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Potentiometric determination of Cd(II) ions using PVC-based polyaniline Sn(IV) silicate composite cation-exchanger ion-selective membrane electrode

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ABSTRACT

Polyaniline Sn(IV) silicate composite cation-exchanger membranes were fabricated by using solution casting method and used for the preparation of ion-selective membrane electrode (ISME). The membrane electrode showed a linear response of potential for cadmium ions in the concentration range from 1×10^{-1} to $1 \times 1 \times 10^{-7}$ M with Nernstian response (28.53 mV decade^{-1} of activity) in pH range from 3.5 to 6.5 with a detection limit of 1×10^{-7} M and fast response time of 10 s. The potentiometric selectivity determined by mixed solution method suggested excellent selectivity for cadmium ions over alkali and alkaline metal interfering ions. The ISME is also applied for the potentiometric titration of cadmium ions using ethylenediamine tetraacetic acid, disodium salt.

Keywords: Composite cation-exchanger; Potentiometric determination of Cd(II); Polyaniline Sn(IV) silicate; Membrane electrode; Selectivity

1. Introduction

Cadmium is considered as an extremely toxic environment pollutant which is being discharged into environment from the natural and anthropogenic sources. The major sources of cadmium exposure including the natural and anthropogenic activities are soil or earth's crust mining, combustion of coal and mineral oils, manufacturing of batteries, smelting, metal plating, alloy processing, nickel–cadmium batteries, paint and pigment industries, consumption of tobacco, etc. Cadmium gets easily dissolved and permeates through the soil, entering water sources, thereby, bioaccumulates in organisms and ecosystems [1]. Cadmium is nonbiodegradable and toxic to human and animals even at low concentration level [2–4].

Various world organizations namely The US Environmental Protection Agency (EPA), World Health Organization (WHO), The Commission of the European Communities, the Food and Agriculture Organization (FAO), and Joint FAO/WHO Expert Committee on Food Additives have proposed the maximum contamination level (MCL) of cadmium in the environment [5–10]. EPA has proposed the MCL for cadmium at 0.005 mg/l or 5 ppb [11]. The exposures to the cadmium above the permissible limit adversely affect the cellular processes, damage the kidney and lungs, produce cardiovascular diseases,

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and destruction of testicular tissues and red blood cells [12]. Experimental and epidemiological studies showed the low-level of cadmium is responsible for extreme risk of cancer [13] and WHO has also defined cadmium as a human carcinogen and especially prostate cancer [14–16]. Thus, monitoring cadmium in the environment is a serious concern worldwide [17]. Several conventional techniques including atomic absorption spectrometry, flame atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, atomic fluorescence spectrometry, gravimetric detection, electrothermal atomic absorption spectrometry, chromatography, photometry, etc. have been used [18–31]. However, these conventional techniques need sophisticated instrumentation and sample preparation, and are expensive, time-consuming and/or inconvenient for *in situ* monitoring. Therefore, over the past decades, determining cadmium has caused increasing interest to develop novel electrochemical sensors to resolve the above-mentioned problems associated with conventional techniques. The electrochemical sensors are considered fairly simple, low cost, and readily available techniques to determine cadmium and are suited for portable environmental applications. Among the various electrochemical methods, ion-selective membrane electrode (ISME) potentiometry has become a well-established electrochemical method to determine low levels of metal ions in environmental samples [32–34]. It takes over several advantages like simple instrumentation, low cost, fast response time, and selectivity over various analytical techniques used. Therefore, in this study, a Cd(II) ISME based on polyaniline Sn(IV) silicate composite cation-exchanger is prepared and successfully used for the potentiometric determination of cadmium.

2. Experimental

2.1. Reagents and instruments

Main reagents used for the synthesis were aniline, stannic chloride pentahydrate, sodium metasilicate, and potassium persulfate. These reagents were purchased from Sigma Aldrich, Germany. All other reagents and chemicals were of analytical reagent grade. The main instrument used during the study was a single electrode pH meter (744, Metrohm, Switzerland).

