15 min. Moreover, the proposed optode sensors showed good selectivity towards Pb^{2+} over Na^+, K^+, Mg^{2+}, Cd^{2+}, Hg^{2+} and Ag^+. It was successfully applied to determine Pb^{2+} in real water samples and the results were compared with well-established inductively coupled plasma optical emission spectrometry (ICP-OES). No significant different value ($t_{critical} = 4.30 > t_{exp} = 1.00–3.42$, $n = 3$ at 95% of confidence level) was found.

1. Introduction

Many countries worldwide are increasing awareness of environmental problems and seeking the way to decrease environmental pollutions. In particular, the contamination of heavy metals in environment is one of the serious problems because even low contents of heavy metal can cause harmful effects to plants, animals and human. Among heavy metals, lead is a common toxic pollutant in the environment as a result of its use in storage batteries, cable sheath, gasoline antiknock products and paint pigments. The widespread uses cause environmental and health problems such as the cumulative poison and the retention of lead in the body for long periods [1].

The majority of lead determinations at the ppm–ppb levels are usually performed by using atomic absorption spectrometry (AAS). However, the detection limit of the instrument is not suitable with the presence of lead in environmental samples. Thus, the preconcentration step followed by spectrometric determinations and flow injection spectrometric methods have been employed [2–6]. Thus, more sophisticated techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) have been employed due to higher sensitivity but these instruments are costly and need specific maintenance. In addition to the existing common methods, lead ion-selective electrodes (ISEs) based on neutral ionophores containing oxygen, nitrogen and sulphur donor atoms have been reported [7–14]. Nevertheless, most of ISEs possessed serious interferences from various cations. Therefore, the highly sensitive, selective and rapid method for determination of trace level of lead is desirable.

Chemical optical sensors (optode) offer advantages such as simple preparation and procedure, relatively fast response, wide response range, reasonable selectivity and high sensitivity [15–16]. Recently, reviews covering the principles and mechanisms of bulk optode have been published [17–19]. The immobilization in various sensing reagents of optode membranes have been developed for many analytically relevant ions, especially heavy metal ions. Examples of optode membranes are 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol in Nafion for nickel ion [20], fatty hydroxamic acid in polymethylmethacrylate for vanadium ion [21], 2-hydroxy-1-(2-hydroxy-5-methylphenylazo)-4-naphthalenesulfonic acid in agarose membrane for copper ion

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[22], zincon-tetraoctylammonium immobilized on triacetylcellulose membrane for zinc ion [23]. However, a few bulk optodes for determination of Pb^{2+} have been published to date. Examples of ionophores in optode membranes used for determination of Pb^{2+} by absorption spectrophotometry or reflectance techniques are dioxaoctanediamide derivative plus protonated Nile blue [24], dithizone [25], oxodiamide derivative [26], and 1,10-dibenzyl-1,10-diaza-18-crown-6 with 1-(2-pyridylazo)-2-naphthol as chromoionophore [27]. In addition, the detection using fluorescence and phosphorescence spectrophotometry was also reported. For example, compounds such as tetra-substituted aluminum 2,3-napthalocyamine dyes [28], 3,3′,5,5′-tetramethyl-*N*-(9-anthrylmethyl)benzidine [29], *tert*-butylcalix[4]arene-tetrakis(*N,N*-dimetylthioacetamide) [30], 4-hydroxysalophen [31], and quinolinesulphonic acid derivatives [32] have been employed as fluorophore and phosphorophore for metal ion detection.

Normally, a design of ion-selective optode membrane for lead ion is focused on the choice of ionophore/chromoionophore. However, the practical use of bulk optode membranes for lead in real water samples, especially in a flow-through system has rarely been seen. In this work, a Pb^{2+} selective thin film optode incorporating *tert*-butylcalix[4]arene-tetrakis (*N,N*-dimetylthioacetamide) or Lead IV as lead-selective ionophore, ETH 5294 as proton-selective chromoionophore and potassium tetrakis (4-chlorophenyl) borate as lipophilic anionic sites plasticized in PVC membrane was manually fabricated by a simple casting technique. The membranes were used in the quantification of Pb^{2+} in various types of water sample using a common UV–vis spectrophotometer combined with a simple lab-made flow-through cell. The validation result was also demonstrated in comparison with a standard method.

2. Experimental

2.1. Chemicals and reagents

For the membrane preparation, high molecular weight poly(vinyl chloride) or PVC, bis(2-ethylhexyl)sebacate (DOS), potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB), *tert*-butyl calix[4]arene-tetrakis (*N,N*-dimetylthioacetamide) shown in Fig. 1(a), 9-(diethylamino)-5-(octadeca noylimino)-5H-benzo[a]phenoxazine (ETH 5294) shown in Fig. 1(b) and tetrahydrofuran (THF) were purchased from Fluka. The solvents were of analytical-reagent grade and used without further purification. All aqueous solutions were prepared using type quality water produced by Milli-Q purify-cation system (Millipore) with a specific resistivity of 18 $M\Omega\,cm^{-1}$.

