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Electro polymerized 4-vinyl pyridine on 2B pencil graphite as ionophore for cadmium (II)

Joanna Lim Wee Ling, Anish Khan, Bahruddin Saad, Sulaiman Ab Ghani*

Pusat Pengajian Sains Kimia, Universiti Sains Malaysia, 11800 USM Pulau Pinang, Malaysia

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ABSTRACT

A new poly(4-vinyl pyridine) (P4VP) based cadmium (Cd)-ion selective electrode (ISE) was developed. The 4-vinyl pyridine (4VP) was first polymerized electrochemically on the surface of graphite, later characterized by FTIR, SEM/EDX and then optimized as ISE for Cd. At optimal pH 6.4, slope of 27.7 ± 0.8 mV decade^{-1}, linear concentration range of 1×10^{-7} to 1.0×10^{-1} M Cd^{2+} and limit of detection (S/N = 3) of 2.51×10^{-8} M were obtained. The ISE was very selective towards Cd^{2+}, with $K^{\text{pot}} < 1 \times 10^{-2}$ in the presence of the usual cations and anions in water samples. Response time and shelf life of less than 1 min and 90 days, respectively, were observed. Its application was tested in various types of samples.

1. Introduction

Various anthropogenic activities such as industrial, fertilizer application, and sewage sludge disposal on land resulted in considerable accumulation of cadmium (Cd) in soil [1]. This is readily taken up by plants where it can be accumulated to a high level. Bioaccumulation of Cd in green plants and the subsequent accumulation in the food chain exceeds all other trace elements because of its high mobility in soil [2,3]. The intake of edible plants by humans is the most direct path for Cd from soil to affect human health in a non-smoking population [4].

There is a concern over food contaminated by Cd as the main source of Cd into animals and human beings [5–7]. The Cd contamination in foods depends on the nature of that food as well as the level of ecological contamination present. Cd can also be transferred to humans through exposure to a Cd contaminated workplace and cigarette smoking.

As a highly toxic element Cd is responsible for several cases of ailment including fever, muscle ache and inflammation that can ultimately lead to respiratory and kidney damage [8,9]. Medical researches have also revealed that Cd may cause lung and prostate cancers [10]. Therefore, there is an urgent need to monitor the level of Cd in the environment.

Analysis of Cd is usually carried out using atomic absorption spectroscopy (AAS). This is an excellent method but the analysis is destructive, expensive and needs skillful operator. Sample preparation is also tedious and time consuming. Moreover, the equipment is bulky and therefore, unsuitable for on site or in situ analysis. Potentiometric method by an ion selective electrode (ISE) is, by far, the best alternative as it is cheap, green and user-friendly. Even though Cd-ISE is not commonly found in the marketplace, but there are reports [11–20] lately indicating intense interest on the fabrications of this ISE. However, their setbacks are mostly due to serious interference by cations such as Ag^{+}, Hg^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+}.

Many known conducting polymers have been utilised in electrode fabrications. They are useful as ion-to-electron transducers and also as sensing membranes in ISE [21]. By coating them in membrane form on electrode surfaces the new electrodes may function either as chemically modified electrodes (CME) or as coated wire electrodes (CWE). The later is sometimes called solid-state ISE. This work has used 4-vinyl pyridine (4VP) as ionophore for Cd because of a metastable (labile) type of complex formed. This is expected as Cd^{2+} is a soft acid whereas pyridine exchange site is borderline base. As a result this should facilitate the exchange of Cd^{2+} in the membrane and in solution. The poly(4-vinyl pyridine) (P4VP) modified graphite pencil rod (GPR), especially of 2B pencil as ISE have been successfully used for the analysis of various analytes [22–31].

2. Experimental

2.1. Reagents and apparatus

The 4VP monomer from Fluka Chemika, Switzerland was used without further purification. Cadmium (II) chloride,

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* Corresponding author. Tel.: +6 04 6534030; fax: +6 04 6574854.
E-mail address: sag@usm.my (Sulaiman AbGhani).

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tetraethylammonium tetrafluoroborate (Et_4NBF_4) and acetonitrile (MeCN) were purchased from Merck, Germany and used as received. The indium tin oxide coated polyethylene terephthalate (ITO-PET) film (175 μm, Coating ITO-60) and potassium hydrogen phthalate (KHP) were purchased from Aldrich, USA. The chloride and nitrate salts of cations were of highest purity and were used as received. Working solutions of Cd (II) ranging from 1×10^{-2} M to 1×10^{-8} M were prepared from 0.1 M Cd (II) stock solution via serial dilution method. Aqueous solutions of different concentrations were prepared by dilution of standard salt solutions in deionized water (18.2 MΩ cm) from Milli-Q plus of Millipore, USA. Adjustments of pH were done with dropwise addition of concentrated hydrochloric acid and sodium hydroxide.

