

Cite this: *RSC Adv.*, 2015, 5, 39209

Cesium selective polymeric membrane sensor based on *p*-isopropylcalix[6]arene and its application in environmental samples

Saeid Ahmadzadeh,^{*a} Majid Rezayi,^b Anuar Kassim^c and Majid Aghasi^d

The present work deals with developing a highly selective membrane electrode based on *p*-isopropylcalix[6]arene for accurate determination of trace amounts of cesium cations. The amounts of ionophore (5 mg), PVC (30 mg), dioctyl phthalate (DOP) as a plasticizer (62 mg) and potassium tetrakis(4-chlorophenyl)borate (KTPClPB) as an ionic additive (3 mg) were optimized in the preparation of the membrane. The effects of various parameters such as pH, composition of the membrane, different cation interferences and concentration of internal solution were investigated. The electrode exhibited a linear response with a near Nernstian slope of 57.29 ± 0.31 (mV per decade of activity) over the pH range from 2 to 11 with a satisfactory concentration range of 1.0×10^{-6} to 1.0×10^{-1} M. The value of 1.0×10^{-6} M was obtained as a lower detection limit for the fabricated cesium-selective electrode. The developed sensor exhibited a good reproducibility over a period of about 12 weeks with a fast response time of less than 10 seconds. The proposed sensor was successfully applied as an indicator electrode for the potentiometric titration of a cesium solution with EDTA. The validation of the developed electrode was done using an inductively coupled plasma technique (ICP) which confirmed the accuracy and precision of the fabricated electrode in the successful determination of cesium trace amounts in the environmental samples.

Received 12th February 2015

Accepted 20th April 2015

DOI: 10.1039/c5ra02799c

www.rsc.org/advances

Introduction

In recent years, nuclear energy has emerged as an essential energy source that can be used widely in different fields. As a result of more nuclear reactors being set up worldwide, increasing amounts of radioactive waste are generated. ^{137}Cs and ^{90}Sr are two of the main fission products. The toxic, non-biodegradable and long lived ($t_{1/2} = 31.2$ year) cesium will lead to catastrophic effects if it is not well-handled.¹ The spillage of cesium into the environment causes critical land and water contamination. Subsequently, it is possible to be transported into human body *via* food chains. Accumulation of cesium in human body will displace potassium from muscles and red cells. Hence, selective removal, safe disposal and accurate determination of its concentration in waste radioactive solution have become a great challenge.^{2,3}

ISEs and the supplementary equipments for the determination of ion concentration are relatively cheaper compared to the other common analytical methods such as atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission and mass spectroscopy (ICP-OES and ICP-MS) and ion chromatography (IC). While the instrumental methods can only determine the total concentration of the ions, ISEs offer the advantage of determining free ions activity with non-destructive sample analysis. The respond of the ISEs to the activity instead of concentration of the ions in solution, has nominate them as a useful chemical sensor for physiological measurements.^{4–7} Other considerable advantages that caused extensive usage of ISEs are their simplicity of preparation and ease of application, fast response time, wide dynamic range with significant low detection limit even to ppb and ppt levels, superior reproducibility with high selectivity towards the ion of interest and their durability for continuous monitoring in environmental, agricultural, industrial and biological fields.^{8–15} So far, most of the reported cesium selective electrodes suffered from poor selectivity, narrow dynamic range, non-Nernstian response, slow response time, and poor reproducibility.^{16–20} Therefore, in the current work, great attempts have been made to develop novel cesium selective membrane sensor, aiming to improve the mentioned disadvantages and can be applied for accurate measuring of trace amount of cesium(I) cations in various environmental samples.

^aPharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran. E-mail: chem_ahmadzadeh@yahoo.com; saeid.ahmadzadeh@kmu.ac.ir; Fax: +98 343 1325003; Tel: +98 343 1325241

^bUM Center for Ionic Liquids, Chemistry Department, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

^cDepartment of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

^dHerbal and Traditional Medicine Research Centre, Kerman University of Medical Sciences, Kerman, Iran

Experimental

Reagent and materials

All reagents used in the current research are analytical reagent grade with the highest available purity which used without any further purification except for vacuum drying over P_2O_5 . The novel ionophore namely *p*-isopropylcalix[6]-arene (*p*-IPC6) was purchased from Merck. Four plasticizers namely dioctyl phthalate (DOP), dibutyl phthalate (DBP), 2-nitrophenyl octyl ether (*o*-NPOE), nitrobenzene (NB) and four lipophilic additives namely potassium tetrakis(4-chlorophenyl)borate (KTPClPB), sodium tetra phenyl borate (NaTPB), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) and tetradodecylammoniumtetrakis(4-chlorophenyl)-borate (TDATpClPB) were purchased from Sigma-Aldrich and Fluka. All nitrate and chloride salts with the highest available purity were purchased from Merck, Sigma-Aldrich, Fluka and Fisher Scientific. High molecular weight polyvinyl chloride (PVC) was purchased from Sigma-Aldrich. Tetrahydrofuran (THF) was used as the solvent obtained from Merck. Nitric acid (HNO_3) and sodium hydroxide (NaOH) all from Merck were used for pH adjustments. In all cases, a 0.100 M stock solution of cationic salts was prepared by dissolving an appropriate and accurate amount of nitrate or chloride salts. The 1.0×10^{-1} M to 1.0×10^{-6} M solutions of cationic salts were prepared daily by sequential dilution of the appropriate stock solution with double distilled de-ionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) (Fig. 1).

