



## ORIGINAL ARTICLE

# Ion imprinted polymer based potentiometric sensor for the trace determination of Cadmium (II) ions



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**Abstract** A cadmium (II) ion selective electrode (ISE) based on an ion-imprinted polymer (IIP) as a novel ionophore has been prepared and studied. The ion-selective electrode (ISE) was prepared by dispersing cadmium (II) IIP particles in 2-nitrophenyloctyl ether as a plasticizer and then embedding them in a polyvinylchloride polymeric matrix. The Cd(II) ISE showed a nernstian response for cadmium (II) over the dynamic concentration range of  $2.0 \times 10^{-7}$ – $1.0 \times 10^{-2}$  mol L<sup>-1</sup>, with a slope of 29.9 mV per decade. The limit of detection was  $1.0 \times 10^{-7}$  M. The proposed electrode revealed good selectivity over a wide variety of other cations including alkali, alkaline earth, heavy and transition metals. The accuracy of the proposed electrode was checked through the analysis of spiked water samples.

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## 1. Introduction

Cadmium is a toxic heavy metal that appears in the environment mainly due to industrial processes. Besides natural exposure from soil or the earth's crust with high cadmium content, anthropogenic processes like the combustion of coal and mineral oils, smelting, mining, alloy processing, paint industries, etc. are the major sources of cadmium to the people in the vicinity of the industrial areas. Human uptake of cadmium takes

place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. Another important source of cadmium emission is the production of artificial phosphate fertilizers. Cadmium strongly adsorbs to organic matter in soil (Rezaei et al., 2008). United States Environmental Protection Agency (EPA) has found that cadmium potentially causes the following health effects when people are exposed to it at levels above the maximum contaminant level (MCL) for relatively short periods of time: nausea, vomiting, diarrhea, muscle cramps, salivation, sensory disturbances, liver injury, convulsions, shock and renal failure. In addition, in long-term, cadmium has the potential to cause the following effects from a lifetime of exposure at levels above the MCL: kidney, liver, bone and blood damage. The MCL has also been set at 0.005 milligrams per liter (mg/L) or 5 parts per billion (ppb) by EPA (United States Environmental Protection Agency, <http://>

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[www.epa.gov](http://www.epa.gov)). Therefore, the determination of trace levels of cadmium in environmental samples is necessary and of great importance. Recently, several techniques including flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma mass spectrometry (ICP-MS) and atomic fluorescence spectrometry (AFS) have been used for the determination of trace amounts of cadmium in different samples (Li et al., 2002; Ye et al., 2003; Yaman, 2005; Xu et al., 2000; Tsalev et al., 2002; Dolan et al., 2003; Dias et al., 2005; Lu et al., 2002). However, most of these techniques are expensive, time consuming and/or inconvenient for in situ monitoring. These problems could be solved by the application of electrochemical methods, which are relatively simple, low cost and readily available techniques. Among the various electrochemical methods, potentiometry with ion selective electrodes is one of the most convenient and reliable electroanalytical tools for estimating metal-ion concentrations.

Imprinted polymers are biomimetic materials used for the sensitive and selective detection of analyte molecules. Through host guest interactions, imprinted polymers often display recognition capabilities comparable to those of antibody-antigen systems. An especially appealing feature of the imprinted polymers is their potential to have the affinity and selectivity analogous to antibodies, while retaining several benefits including greater stability, ease of production, lower cost and stability in harsh environments such as high temperatures and pressures (Prasada Rao et al., 2006). Mosbach and co-workers (Rosatzin

et al., 1991) described the first imprinted polymer potentiometric electrode for calcium and magnesium ions. Since that, until now, numerous studies on the ion imprinted polymers (IIP) and their use in ISE have been reported (Anuradha Baghel et al., 2007; Prasad et al., 2006). This paper reports a novel Cadmium (II) ion selective electrode based on Cadmium (II) IIP particles dispersed in 2-nitrophenyloctyl ether (NPOE) and embedded in a polyvinylchloride (PVC) matrix, for the monitoring of traces of Cadmium (II) ions.