Cyclic voltammetry studies were done using a Potentiostat/Galvanostat Model 273A c/w related softwares and FRD100 (Princeton Applied Research, USA). A conventional three-electrode cell involving (i) working electrode, a 2B pencil graphite lead (Steadtler, Germany) which has undergone 8 h soxhlet extraction using methanol and sonification in HCl and water for 15 min, (ii) platinum wire (99.99%) (Advent, UK) as the auxiliary electrode and (iii) Ag/AgCl (3 M KCl) as the reference electrode were used. All potentiometric (emf) and pH measurements were done with pH/ion meter model 720A (Orion, USA). Validation of the proposed Cd-ISE was done with an AAS model A Analyst 200 (Perkin Elmer, USA). The scanning electron microscope (SEM) Jeol JSM 6300 with a Link-Oxford-ISIS X-ray microanalysis system (SEM/EDX) was used for surface studies. FTIR spectrophotometer model 2000 (Perkin Elmer, USA) was used for functional group analysis. UV–vis spectrophotometer model Lambda 35 was used for the determination of formation constant.

2.2. Preparation of electrode

The coating of surface of the graphite by poly(Cd–4VP) complex was done by immersing the working electrode in 0.01 M Cd^{2+} solution and 4VP monomer in acetonitrile (MeCN) and tetraethylammonium tetrafluoroborate (Et_4NBF_4) in the potential range of −0.4 V to +0.6 V Ag/AgCl at a scan rate of 50 mV s^{-1}. The electrochemical solution was first purged with oxygen-free-nitrogen (OFN) gas for 15 min before being subjected to cyclic voltammetry. Once a steady state was achieved the electrode was taken out of the solution and was washed with water and then MeCN mixture. P4VP modified electrodes were left to dry under reduced pressure for 30 min prior to use.

2.3. Spectroscopic measurements

P4VP polymer was synthesized onto ITO-PET films in the potential range from −0.4 V to +0.6 V versus Ag/AgCl at a scan rate of 50 mV s^{-1}. Polymer film on the ITO-PET was then analyzed using an ATR-FTIR spectrometer with a universal ATR attachment on a diamond and zinc selenide (ZnSe) crystal. Polymer film coated onto the graphite pencil was also analyzed by scanning electron microscopy (SEM) to compare morphology, porosity as well as thickness of the polymer film deposited. The SEM JOEL JSM 6300 operated with a Link-Oxford-ISIS X-ray microanalysis system (SEM/EDX). The analytical conditions were at accelerating voltage 20 kV, beam current 2×10^{-9} A, and working distance 15 mm. Samples were carbon-coated to eliminate charging effects. Semi-quantitative microanalysis was carried out using the ZAF method for correcting inter-elemental effects. The counting time was 100 s for major and minor elements.

2.4. Conditioning and electrode emf measurements

All emf measurements were done at 25 ± 3 °C. Membranes were conditioned in buffered 0.1 M cadmium (II) solution overnight and for 1 h before use. Buffer used was prepared from a mixture of 45.2 ml of 0.1 M NaOH and 100 ml of 0.1 M KHP. The electrodes were also kept in a similar solution in between measurements. The schematic assembly of the proposed cell was:

Ag, AgCl|3 M KCl||test solution|P4VP–Cd membrane|2B GPR

2.5. The response time and life time

The method of determining response time in the present work is being outlined as follows.

The electrode was first dipped in a 1×10^{-2} M solution of $Cd(NO_3)_2$ and then 10 fold higher concentration. The potential of the solution was read at zero second; just after dipping of the electrode in the second solution and subsequently recorded at the intervals of 1 s. The potentials were then plotted versus the time. For life time studies, the electrode responses were noted for one or more weeks and response curve was drawn for the data. The period referred to as shelf life of electrode was obtained when the Nernstian slope values were remained constant.

2.6. Real sample analysis

Soil samples were obtained from various places in Penang Island. Each sample represents only one type of soil or location and in this case agricultural, roadside and also industrial. Roadside samples were obtained at location of highly congested traffic at any given time of the day. Industrial samples were obtained from Bayan Lepas Free Trade Zone. For each location five to six samples were taken and then placed in a beaker and mixed thoroughly.