Apparatus and EMF measurement

All potential measurements were performed at laboratory ambient temperature (25°C) versus Metrohm double junction reference electrodes. pH adjustments of the solutions were performed versus a Mettler Toledo pH electrode. Both of them were done by using Mettler Toledo Ion Meter (seven multi, Ion pH/mV/ORP). A Perkin-Elmer Lambda spectrophotometer (model 1650 PC SHIMADZU) was used to obtain the optical absorption data which predicate on the complex reaction

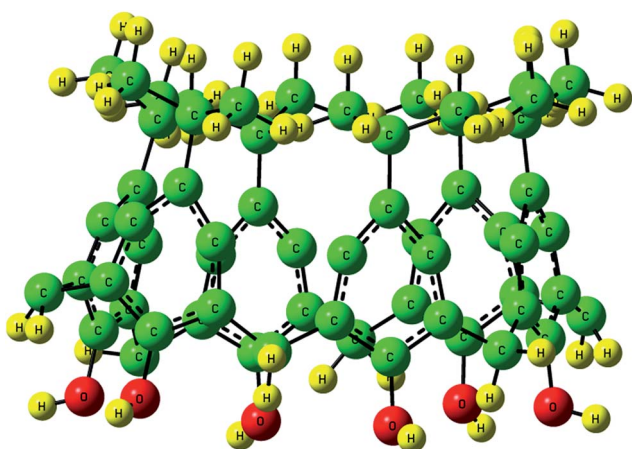
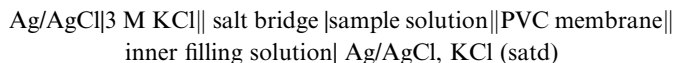


Fig. 1 Chemical structure of *p*-isopropylcalix[6]arene.

between ionophore and cesium(i) cation. A Perkin-Elmer emission spectrometer (model Optima 2000DV, sequential scanning inductively coupled plasma-atomic emission spectrometer ICP-AES) was used to validate the accuracy of the developed cesium(i) selective electrode by comparing the obtained data with the data acquired from ICP. Moreover, SEM studies of membrane morphology were performed using Philips scanning electron microscope (Model XL30E SEM).

The electrochemical cell for the EMF measurements is presented as below:



Phase boundary model was employed to explain the mechanism of ISEs response and the modified Nicolsky–Eisenman equation was used to evaluate the response of the developed ISEs with any combination of target and interfering ion charge.^{21–23}

Electrode preparation

To prepare the membrane 30.0 mg of PVC as a polymeric matrix, 5.0 mg of *p*-IPC6 as an ionophore, 62 mg of DOP as a plasticizer and 3 mg of KTPClPB as a lipophilic additive were dissolved in 3 mL of fresh THF. The solvent was evaporated slowly under inert atmosphere at room temperature, until an oily concentrated mixture was obtained. A Pyrex tube (with a tip diameter of 3 mm o.d) was dipped into the oily mixture for about 10 seconds. Then, the tube was pulled out from the mixture and kept at room temperature for ~ 24 hours so that a non-transparent film of ~ 0.3 mm thickness was formed. After that, the tube was filled with the 1.0×10^{-2} M CsCl internal solution. The electrode was eventually conditioned for 24 hours by soaking in the same solution. Ag/AgCl reference electrode was used as the internal reference electrode.

Results and discussion

Working concentration range and slope

The potential responses of fabricated ISE towards monovalent, bivalent and trivalent ions over a very wide concentration range of 1.0×10^{-6} M to 1.0×10^{-1} M were investigated and showed in Fig. 2. As it can be seen among all of the cations tried, Cs(i) cation exhibited the best Nernstian response with the slope and correlation coefficient of (57.29 mV per decade of activity, 0.998) and seemed to be suitably determined with the membrane electrode based on *p*-IPC6. It might be due to strong selective complexation behavior of the ionophore towards Cs(i) in compare to other metal ions as well as the rapid exchange kinetics of the obtained complex.^{24–26} Therefore, *p*-IPC6 was used as an ionophore in the fabrication of Cs^+ -ISE for further studies.

Effect of the membrane composition

The polymeric membrane physically separates the internal filling solution from the sample solution and it is the source of the signal generated by the ISE. The nature and amount of each

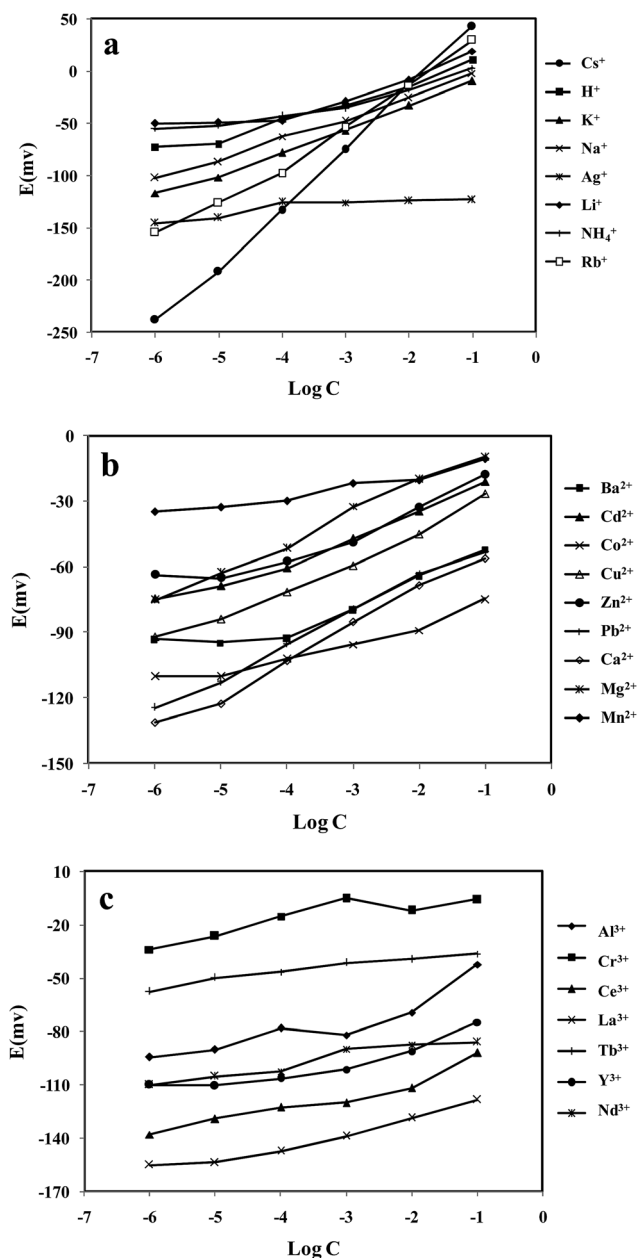


Fig. 2 The potential responses of PVC membrane sensor based on *p*-IPC6 towards (a) monovalent, (b) bivalent and (c) trivalent cations.

component have a significant effect on the characteristics performance of the ISE. The effect of various amount of ionophore, plasticizers and lipophilic additives on characteristics performance of the fabricated electrode were investigated and the potential responses are summarized in Table 1.

