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Complete List of Authors:	Kaushal, Sandeep; Sri guru granth sahib world university, Fatehgarh sahib, Punjab, India Badru, Rahul; Punjabi University, Chemistry Kumar, Sanjeev; Sri guru granth sahib world university, Fatehgarh sahib, Punjab, India, Physics Mittal, Susheel; Thapar University, Patiala Dhillon, Pritpal; Sri Guru Sahib World University Fatehgarh Sahib, Chemistry
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Fabrication of Mercury (II) Ion Selective Electrode based on Poly-*o*-toluidine Zirconium Phosphoborate

Sandeep Kaushal[1,4], Rahul Badru[1], Sanjeev Kumar[2], Susheel K Mittal[3] and Pritpal Singh[1*]
[1]Department of Chemistry, Sri Guru Granth Sahib World University, Fatehgarh Sahib (Pb), India.
[2]Department of Physics, Sri Guru Granth Sahib World University, Fatehgarh Sahib (Pb), India
[3]School of Chemistry & Biochemistry, Thapar University, Patiala 147004, India
[4]Punjab Technical University, Jalandhar (Pb) India

Fax: +91-1763-234236, Email: dhillonps2003@gmail.com

Abstract: This work covers various aspects of a new ion selective electrode for mercury (II) ions, designed by incorporation of poly-*o*-toluidine (PTD) into zirconium phosphoborate (ZrPB) ion exchanger. The designed sensor showed pretty good detection ability towards Hg^{2+} ions in comparison to alkali, alkaline earth, transition and even some heavy metal ions. The crystallinity and morphology of synthesized composite has been explored using X-ray diffraction, scanning electron microscope and transmission electron microscope. A linear near Nernstian response for Hg (II) ions with a slope of 28.0 mV decade^{-1} over a wide concentration range (1×10^{-7} M to 1×10^{-1} M) has been observed. The limit of detection is 7.08 $\times10^{-8}$ M (0.014 ppm). Moreover, the electrode showed significantly same results in the pH range 2.5-10.0, a fast response time of 6s and a life-time of at least 6 months without any divergence in potential. It has been successfully applied as an indicator electrode in potentiometric titrations, and quantitative estimation of Hg (II) ions in tap water, CFL unit waste water and thermometer unit waste.

Keywords: hybrid ion exchanger, zirconium phosphoborate, toluidine, ion selective electrode, potentiometry.

1. Introduction

The need to detect and quantify mercury in soil and water has been a matter of serious concern, due to its severe toxicity known as ‘mercury poisoning’ [1]. Several methods have been employed for detection of mercury ions in solution that include atomic absorption spectrometry (AAS) [2], inductively coupled plasma mass spectrometry (ICP-MS) [3],inductively coupled plasma atomic emission spectrophotometry (ICP-AES) [4], atomic fluorescence spectrometry (AFS) [5], spectrophotometry [6], anodic stripping voltammetry [7] and X-ray fluorescence (XRF) [8] etc. In addition, many potentiometric mercury electrodes having detection limits as low as 2 ppm have also been demonstrated [9].

Although potentiometry is a highly-selective, sensitive, fast and cost friendly technique for estimation, yet these potentiometric probes have not proven useful for analysis, as mercury ion concentration in samples is generally in ppb range. Moreover, most of these probes rely on chelating agent to achieve mechanical entrapment of metal ion [10] or use ionophores [11] or neutral carriers [12]. Short working lifetime due to loss of chelating agent from the membrane by leaching with passage of time is a major drawback of these membrane electrodes.

In view of limitations of above mentioned reported methods like high cost of operation and number of parameters involved for optimization of experimental conditions, poor results in the presence of interfering ions, there is a pressing need for a simple, reproducible and inexpensive probe for Hg^{2+} ions. In this study, poly-*o*-toluidine incorporated zirconium phosphoborate (ZrPB) [13] composite membrane was prepared, which was found to be selective for Hg^{2+} ions, with detection limit as low as 0.014 ppm. The potency of the proposed membrane has been checked by carrying out potentiometric estimation of Hg^{2+} ions titrimetrically with EDTA and quantitative estimation of Hg (II) ions in tap water, CFL unit waste water and thermometer unit waste. To the best of our knowledge, no such membrane has been reported previously for estimation of Hg^{2+} ions in aqueous solution.