Food samples such as green tea, black tea, Chinese cabbage and also spinach were purchased from local supermarkets.

Both samples of soil and plant origin were wet digested before further analyses. This was performed by placing 1.0 g sample in 12 mL mixture of HNO_3:H_2O_2 (6:2). The mixture was then heated up to 130 °C for 4 h. After cooling, 5 mL of distilled water was added to the sample, stirred and heated again for 10 min. The residue formed was filtered off and the filtrate was diluted to 25 mL with distilled water. A blank digestion was carried out in the same way.

Biological samples were taken from fully matured cattle and chicken specimens raised within Penang Island. The targeted poultry farms were situated near a trunk road with moderate to high pollution index. Samples were taken from the animals' organs such as the liver, kidney and heart. These were stored in a freezer until the analyses. The organ samples were chopped into small pieces and dried overnight at 105 °C in the oven. Then, 5 g of the dried samples were weighed at constant weight before subjected to wet digestion. After dilution the solution of sample were spiked with cadmium.

3. Results and discussion

3.1. Characterization of electrodes

3.1.1. Electropolymerization of 4VP

Thin films of P4VP were prepared from the 4VP solution and coated on the surface of graphite rods by forward and reverse scanning at the potential range of −0.4 V to +0.6 V versus Ag/AgCl (Fig. 1). As the anodic peak, I_{pa}, increases, indicating the polymer was progressively thickened on the GPR pencil replacing the double layer, it was also observed that the peak potential, E_{pa}, have shifted slightly to a higher potential with increasing number of

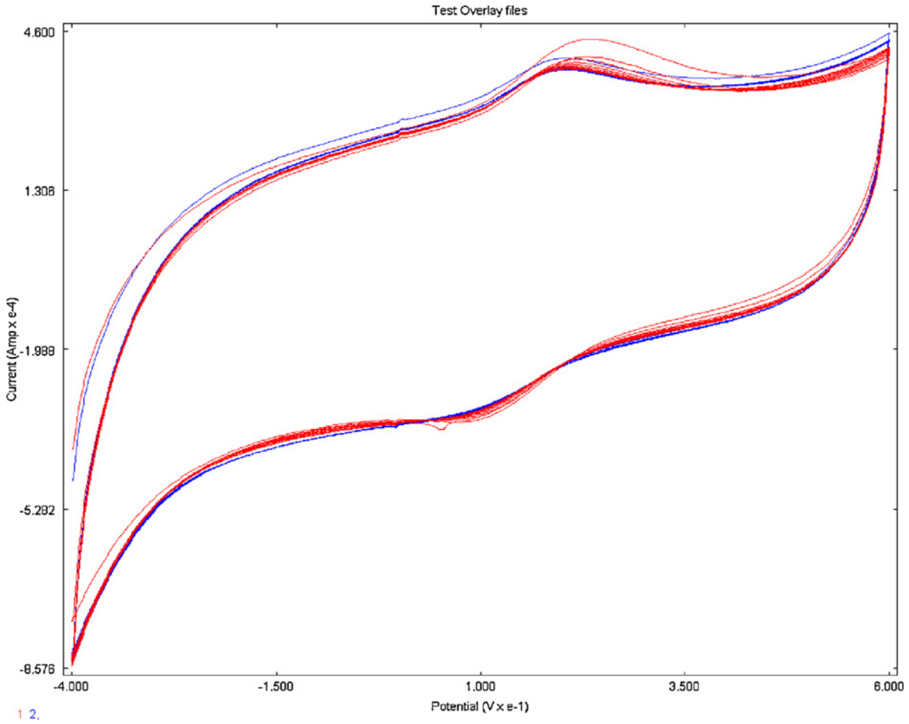

Fig. 1. Cyclic voltammetry for the electrodeposition of 4VP monomer onto graphite rod at E_{app} of −0.4 V to +0.6 V, scan rate of 50 mV s^{-1} in 0.1 M of supporting electrolyte (Et_4NBF_4).

cycles (result not shown), i.e. the peak separation, ΔE_p, become larger. The redox system in which radical was formed via protonation of the monomer leading to electropolymerization tended to favour irreversibility. However, the coating of P4VP film on the GPR was stopped once it acquired steady state. The ratio of anodic and cathodic peak currents, I_{pa}/I_{pc}, appeared to have been almost equal to unity after achieving steady state, which was expected of from most electropolymerization of this nature. The optimum monomer concentration used was 0.05 M. At higher concentrations precipitation would appear in solution.