The amount of ionophore in membrane influences the sensitivity and selectivity of the fabricated electrode.^{27–29} Hence, in order to optimize the characteristics performance of the fabricated electrode, membranes with different amount of ionophore were prepared and their potential responses towards cesium(i) cation were obtained as it is showed in Table 1, where the membrane without ionophore did not have any significant potential response.

Plasticizer affects the dielectric constant of membrane phase and also has a very important role in optimizing the physical properties of PVC membrane as well as ensuring high mobility of ionophore and its complex in membrane.^{30–32} Hence, different plasticizers were applied to obtain the best electrochemical characteristics of the fabricated membranes with high selectivity and sensitivity towards corresponding target ion. The membranes exhibited better potential response while the plasticizers with lower dielectric constant were used. As it is obvious, dioctyl phthalate (DOP, $\epsilon = 5.1$) with the lowest dielectric constant, demonstrated the best Nernstian response and linear dynamic range in compare to dibutyl phthalate (DBP, $\epsilon = 6.4$), 2-nitrophenyl octyl ether (*o*-NPOE, $\epsilon = 24$) and nitrobenzene (NB, $\epsilon = 36.1$). As like as previous reports, in this experiment, the DOP with low dielectric constant was selected as the best plasticizer for the proposed cesium selective electrode.^{33–35}

By the addition of appropriate amount of different lipophilic additives as an anion excluder to the membranes, the influence of the nature and amount of additives on the potential responses of the fabricated ISEs were investigated (see Table 1). Among four different lipophilic additives which were applied for ISEs optimization, potassium tetrakis(4-chlorophenyl) borate (KTPClPB) revealed better Nernstian response and linear dynamic range. It is noteworthy to mention that the presence of lipophilic additive enhances the selectivity of the membrane by diminishing the anionic interference effects, improves the potential responses behavior of ISEs by reducing the response time and decreases the membrane ohmic resistance by increasing the cation extraction efficiency.^{17,30,35–40}

Effect of internal solution

It was found that the variation on the internal solution concentration, from 1.0×10^{-3} M to 1.0×10^{-1} M affected the stability and potential responses of the fabricated electrode (Table 2). The optimum internal solution with the concentration of 1.0×10^{-2} M CsCl showed the best performance in the terms of slope, working concentration range and response time. Hence, the found optimum concentrations for internal solutions were used for further studies. Moreover, all membranes were equilibrated for 24 hours in the mentioned optimum solution.

Calibration graph

The optimized ISEs based on *p*-IPC6 exhibited a linear potential response to the concentration of Cs^+ cation in the range of 1.0×10^{-6} M to 1.0×10^{-1} M with the Nernstian slope of 57.29 ± 0.31 mV per decade of activity. As it is clarified by the standard deviation value, the fabricated electrodes exhibited good stability and repeatability in potential responses with high accuracy and precision (see Table 3). By extrapolating the linear regions of the calibration graph to the base line potential, the values of 1.0×10^{-6} M was obtained as a limit of detection (LOD) for fabricated cesium(i) selective electrode (Fig. 3).

Table 1 Optimization of the membrane composition to fabricate high cesium(i) selective electrode

Sensor no.	<i>I</i>	Plasticizer					Lipophilic additive				Nernstian slope ^a (mV per decade)	<i>R</i> ²	Response time (s)
		PVC	DOP	DBP	<i>o</i> -NPOE	NB	KTpClPB	NaTFPB	TDATpClPB	NaTPB			
1	0	30.0	67.0	—	—	—	3.0	—	—	—	7.19 ± 0.63	0.960	N/A
2	3.0	30.0	64.0	—	—	—	3.0	—	—	—	31.28 ± 0.41	0.995	17
3	4.0	30.0	63.0	—	—	—	3.0	—	—	—	44.82 ± 0.35	0.998	13
4	5.0	30.0	62.0	—	—	—	3.0	—	—	—	57.29 ± 0.31	0.998	10
5	5.0	30.0	—	62.0	—	—	3.0	—	—	—	48.25 ± 0.46	0.976	13
6	5.0	30.0	—	—	62.0	—	3.0	—	—	—	45.99 ± 0.39	0.989	16
7	5.0	30.0	—	—	—	62.0	3.0	—	—	—	5.40 ± 0.48	0.859	15
8	5.0	30.0	63.0	—	—	—	2.0	—	—	—	47.41 ± 0.38	0.997	13
9	5.0	30.0	64.0	—	—	—	1.0	—	—	—	52.50 ± 0.41	0.996	13
10	5.0	30.0	65.0	—	—	—	0	—	—	—	41.44 ± 0.45	0.993	17
11	5.0	30.0	62.0	—	—	—	—	3.0	—	—	20.70 ± 0.73	0.934	14
12	5.0	30.0	62.0	—	—	—	—	—	3.0	—	29.93 ± 0.48	0.969	11
13	5.0	30.0	62.0	—	—	—	—	—	—	3.0	37.59 ± 0.39	0.993	15

^a Average and standard deviation for triplet measurement.

Repeatability & reproducibility

The repeatability and reproducibility study for fabricated ISEs were carried out over a wide concentration range of 1.0×10^{-6} M to 1.0×10^{-1} M of target cation standard solutions. Repeatability studies were done by using one selective electrode for five times and on the other hand, reproducibility studies were carried out by using five different electrodes, where each electrode was used only once (see Table 3). The average and standard deviation (SD) of the Nernstian slopes were calculated and their values were 57.29 ± 0.31 and 57.36 ± 1.01 mV per decade of activity, respectively. As it can be seen, the values of relative standard deviation (RSD) were much lower than 5% which can consider as an acceptable value for repeatability and reproducibility studies. The difference of Nernstian slope from one electrode to another may be due to the difference in the thickness and morphology of the membranes at different locations, that result in fluctuation in extraction equilibrium of corresponding ions at the vicinity of the interface between the membrane and aqueous layer.⁴¹ Thus, the variation of the thickness can cause minor changes in Nernstian slope of the electrodes.

Dynamic response time

The dynamic response time of fabricated cesium(i) selective electrode is one of the most important parameters in its evaluation for analytical applications. As it can be seen from Fig. 4,

the average of dynamic response time obtained based on *p*-IPC6 to reach to its equilibrium potential responses in the whole linear concentration range were less than 10 seconds. This is probably due to the fast exchange kinetics of metal ions complexation–decomplexation at the interface of PVC membrane with the test solution.