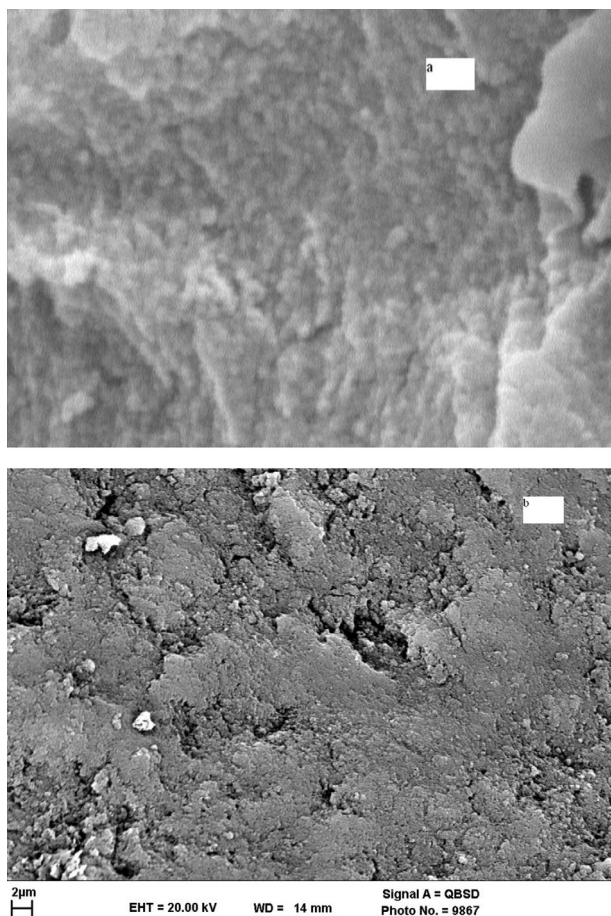
## 2. Experimental

### 2.1. Reagent and materials

Cd (II) stock solution ( $0.10 \text{ mol L}^{-1}$ ) was prepared by dissolving 2.013 g of  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  (Fluka) in acidified deionized water and making up the final volume to 100 mL. More dilute solutions were prepared daily by appropriate dilution of this stock solution with distilled water. 5,7-Dichloroquinoline-8-ol was purchased from Acros organics (New Jersey, USA). 4-vinyl pyridine, methyl methacrylate (MMA), ethyleneglycoldimethacrylate (EGDMA), triethylamine and 2, 2-azo bisisobutyronitrile (AIBN) were obtained from Merck (Germany). In addition, O-nitrophenyloctylether (o-NPOE), dioctylphthalate (DOP), dibutylphthalate (DBP), sodium tetraphenylborate (NaTPB) and high relative molecular weight polyvinylchloride (PVC) were obtained from Aldrich (Milwaukee, USA). Other chemicals were of analytical grade and purchased from Merck (Germany). Deionized water has been used throughout all experiments.

### 2.2. Preparation of the ion-imprinted polymer based electrodes

The Cadmium (II) ion imprinted polymer (IIP) was synthesized via a single pot method by dissolving of the ternary complex of Cadmium with DCQ and VP in acetonitrile (porogen) and then, copolymerizing thermally after the addition of MMA (monomer) and EGDMA (crosslinking monomer) in the presence of AIBN (initiator). Then the obtained polymer was ground and the imprinted Cd(II) ions were leached from the polymer particles by stirring for 6 h with three portions of  $\text{HNO}_3$  (3 M, 25 mL). Finally, the particles were washed several times with double distilled water and dried at  $45^\circ\text{C}$ . The non-imprinted polymer (NIP) was prepared using the same protocol except that Cd(II) did not exist in the polymerization mixture. A graphite disk electrode was fabricated from a graphite rod with 4 mm diameter housed and glued onto a Teflon holder. The exposed surface of the disk electrode was polished to a shiny finish with SiC paper. The electrode was rinsed with deionised water and allowed to dry. The PVC membrane electrodes were prepared by thorough mixing of PVC, NPOE, NaTPB and Cadmium (II) IIP particles ( $60\text{--}85 \mu\text{m}$  size) in proportions of 21%, 21%, 43% and 15% (w/w), respectively and dissolving in 2.5 mL of tetrahydrofuran (THF). The mixture was homogenized in a sonicator, poured into a watch glass until a viscose mixture was obtained. Then, the polished surface of a graphite electrode was dipped into this mixture and the solvent was allowed to evaporate completely. Thereafter, a thin PVC film formed on the graphite electrode surface.