2.2. Preparation of standard solution

The solutions of stannic chloride pentahydrate and sodium metasilicate were prepared in de-ionized water (Milli Q). Aniline and potassium persulfate solutions were prepared in 1.0 M HCl. A solution of 0.1 M $Cd(NO_3)_2$ was prepared by dissolving $Cd(NO_3)_2$ salt in 100 ml de-ionized water while other standard $Cd(NO_3)_2$ solutions of 1×10^{-1}–1×10^{-10} concentrations were prepared by dilution step-by-step.

2.3. Preparation of polyaniline Sn(IV) silicate composite cation-exchanger

Composite cation-exchanger polyaniline Sn(IV) silicate was prepared as reported by Naushad et al. [35]. The typical method of preparation is given below.

Polyaniline gel was prepared by mixing 1:1 volume ratio of 10% aniline and 0.2 M potassium persulfate with continuous stirring. Green colored polyaniline gel was obtained by keeping the solution below 10°C for 1 h. The precipitate of Sn(IV) silicate was prepared by adding 0.2 M sodium silicate solution gradually into an aqueous solution of 0.2 M stannic chloride pentahydrate at a pH of 1.75 and at room temperature (25 ± 2°C). The gel of polyaniline was added to the inorganic precipitate of Sn(IV) silicate and mixed thoroughly with constant stirring. The resultant gel was kept in mother liquor for 24 h at room temperature for digestion. The supernatant liquid was filtered and washed with Milli Q water to remove adhering ions. The material was dried in an oven at 50 ± 2°C for 48 h. The composite cation-exchanger was cracked and the particle size of about 125 μm was obtained by sieving and stored in desiccator. The ion-exchange capacity was determined by standard column process. One gram of the dry cation-exchanger in the H^+-form was taken into a glass column having an internal diameter (i.d.) ~1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1 M $NaNO_3$ as eluent was used to elute the H^+ ions from the cation-exchange column, maintaining a slow flow rate (~0.5 ml min^{-1}). The effluent was titrated against a standard 0.1 M NaOH solution for the total ions liberated in the solution using phenolphthalein indicator and the ion-exchange capacities in meq dry g^{-1} of the exchanger is determined. The ion-exchange capacity of this composite cation-exchanger was found to be 1.75 meq dry g^{-1} of exchanger.

2.4. Preparation of polyaniline Sn(IV) silicate membrane

The method of preparation of polyaniline Sn(IV) silicate composite ion-exchange membrane was similar to that of Coetzee and Benson [36]. The electroactive material, i.e. polyaniline Sn(IV) silicate composite cation-exchanger was grinded to fine powder, and was mixed thoroughly with PVC, dissolved in 10 ml of tetrahydrofuran (THF), and finally mixed with 10 drops of dioctylphthalate used as a plasticizer [37]. The mixing ratio of the ion-exchanger was varied with a fixed content of PVC to obtain a composition, which gave the membrane showing the best performance, and the resulting solutions were carefully poured into glass casting rings (diameter 10 mm) resting on a glass plate. These rings were left for slow evaporation of THF to obtain thin films. In this way four sheets of different thickness of master membranes were obtained.

2.5. Characterization of membrane

The prerequisite performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters were membrane water content, porosity, thickness, swelling, etc. and were determined as described elsewhere [38–41] after conditioning the membrane as given below.

2.5.1. Conditioning of the membrane

The membranes were conditioned by equilibrating with 1 M sodium chloride; about 1 ml of sodium acetate was also added to adjust the pH 5–6.5 (to neutralize the acid present in the film).

2.5.2. Water content (% total wet weight)

The conditioned membranes were first soaked in water to elute diffusible salts, blotted quickly with Whatman filter paper to remove surface moisture, and immediately weighed. These were further dried to a constant weight in vacuum over P_2O_5 for 24 h. The water content (% total wet weight) was calculated as:

$$\%\ \text{Total wet weight} = \frac{W_w - W_d}{W_w} \times 100 \tag{1}$$

where W_w = weight of the soaked/wet membrane and W_d = weight of the dry membrane.