Life time

The stability and life time of the developed cesium(i) selective electrode were evaluated by using four electrodes. Their potential responses were measured over a period of 15 weeks. The electrodes were used daily over an extended time period (1 hour per day) and were stored in 1.0×10^{-2} M CsCl solution, when they were not in use. The characteristics performance of fabricated ISEs with respect to Nernstian slope and detection limit was investigated. As it can be seen from Table 4, the results demonstrated that after 12 weeks, only slight changes were observed in the slope and detection limit. The slope of the fabricated electrode changed from 57.29 ± 0.31 to 53.31 ± 0.34 mV per decade of activity, whereas its detection limit changed from 1.0×10^{-6} M to 4.5×10^{-6} M of Cs⁺ activity. The limitation of life time in the fabricated ISEs might be due to the loss of membrane ingredients by leaching into the sample. According to the obtained results, ISEs based on *p*-IPC6 demonstrated comparatively long life time with high stability,

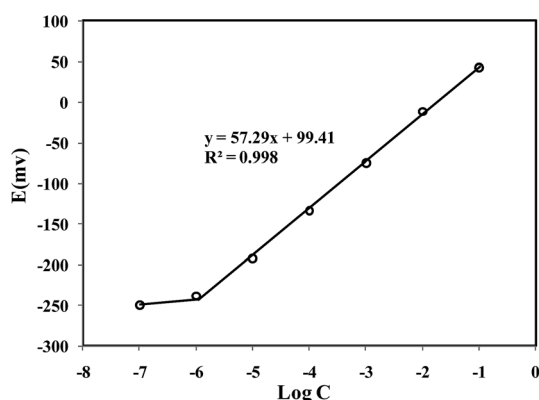
Table 2 Effect of different concentrations of internal solutions on characteristics performance of Cs⁺ selective electrode

Sensor no.	Internal solution (M)	Working range (M)	Nernstian slope ^a (mV per decade)	<i>R</i> ²	Response time (s)
1	1.0×10^{-1}	1.0×10^{-5} to 1.0×10^{-1}	49.30 ± 0.49	0.984	14
2	1.0×10^{-2}	1.0×10^{-6} to 1.0×10^{-1}	57.29 ± 0.31	0.998	10
3	1.0×10^{-3}	1.0×10^{-6} to 1.0×10^{-1}	50.25 ± 0.38	0.993	13

^a Average and standard deviation for triplet measurements.

Table 3 The repeatability and reproducibility of the fabricated ISEs based on *p*-IPC6 at 25 °C

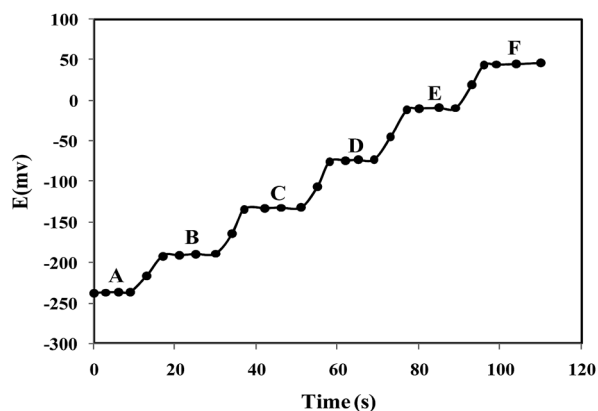
Study	Nernstian slope (mV per decade)	Average	Standard deviation	RSD
Repeatability	56.93, 57.11	57.29	0.31	0.54
	57.25, 57.41			
	57.74			
Reproducibility	56.11, 56.75	57.36	1.01	1.76
	57.29, 57.93			
	57.82			

**Fig. 3** Calibration graph of the Cs⁺ selective electrode based on *p*-IPC6 at 25 °C.

which indicates that it can be practically used for the determination of cesium concentrations in different fields such as environmental and industrial analysis.

Effect of pH

The pH dependence of fabricated ISE was investigated by measuring the potential responses of electrodes over wide pH range of 1.0 to 12.0 in different concentrations of 1.0×10^{-2} M and 1.0×10^{-4} M CsCl solution. The pH was adjusted by adding small volumes of dilute HNO₃ or NaOH to cesium solution.

**Fig. 4** Dynamic response time of the Cs⁺ selective electrode for step changes in the concentration of cesium solution: (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M and (F) 1.0×10^{-1} M at 25 °C.

As it is illustrated in Fig. 5, the potential response of the fabricated electrode was pH independent over the wide range of 2.0 to 11.0 for 1.0×10^{-2} M of CsCl solution and 3.0 to 10.0 for 1.0×10^{-4} M of CsCl solution. The obtained pH range indicates that the developed electrode can be applied for cesium concentration determination in environmental and industrial waste water over a very wide range without pH adjustments. The drift in the potential response at lower pH might be due to high concentration of H₃O⁺ ions that contributed to charge transport process of the membrane, thereby simultaneous response of electrode to both positively charged H₃O⁺ and Cs⁺ ions caused an increase in the potential response. While at higher pH value, the drift in potential was probably due to response of the electrode towards Na⁺ cation associated with OH[−] and Cs⁺ ions.

FT-IR spectroscopy

Due to possible leaching of membrane ingredients during long-term performance, the fabricated membranes were analyzed by FT-IR to evaluate their life time and sensitivity to target ion (see Fig. 6). Obviously, it is possible to deduce the presence of *p*-IPC6 in with the observed absorption band in the region of 3200–3400 cm^{−1} due to O–H stretching in compares to the spectrum of membranes without ionophore. However, the absorption band related to O–H stretching is low because of high intensity of C=O, C=C absorption bands and also low amount of OH in

Table 4 The life time of ISEs based on *p*-IPC6

Period (weeks)	Nernstian slope ^a (mV per decade)	Detection limit (M)
1	57.29 ± 0.31	1.0×10^{-6}
2	57.18 ± 0.22	1.0×10^{-6}
3	57.21 ± 0.34	1.0×10^{-6}
4	56.81 ± 0.18	1.0×10^{-6}
5	56.37 ± 0.25	1.5×10^{-6}
6	56.11 ± 0.42	1.5×10^{-6}
7	55.63 ± 0.36	2.0×10^{-6}
8	55.24 ± 0.35	2.0×10^{-6}
9	54.52 ± 0.41	3.0×10^{-6}
10	54.09 ± 0.47	3.0×10^{-6}
11	53.73 ± 0.39	3.5×10^{-6}
12	53.31 ± 0.54	4.5×10^{-6}
13	52.16 ± 0.72	4.5×10^{-6}
14	50.87 ± 1.24	5.0×10^{-6}
15	48.39 ± 1.46	5.5×10^{-6}

^a Average and standard deviation for quadruplet measurements.