Buffer solutions (1.0×10^{-3} mol L^{-1}) used were (i) Tris buffer (tris(hydroxyl methyl)-aminomethane, adjusted with 0.01 mol L^{-1} HCl), (ii) acetate buffer (sodium acetate adjusted with 0.01 mol L^{-1} NaOH) and (iii) citrate buffer (tri sodium citrate adjusted with 0.01 mol L^{-1} citric acid).

A stock solution of 1.0×10^{-2} mol L^{-1} Pb^{2+} was prepared by dissolving $Pb(NO_3)_2$ in Milli-Q water in an appropriate volume. Test solutions were prepared by serial dilution of the stock solution with the buffer solution. The Pb^{2+} solutions were buffered in order to provide nearly constant ionic strength. The activity coefficients in the aqueous solution were assumed to be constant so that the total concentration of measuring ions was used for calculations. The glassware was pretreated with 5% HNO_3 overnight before used.

2.2. Apparatus

The visible spectra and absorbance measurements were recorded on a Hewlett Packard diode array spectrophotometer, model 8453 (USA). Inductively coupled plasma optical emission spectrometric measurements were performed on Perkin Elmer, model PLASMA-1000 (USA). The pH values of sample solutions were determined with a pH glass electrode, Orion 2 star, model 9162BNWP and a pH meter, Orion, OR3557 (Taiwan).

A lab-made flow-through cell (Fig. 2) consisted of a rectangular 38 mm × 30 mm acrylic block of 10 mm height with cylindrical opening of 12 mm diameter in the middle (a), rectangular 38 mm × 30 mm acrylic block of 10 mm height as optical window with inlet (b) and outlet tubes (c), rectangular 20 mm × 25 mm vacuum plastic sheet as seal gasket with elliptical opening of 17 mm (d), cover glass slide as support for optode membranes (e). All parts of the flow-through cell were fixed with screws for clamping the block (f). The flow-through cell system consisted of a peristaltic pump Ismatec model ISM 827, the lab-made flow-through cell, the connecting Tygon tube R3607 (2.79 mm i.d.), and a Teflon FEP tube (0.50 mm i.d.). Experiments were performed by setting the flow-through cell in the optical path of the spectrophotometer. The reference of the flow-through cell consisted of a glass slide without the membrane. Prior to analysis, the flow-through cell system was cleaned sequentially using 1.0 mol L^{-1} HNO_3 and Milli-Q water for 5 min.

2.3. Optode membrane preparation

A mixture of membrane cocktail solution containing 0.95 mg (10 mmol kg^{-1}) of lead-selective ionophore, 0.22 mg (5 mmol kg^{-1}) of KT*p*ClPB, 0.12 mg (2.5 mmol kg^{-1}) of ETH 5294, 29.57 mg of PVC and 59.14 mg of DOS was dissolved in 2.0 mL THF in a glass vial. The mixture was immediately shaken to obtain a clear homogeneous solution.

An aliquot of 50 μL cocktail solution was spread on a square microscope cover glass (22 × 22 mm) using micropipette. Prior to spread, the microscope cover glasses were cleaned with THF to remove organic impurities and dust. The membranes were dried at 23 ± 1 °C and 40 ± 4% humidity for at least 30 min before use. The homogenous, transparent and pinkish purple membranes were obtained. The fabricated membranes were kept in a desiccator.

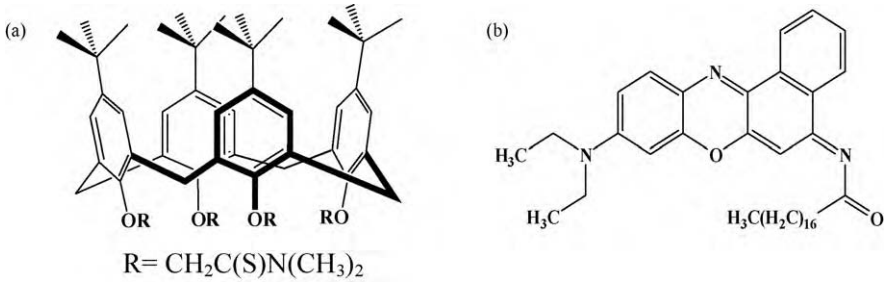

Fig. 1. Structures of (a) lead-selective ionophore and (b) chromoionophore.