2.5.3. Porosity

Porosity (ε) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data.

$$\varepsilon = \frac{W_w - W_d}{AL\rho_w} \tag{2}$$

where A = area of the membrane, L = thickness of the membrane, and ρ_w = density of water.

2.5.4. Thickness and swelling

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze.

Swelling was measured as the difference between the average thicknesses of the membrane equilibrated with 1 M NaCl for 24 h and the dry membrane. The results of the membrane characterization are given in Table 1.

2.6. Fabrication of ion-selective electrode

The membrane sheet (M-1) of 0.32 mm thickness as obtained by the above procedure was cut in the shape of disk and mounted at the lower end of a Pyrex glass tube (o.d. 1.6 cm, i.d. 0.8 cm) with Araldite. Finally, the assembly was allowed to dry in air for 24 h. The glass tube was filled with 0.1 M $Cd(NO_3)_2$ solution. A saturated calomel electrode was inserted in the tube for electrical contact and another saturated calomel electrode was used as an external reference electrode. The whole arrangement can be shown as:

Table 1
Characterization of ion-exchanger membranes

S. no.	Membrane composition			Thickness (mm)	Water content as % weight of wet membrane	Porosity	Swelling as % weight of wet membrane
	Polyaniline Sn (IV) silicate (mg)	PVC (mg)	Plasticizer (drops)				
M-1	100	200	10	0.32	13.10	0.078	0.2
M-2	150	200	10	0.39	14.50	0.095	0.2
M-3	200	200	10	0.43	18.00	0.123	0.2
M-4	250	200	10	0.56	19.93	0.145	0.2

Internal reference electrode (SCE)	Internal electrolyte 0.1 M Cd^{2+}	Membrane	Sample solution	External reference electrode (SCE)

2.7. EMF measurement

All response potentials of the ISME were measured by varying the concentration of $Cd(NO_3)_2$ in a range between 1×10^{-10} and 1×10^{-1} M obtained from the sequential dilution from stock solution of 1×10^{-1} M $Cd(NO_3)_2$. Essentially, the membrane electrode was conditioned by soaking in a 0.1 M $Cd(NO_3)_2$ solution for five to seven days and for 1 h at least before use. The experiments were conducted in an air thermostat maintained at 25 ± 1℃. After performing, the experiment membrane electrode was removed from the test solution and kept in a 0.1 M $Cd(NO_3)_2$ solution to maintain the activity. Potential measurements of the membrane electrode were plotted against the logarithmic function of selected concentrations of the respective ions in an aqueous medium using the electrode assembly. The calibration graphs were plotted three times to check the reproducibility of the system. To study the characteristics of the electrode, the following parameters were evaluated: lower detection limit, slope response curve, response time, and working pH range.

The response time was measured by recording the e.m.f. of the electrode as a function of time when it was immersed in the solution to be studied. The electrodes were first dipped in 1×10^{-3} M solution of the ion concerned and immediately shifted to another solution (pH 4.0) of 1×10^{-2} M ion concentrations of the same ion (10-fold higher concentration). The potential of the solution was read at zero second, that is, just after immediate dipping of the electrode in the second solution and afterwards recorded at the intervals of 5 s. The potentials were then plotted against the time. The time during which the potentials attain a constant value represents the response time of the electrode. The lifetime of the membrane electrode was determined by periodically recalibrating the potentiometric response to Cd^{2+} ions in standard $Cd(NO_3)_2$ solutions. The influence of pH of the test solution on the potential response of ISME was tested at 1×10^{-2} M, concentration of cadmium over the pH range 1–9. The pH variations were brought out by adding dilute acid (HCl) or dilute alkali (NaOH) solutions. The value of the electrode potential at each pH was recorded and was plotted against pH.