**Figure 1** SEM photographs of IIP (a) unleached and (b) leached.

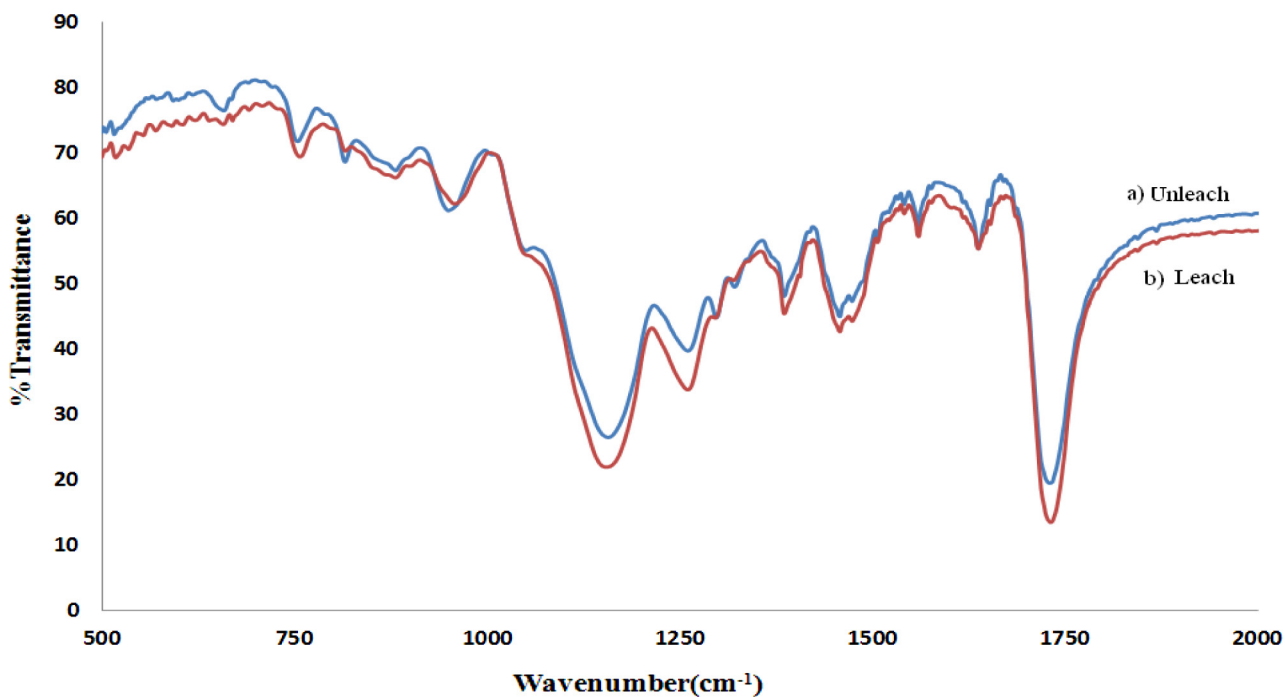
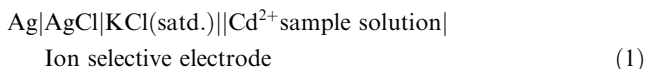


Figure 2 FT-IR spectra of the unleached (a), leached (b) IIP particles.