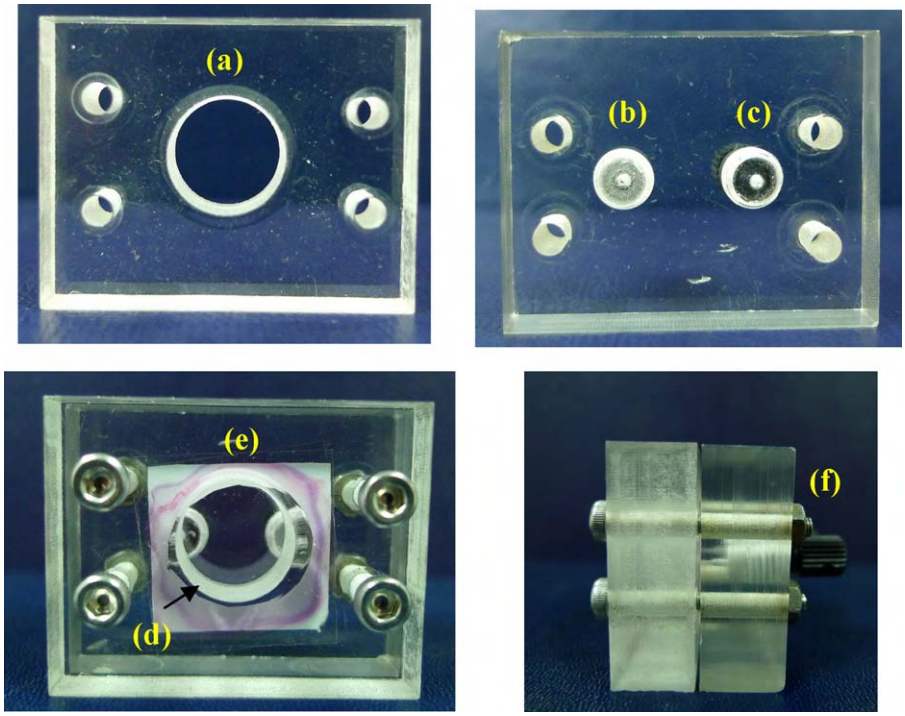

Fig. 2. Parts of lab-made flow-through cell (a) acrylic block, (b) and (c) inlet and outlet tubes on optical window, (d) seal gasket, (e) optode membrane and (f) fixing screws.

2.4. Absorbance measurements

The absorbance measurements of the optode membrane were performed over the wavelength range of 400–800 nm in three steps as follows:

Step 1. An optode membrane was conditioned by immersing in a 0.01 mol L^{-1} HCl as conditioning solution for 5 min to obtain fully protonated chromoionophore and then rinsed with Milli-Q water. The absorbance of the conditioned optode membrane (A_{prot}) was recorded when a cover glass without membrane was used as blank [24,33–34].

Step 2. The conditioned optode membrane was rinsed with Milli-Q water and then exposed to a Pb^{2+} solution for 30 min or until reach equilibrium and then rinsed with Milli-Q water. The absorbances of the optode membrane were measured.

Step 3. This optode membrane was regenerated by immersing in a regenerating solution to elute Pb^{2+} from the membrane and then rinsed with Milli-Q water. The same process was repeated for 3 times ($n = 3$).

A fully deprotonated chromoionophore membrane was prepared by immersing in a 0.01 mol L^{-1} NaOH for 5 min and then rinsed with Milli-Q water. The absorbance of this optode membrane (A_{deprot}) was also recorded.

The measured absorbance is directly related to the membrane response [19], thus

$$\alpha = \frac{A_{prot} - A}{A_{prot} - A_{deprot}} \quad (1)$$

where α is the degree of deprotonation of chromoionphore, A is the absorbance of the chromoionophore for a giving equilibrium, A_{prot} and A_{deprot} are the absorbance values of the fully protonated ($\alpha = 0$) and fully deprotonated ($\alpha = 1$) forms of the chromoionophore, respectively.

The condition, measurement and regeneration steps for the flow-through measurement were investigated by passing 0.01 mol L^{-1} HCl, Tris buffer solution containing Pb^{2+} and 0.10 mol L^{-1} HNO_3, respectively, through the membrane.

2.5. Sample preparation

Water samples (pond water, tap water and drinking water) were collected in the polyethylene bottles and adjusted to pH 2 with nitric acid. Pond water sample was filtered to remove particles before use. Determinations of Pb^{2+} in water samples were carried out with spiked method. Standard Pb^{2+} was spiked into 50.0 mL of the water sample. The water samples were diluted with Tris buffer (pH 7.0) to a final volume of 100 mL. The absorbance measurements of the optode membrane were performed in both batch and flow-through systems under the optimum conditions. The experiments were performed in triplicate ($n = 3$).

3. Result and discussions

3.1. Effect of pH and type of buffer

The response characteristics of optode such as sensitivity, response range and detection limit depend on pH [26]. The optode response is based on the exchange of Pb^{2+} and H^+ between the membrane and aqueous phases. Therefore, the pH of the test solution has to be kept constant by buffering. Thus, the buffer solution in the experiment should not interfere the measurement of Pb^{2+}.