To study the cationic interference because of other ions, the selectivity coefficients of various interfering cations for the ISME was determined by the mixed solution method as discussed elsewhere [42]. A beaker of constant volume contained a mixed solution having a fixed concentration of interfering ion (M^{n+}) ($1{\times}10^{-3}$ M) and varying concentrations ($1{\times}10^{-1}$–$1{\times}10^{-10}$ M) of the primary ion. Now the potential measurements were made by using the membrane electrode assembly and plotted against the logarithmic of the concentration of ions under study.

3. Results and discussion

The composite cation-exchanger polyaniline Sn(IV) silicate was prepared as reported by Naushad et al. [35]. This cation-exchanger showed the ion exchange capacity of 1.75 meq/dry g of ion exchanger. Based on distribution studies composite cation-exchanger was found selective for cadmium, a toxic metal pollutant of the water [35]. To explore the applicability of this cation-exchanger in environmental pollution analysis, the fabrication and characterization of ISME was carried out as given below.

Four samples of polyaniline Sn(IV) silicate cation selective membranes were prepared using different mixing ratios of electroactive material polyaniline Sn (IV) silicate and PVC dissolved in THF with a fixed amount (10 drops) of plasticizer dioctylphthalate. The ion-exchanger was varied to change the thicknesses of the membranes. These membranes were characterized to find out one membrane of good electrochemical performance for preparation of an ISME and the results are given in Table 1. It is observed that as the electroactive polyaniline Sn(IV) silicate increased, the thickness, swelling, water content, porosity increased. Thus, the low orders of water content, swelling, and porosity with less thickness of this membrane suggest that interstices are negligible and diffusion across the membrane would occur mainly through the exchange sites. Therefore, membrane sample M-1 (thickness 0.32 mm) was selected for preparing the ion-selective electrode for further studies.

The membrane electrode prepared from membrane sample M-1, showed a linear Nernstian response to the concentration of Cd^{2+} in the range of 1×10^{-1}–1×10^{-7} M with a slope of 28.53 ($R^2 = 0.9998$) mV/decade

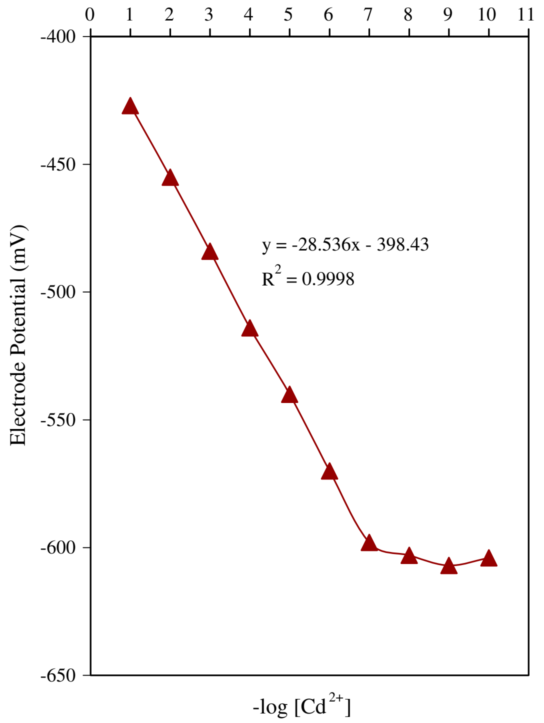

Fig. 1. Calibration curve for Cd^{2+} ion-selective polyaniline Sn(IV) silicate membrane electrode.

change in concentration of cadmium ions as shown in Fig. 1. The linear range of this electrode was assumed to be the working concentration range with a limit of detection of 1×10^{-7} M (Fig. 1). The dynamic response time of an ion-selective electrode is the time to reach a cell potential of 90% of the final equilibrium potential, after successive addition in a series of solutions each having a 10-fold higher difference. It was noted the polyaniline Sn(IV) silicate composite ISME displayed dynamic response time of 10 s on successive addition of 10-fold higher Cd(II) concentrations from 1×10^{-3} to 1×10^{-2} M as shown in Fig. 2. The fast response time is ascribed because of the stoichiometric exchange of cadmium ions with the counter ions present at the membrane interface. Naushad et al. [35] reported that polyaniline Sn(IV) silicate composite cation-exchanger is selective for cadmium ions. Thus, the use of this cation-exchanger as electroactive material for the preparation of ISME may reduce the response time of electrode. To check the sensitivity of this electrode, its performance should also be checked before using for any analysis. It was observed the potential for this electrode showed no significant changes in the slope of Nernst plot during the experiments over a time period of three months. Therefore, three months are assumed to be the lifetime of this electrode with stable electrode response.