3.1.2. *UV–vis spectrophotometric analysis*

When the monomer 4VP and Cd^{2+} were mixed together in MeCN, a light brown solution was obtained. UV–vis spectrometric analysis was carried out to confirm on charge transfer complexes between the monomer and Cd^{2+}. The concentration of

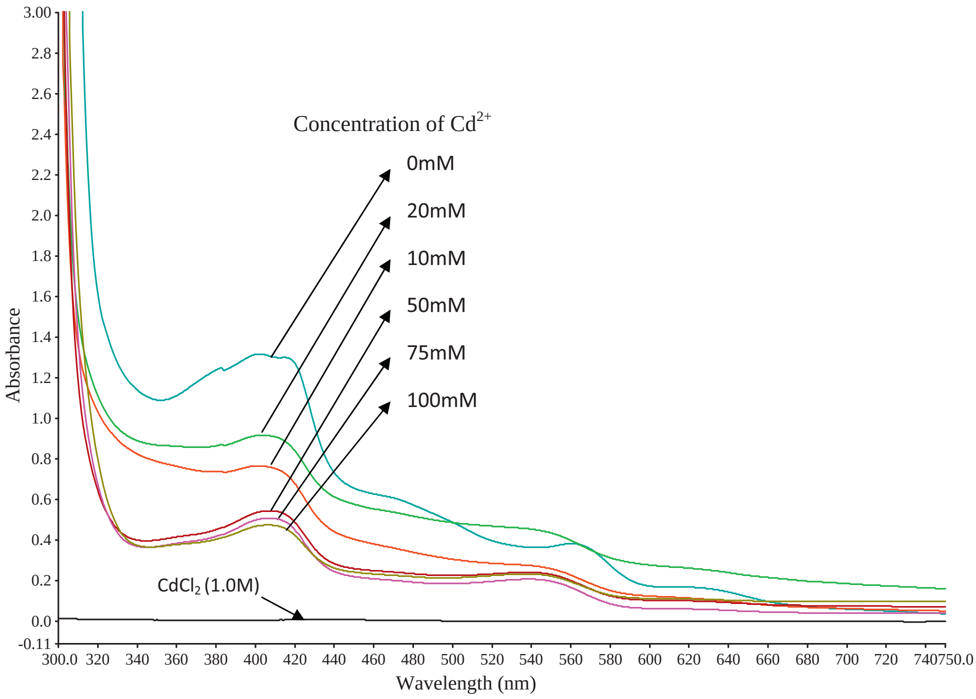

Fig. 2. UV–vis spectra obtained for the solutions containing 4VP (50 mM) with different concentrations of Cd^{2+}.

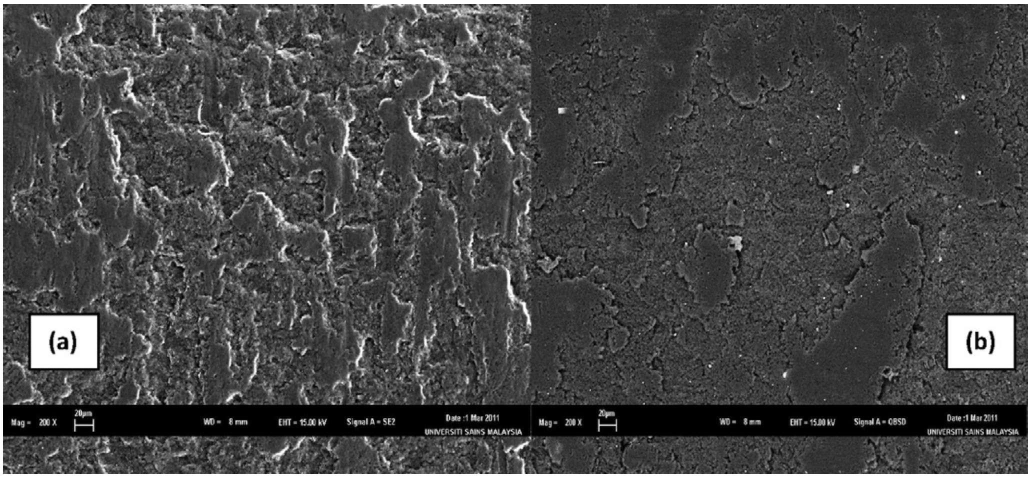

Fig. 3. SEM micrographs of the P4VP films: (a) before immersion in Cd^{2+} solution, (b) after immersion in Cd^{2+} solution, all with a 200× magnification.