Fig. 3 illustrated the degree of deprotonation (α) in a function of pH. The absorbance of the optode membrane was recorded at 660 nm after equilibration for 30 min. The maximum response, which is the highest sensitivity, was experimentally found at pH 7. The decreased response at lower pH was probably due to the extraction of proton (H^+) from the aqueous solution into the membrane. At pH > 7.0, the reduced response may be due to the hydrolysis reaction of Pb^{2+} giving $Pb(OH)^+$ resulting in the decreasing of the actual concentration of Pb^{2+} in the solution. Moreover, we also studied the responses of the optode at pH 5.0, 6.0, 7.0 in various concentrations of Pb^{2+} (Fig. 4). It was found that the maximum response and widest response range were obtained at pH 7. Therefore, pH 7 was chosen as the working pH. An appropriate buffer solution was examined by using 1.00×10^{-3} mol L^{-1} of acetate, citrate and

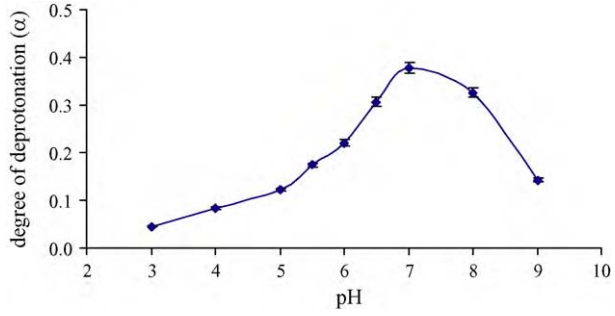

Fig. 3. The pH effect on the optode response at 660 nm in the presence of 3.16×10^{-6} mol L^{-1} Pb^{2+}.

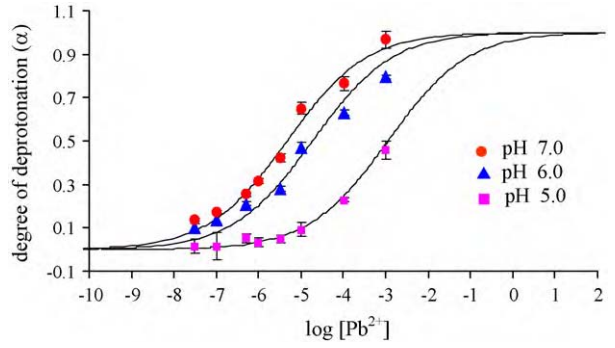

Fig. 4. The response of lead-selective optode at pH 5.0, 6.0, 7.0 in various concentrations of Pb^{2+}.

Tris buffers adjusted to pH 7.0. The optode response in Tris buffer had a greater response range than that of acetate buffer and citrate buffer.

3.2. Response time

The response time of the optode was controlled by the time required for the analyte to diffuse from bulk solution to the membrane adducting by the ionophore. The response time of the fabricated optode membrane was defined as the time required to reach 99% (t_{99}) of steady signal absorbance. It would be desirable for the optode to have a short response time. The response time of the optode depended on the membrane thickness, membrane composition, activity of the measuring ion and the pH of the measurement [35].

The observation of 99% steady signal absorbance was found within 15–30 min depending on the concentration of Pb^{2+}.

3.3. Response behavior

The diversities of the optodes in plasticized PVC membrane with high selectivity for lead have been described [24]. The response of the proposed optode was based on a cation-exchange mechanism. Ionophore (L) induced the extraction of Pb^{2+} into the membrane, at the same time hydrogen ion of the chromoionophore (CH^+) was released from the membrane to maintain the electroneutrality of the system. Then, Pb^{2+} in the membrane phase formed a complex with an ionophore. Therefore, the absorption spectra of the membrane changed with the concentration change of Pb^{2+} in solution.

The absorption spectra of the optode membrane were recorded after equilibration in Tris buffer solution (pH 7.0) containing different concentrations of Pb^{2+} in the range of 3.16×10^{-8}–5.00×10^{-3} mol L^{-1} in comparison with the absorption spectrum of fully protonated chromoionophore (0.01 mol L^{-1} HCl) and the absorption spectrum of fully deprotonated chromoionophore (0.01 mol L^{-1} NaOH). The results were shown in Fig. 5.

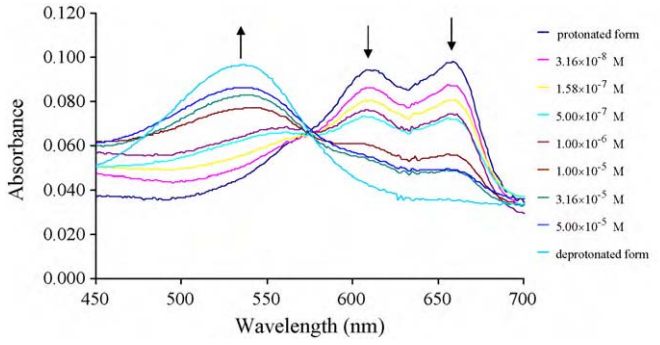

Fig. 5. Absorption spectra of the optode membranes after equilibrium in Tris buffer solutions containing different concentrations of Pb^{2+} (pH 7.0).

The absorption spectrum of the fully protonated membrane showed two absorption bands at 616 and 660 nm which correspond to the protonated form of the chromoionophore (CH^+), and the color of the membrane was blue. When the concentration of Pb^{2+} increased, the deprotonation of the chromoionophore occurred, resulting in a change from blue to pinkish purple. Thus, a reduction in the absorption band at 616 and 660 nm and an increase in the absorption band at 545 nm were observed.