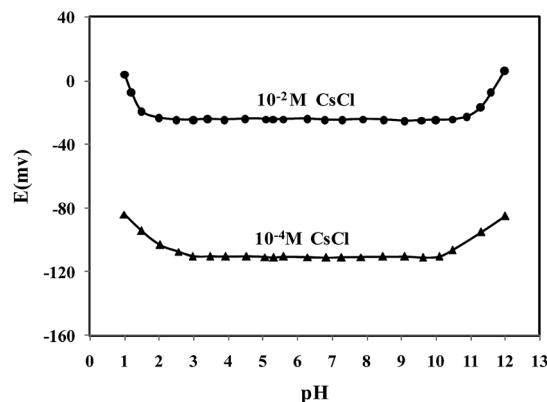


Fig. 5 pH effect of the sample solutions on the potential response of Cs^+ selective electrode at 25 °C.

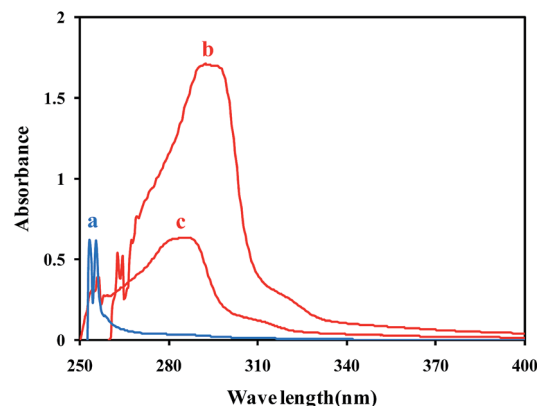


Fig. 7 UV-Vis absorption spectra: (a) 1.0×10^{-3} M Cs^+ , (b) 1.0×10^{-4} M $p\text{-IPC6}$ and (c) mixture of ionophore and cation.

the matrix of membrane. The presence of DOP as plasticizer in the membrane compositions is confirmed by the strong absorption bands related to C–O stretching appear at $1100\text{--}1300\text{ cm}^{-1}$ region and C=O stretching appear at 1722 cm^{-1} . As it can be observed from FT-IR spectra, DOP and ionophore show the common peak of C–H sp^3 stretching in $2859\text{--}2856\text{ cm}^{-1}$ region. Besides, the common peak of =C–H sp^2 stretching which appears at 2925 cm^{-1} indicates the presence of DOP and KTpCIPB. On the other hand, two peaks related to C=C aromatic stretching in 1458 cm^{-1} and $1583\text{--}1590\text{ cm}^{-1}$ region for the membrane are common absorption bands for all of the membrane ingredients.

The comparison of FTIR spectra for newly fabricated membrane (b) and used membrane after three month (c) as illustrated in Fig. 6, revealed that no significant change happened in the compositions of the membranes and it established the stability and long life time for the membranes based on $p\text{-IPC6}$. However, the slight leaching of membrane ingredients into the test solutions has detrimental effect on the fabricated ISEs behavior which results in minor change in their Nernstian slope and detection limit.

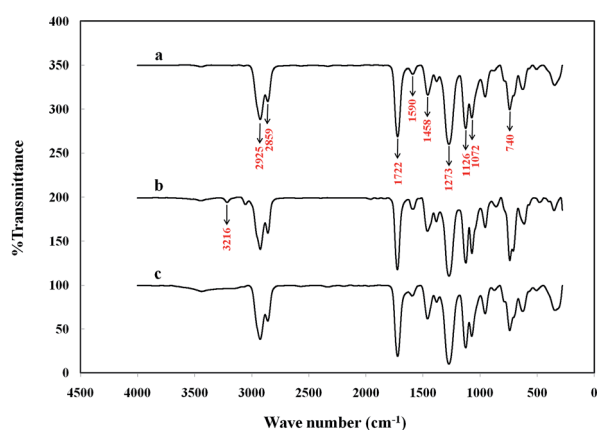


Fig. 6 Comparison of FT-IR spectra for membrane ingredients under different conditions: (a) blank membrane without $p\text{-IPC6}$ as ionophore, (b) fabricated membrane with ionophore and (c) used membrane after 3 months.

UV-Vis Spectroscopy

UV-Vis Spectroscopy analysis is used to investigate the strength of selective interaction between ion carriers and ionic species. It is known that the ionic species which cause larger change in spectrum result in larger potential responses and therefore have better selectivity.^{41,42} The UV spectra absorption of the $p\text{-IPC6}$ with the concentration of 1.0×10^{-4} M, Cs^+ cation with the concentration of 1.0×10^{-3} M and their mixture were recorded over 250 to 400 nm. As it is shown in Fig. 7, the spectrum of ionophore shows a distinct absorption maximum at 295 nm, while cation spectrum shows a significant absorption at 254 nm. With the addition of cesium(i) to $p\text{-IPC6}$, the absorption band shifts to 285 nm and its intensity decreases. The observed behavior can be attributed to preferred coordination of cesium ion by ionophore and confirmed their strong and selective interaction.

