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Synthesis, Characterization and Pb(II) Ion Selectivity of *N, N´*-bis(2-hydroxy-1-napthalene)-2,6-pyridiamine (BHNPD)

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N,N´-bis(2-hydroxy-1-napthalene)-2,6-pyridiamine (BHNPD)(**I**) has been synthesized by the reaction of 2,6-diaminopyridine with 2-hydroxy-1-napthaldehyde at 60 ºC in methanol. The BHNPD (**I**) was characterized by FT-IR, ^1H NMR and elemental analyzer (C, H, N). PVC-based membranes of BHNPD (**I**) were prepared and investigated for response toward Pb^{2+} ions. The best performance was obtained for the membrane of composition (BHNPD) (**I**): PVC: NaTPB: NPOE in the ratio 3:120:2:150. The sensor shows a linear potential response for Pb^{2+} over wide concentration range 3.2×10^{-6} - 1.0×10^{-1} M with Nernstian compliance (29.1 mV decade^{-1} of activity) between a wide pH range (3.5-7.5) and a fast response time of 10 s. This sensor can also be used in partially non-aqueous media having upto 20 %(v/v) methanol, ethanol or acetone content with no significant change in the value of slope or working concentration range. The selectivity coefficient values are in the range of 1.0×10^{-2} to 1.0×10^{-4} for mono-, bi-, and trivalent cations and anions, which indicate good selectivity for Pb^{2+}. The sensor has a lifetime of six months and could be used as an indicator electrode in the potentiometric titration of Pb^{2+} vs. EDTA and also in the estimation of lead in waste water.

Keywords: Polyvinyl chloride; *N,N´*- bis(2-hydroxy-1-napthalene)-2,6-pyridiamine (BHNPD); lead selective sensor; Nernstian slope.

1. INTRODUCTION

The amount of lead present in the environment is a result of its release by natural processes and a long history of anthropogenic use of lead. Its increasing use in the various industries such as storage batteries, gasoline, cable manufacture, paint industry and ammunition have resulted in recurring environmental contamination in developing and industrialized areas of the world. It is accumulated throughout the food chain and ultimately reaches the human organism causing poisoning which results in brain damage, nephropathy, sluggishness, hyperirritability, restlessness, loss of skin colour and appetite. Due to its toxicity, its determination is important. A number of instrumental methods, such as atomic absorption spectrometry (AAS), cold vapour AAS or flame AAS-ETA (electrothermal atomization) [1-4], inductively coupled plasma-optical emission spectroscopy (ICP-OES)[5], anodic stripping voltammetry [6], chromatography [7], gravimetric detection [4] or photometry [4,8-12] are used for its determination at low concentration level. These methods generally require sample pretreatment and infrastructure backup and are not very convenient for routine analysis of large number of environmental samples. To monitor metals in large number of environmental samples, ion selective sensors are the convenient means as they provide fast analysis. For the analysis of lead ions, therefore attempts have been made to develop a number of Pb(II) selective sensors. Thus, a number of lead sensor based on heterogeneous membranes of lead chelates [13], crown ethers [14-27], calixarenes [28-31], acyclic benzopolyether diamides [32], 5,5'-dithiobis-(2-nitrobenzoic acid) [33], 4,7,13,16-tetrathenoyl-1,10-dioxa-4,7,13,14-tetraazacyclooctadecane [34], benzyldisulphide [35], bis(anthraquinone)sulphide derivatives [36], aquatic humic substances [37], schiff bases [38-40], piroxicam [41], capric acid [42], tetrabenzyl pyrophosphate [43], 2,6-bis-pyridinecarboximide [44] and tetrakis(2-hydroxy-1-naphthyl)porphyrins [45] in PVC have been reported. However, most of these suffer from one or other electrode characteristics, i.e., working concentration range, selectivity, response time, pH range and life time. It is known that schiff bases form strong complexes with Pb^{2+} ions as these can be used for fabricating the Pb^{2+} selective membranes. Therefore, we synthesized a new schiff base *N, N'*- bis(2-hydroxy-1-napthalene)-2,6-pyridinediamine (BHNPD) and PVC based membranes of BHNPD using different plasticizers have been prepared and investigated as a selective material for Pb^{2+} ions. The results of these investigations are presented in this communication and show that the sensor prepared is better in many respects as compared to the existing sensors.