Working of an ion-selective electrode is significantly dependent on the pH of the test solution [43]. This electrode showed a constant potential response for 1×10^{-2} M Cd(II) ion concentration in the pH range from 3.5 to 6.5 as shown in Fig. 3. Therefore, the working pH range for this electrode was considered to be pH 3.5–6.5. The comparison of response characteristics of this electrode was found comparable with previously reported Cd^{2+} ion-selective electrodes [11,12,44,45] (Table 2).

The interference of other ions on the selectivity of this ISME was determined at pH 4 by the mixed solution method [42]. The response potentials in presence of interfering ions were observed and were plotted against the logarithms of the concentration Cd^{2+} ion concentration as shown in Fig. 4. Fig. 4 showed that Na(I), K(I), Ca(II), Mg(II) and Sr(II) do not interfere with the determination of Cd(II) ions. The interference

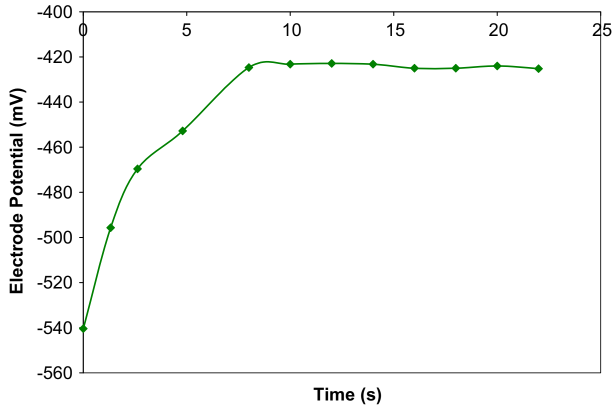

Fig. 2. Response time characteristics of Cd^{2+} ion-selective polyaniline Sn(IV) silicate membrane electrode at different time interval for 1×10^{-2} M concentration of cadmium.

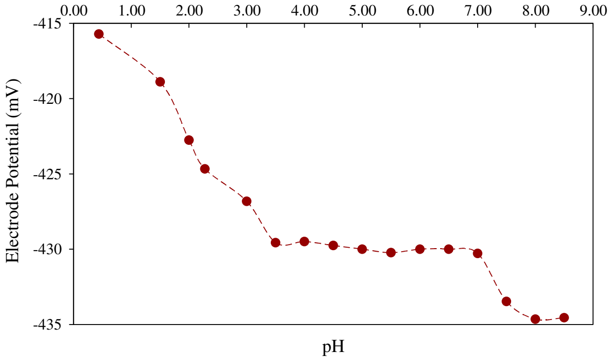

Fig. 3. Effect of pH of the test solution on the potential response of the polyaniline Sn(IV) silicate ion-selective membrane electrode at 1×10^{-2} M, concentration of cadmium.

Table 2
Comparison of the response characteristics of different Cd^{2+} ion-selective electrodes

S. no.	Working concentration range (M)	Life time	pH range	Response time	Slope (mV)/ decade	References
1	1×10^{-2}–2×10^{-7}	Not mentioned	4.0–7.0	15 s	29.9	[11]
2	1×10^{-1}–1×10^{-6}	2 Months	2.8–8.1	20 s	30.1 ± 1.0	[12]
3	1×10^{-3}–1×10^{-7}	1 Month	2.0–7.1	5–10 s	29.4 ± 0.3	[44]
4	1×10^{-1}–3.2×10^{-6}	3 Months	4.5–6.5	8 s	29.5	[45]
5	1.4×10^{-1}–3.3×10^{-8}	2–3 Months	3.5–7.6	<5 s	Not mentioned	[46]
6	1×10^{-1}–1×10^{-7}	3 Months	3.5–6.5	10 s	28.53	Proposed study