2. Experimental

2.1. Reagents and Instruments

Analytical grade reagents i.e. ortho-toluidine, zirconyl oxychloride, boric acid, phosphoric acid and potassium persulphate were used for synthesis, without any further purification. The phase purity and crystallinity of the particles was studied by PAN-Analytical DY 3190 X-ray diffraction-meter. Perkin Elmer RXI FTIR spectrometer was used to record IR spectra. Thermal studies of *o*-toluidine-ZrPB composite were carried out using thermogravimetric analyser (Hitachi SGA7400). Digital potentiometer (model 318, Systronics, India) and pH meter (Elico, model number-1012) were employed for potentiometric studies and pH measurements, respectively.

2.2. Preparation of Composite Ion exchanger

2.2.1. Synthesis of ZrPB

Sol-gel method was employed for the synthesis of zirconium (IV) phosphoborate ion-exchanger. 0.1 M zirconyl oxychloride solution was added to a continuously stirred mixture of 0.1 M boric acid and 0.1 M phosphoric acid solutions at 60^0 C, in the volume ratio 2:1:1.

The gel formed was permitted to stand overnight. The gel was repeatedly washed with distilled water to remove chloride ions. The gel was then filtered and dried in an air oven at 40 °C.

2.2.2. Preparation of Poly-*o*-toluidine

10% *o*-toluidine solution (v/v) was prepared in 1M HCl solution, at a temperature below 10 °C. Potassium persulphate solution (0.1 M) was added to this solution with continuous stirring, maintaining pH ~1 and ice cold conditions [1a]. The completion of reaction and formation of poly-*o*-toluidine (PTD) was indicated by the change of brown colour of solution to green gel. The reaction mixture was stirred for another 30 minutes. This PTD gel was used in the next step.

2.2.3. Preparation of Poly-*o*-toluidine-ZrPB Composite Ion-Exchanger

Six different samples of PTD-ZrPB composite ion exchanger were prepared by varying the volume ratio of poly-*o*-toluidine and ZrPB (**Table 1**). In all the cases, mixture of ZrPB ion exchanger and PTD gel was refluxed at 50°C for 2 hours with constant stirring. Poly-*o*-toluidine-zirconium phosphoborate composite was obtained after repeated washing with double distilled water, followed by filtration.

Table 1. Optimization of reaction parameters and ion exchange capacity of PTD-ZrPB cation-exchanger

S. No.	**Mixing volume ratio**			**Mixing volume ratio**		**Colour**	**Ion Exchange Capacity (meq/g)**
	0.1 M zirconyl oxychloride	**0.1 M boric acid**	**0.1 M phosphoric acid**	**10 % toluidine in 1 M HCl**	**0.1 M Potassium persulphate**		
S-1	1	0.5	0.5	0	0	White	0.38
S-2	1	0.5	0.5	0.10	0.10	Green	0.40
S-3	1	0.5	0.5	0.25	0.25	Green	0.46
S-4	1	0.5	0.5	0.50	0.50	Green	0.55
S-5	1	0.5	0.5	0.75	0.75	Green	0.50
S-6	1	0.5	0.5	1.00	1.00	Green	0.41

2.3. Ion-exchange capacity (IEC)

The ion-exchange capacity of the composite ion exchanger was determined by column method, using 0.1 M sodium nitrate solution as an eluent. The H^+ ions eluted from the column were determined titrimetrically against standard solution of sodium hydroxide.

$$\mathrm{IEC} = \frac{\mathrm{N \times V}}{w} \mathrm{meq/g}$$

where IEC is ion exchange capacity, N and V are normality and volume in ml of NaOH, respectively, and w is mass in gram of PTD-ZrPB composite. The ion exchange capacity of all the six samples was determined before proceeding for further electro-chemical studies (**Table 1**).

2.4. Characterization of PTD-ZrPB composite

2.4.1. Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray (EDX) studies

Fig. 1a shows the low resolution SEM micrograph of PTD-ZrPB composite (S-4). This micrograph reveals the formation of clusters in the synthesized composite. A high resolution FESEM micrograph (**Fig. 1b**) of same sample (S-4) has been taken to further explore the structure of nanocomposite. This micrograph shows the regions of agglomerations (marked as region P) as well as aggregations (marked as region Q) of the nanocomposite particles. The EDX (**Fig. 1c**) confirmed the presence of Zr, P, C, N, O and B in the composite.