2. EXPERIMENTAL

2.1 Reagents

2-naphthol was obtained from BDH E-Merck, India Limited (India) and 2,6-diaminopyridine was obtained from Aldrich (USA). Solvents and reagents were purified and dried by distillation. High molecular weight polyvinyl chloride (PVC), Aldrich (USA); 2-nitrophenyl octyl ether (NPOE) (ACROS Organics, New Jersey, USA); dioctylphthalate (DOP) (Reidel, India), chloronapthalene (CN) (Merck, Germany), tri-n-butylphosphate (TBP) (BDH, England), sodium tetraphenyl borate (NaTBP) (BDH, UK) were used as received. 0.1 M stock solution were prepared by dissolving AR grade metal nitrates solution in double distilled water and standardized wherever necessary. The working solutions of different concentration were prepared by stock solution.

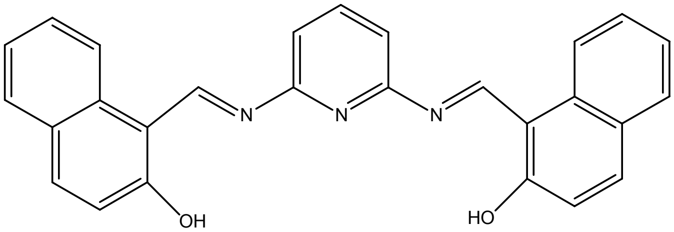
2.2 Equipments

The melting point of BHNPD was determined on JSGW apparatus. Microanalysis (C, H and N) were performed using an Elemental NLR Vario (III) (Germany) elemental analyzer. FT-IR spectra were obtained on a Nicolet (USA) spectrometer (200-4000 cm^{-1}) prepared as KBr pellets. ^{1}H spectrum was obtained on a Bruker Avance 250 Spectrometer (Germany), using TMS as the internal standard. The potential measurements were carried out at 25 ± 0.1 °C with a digital pH meter (Model 5652 A, ECIL, India) and microvoltmeter, model CVM 301, Century, (India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrodes.

SCE / internal solution (0.1 M Pb^{2+}) / membrane / test solutions / SCE

*2.3 Synthesis of N, N′- bis(2-hydroxy-1-napthalene)-2,6-pyridinediamine (BHNPD)(**I**)*

2, 6-diaminopyridine (4 mmol, 0.436 gm) was added to a stirring solution of 2-hydroxy-1-napthaldehyde (0.979 gm, 8 mmol), prepared by the reported method [46]. in methanol (10 mL). The resulting mixture was refluxed at 60 ºC and stirred for 3 h. The reaction mixture was cooled to room temperature and the resulting precipitate was filtered and washed with cold methanol. The brown residue was purified by column chromatography (20% ethyl acetate/ 80% petroleum ether (60-90 ºC)) to give pure product. Yield = 68% and m.p = 320-325 ºC.



N,N′- bis(2-hydroxy-1-napthalene)-2,6-pyridiamine (BHNPD)(**I**)

Anal. Calc. for $C_{27}H_{19}N_3O_2$: C, 77.69; H, 4.56; N, 10.07; Found C, 77.75; H, 4.60; N, 10.12 %. Infrared spectrum (cm^{-1} KBr disk); ν(C=N) 1634 (s), ν (phenolic C-O) 1354 (s); ν (CH_2) 836 (m), ^1H NMR ($CDCl_3$, ppm); δ (phenolic OH) 15.18-15.20 (d, 2H, OH exch.); 10.03 (s,1H, HC=N); 8.18-8.20 (d, 2H, Ar); 7.79-7.85 (q, 2H, Ar); 7.67-7.69 (d, 2H, Ar); 7.57-7.61 (t, 2H, Ar); 7.36-7.40 (t, 2H, Ar); 7.01-7.05 (d,2H,Ar); 6.93-6.97(d, 2H, Ar).

2.4 Membrane Preparation

The PVC based membranes were prepared by dissolving appropriate amounts of schiff Base (BHNPD), anion excluder NaTPB, solvent mediators (2-nitrophenyl octyl ether (NPOE), dioctyl phthalate (DOP), 1-chloronaphthalene (CN) and tri-*n*-butylphosphate (TBP) and appropriate amount of PVC in THF (5-10 mL). After complete dissolution of all the components and thorough mixing, the homogeneous mixture was poured into polyacrylate rings placed on a smooth glass plate. THF was allowed to evaporate at room temperature. The transparent membranes of 0.4 mm thickness were removed carefully from the glass plate. A 5 mm diameter piece was cut out and glued to one end of a "Pyrex" glass tube. The membranes thus prepared were equilibrated in 0.1 M Pb^{2+} solution. Membranes of different compositions were prepared and investigated. Those, which gave reproducible results and best performance characteristics, were selected for detailed studies. The optimum compositions of best performing membranes are given in Table 1.