### 2.3. Conditioning of the electrodes and emf measurement

The Cadmium (II) IIP based ISE was conditioned for 48 h in a 0.01 mM Cadmium (II) solution at the pH value of 6.0. The potentials were measured by varying the concentration in the range of  $1 \times 10^{-8}$ – $1.0 \times 10^{-1}$  M. Potential measurements were made with a potentiometer, model pHM-632 (Metrohm, Swiss) having  $\pm 0.01$  mV accuracy with an Ag/AgCl reference electrode. All measurements were carried out at 25 °C with cell type:



## 3. Results and discussion

In this paper, the suitability of the IIP particles dispersed in NPOE and embedded in PVC for selectively recognizing cadmium ions was examined.

### 3.1. Characterization of Cd (II) imprinted polymer

The Cadmium IIP particles were characterized by FT-IR and SEM techniques. The surface morphologies of the leached and unleached polymers were shown by SEM as depicted in Fig. 1. The SEM images confirm the Cd (II) removal as well as the enhanced surface area in the leached polymer. Thus, the ordered nano-pattern observed in the SEM image of the leached polymer is probably due to the metal ion imprinting of Cadmium (II) into the polymer. The FT-IR spectra of the unleached and leached IIP particles were recorded by the KBr pellet method using a Bomem spectrometer. The peak near  $756 \text{ cm}^{-1}$  corresponded to  $\nu_{\text{C-Cl}}$  in the spectra of both the leached and unleached polymers, illustrating that DCQ was kept intact in the polymer even after leaching (Fig. 2).

### 3.2. Potential response

The potential responses of the electrodes prepared with Cadmium (II) IIP membrane has been given in Fig. 3 in which a slope of 29.9 mV per decade over a concentration range of  $2.0 \times 10^{-7}$ – $1.0 \times 10^{-2}$  M of Cadmium (II) is observed. The limit of detection was  $1 \times 10^{-7}$  M Cadmium (II) calculated based on the IUPAC definition. The same experiment was carried out in the case of the electrode fabricated with NIP. This electrode showed almost a constant potential with respect to increase in cadmium (II) concentration from  $2.0 \times 10^{-7}$  to  $1.0 \times 10^{-2}$  M.

### 3.3. Effect of electrode composition

Literature shows that the sensitivity and selectivity of the ion selective electrodes depend upon various features of the

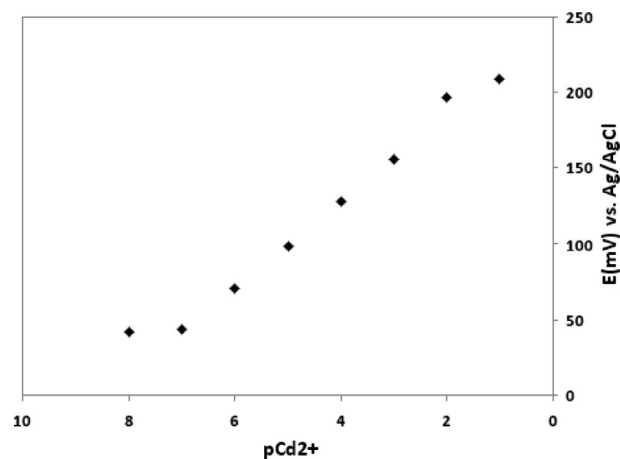


Figure 3 Potential response of ISE with Cadmium (II) IIP.

**Table 1** Composition of the graphite disk electrodes and their potentiometric response characteristics.

No.	PVC (%)	Plasticizer (%)	IIP particle (%)	NaTPB (%)	Slope(mV decade <sup>-1</sup> )	Linear range
1	21	NPOE, 50	21	8	27.5	$1 \times 10^{-3}$ to $1 \times 10^{-6}$
2	31	NPOE, 40	21	8	23.1	$1 \times 10^{-2}$ to $1 \times 10^{-6}$
3	21	NPOE, 40	21	8	28.1	$1 \times 10^{-2}$ to $1 \times 10^{-6}$
4	21	NPOE, 43	21	15	29.9	$1 \times 10^{-2}$ to $2 \times 10^{-7}$
5	21	DOP, 43	21	15	39.1	$1 \times 10^{-2}$ to $1 \times 10^{-6}$
6	21	DBP, 43	21	15	19.2	$1 \times 10^{-3}$ to $1 \times 10^{-6}$