Table 5 Selectivity coefficient of the developed cesium(i) selective electrode based on Separate Solution Method (SSM) at 25 °C

Examined cation	$\log K_{\text{Cs,M}}^{\text{Pot}}$	$K_{\text{Cs,M}}^{\text{Pot}}$
Cs^+	1	0
K^+	−2.62	2.39×10^{-3}
H^+	−2.41	3.89×10^{-3}
Na^+	−2.74	1.82×10^{-3}
NH_4^+	−3.21	6.17×10^{-4}
Li^+	−3.53	2.95×10^{-4}
Rb^+	−2.16	6.92×10^{-3}
Zn^{2+}	−3.86	1.38×10^{-4}
Ni^{2+}	−4.56	2.75×10^{-5}
Ba^{2+}	−4.34	4.57×10^{-5}
Cd^{2+}	−3.98	1.05×10^{-4}
Co^{2+}	−4.61	2.45×10^{-5}
Cu^{2+}	−3.81	1.55×10^{-4}
Mn^{2+}	−4.72	1.90×10^{-5}
Pb^{2+}	−4.13	7.41×10^{-5}
Mg^{2+}	−4.18	6.61×10^{-5}
Ca^{2+}	−4.25	5.62×10^{-5}
Cr^{3+}	−4.22	6.03×10^{-5}
Ce^{3+}	−3.81	1.55×10^{-4}
Nd^{3+}	−4.04	9.12×10^{-5}

Determination of selectivity coefficients

The selectivity coefficient of the developed ISE based on (*p*-IPC6) towards cesium ions with respect to a wide range of interfering ions were determined by separate solution method (SSM). For selectivity evaluation of the fabricated cesium(I) selective electrodes, the concentration of 1.0×10^{-1} M was used for both target ions and interfering ions. As it can be concluded from Table 5, it is obvious that the fabricated electrodes exhibited high selectivity towards Cs^+ ions, in compare to a variety of investigated interfering cations which indicated a considerable improvement compared to the previously reported cesium(I) selective electrodes.

Scanning electron microscopy (SEM)

With the development of new surface analysis techniques such as scanning electron microscopy (SEM), it is possible to image the surfaces of some non-conducting samples like selective PVC membrane to distinguish their surface characteristics such as fouling and swelling.^{43,44} In order to investigate the surface morphology of cesium(I) selective membrane, SEM studies were carried out at different magnifications. As it is demonstrated in Fig. 8, the cesium(I) selective membrane without *p*-IPC6 reveals

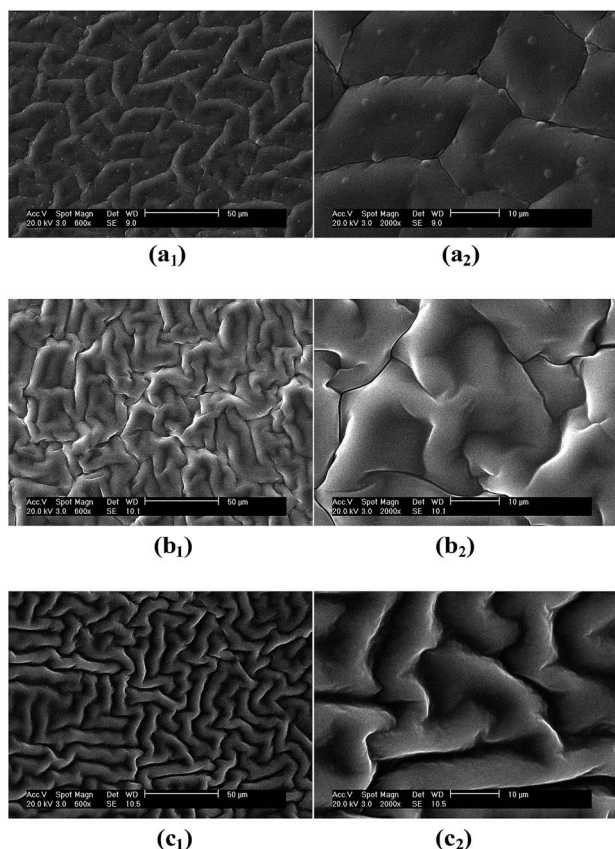


Fig. 8 Scanning electron microphotographs (SEM) of cesium(I) selective PVC membrane at two magnifications: (a) membrane without ionophore that conditioned for one day, (b) membrane with ionophore that conditioned for one day and (c) membrane that conditioned for three months and used daily over the mentioned period.

Table 6 Determination of cesium ion concentration in five sample solutions using ICP and developed selective electrode based on *p*-IPC6 and recovery test using standard addition technique

Amount added (ppm)	Concentration of Cs^+ ions (ppm)		
	ISE method ^a	ICP method ^a	Recovery (%)
0.00	ND	0.00	0.0
5.00	5.09 ± 0.42	5.02 ± 0.17	101.8
20.00	19.65 ± 0.27	19.28 ± 0.23	97.8
50.00	49.68 ± 0.36	49.34 ± 0.31	99.4
75.00	74.93 ± 0.45	74.68 ± 0.20	99.9
100.00	101.31 ± 0.32	101.07 ± 0.37	101.0

^a Average and standard deviation for triplet measurements.

a physically tight structure, while the membrane with ionophore exhibited a physically permeable and loose structure that includes channels through which Cs^+ ions can diffuse. Furthermore, the physical appearance of the membranes (*c*₁) and (*c*₂) shows swollen structure due to daily use over three months and stored in 1.0×10^{-2} M of CsCl solution when not in use. Consequently, it causes a relative fluctuation in the Nernstian slope and detection limit of the electrode.

Validation of fabricated selective electrode

In order to validate the accuracy of the developed electrode in determining the concentration of cesium, the obtained results are compared with the data acquired from inductively coupled plasma technique (ICP). Tap water samples were analyzed by the fabricated electrode and ICP method to detect Cs(I) concentrations *via* the spiked samples. As it can be seen from Table 6, there is a satisfactory agreement between the results obtained by ISE with those obtained by certified ICP method. Hence, it confirmed the accuracy and precision of fabricated ISE in successful determination of cesium trace amount in the real environmental and industrial samples.

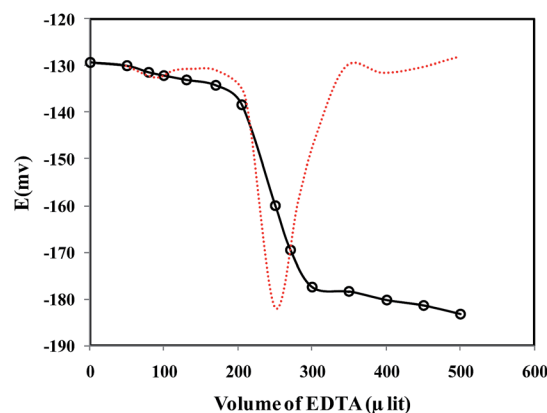


Fig. 9 Potentiometric titration curve of cesium ion (1.0×10^{-4} M, 25 mL) with standard EDTA solution (1.0×10^{-2} M) using fabricated electrode based on *p*-IPC6 as an indicator electrode.