3. RESULTS AND DISCUSSION

3.1 Potential Response of the membranes

The potential of the sensor was determined as a function of Pb^{2+} concentration and shown in Figure 1. The working concentration range and slopes were calculated from these plots and compiled in Table 1 along with composition of membrane and response time. It is seen from Figure 1 that the sensor no.1 having membrane of Schiff Base (BHNPD) (**I**) without plasticizer exhibits linear response over a working concentration range of 7.9×10^{-5} to 1.0×10^{-1} M with a slope of 27.4 ± 0.1 mV/decade of activity and a response time of 23 seconds. The slope of the membrane is near-Nernstian and the working concentration range is narrow. The improvement in the performance was attempted by the addition of plasticizers to the membranes. The addition of plasticizers not only improves the workability of the membranes but also contributes significantly towards the improvement in the working concentration range, stability and life time of the sensor [47, 48]. However, the selectivity remains usually unaffected and mainly depends on the metal-ionophore interaction. The plasticizer to be used in membranes should exhibit high lipophilicity, have high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane. Additionally, its viscosity and dielectric constant should be adequate [49]. Thus, four plasticizers namely, DOP, CN, TPB and NPOE were added to improve the performance of the sensors. The results obtained are shown in Figure 1 and all performance characteristics of the sensors are compiled in Table 1. The addition of the four plasticizers to the membranes of BHNPD (sensor nos. 2-5) improved the working concentration range and the slope (Figure 1 and Table 1). The best performance characteristics are obtained with the membrane having NPOE as plasticizer (sensor no 5).

Table 1. Composition of PVC membranes of (I) and performance characteristics of Pb^{2+} selective sensors based on them

Sensor No.	Components in membranes (w/w)							Working Concentration range (M)	Slope($\pm$1.0 mV/decade of activity)	Response Time (s)
	(**I**)	PVC	NaTPB	DOP	CN	TPB	NPOE			
1.	3	120	2	-	-	-	-	7.9×10^{-5} to 1.0×10^{-1}	27.4	23
2.	3	120	2	150	-	-	-	5.6×10^{-5} to 1.0×10^{-1}	35.0	22
3.	3	120	2	-	150	-	-	3.5×10^{-5} to 1.0×10^{-1}	29.4	20
4.	3	120	2	-	-	150	-	5.0×10^{-5} to 1.0×10^{-1}	31.1	35
5.	**3**	**120**	**2**	**-**	**-**	**-**	**150**	$\mathbf{3.2 \times 10^{-6}}$ **to** $\mathbf{1.0 \times 10^{-1}}$	**29.1**	**12**

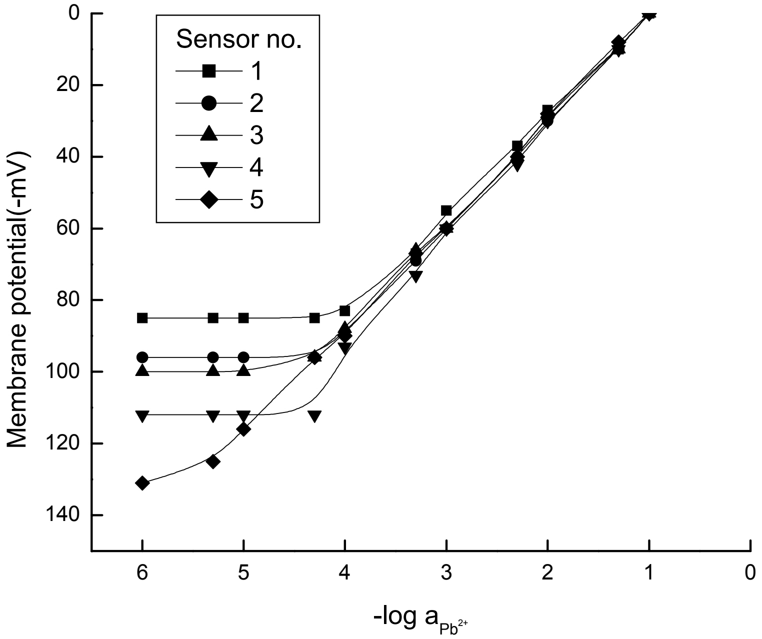


Figure 1. Variation of membrane potential with Pb^{2+} ions concentration; PVC based membranes of (**I**) (BHNPD) without solvent mediator (1), with solvent mediators, DOP (2), 1-CN (3), TBP (4), and NPOE (5).