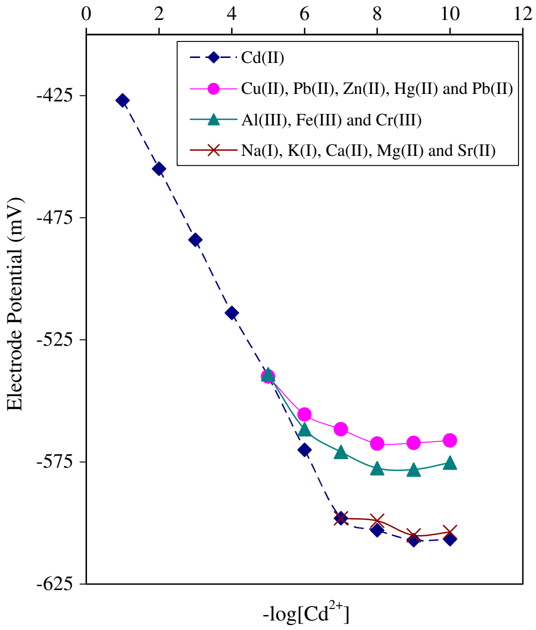

Fig. 4. Response curve of the Cd(II) selective membrane electrode for the interference of other metal ions.

was observed by divalent and trivalent heavy metal ions heavy metal ions. These metal ions start interfering from 1×10^{-5} M Cd(II) concentration which is suggesting that in presence of divalent and trivalent heavy metal ions limits the measurement only up to 1×10^{-5} M Cd(II) ion concentration.

The analytical applicability of this electrode was also examined for potentiometric titration of Cd(II) ions using ethylenediamine tetraacetic acid disodium salt (EDTA). A 15 ml $Cd(NO_3)_2$ solutions at 1×10^{-2} M concentration was titrated against 1×10^{-2} M EDTA solution and the electrode potential was measured after each successive addition of 1 ml of EDTA at pH 4. The addition of EDTA causes a decrease in potential because of the decrease in free Cd(II) ion concentration due to formation of a complex with EDTA (Fig. 5). The Cd(II) ions in solutions can be accurately determined from the resulting neat titration curve providing a sharp end point. It is also clear from the figure that the sharp end point at 15 ml of EDTA agrees to the stoichiometry of Pb(II)–EDTA complex.

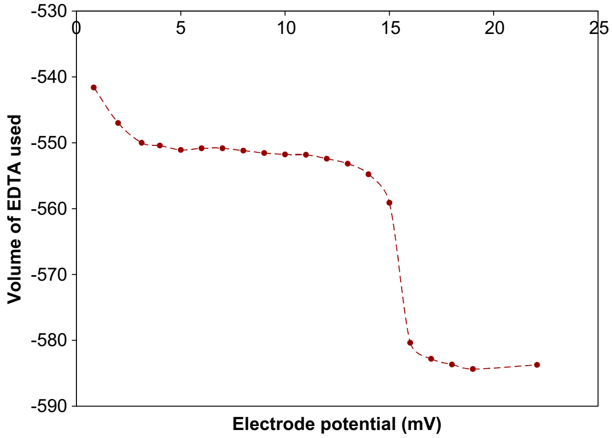

Fig. 5. Precipitation titration curves of 15 ml $Cd(NO_3)_2$ solution at 1×10^{-2} M concentration against 1×10^{-2} M EDTA solution.

4. Conclusions

In this study, PVC-based polyaniline Sn(IV) silicate composite cation-exchanger ISME was fabricated for the potentiometric determination of cadmium ions. The electrode was found to be selective, sensitive with good life span. The membrane electrode is also found selective for cadmium ions in presence of various interfering ions. The membrane electrode could be applied as an indicator electrode for the potentiometric titration of cadmium ions.

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