monomer solution was kept constant with the addition of different concentrations of Cd^{2+} solutions (Fig. 2). The maximum absorption wavelength, λ_{max}, was observed at 410 nm. This is the blue region which is complementary colour for the observed colour of yellowish orange of the 4VP solution used. By virtue of the peak obtained it was concluded that 100 mM was the optimum concentration of $Cd^{2+}$with 0.05 M 4VP used (see Section 3.1.1). The colour of the Cd–4VP complex and monomer 4VP was assumed similar. The absorbance decreases as and when $[Cd^{2+}]$ increases indicating diminishing of the monomer. However, there is a consistency in the absorption intensity at 560 nm which could be due to the formation of charge transfer in the complexes.

3.1.3. SEM studies

Fig. 3 is a typical SEM of P4VP membrane deposited on the GPR before and after immersion in Cd^{2+} solution showing the rough surface of the polymer. This was taken with the secondary electron (SE) detector which has a strong function of the angle of incidence. SEM photomicrograph of the polymer after immersion showed a much smoother and even surface area. The white spots were believed to be cadmium.

Examination by SEM/EDX at equilibrium potentials and at lowest concentration of Cd^{2+} had no significant morphological changes. The presence of Cd^{2+} altered the surface of the film after diffusion, with the presence of holes. These similar features, i.e. ion insertion during electrochemical processes in the reduction of metal–organic frameworks were also reported elsewhere [32,33].

3.1.4. FTIR studies

The FTIR spectrum of Cd–P4VP and P4VP (Fig. 4) showed the vibrational bands at 2911, 2869 and 1426 cm^{-1} were due to CH_2 stretching. The presence of Cd^{2+} incorporated into the P4VP matrix has caused the intensity of the pyridine vibrational bands at 1600 cm^{-1} to disappear [34]. The Cd^{2+} has caused the C–N stretching band to shift and more importantly narrowing the N–H stretching band at around 3400 cm^{-1}. The existence of IR bands at 1400–1450 cm^{-1} showed the characteristic peaks of a metal linked to nitrogen which is coherent with the P4VP loaded with Cd^{2+}. This further confirms the formation of Cd–4VP complex.

3.1.5. Stoichiometry of complex

The continuous variation (Job's Method) was applied in the determination of the stoichiometry of Cd–4VP complex. This method keeps the number of moles of each reactant constant but the mole fractions of the two reactants are varied. The molar absorptivity of the Cd–4VP complex was determined at 560 nm. Plot of mole fraction versus absorbance suggested that two moles of 4VP react with 1 mole of Cd^{2+}, suggesting a 1:2 (Cd:4VP) ratio complex was formed. A 3D schematic representation of the Cd–4VP complex is shown (Fig. 5).

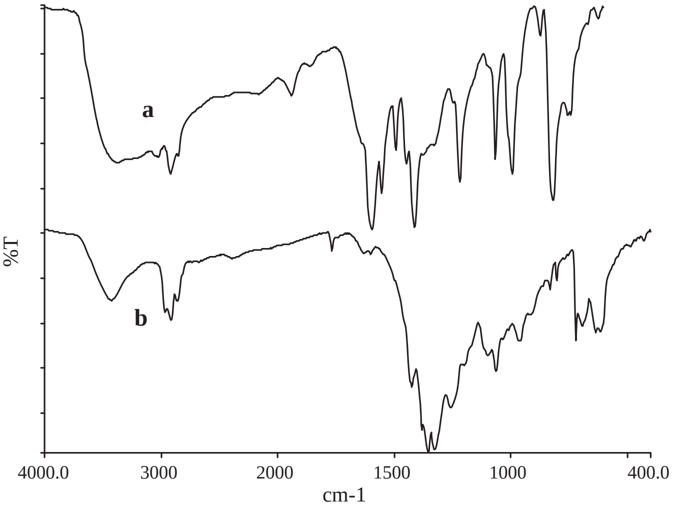

Fig. 4. FTIR spectra (a) before and (b) after absorption of Cd^{2+} on P4VP membrane on graphite modified electrode after immersing in Cd^{2+} solution.