2.4.2. X-ray Diffraction Studies

X-ray diffraction pattern of composite ion exchanger was recorded between 5° to 50° at 2θ, using Cu Kα radiation (Fig. 2). The sharp peaks in the X-ray diffraction pattern indicate the crystalline nature of synthesized composite. The diffraction pattern further reveals that the sample exhibits characteristic peaks of PTD-ZrPB which are well matched with JCPDS card numbers 39-1893 and 23-0063, thus confirming the crystalline nature of sample.

2.4.3. Transmission Electron Microscopic (TEM) Studies

Fig. 3 shows the TEM image of PTD-ZrPB composite taken at a magnification of 2,00,000X. The TEM micrograph reveals the rod shaped structure of the synthesized sample. Rods of different aspect ratios (i.e. length to diameter) are clearly visible in the micrograph. A ray diagram has been drawn on the nano rod for better depiction of the axis. As shown in the micrograph, c-axis of the rod is parallel to the growth of the rods. The length and diameter of the rods vary between 70-200 nm and 30-55 nm, respectively. This confirms the nano size of the composite particles. The different aspect ratios of various rods formed are due to confinement free synthesis route adopted in the present study.

2.4.4. FTIR (Fourier Transform Infrared) Studies

Peaks at 3539, 3427, 3012 and 1519 cm^{-1} in the FTIR spectrum of PTD-ZrPB nanocomposite (**Fig. 4**) correspond to organic counterpart, while peak at 1025 and 636 cm^{-1} corresponds to inorganic exchanger, clearly indicating the incorporation of PTD into the inorganic matrix. Peak at 3012 cm^{-1} is due to aromatic C-H stretching, whereas peaks at 3539 cm^{-1} and 3427 cm^{-1} may be assigned to O-H and N-H stretching vibrations respectively. Despite benzenoid ring stretching at 1519 cm^{-1} [14], peak at 1220 cm^{-1} corresponds to C-N stretching in the neighbourhood of a quinoid ring [15]. Ionic phosphate stretching appears at 1025 cm^{-1} [16]. Peak at 636 cm^{-1} may be assigned to M-O stretching [17].

2.5. Distribution Studies (K_d values)

This experiment was conducted to know distribution coefficients of the composite ion exchanger for different metal ions in aqueous medium. In typical procedure, 200 mg of PTD-ZrPB composite in H^+ form was equilibrated with 20 ml of 0.01M solution of different metal ions. The mixture was kept for 24 hours at 300K with occasional shaking.

The concentration of metal ions in solution, before and after equilibrium, was determined by standard EDTA solution [18]. The distribution coefficients (K_d) of different metal ions were calculated using the formula:

$$K_d = \frac{I-F}{F} \times \frac{V}{M} mL/g$$

Where I and F are the initial and final concentrations of metal ions in solution, respectively. V is volume of the solution in ml and M is mass of PTD-ZrPB in gram.

2.6. Fabrication and IEC of PTD-ZrPB Composite Ion exchange Membrane

The ion exchange membranes of different thickness were prepared using PTD-ZrPB composite. The cation exchanger was ground to a fine powder (approximately 200 micrometre) and mixed thoroughly with araldite [PTD-ZrPB: epoxy resin = 80:20 (w/w)] till a homogeneous slurry was obtained. The slurry was spread between the folds of a glossy paper and a pressure of 2.0 Kg/cm^2 was applied over the glass plates for 24 hours. The glossy paper was removed by dipping the membrane in distilled water. Circular membranes of different thickness (0.64. 0.83, 0.72 mm) were obtained by cutting with sharp knife. The photographs of the membranes are given in **Fig. 5**.

2.7. Potential Measurements and Calibration of Electrode

All measurements were carried out at 300±1K with the following cell assembly:

Hg-Hg_2Cl_2, KCl (Sat.) |0.05M Hg (II) membrane|| test solution |KCl (Sat.), Hg_2Cl_2-Hg

Mercury (II) solutions of concentration range 5×10^{-9} to 5×10^{-1} M were used to study the performance of electrode. The electrode was stored in 5×10^{-2} M mercury (II) chloride solution after the experiment.