membrane such as the nature and the amount of the plasticizers and the ion recognizing material used (Ganjali et al., 2003a, 2003b; Shamsipur et al., 2000). Thus, different aspects of electrode preparation using Cadmium (II) IIP particles were optimized and the results have been shown in Table 1. It is well known that the plasticizer has major effects on the electrochemical properties of conventional ISEs. These solvent mediators strongly influence the working concentration range of ISEs. Thus, the effect of different plasticizers, i.e. O-NPOE, DOP and DBP, on the potential response of the cadmium (II) IIP based ISE has been investigated. In addition, the addition of appropriate amounts of plasticizer leads to optimum physical properties and ensures the high mobility of ions in the membrane. As results show, the membrane with O-NPOE as plasticizer gives a Nernstian slope over the concentration range of  $2.0 \times 10^{-7}$ – $1.0 \times 10^{-2}$  M with a detection limit of  $1 \times 10^{-7}$  M. This is in accordance with the previously reported ISEs as in the case of ISE reported by Shamsipur et al. (2000). The ISE with plasticizer having higher dielectric constant viz., O-NPOE ( $\epsilon = 24.0$ ) gives better sensitivity compared to DOP ( $\epsilon = 5.2$ ) and DBP ( $\epsilon = 6.4$ ).

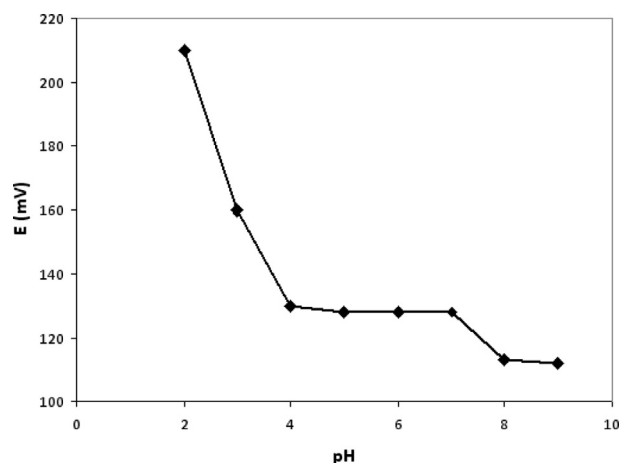
Moreover, the effect of the addition of NaTPB to Cadmium (II) IIP particle based membrane on the potentiometric response of the electrode was examined. There are several reports on the effect of lipophilic salts or ionic additives upon the characteristics of ISEs as they reduce the anionic interference and lower the electrical resistance of the membrane in conventional ISEs (Gupta et al., 2007).

### 3.4. pH effect of the test solution

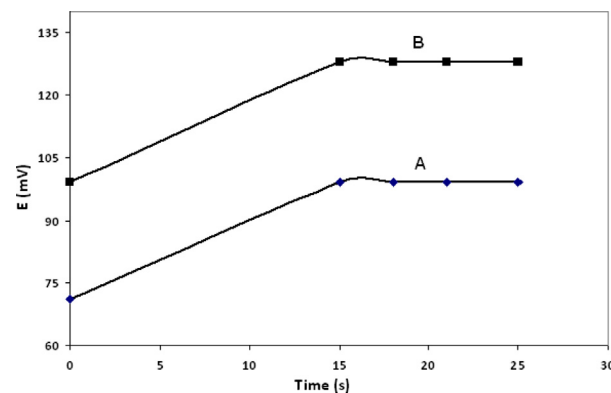
The pH dependence of the sensor number 4 (Table 1) has been tested over the range of 3–9 for  $1.0 \times 10^{-4}$  M  $\text{Cd}^{2+}$ . The pH was adjusted with a dilute solution of nitric acid or sodium hydroxide. The potential of the sensor was plotted as a function of pH (Fig. 4). It is clear that the potential remains constant over the pH range of 4–7, which may be taken as the working pH range of the sensor assembly. The observed increase in the potential at low pH values indicates that the ionophore responds to the hydronium ions.