3.2. Potentiometric characterizations

3.2.1. Calibration

Nernstian response occurs when the exchange of the ion in the membrane and solution has attained thermodynamic equilibrium usually refers as Donnan equilibrium. This can be expressed as in Eq. (1) whereby a linear plot of the emf of cell (E) versus the log concentration of analyte is obtained. In theory for a divalent Cd^{2+}, ideally a slope (S) of 29.5 mV $decade^{-1}$ at 25 °C should be obtained.

$$E = E + S \ \log[Cd^{2+}] \tag{1}$$

P4VP fabricated electrodes were tested after 24 h of conditioning in 0.01 M Cd^{2+}. The emf response of the fabricated ISEs was determined in 1.0×10^{-1} M to 1.0×10^{-8} M Cd^{2+}. Fig. 6 showed that the electrode exhibited near Nernstian behaviour with a slope of 27.7 ± 0.8 mV $decade^{-1}$ ($n = 3$) and a limit of detection at 1.0×10^{-7} M of Cd^{2+}. Since the complex formed is relatively unstable the response generated has to be due to exchange mechanism between analyte in solution and in membrane.

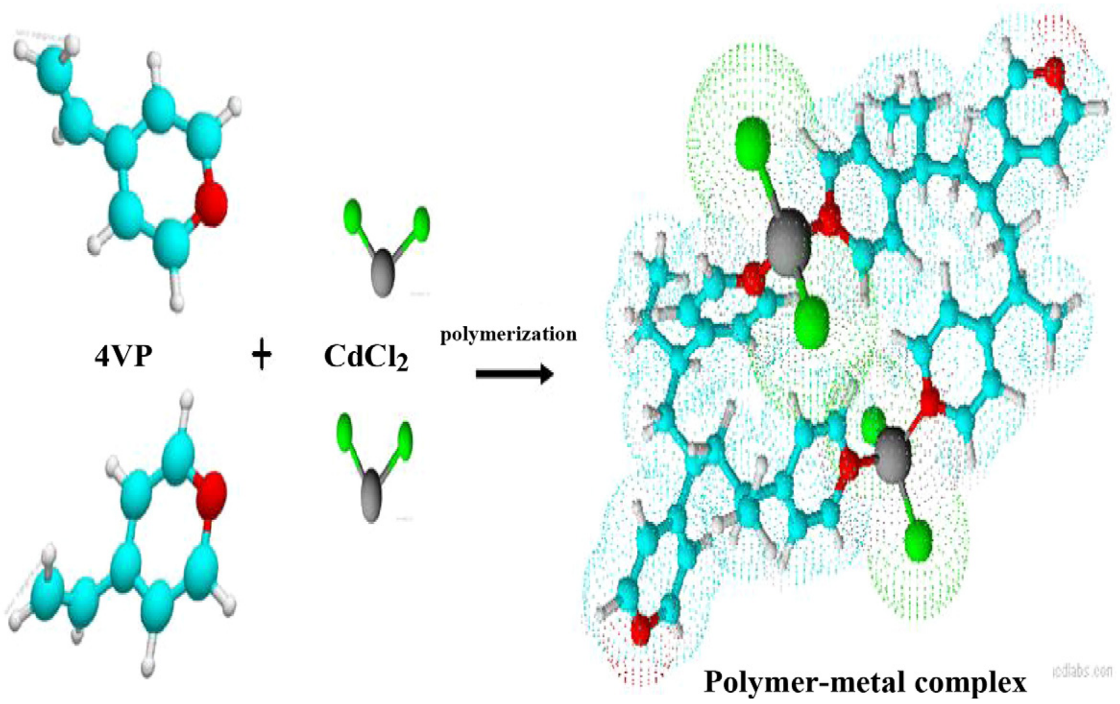

Fig. 5. The 3D structural formation of Cd–4VP complex.

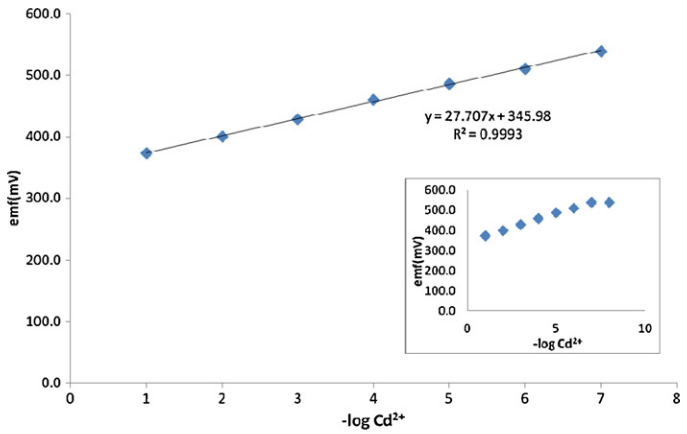

Fig. 6. Calibration plot for the emf response of Cd^{2+} solution.