Table 7 Comparison of the characteristics performance of fabricated cesium(I) selective electrode in this study with reported cesium(I) electrodes

Ionophore	Working range (M)	Detection limit (M)	Slope (mV per decade)	Response time (s)	pH	Ref.
15-Crown-5-phosphotungstic acid	1.0×10^{-4} to 1.0×10^{-1}	1.0×10^{-5}	60.0	60	3.0–5.5	45
Hexameric calix[6]arene ester	1.0×10^{-4} to 1.0×10^{-1}	—	50.0	—	—	18
Anilino-(1,3-dioxo-2-indanylidene) acetonitrile	2.5×10^{-5} to 1.0×10^{-1}	6.3×10^{-6}	52.0	60	2.0–11.0	19
Calix[4]arene dibenzocrown ether	1.0×10^{-6} to 1.0×10^{-1}	8.0×10^{-7}	58.5	—	3.0–10.0	46
Calix[6]arene tetraester	1.0×10^{-6} to 1.0×10^{-1}	4.9×10^{-7}	55.7	—	7.2	20
Quadruply-bridged calix[6]arenes	1.0×10^{-6} to 1.0×10^{-1}	5.0×10^{-7}	55.6	—	7.2	17
Calix[4]crown ether-ester	5.0×10^{-6} to 1.0×10^{-1}	5.0×10^{-6}	59.0	20	4.0–9.0	2
Cs-12-molybdophosphate	1.0×10^{-5} to 1.0×10^{-1}	3.0×10^{-6}	46.5	30	4.0–6.0	16
Crown bridged thiocalix[4]arenes	1.0×10^{-6} to 1.0×10^{-1}	5.0×10^{-7}	58.2	—	4.5–11.0	47
5-(4-Nitrophenylazo)25,27-bis(2-propyloxy)-26,28-dihydroxycalix[4]arene	1.0×10^{-5} to 1.0×10^{-1}	4.6×10^{-6}	56.0	20	3.0–11.0	48
Current study	1.0×10^{-6} to 1.0×10^{-1}	8.0×10^{-7}	57.3	10	2.0–11.0	—

Application

The developed ISEs based on *p*-IPC6 can be applied successfully as an indicator electrodes for the potentiometric titration of 25 mL of cesium cation (1.0×10^{-4} M CsCl) with 1.0×10^{-2} M of standard EDTA solution. As can be seen from Fig. 9, the obtained plots have a standard sigmoidal shape with sharp break point which indicates that the fabricated electrode is selective towards cesium ions. Moreover, the end point of the plots corresponds to 1 : 1 stoichiometry of EDTA-Cs⁺ ions complex. The obtained potential decreased by decreasing the metal ion concentration due to their complexation with standard EDTA solution. As a result, it is possible to determine the amount of metal ions in solution accurately by the fabricated electrode.

Comparison of previous works with current study

The characteristics performance of fabricated selective electrode was compared with the reported Cs⁺ selective electrodes based on various macrocyclic compounds. As it can be seen from Table 7 the developed electrode in this study demonstrated a very good dynamic working range with low detection limit and fast response time in compare to the pervious reported electrodes. Moreover, the potential responses of the developed electrodes are pH independent over a satisfactory wide range. It can be concluded that the developed electrode can be applied successfully for accurate and precise determination of cesium concentration in environmental and industrial fields.

Conclusion

The polymeric membrane sensor proposed in this paper can be used to determine the concentration of Cs(I) cation in tap water sample. The properties of the ISE are characterized by its strong selectivity, good reproducibility and rapid response time. The sensor can be used in a wide range of pH from 2 to 11. It gives a

good Nernstian slope of 57.29 ± 0.31 mV per decade for concentrations of cesium(I) cation between 1.0×10^{-6} and 1.0×10^{-1} M. The performance of the sensor constructed using *p*-IPC6 ionophore is favorable compared to previously developed Cs(I) ion sensors.

Acknowledgements

The authors express their appreciation to Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran and Universiti Putra Malaysia for the financial support of this work.

Notes and references

- 1 S. Peper, C. Gonczy and W. Runde, *Talanta*, 2005, **67**, 713–717.
- 2 R. K. Mahajan, M. Kumar, V. Sharma nee Bhalla and I. Kaur, *Talanta*, 2002, **58**, 445–450.
- 3 A. A. Helal, H. A. Arida, H. E. Rizk and S. M. Khalifa, *Radiochemistry*, 2007, **49**, 523–529.
- 4 E. Bakker and E. Pretsch, *Angew. Chem., Int. Ed.*, 2007, **46**, 5660–5668.
- 5 M. R. Ganjali, P. Norouzi and M. Rezapour, *Encyclopedia of Sensors*, American Scientific Publisher (ASP), 2006, vol. 8, pp. 197–287.
- 6 C. Bocchi, M. Careri, A. Casnati and G. Mori, *Anal. Chem.*, 1995, **67**, 4234–4238.
- 7 C. Bocchi, M. Careri, A. Casnati and G. Mori, *Anal. Chem.*, 1995, **67**, 4234–4238.
- 8 A. Ceresa, E. Bakker, B. Hattendorf, D. Günther and E. Pretsch, *Anal. Chem.*, 2001, **73**, 343–351.
- 9 A. C. Ion, E. Bakker and E. Pretsch, *Anal. Chim. Acta*, 2001, **440**, 71–79.