This sensor exhibits the maximum working concentration range of 3.2×10^{-6} - 1.0×10^{-1} M with almost Nernstian slope (29.1 ± 0.1 mV $decade^{-1}$ of activity) and low response time (12 s). In view of the best performance of sensor no.5 in terms of wide working concentration range, low response time and Nernstian slope; all further studies were carried out with this electrode only. The sensor could be used satisfactorily for a period of over six months. The membranes were kept equilibrated with 0.5 M Pb^{2+} solution when not in use.

3.2 pH and solvent effect

The pH dependence of the membrane sensor (no. 5) was investigated at two concentrations of Pb^{2+} (1.0×10^{-3} and 1.0×10^{-4} M) and the results obtained are given in Figure 2. It is seen from this figure that the potential remains constant over a pH range of 3.5 to 7.5. The sharp change in potential below pH 3.5 may be due to co-fluxing of H^+ with Pb^{2+} while above 7.5 may be due to hydrolysis of Pb^{2+} ions.

The performance of the sensor was further assessed in partially non-aqueous media i.e. methanol-water, ethanol-water and acetone-water mixture. The results obtained are compiled in Table 2. It is seen that with increase in aqueous content, the slope is slightly increased but the working concentration range is reduced. Thus, the electrode can be used in partially non-aqueous media containing up to 20% methanol, ethanol and acetone. Above this non-aqueous content, the decrease in concentration range is significant.

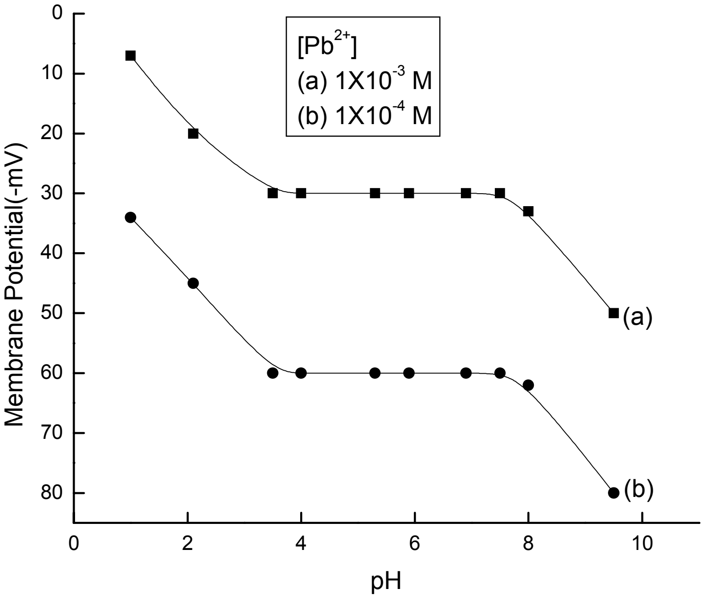


Figure 2. Effect of pH on cell potential; $[Pb^{2+}] = 1.0 \times 10^{-3}$ (a) and 1.0×10^{-4} M (b)

Table 2. Effect of partially non-aqueous medium on the working of Pb^{2+} sensor (Sensor no. 5)

Non- aqueous Content (% v/v)	Slope (mV/decade of activity)	Working Concentration Range (M)
0	29.1	3.2×10^{-6} to 1.0×10^{-1}
Methanol		
10	29.1	3.2×10^{-6} to 1.0×10^{-1}
20	29.1	5.0×10^{-6} to 1.0×10^{-1}
25	28.5	3.8×10^{-5} to 1.0×10^{-1}
Ethanol		
10	29.1	3.2×10^{-6} to 1.0×10^{-1}
20	29.2	3.6×10^{-6} to 1.0×10^{-1}
25	28.4	4.5×10^{-5} to 1.0×10^{-1}
Acetone		
10	29.1	3.2×10^{-6} to 1.0×10^{-1}
20	29.3	5.0×10^{-6} to 1.0×10^{-1}
25	30.5	5.0×10^{-5} to 1.0×10^{-1}

3.3 Potentiometric Selectivity

The selectivity of membrane sensors is one of the most important parameter that determines the utility of the sensor. Thus, selectivity studies were carried out only for sensor no. 5, which exhibited the best performance characteristics. The selectivity coefficients ($K^{Pot}_{Pb^{2+},B}$) were determined by the modified form of Fixed Interference Method as suggested by Sa'ez de Viteri and Diamond [50] and are given in Table 3.