Table 1
Life time of proposed Cd-ISE.

Period after deposition, days	Slope (mV/decade)
7 days	27.7
30 days	26.3
60 days	26.2
90 days	5.5 (no response)

To investigate the lifetime of the ISE, the emf responses of a control ISE was studied repeatedly over a period of time. The resulting data are depicted in Table 1. No significant change in the slope value was seen up to 3 months. However, after 3 months, there was a 80% decrease in the slopes obtained, and the ISE also showed erratic responses.

The average response time for the developed Cd-ISE was found to be 25 s after successive immersion in a series of Cd^{2+} solutions. However, at lower concentration of Cd^{2+} solutions smaller than 1.0×10^{-3} M the response time was sluggish and reached an average of 50 s.

3.2.2. *pH studies*

The pH profile of Cd–4VP complex membrane to standard Cd^{2+} solutions was prepared over a pH range of 2.0–8.0. The emf response of the developed Cd^{2+}-ISE was not affected by solution pH at pH range of 4.00–7.50. Sharp changes in potential at pH < 4.00 were due to the interference by H^+ ions. Whereas at pH > 8.0, Cd^{2+} tend to form inorganic hydroxide and precipitated which decrease the free Cd^{2+} in solution, hence reduction in the emf response. Extrapolation of these flat regions of the profile brought to optimum pH value at 6.40. This pH value was used throughout the following experiments.

3.2.3. *Interference studies*

The selectivity coefficient ($K^{pot}_{A,B}$) of an ISE is a quantitative representative to which an ISE responds to a primary ion (A) in the presence of interfering ions (B). They should also have rapid exchange kinetics and sufficiently lipophilic to prevent leaching into solutions. The larger the value of $K^{pot}_{A,B}$ the more interfered is

Table 2
Potentiometric selectivity coefficients of the proposed Cd-ISE.

Interfering ions, M^{n+}	$K^{pot}_{Cd^{2+},M^{n+}}$
Co^{2+}	3.16×10^{-3}
Cu^{2+}	1.78×10^{-3}
Ni^{2+}	1.00×10^{-2}
Zn^{2+}	4.22×10^{-3}
Na^+	8.91×10^{-3}
Ca^{2+}	3.31×10^{-3}
Mg^{2+}	6.31×10^{-3}
Pb^{2+}	7.08×10^{-3}
Ba^{2+}	3.80×10^{-3}
K^+	6.31×10^{-3}
Li^+	7.08×10^{-4}
Fe^{3+}	2.33×10^{-3}
Hg^{2+}	1.00×10^{-4}
Ag^+	1.26×10^{-3}
Cl^-	1.58×10^{-3}
Br^-	7.94×10^{-4}

Table 3
Comparison on characteristics of Cd-ISE.

Electrode	Nernstian slope (mV decade^{-1})	Selectivity studies	Response time (s)	Optimum pH range	Ref.
Cyanocopolymer modified electrode	29.00 ± 0.001	Slight interference to Pb^{2+}, Mg^{2+}, Cu^{2+}	12	2.5–6.5	12
Synthesized tetrol compound based electrode	27.8	No significant interference	<15	4.0–7.0	13
TRIAR 3-(2′,4′ dihydroxyphenylazo-1′)-1,2,4 triazol in PVC matrix	28.5	Slight interference to Zn^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}	5	4.3–8.5	16
Cetylpyridium tetraiodo and tetrabromo complex based solid state electrodes	−25.1	Interference to Hg^{2+}, Ag^{+}, Pb^{2+}, Fe^{3+}, Cu^{2+}	7	2.0–8.0	17
N,*N*_-(4-methyl-1,2 phenylene)diquinoline-2-carboxamide based electrode	29.9 ± 0.5	Interference to univalent cations	3–8	4.0–9.0	19
Poly(vinyl chloride) α-sexithiophene (α-6T)	29.4 ± 0.3	Not stated	5–10	2.0–9.0	[35]
This study	27.71 ± 0.83	Slight interference to Ni^{2+}	25	4.0–7.5	