- 10 A. Kassim, M. Rezayi, S. Ahmad Zadeh, W. T. Tan, N. A. Yusof and Y. H. Lee, *Malays. J. Chem.*, 2009, **11**, 19–25.
- 11 A. Kassim, M. Rezayi, S. Ahmadzadeh, G. Rounaghi, M. Mohajeri, N. A. Yusof, T. W. Tee, L. Y. Heng and A. H. Abdullah, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2011, **17**, 012010.
- 12 B. J. Sanghavi, S. M. Mobin, P. Mathur, G. K. Lahiri and A. K. Srivastava, *Biosens. Bioelectron.*, 2013, **39**, 124–132.
- 13 B. J. Sanghavi, S. Sitaula, M. H. Griep, S. P. Karna, M. F. Ali and N. S. Swami, *Anal. Chem.*, 2013, **85**, 8158–8165.
- 14 B. J. Sanghavi, W. Varhue, J. L. Chávez, C.-F. Chou and N. S. Swami, *Anal. Chem.*, 2014, **86**, 4120–4125.
- 15 B. J. Sanghavi, O. S. Wolfbeis, T. Hirsch and N. S. Swami, *Microchim. Acta*, 2015, **182**, 1–41.
- 16 H. A. M. Arida, R. F. Aglan and S. A. El-Reefy, *Anal. Lett.*, 2004, **37**, 21–33.
- 17 E. M. Choi, H. Oh, S. W. Ko, Y. K. Choi, K. C. Nam and S. Jeon, *Bull. Korean Chem. Soc.*, 2001, **22**, 1345–1349.
- 18 A. Cadogan, D. Diamond, M. R. Smyth, G. Svehla, M. A. McKervey, E. M. Seward and S. J. Harris, *Analyst*, 1990, **115**, 1207–1210.
- 19 M. B. Saleh, *Talanta*, 1998, **46**, 885–895.
- 20 H. Oh, E. M. Choi, H. Jeong, K. C. Nam and S. Jeon, *Talanta*, 2000, **53**, 535–542.
- 21 E. Bakker, P. Buhlmann and E. Pretsch, *Talanta*, 2004, **62**, 843–860.
- 22 E. Bakker, R. K. Maruva, E. Pretsch and M. E. Mayerhoff, *Anal. Chem.*, 1994, **66**, 3021–3030.
- 23 Y. Umezawa, K. Umezawa and H. Sato, *Pure Appl. Chem.*, 1995, **67**, 507–518.
- 24 M. R. Ganjali, M. Emami, M. Salavati-Niasari and M. Yousefi, *Anal. Lett.*, 2003, **36**, 2735–2747.
- 25 S. Ahmadzadeh, A. Kassim, M. Rezayi and G. H. Rounaghi, *Molecules*, 2011, **16**, 8130–8142.
- 26 S. Ahmadzadeh, A. Kassim, M. Rezayi, Y. Abdollahi and G. Hossein, *Int. J. Electrochem. Sci.*, 2011, **6**, 4749–4759.
- 27 M. R. Ganjali, R. Kiani-Anbouhi, M. Shamsipur, T. Poursaberi, M. Salavati-Niasari, Z. Talebpour and M. Emami, *Electroanalysis*, 2004, **16**, 1002–1008.
- 28 M. Javanbakht, A. Shabani-Kia, M. R. Darvich, M. R. Ganjali and M. Shamsipur, *Anal. Chim. Acta*, 2000, **408**, 75–81.
- 29 M. Rezayi, R. Karazhian, Y. Abdollahi, L. Narimani, S. B. T. Sany, S. Ahmadzadeh and Y. Alias, *Sci. Rep.*, 2014, **4**, 4664–4672.
- 30 E. Bakker, P. Buhlmann and E. Pretsch, *Chem. Rev.*, 1997, **97**, 3083–3132.
- 31 H. A. Zamani, G. Rajabzadeh, M. Masrornia, A. Dejbord, M. R. Ganjali and N. Seifi, *Desalination*, 2009, **249**, 560–565.
- 32 K. S. Park, S. O. Jung, I. Yoon, K. M. Park, J. Kim, S. S. Lee and J. S. Kim, *J. Inclusion Phenom. Macrocyclic Chem.*, 2001, **39**, 295–301.
- 33 D. Ammann, W. E. Morf, P. Anker, P. C. Meier, E. Pretsch and W. Simon, *Ion-Sel. Electrode Rev.*, 1983, **5**, 3–92.
- 34 P. L. H. M. Cobben, R. J. M. Egberink, J. G. Borner, P. Bergveld, W. Verboom and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1992, **114**, 10573–10582.
- 35 Y. Choi, H. Kim, J. K. Lee, S. H. Lee, H. B. Lim and J. S. Kim, *Talanta*, 2004, **64**, 975–980.
- 36 M. R. Ganjali, M. Emami and M. Salavati-Niasari, *Bull. Korean Chem. Soc.*, 2002, **23**, 1394–1398.
- 37 T. Rosatzin, E. Bakker, K. Suzuki and W. Simon, *Anal. Chim. Acta*, 1993, **280**, 197–208.
- 38 Y. Umezawa, K. Umezawa and H. Sato, *Pure Appl. Chem.*, 1995, **67**, 507–518.
- 39 H. A. Zamani, G. Rajabzadeh and M. R. Ganjali, *Sens. Actuators, B*, 2006, **119**, 41–46.
- 40 M. Huser, P. M. Gehrig, W. E. Morf, W. Simon, E. Lindner, J. Jeney, K. Toth and E. Pungor, *Anal. Chem.*, 1991, **63**, 1380–1386.
- 41 A. K. Singh, V. K. Gupta and B. Gupta, *Anal. Chim. Acta*, 2007, **585**, 171–178.
- 42 M. Rezayi, L. Y. Heng, A. Kassim, S. Ahmadzadeh, Y. Abdollahi and H. Jahangirian, *Sensors*, 2012, **12**, 8806–8814.
- 43 E. Bakker, D. Diamond, A. Lewenstam and E. Pretsch, *Anal. Chim. Acta*, 1999, **393**, 11–18.
- 44 M. Rezayi, Y. Lee, A. Kassim, S. Ahmadzadeh, Y. Abdollahi and H. Jahangirian, *Chem. Cent. J.*, 2012, **6**, 40.
- 45 D. Wang and J. S. Shih, *Analyst*, 1985, **110**, 635–638.
- 46 J. S. Kim, A. Ohki, R. Ueki, T. Ishizuka, T. Shimotashiro and S. Maeda, *Talanta*, 1999, **48**, 705–710.
- 47 R. Bereczki, V. Csokai, A. Grun, I. Bitter and K. Toth, *Anal. Chim. Acta*, 2006, **569**, 42–49.
- 48 P. S. Ramanjaneyulu, P. Singh, Y. S. Sayi, H. M. Chawla and K. L. Ramakumar, *J. Hazard. Mater.*, 2010, **175**, 1031–1036.