If a 1:1 stoichiometry was assumed for the complexation of Pb^{2+} in the membrane phase, the equilibrium between the membrane phase (mem) and the sample solution phase (aq) can be described by Eq. (2):

$$Pb^{2+}_{(aq)} + L_{(mem)} + CH^{+}_{(mem)} + R^{-}_{(mem)} \overset{K^{Pb}_{exch}}{\rightleftharpoons} PbL^{2+}_{(mem)} + C_{(mem)} + H^{+}_{(aq)} + R^{-}_{(mem)} \quad (2)$$

The ion-exchange constant (K^{Pb}_{exch}) corresponding to the upper equilibrium was expressed by Eq. (3):

$$K^{Pb}_{exch} = \frac{[PbL^{2+}][H^+][C]}{[Pb^{2+}][CH^+][L]} \quad (3)$$

where PbL^{2+} and CH^+ represented the ionophore–lead complex and the protonated chromoionophore, respectively.

The response function for Pb^{2+} can be derived as shown in Eq. (4): [17]

$$[Pb^{2+}] = \frac{1}{K^{Pb}_{exch}} \left(\frac{\alpha[H^+]}{1-\alpha} \right)^{z} \left[\frac{R^{-}_{tot} - (1-\alpha)C_{tot}}{z(L_{tot} - \frac{n}{z}\{R^{-}_{tot} + (1-\alpha)C_{tot}\})^{n}} \right] \quad (4)$$

where $1-\alpha$ is the degree of protonation of the chromoionophore, R^{-}_{tot} is the total concentration of anionic sites, L_{tot} is the total concentration of ionophore, and C_{tot} is the total concentration of chromoionophore in the membrane. z is the charge of Pb^{2+} ($z=2$) and n is the ion–ionophore complex stoichiometry ($n=1$). The logarithmic form of Eq. (4) shows the dependence between the concentration of Pb^{2+} and the degree of protonation of chromoionophore ($1-\alpha$) since all the other terms are constant for each analytical system. When plotting $1-\alpha$ versus $\log[Pb^{2+}]$, a sigmoidal curve is obtained. All calculated curves are fitted to the experimental data by varying K^{Pb}_{exch} in Eq. (4). This confirms the validity of Eq. (2) in explaining the response mechanism of the fabricated optode membrane towards Pb^{2+} and stoichiometry obtained in the solution phase.

3.4. Repeatability and reproducibility

The repeatability of the optode membrane was performed by repetitive exposure of the single optode membrane ($n = 10$), which was prepared from the same cocktail solution. The reproducibility of the optode membrane was evaluated by measuring the absorbance of twelve membranes. Therefore, the regeneration process is an important step in these studies. The efficiency of the regenerating solution was counted on the regeneration time which was defined as the time taken for reaching the baseline signal (the signal observed in 0.01 mol L^{-1} HCl as conditioning solution), where the minimum absorbance has been reached at the wavelength of 545 nm.

When 0.01 mol L^{-1} HCl solution was used, the color of the regenerated membrane did not change after immersing in Pb^{2+} solution at any response time. Therefore, HCl solution was not a good regeneration solution. However, 0.10 mol L^{-1} HNO_3 could fully regenerate optode membrane within 5 min.

The relative standard deviation (R.S.D.) of the absorbance for repeatability and reproducibility, 2.3% and 4.1% respectively, were obtained. These R.S.D. values were acceptable for the fabricated membrane to operate in the condition described.

3.5. Short-term stability and lifetime

The *short-term stability* of the optode membrane was defined in term of the stability of absorbance of the optode membrane. The absorbance was recorded at 660 nm over a period of at least 6 h [36–38] by recording the UV–vis spectrum every 30 min intervals ($n = 12$), giving 1.0% R.S.D. This indicated a satisfied short-term stability.

The *lifetime* of the optode membrane described by the stability of the absorbance of the optode membrane at 545 nm in the ambient conditions on recording for a period of 30 days [36–37] in comparison with the absorbance at 545 nm of a freshly prepared optode membrane. The observed absorption changes are 1.7%, 3.9%, 4.8% and >10% after 7, 15, 20 and 30 days, respectively. The R.S.D was 1.6% for 20 absorption values. Therefore, the lifetime of optode membrane which stored in ambient condition was at least 20 days before use. However, the fabricated membrane could be used efficiently within 7 days.

3.6. Flow-through measurement

A membrane was placed in the flow-through measuring cell. Then, 0.01 mol L^{-1} HCl and milli-Q water were consecutively passed through the membrane at a flow rate of 1.6 mL min^{-1} for 3 min. Tris buffer solution at pH 7.0 containing 1.00×10^{-6} mol L^{-1} Pb^{2+} was passed through the membrane at different flow rates from 0.9 to 7.5 mL min^{-1} for 30 min. The absorbance of each optode membrane was recorded at 660 nm. The response of the membrane in various flow rates was then determined. Fig. 6 showed that the optode response decreased as the flow rate increased in the range of 3.8–7.5 mL min^{-1} because of less contact time between Pb^{2+} and the optode membrane. The maximum degree of deprotonation was obtained at a flow rate of 1.6 mL min^{-1} with high response and less time-consuming of sampling solutions.