Table 3. Selectivity coefficients of sensors no. 5 on the membrane of (I) by Fixed Interference Method.

Interfering ions (B)	Selectivity Coefficient(I) $K^{Pot}_{Pb^{2+},B}$
Li^+	6.3×10^{-3}
Na^+	7.9×10^{-3}
K^+	1.9×10^{-3}
NH_4^+	1.0×10^{-3}
Ba^+	1.0×10^{-2}
Ni^{2+}	7.0×10^{-2}
Ca^{2+}	5.0×10^{-2}
Zn^{2+}	2.5×10^{-2}
Cd^{2+}	1.3×10^{-2}
Hg^{2+}	1.0×10^{-2}
Al^{3+}	8.9×10^{-2}
Fe^{3+}	3.2×10^{-2}
CH_3COO^-	3.2×10^{-4}
Cl^-	3.2×10^{-4}

A value of 1.0 for selectivity coefficient indicates equal response to both primary and interfering ion. It is seen from Table 3 that the selectivity coefficients values are substantially less then 1.0, which show that the sensor has good selectivity to Pb^{2+} over mono-, di- and trivalent cations studied. Hence, this sensor can be used for Pb^{2+} estimation in presence of these metal ions provided their concentrations are similar to or lesser than Pb^{2+} concentration.

The interference of anions were also investigated. Figure 3 shows that the presence of CH_3COO^- and Cl^- does not cause any interference in the determination of Pb^{2+}. This may be due to the addition of anion excluder (NaTPB), which prevents the interference of anions.

3.4 Potentiometric Titration

The utility of sensor has been further assessed by as an indicator electrode in the potentiometic titration of Pb^{2+} solution by titrating 10 ml of 1.0×10^{-3} M $Pb(NO_3)_2$ against 1.0×10^{-2} M EDTA solution. The pH of the solution was maintained at 4.0 throughout the titration with dil. HCl and NaOH. The titration plot obtained (Figure 4) at pH 4.0 is of standard sigmoid shape and the end point corresponds to 1:1 stoichiometry of Pb-EDTA complex.

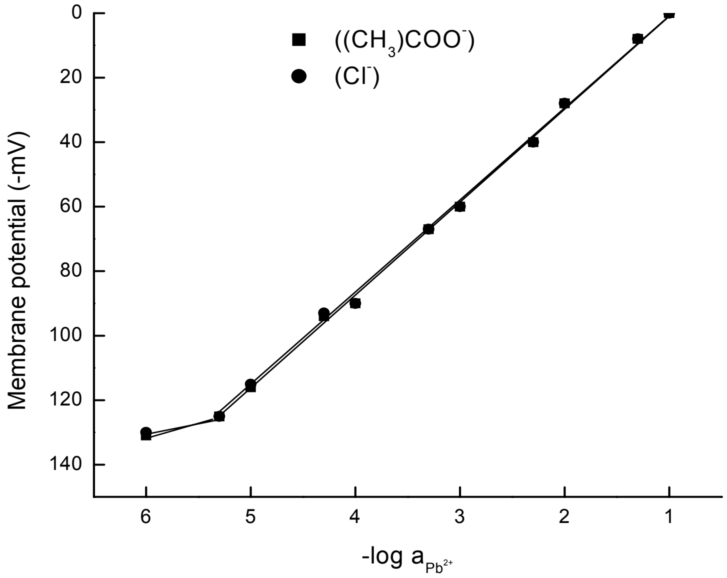


Figure 3.. Effect of anions; variation of potential with Pb^{2+} ions concentration.