the ionophore by the interferent. Studies on the $K^{pot}_{A,B}$ developed Cd-ISE were performed using the fixed interference method (FIM). Measurements with FIM method are based on the relative value of difference between the emf of the working electrode and the reference electrode for a solution containing both the primary ion and interference ion. Activity of the interference ion (a_B) was constant while the activity of the primary ion (a_A) was varied. Emf values were plotted against logarithm of a_A. Intersection from the extrapolated linear segments gave the a_A value for the calculation of $K^{pot}_{A,B}$ according to:

$$K^{pot}_{A,B} = \frac{a_A}{(a_B)^{z_A/z_B}} \qquad (2)$$

$K^{pot}_{A,B}$ values calculated for each interfering ions were shown in Table 2. As can be seen, little interference from usual ions (see Section 1). It is noteworthy that silver (I) ions and lead (II) ions which pose serious interferents for earlier Cd-ISE had shown small selectivity values.

A list of performance of various Cd-ISE is given in Table 3. As can be seen the proposed Cd-ISE performed as well as the others. An additional advantage is that no plasticizer or exotic materials such as additives and ion exchangers are needed.

Table 4
Determination of cadmium in environmental samples.

Sample	Concentration of Cd^{2+} (μg mL^{-1})[a]	
	AAS	Proposed ISE
Agricultural soil	0.28 ± 0.01	0.31 ± 0.01
Roadside soil	1.35 ± 0.02	1.38 ± 0.01
Industrial area soil	2.61 ± 0.01	2.64 ± 0.01
Green tea	0.12 ± 0.01	0.11 ± 0.02
Black tea	0.25 ± 0.02	0.25 ± 0.02
Chinese cabbage	0.21 ± 0.01	0.21 ± 0.03
Spinach	0.23 ± 0.01	0.28 ± 0.02

[a] RSD values are based on triplicate measurements.

3.3. Analysis of real samples

To evaluate the utility of the proposed ISE, experiments were carried out to determine cadmium in various environmental, food (tea, vegetables) (Table 4) and biological samples (Table 5). The cadmium content in each sample was measured using the proposed ISE and compared to the AAS using the standard addition method. The emf measurements were done at optimum pH. The results showed that the proposed electrode can be used as a probe for the determination of cadmium in real samples.

Table 5
Determination of cadmium in biological samples.

Sample	Added (μg mL^{-1})	Found by AAS (μg mL^{-1})[a]	Found by proposed ISE (μg mL^{-1})[a]	% Recovery
Cow liver	–	0.10 ± 0.02	–	0
	0.025	–	0.12 ± 0.03	96.0
	0.25	–	0.37 ± 0.02	105.7
	2.50	–	2.52 ± 0.15	97.0
Cow kidney	–	0.12 ± 0.01	–	0
	0.025	–	0.15 ± 0.01	103.4
	0.25	–	0.39 ± 0.01	105.4
	2.50	–	2.63 ± 0.10	100.4
Cow heart	–	0.031 ± 0.001	–	0
	0.025	–	0.05 ± 0.02	92.9
	0.25	–	0.26 ± 0.02	92.5
	2.50	–	2.50 ± 0.26	98.8
Chicken liver	–	0.040 ± 0.002	–	0
	0.025	–	0.07 ± 0.01	104.6
	0.25	–	0.27 ± 0.01	93.1
	2.50	–	2.51 ± 0.06	98.8
Chicken heart	–	0.045 ± 0.001	–	0
	0.025	–	0.07 ± 0.02	105.7
	0.25	–	0.28 ± 0.06	94.9
	2.50	–	2.51 ± 0.15	98.6

[a] RSD values are based on triplicate measurements.

4. Conclusions

The P4VP film formed by electro-polymerization has been found to have better properties for polymer-modified electrode applications. This is likely due to the differences in the polymer structure and adhesion to the graphite substrate depending on the method of formation. Cd-ISE based on P4VP have shown to give Nernstian responses to cadmium over a wide concentration range of at least three orders of magnitude and fast response time. Detection limits of 10^{-7} M and appropriate pH range of 4.00–7.50 were observed. The superiority of the P4VP over the other conventional polymers membrane electrode is important since the lower cost and easier construction of the ISEs make it much more attractive. The P4VP-based electrode also shows great promise for the determination of cadmium in real samples in situ. The Cd-ISE is able to function well over the linear range obtained without adding plasticizers to the membrane. Studies on P4VP copolymerization as the next generation of coated wire electrode are currently under way.

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