The response time of the optode membrane to reach 99% of steady signal absorbance was 15 min. The response time in the flow-through system was better than that in the batch system probably due to the faster mass transfer rate of a solute between solution/membrane interfaces which the concentration gradient in the flow system is higher than that in the batch system. The repeatability and reproducibility of the optode membrane in the flow-through system were evaluated in the same manner as described in the batch system. The R.S.D. values of responses were 1.2% ($n = 10$) and 2.7% ($n = 9$), respectively.

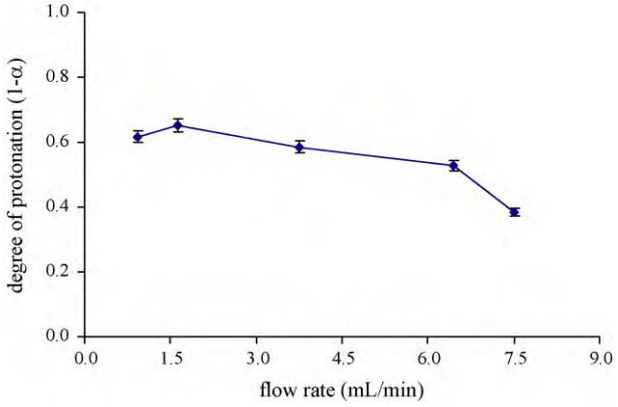

Fig. 6. Responses of the optode membrane for 1.00×10^{-6} mol L^{-1} Pb^{2+} at different flow rates of 0.9–7.5 mL min^{-1}.

3.7. Analytical performance of proposed method

The linearity of the sigmoidal response curve is usually employed for analysis, defined as a linearity between a lower and an upper detection limit. The lower detection limit can be estimated from different approximates [9,18,24,33]. In order to determine the detection limit, two series of Pb^{2+} standard solutions were prepared. A maximum slope zone (8 standards, 3.16×10^{-8} to 5.00×10^{-5} mol L^{-1}) was obtained with linear functions of $1 - \alpha = -0.2346 \log [Pb^{2+}] - 0.8243$ (Fig. 7). The lower detection limit was defined as the concentration at the intersection of two linear functions of the maximum slope and the minimum slope. The interception of both functions gave a detection limit (DL) of 2.49×10^{-8} mol L^{-1}. A practical upper detection limit obtained from the intercept of the linear calibration function with the axis of abscissa was found at 1.00×10^{-3} mol L^{-1}. The central zone of the sigmoidal curve showed a straight line that was a dynamic range of the optode. A dynamic range of 3.16×10^{-8} to 5.00×10^{-5} mol L^{-1} was obtained in the batch system.

In the flow-through system, the linear equations were $1 - \alpha = -0.1994 \log [Pb^{2+}] - 0.6294$. The lower and upper detection limit values were 8.97×10^{-9} and 3.16×10^{-3} mol L^{-1}, respectively. A dynamic range of 1.26×10^{-8} to 3.16×10^{-5} mol L^{-1} was obtained.

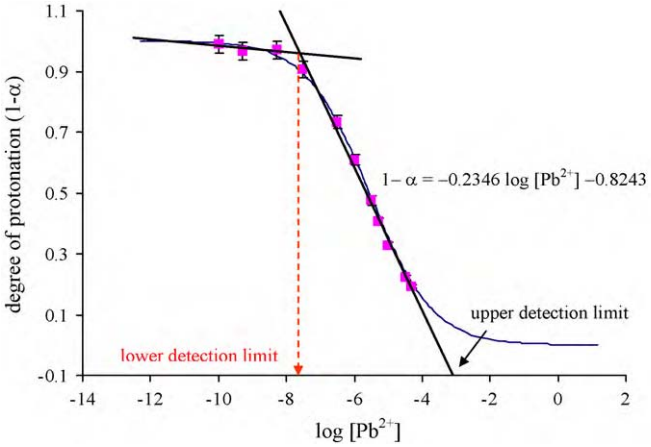

Fig. 7. Sigmoidal response curves of the optode membrane with the intersection of two linear functions for determination of detection limit in the batch system.