### 3.5. Response time

Response time is the average time required for the electrodes to reach a potential response within  $\pm 1$  mV of the final equilibrium value. The response time was recorded by changing the cadmium (II) concentration in solution over a concentration range of  $1.0 \times 10^{-6}$ – $1.0 \times 10^{-4}$  M. The actual potential versus time traces has been shown in Fig. 5. As seen from the figure, the cadmium (II) IIP based ISE reaches the equilibrium re-



**Figure 4** Effect of pH of the test solution ( $1 \times 10^{-5}$  M of Cadmium (II)) on the potential response of the Cadmium (II) IIP based ISE.



**Figure 5** Dynamic response of the Cadmium (II)IIP based ISE for stepwise concentration change of Cadmium (II) (A)  $1.0 \times 10^{-6}$  M to  $1.0 \times 10^{-5}$  M, (B)  $1.0 \times 10^{-5}$  M to  $1.0 \times 10^{-4}$  M.

sponse in a time of about 15 s. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements performed in the sequence of high to low concentration (from  $1 \times 10^{-4}$  to  $1 \times 10^{-6}$  M) indicate that the response of the cadmium (II) IIP based ISE was reversible.

### 3.6. Interference studies

Potentiometric selectivity coefficients, describing the preference of the Cadmium (II) IIP based ISE for cadmium ion

**Table 2** Potentiometric selectivity coefficient values,  $K_{Cd,M}^{pot}$ .

$M^{n+}$	$K_{Cd,M}^{pot}$
Na <sup>+</sup>	$4.0 \times 10^{-4}$
K <sup>+</sup>	$5.0 \times 10^{-4}$
Cu <sup>2+</sup>	$1.0 \times 10^{-2}$
Ni <sup>2+</sup>	$1.0 \times 10^{-2}$
Mg <sup>2+</sup>	$6.0 \times 10^{-4}$
Ca <sup>2+</sup>	$1.0 \times 10^{-3}$
Ag <sup>+</sup>	$1.0 \times 10^{-5}$
Zn <sup>2+</sup>	$4.0 \times 10^{-3}$

**Table 3** Result of the determination of Cadmium (II) in tap water.

Sample	Added cadmium(M)	Found cadmium(M)	Recovery (%)
Tap water <sup>a</sup>	–	Detection limit	–
Tap water	$1 \times 10^{-5}$	$9.25 \times 10^{-6}$	92.5

<sup>a</sup> Mashhad city.

(A) relative to an interfering ion B were determined by the matched potential method, recommended by IUPAC (Umezawa et al., 1995). According to this method, a specified activity (concentration) of the primary ion ( $A = 1 \times 10^{-5}$  M) is added to a reference solution ( $5.0 \times 10^{-6}$  M of cadmium (II)) and the potential is measured. In a separate experiment, interfering ions are successively added to an identical reference solution, until the measured potential matched with that obtained on the addition of the primary ions. The selectivity coefficient has been given by the resulting primary ion to interfering ion activity (concentration) ratio. As shown in Table 2 the selectivity coefficients are in the order of  $\sim 1.0 \times 10^{-2}$  or smaller.

### 3.7. Analytical application

The proposed cadmium (II)-selective electrode was applied to obtain recovery of cadmium (II) in a tap water sample with satisfactory results. The analysis was performed by using the standard addition technique. The results are summarized in Table 3. Good recovery was obtained in tap water.

## 4. Conclusions

In conclusion, we have successfully demonstrated the design and development of Cadmium (II) ion sensitive ISE based on IIP particles which is highly selective for Cadmium (II) compared to several coexisting inorganic cations even with a nonselective DCQ and VP as chelating agents. By proper choice of chelating agents and employing the concept of ion imprinting, one can fabricate ISE, which can be specific for Cadmium (II) in the presence of other inorganics. Studies are in progress in choosing one such chelating agent.

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