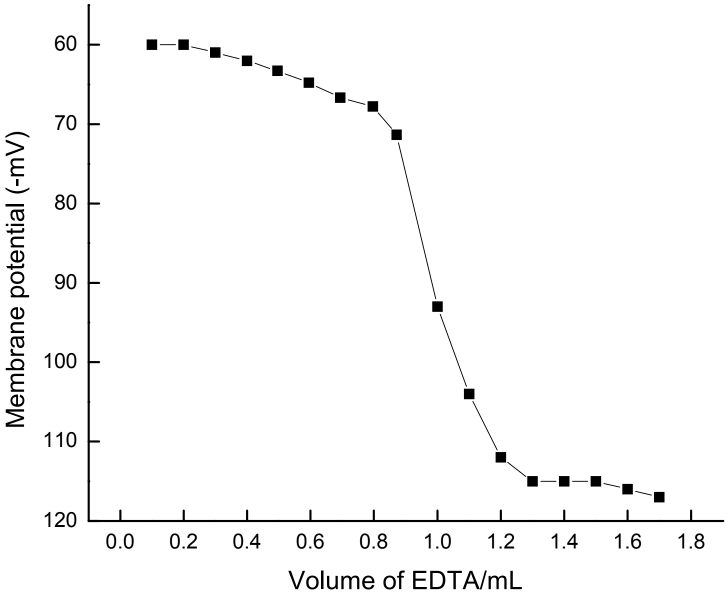


Figure 4. Potentiometric titration plot of 1.0×10^{-3} M Pb^{2+} solution (10 mL) with EDTA (1.0×10^{-2} M).

4. ANALYTICAL APPLICATION

The sensor was also used to determine the concentration of lead in waste water. The result obtained by the proposed sensor is in good agreement with AAS (Table 4).

Table 4. Quantification of lead in waste water using AAS and Pb^{2+} sensor (no.5)

Sample	**Lead content (ppm)**	
	Sensor no. 5	**AAS**
Waste water	4.2 ± 0.1	4.4 ± 0.2

Table 5: Comparison of the proposed ion selective sensor with the existing solid state

Sensor No.	Working concn. range (M)	Slope (mV/decade of activity)	pH range	Response time (s)	Detection limit (M)	Interference	Ref No.
1.	$1.0x10^{-5}$-$1.0x10^{-1}$	30.0	3.0-9.0	60	$>1.0x10^{-5}$	-	[26]
2.	$1.0x10^{-6}$-$8.0x10^{-3}$	29.0	3.0-6.0	40	$>8.0x10^{-7}$	-	[28]
3.	$1.0x10^{-6}$-$1.0x10^{-1}$	30.0	1.5-6.0	15	$>6.0x10^{-7}$	-	[31]
4.	$2.0x10^{-6}$-$1.0x10^{-2}$	29.3	3.5-6.3	45	$>1.2x10^{-6}$	-	[35]
5.	-	29.4	5.0-7.0	10	$>9.12x10^{-7}$	-	[39]
6.	$2.5x10^{-6}$-$1.0x10^{-2}$	30.0	1.6-6.0	-	-	-	[40]
7.	$1.0x10^{-5}$-$1.0x10^{-1}$	30.0	4.0-8.0	45	$>4.0x10^{-6}$	Ag^{+}	[41]
8.	$4.0x10^{-6}$-$1.0x10^{-2}$	26.0-33.1	4.5-7.0	10	0.4-3.7μg/ml	-	[44]
9.	$3.2x10^{-5}$-$1.0x10^{-1}$	29.2	fixed 6.0	10	$>3.5x10^{-6}$	-	[45]
10.	$3.2x10^{-6}$-$1.0x10^{-1}$	29.1	3.5-7.5	10	$>3.2x10^{-6}$	-	Proposed sensor

5. CONCLUSION

The investigations demonstrate the utility of the membrane sensor incorporating *N, N′*- bis(2-hydroxy-1-napthalene)-2,6-pyridinediamine (BHNPD) as electroactive phase in determining Pb^{2+}in the concentration range 3.2×10^{-6} to 1.0×10^{-1} M. The functional pH range is 3.5 to 7.5 and most of the ions, commonly present with Pb^{2+} in real samples do not cause any disturbance with this sensor. It could be used as an indicator electrode in the potentiometric titration of Pb(II) ions with EDTA. Analytical application shows that it holds promise for regular and routine analysis of Pb^{2+} in diverse samples. It exhibits good reproducibility, fast response time and can be used for more than six months in aqueous as well as non-aqueous medium. This sensor exhibits either comparable or better performance to the existing electrodes, already reported by many researchers for the determination of lead ions, regarding working concentration range [26,27,40,44], pH range [27-28,31,39,43-44], response time [26-28,31,40] and detection limit [26,40,44] (Table 5). Therefore, the proposed sensor is a good addition to the existing list of the lead ions selective sensors reported till date.

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