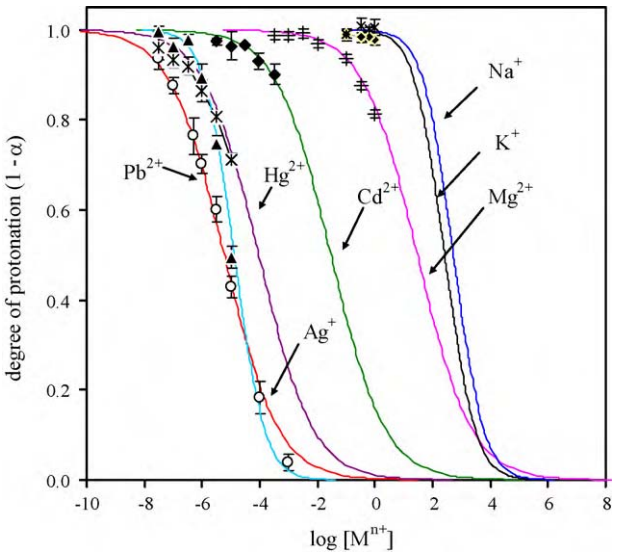

Fig. 8. Response curves of the optode membrane in various interfering ions at pH 7.0.

3.8. Selectivity

The influence of the common interfering ions on the optode response of the proposed Pb^{2+} optode membrane was investigated. The selectivity coefficient depended on the pH and the degree of protonation of the chromoionophore [26]. The optical selectivity of the fabricated optode membrane over common interfering ions was carried out by separated sample solution method (SSM) [19]. The response of optode membrane in the presence of different concentrations of each interfering ion was measured and selectivity coefficients ($K^{opt}_{Pb,M}$) were determined by graphically plotting the corresponding $(1-\alpha)$ versus log concentration of interfering ions ($\log C_M$) shown in Eq. (5).

$$K^{opt}_{Pb,M} = \frac{z^M}{z^{Pb}} \frac{K^M_{exch}}{K^{Pb}_{exch}} \left(\frac{\alpha[H^+]}{1-\alpha}\right)^{z^{Pb}-z^M} \frac{\left([L_{tot}] - \frac{n_M}{z^M}\left\{[R^-_{tot}] - (1-\alpha)[C_{tot}]\right\}\right)^{n_M}}{\left([L_{tot}] - \frac{n_{Pb}}{z^{Pb}}\left\{[R^-_{tot}] - (1-\alpha)[C_{tot}]\right\}\right)^{n_{Pb}}} \quad (5)$$

where z^M,z^{Pb} are the charge of the interfering ion M and Pb^{2+}, n_M , n_{Pb} are the ion interfering–ionophore complex stoichiometry and lead–ionophore complex stoichiometry ($n = 1$), respectively.

The response curves of the optode membrane in various interfering ions are illustrated in Fig. 8 and the selectivity coefficients ($K^{opt}_{Pb,M}$) were calculated at the highest sensitivity ($\alpha = 0.5$). Log $K^{opt}_{Pb,M}$ values of Ag^+, Hg^{2+}, Cd^{2+}, Mg^{2+}, K^+ and Na^+ were −0.35, −1.20, −3.70, −6.70, −7.65 and −7.95, respectively. The strong preference of Pb^{2+} over Na^+, K^+, Mg^+, Cd^{2+} and Hg^{2+} was due to its specific binding capability [14].

Some characteristics of the optodes used for determination of Pb^{2+} by absorption spectrophotometry are compared with other optodes listed in Table 1. Although, the insignificant difference of the working range and the detection limit were observed but our optode showed high preference to Pb^{2+} over alkali, alkaline earth metals, especially over Cd^{2+} and Hg^{2+}. This indicated that the fabricated optode could apply to determine Pb^{2+} in natural water. Moreover, regeneration of the fabricated optode was achieved within only 5 min in comparison with that reported by Alizadeh et al. [27].

3.9. Application to real water samples

This proposed method was successfully applied to determine Pb^{2+} in different real water samples under the optimum conditions either batch or flow-through systems with the satisfied recover-

Table 1
Comparison of some characteristics of lead optode in plasticized PVC membranes.

Ionophore	Response time	Working range (mol L^{-1})	Detection limit (mol L^{-1})	Remarks	Ref.
ETH 5435 (flow-through system)	Order of minutes, up to 220 min if lower concentration	5.0×10^{-9}–5.0×10^{-3} at pH 5.68	3.2×10^{-12}	Cd^{2+}, Ag^+ and Cu^{2+} interfere, Hg^{2+} irreversible change in membrane	[24]
ETH 5493 (flow-through system)	–	1.0×10^{-7}–1.0×10^{-2} at pH 5.0	–	Cd^{2+} interfere, Cu^{2+} causes drifting signals	[26]
DBzDA18C6 (batch system) Lead IV	20 min Batch system	1.0×10^{-8}–5.0×10^{-5} at pH 5.0	1.0×10^{-8}	Use long time to regenerate (2 h)	[27]
	30 min Flow-through system	3.2×10^{-8}–5.0×10^{-5} at pH 7.0	2.5×10^{-8}	Ag^+ slightly interfere lifetime = 7 days, regenerate time = 5 min	This work
	15 min	1.3×10^{-8}–3.2×10^{-5} at pH 7.0	9.0×10^{-9}		

Table 2
The determination of Pb^{2+} in real water samples in batch and flow-through systems.

Sample	Batch system			Flow-through system		
	Added ($mg\,L^{-1}$)	Found ± SD ($mg\,L^{-1}$)[a]	Recovery (%)	Added ($mg\,L^{-1}$)	Found ± SD ($mg\,L^{-1}$)[a]	Recovery (%)
Pond water	–	<DL	–	–	<DL	–
	3.16×10^{-6}	$(3.06\pm0.02)\times10^{-6}$	97	3.16×10^{-7}	$(2.88\pm0.01)\times10^{-7}$	91
	1.00×10^{-5}	$(0.97\pm0.01)\times10^{-5}$	97	1.00×10^{-6}	$(0.93\pm0.01)\times10^{-6}$	93
	3.16×10^{-5}	$(2.95\pm0.02)\times10^{-5}$	93	3.16×10^{-6}	$(2.88\pm0.01)\times10^{-6}$	91
Tap water	–	<DL	–	–	<DL	–
	3.16×10^{-6}	$(3.02\pm0.01)\times10^{-6}$	96	3.16×10^{-6}	$(2.87\pm0.01)\times10^{-6}$	91
	1.00×10^{-5}	$(0.96\pm0.01)\times10^{-5}$	96	1.00×10^{-5}	$(0.91\pm0.01)\times10^{-5}$	91
	3.16×10^{-5}	$(3.05\pm0.01)\times10^{-5}$	97	3.16×10^{-5}	$(3.19\pm0.01)\times10^{-5}$	101

[a] Mean value of three determinations.

Table 3
The comparison results of the proposed method (flow-through system) and ICP-OES for determination of Pb^{2+} in real water samples.

Sample	Added	Optode method		ICP-OES	t-statistics ($t_{0.05,3}=4.30$)
		Found ± SD ($mol\,L^{-1}$)[a]	Recovery (%)	Found ± SD ($mol\,L^{-1}$)[a]	
Drinking water (1)	–	<DL	–	<DL	–
	3.16×10^{-6}	$(3.19\pm0.01)\times10^{-6}$	101	$(3.16\pm0.02)\times10^{-6}$	2.61
	5.01×10^{-6}	$(4.82\pm0.01)\times10^{-6}$	96	$(4.66\pm0.01)\times10^{-6}$	1.86
Drinking water (2)	–	<DL	–	<DL	–
	3.16×10^{-6}	$(3.13\pm0.01)\times10^{-6}$	99	$(3.36\pm0.03)\times10^{-6}$	1.90
	5.01×10^{-6}	$(4.99\pm0.02)\times10^{-6}$	97	$(5.06\pm0.02)\times10^{-6}$	1.00
Pond water	–	<DL	–	<DL	–
	1.00×10^{-6}	$(0.92\pm0.01)\times10^{-6}$	92	$(1.01\pm0.02)\times10^{-6}$	3.24
	3.16×10^{-6}	$(2.89\pm0.01)\times10^{-6}$	91	$(3.25\pm0.02)\times10^{-6}$	3.42
	1.00×10^{-5}	$(9.33\pm0.01)\times10^{-6}$	93	$(9.75\pm0.02)\times10^{-6}$	1.06
Tap water	–	<DL	–	<DL	–
	1.00×10^{-6}	$(0.91\pm0.02)\times10^{-6}$	91	$(1.08\pm0.02)\times10^{-6}$	1.11
	3.16×10^{-6}	$(2.87\pm0.02)\times10^{-6}$	91	$(3.18\pm0.02)\times10^{-6}$	1.01
	1.00×10^{-5}	$(9.66\pm0.02)\times10^{-6}$	97	$(9.55\pm0.02)\times10^{-6}$	1.74

[a] Mean value of three determinations.

ies (Table 2). Sample throughput in flow-through system was 4 samples h^{-1}.

The results obtained from flow-through measurements were compared with the results determined by ICP-OES. The statistical t-test was used to compare the experimental means obtained from the proposed optode membrane and ICP-OES. The results were summarized in Table 3. No significant different value ($t_{critical}=4.30>t_{exp}=1.00$–$3.42$, $n=3$, 95% of confidence level) was found in both flow-through method and ICP-OES.

4. Conclusions

We have successfully fabricated the bulk optode by a simple casting technique for the determination of Pb^{2+}. In the batch system, the response range of 3.16×10^{-8} to 5.00×10^{-5} $mol\,L^{-1}$ Pb^{2+} with the detection limit of 2.49×10^{-8} $mol\,L^{-1}$ and the response time of 30 min were obtained. In the flow-through system, the dynamic range of 1.26×10^{-8} to 3.16×10^{-5} $mol\,L^{-1}$ Pb^{2+} with detection limit of 8.97×10^{-9} $mol\,L^{-1}$ were obtained at a flow rate of 1.6 mL min^{-1}. The response time of the flow-through system was 15 min. The proposed optode showed high preference to Pb^{2+} over Na^+, K^+, Mg^{2+}, Cd^{2+}, Hg^{2+} and Ag^+. Moreover, the application of the proposed optode to determine Pb^{2+} in real water samples, pond water, tap water and drinking water, provided high accuracy and high precision.

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