2.8. Response Time

The electrode was immersed in Hg (II) ion solution and electrode potential was recorded as a function of time. In present work, 5×10^{-2} M solution was taken inside the membrane electrode and 5×10^{-3} M solution was used for investigation. The membrane potential was then plotted against time [**Fig. 6**].

2.9. Selectivity Coefficients

The potentiometric selectivity coefficients ($K_{a,B}^{Pot}$) indicate the preference of electrode for Hg^{2+} ions relative to an interfering ion B. Fixed interference method (FIM) was used to evaluate the potentiometric selectivity coefficients of membrane electrode [19]. Concentration of interfering ions was kept constant and that of primary ion (Hg^{2+}) was varied during selectivity coefficient determination. Selectivity coefficients were calculated from the following equation:

$$K_{i,j}^{Pot} = \frac{a_i}{a_j^{\frac{z_i}{z_j}}}$$

Where a_i is activity of primary ion, a_j is the activity of foreign ion, z_i and z_j are the valencies of primary ion and secondary ion, respectively.

2.10. Potentiometric Titration

The membrane electrode was used as an indicator electrode in potentiometric titration of Hg^{2+} solution (1.0 x 10^{-3} M) against EDTA (1.0x 10^{-2} M) as titrant to confirm its analytical usefulness. Electrode potential values were plotted against volume of EDTA solution used.

2.11. Procedure 1: The collected sample was digested by UV-digester in the presence of suitable volumes of both concentrated HNO_3 and H_2O_2 (30%) for 1 h. The solution obtained was neutralized by NaOH (5 M) and 10 mL of this solution was treated under the conditions of recommended procedure [20].

2.12. Analysis of Mercury in Thermometer Unit (TU) Waste

TU waste samples were collected from thermometer manufacturing unit, Ambala (Haryana), India. Sample was treated as per procedure 1 and subjected to Hg(II) ion determination by AAS, mercury analyser and proposed sensor.

2.13. Analysis of Mercury in Compact Fluorescent Lamp (CFL) Waste

CFL waste samples were collected from CFL manufacturing unit, Ambala (Haryana), India. Sample was treated as per procedure 1 and subjected to Hg (II) ion determination by AAS, mercury analyzer and proposed sensor.

2.14. Storage and Life Time of Electrode

PTD-ZrPB membrane electrode was normally kept in 0.05 M Hg (II) solution. However, it was stored in distilled water if not used for more than 24 hours. The life time of the electrode was tested to be 6 months. It was observed that the proposed electrode worked without any significant change in response time and slope during this period.

3. Results and Discussion

PTD-ZrPB composite ion exchanger was prepared by sol-gel method and characterized by techniques like XRD, EDX, SEM, TEM and FTIR. PTD-ZrPB composite ion exchanger possesses enhanced IEC for Na^+ ions than its inorganic counterpart ZrPB under identical conditions. Sample S-4 (**Table 1**) with maximum ion exchange capacity (0.55 meq/g for Na^+ ions) was selected for further studies. The increase in IEC of PTD-ZrPB ion exchanger may be due to the binding of organic material (PTD) with its inorganic counterpart. In addition, the organic part in composite ion exchanger improves the mechanical properties and surface area by providing more exchanging sites on the inorganic counterpart [21].

To study the effect of temperature, 1.0 g of PTD-ZrPB (**S-4, Table 1**) in H^+ form was heated at various temperatures in a muffle furnace (100–600 °C) for 1 h and ion exchange capacity was determined by column method, after cooling the ion exchanger to room temperature (**Table 2**).

Table 2. Ion exchange capacity (for Na^+ ions) of PTD-ZrPB composite ion exchanger heated at different temperatures

Temperature (in °C)	Colour	IEC (Na^+ in meq/g)	% Retention in IEC
50	Green	0.55	100
100	Green	0.50	91.0
200	violet-grey	0.45	82.1
300	violet-grey	0.33	60.0
400	violet-grey	0.27	47.7
500	violet-grey	0.17	30.0

The composite ion exchanger was found to be thermally stable upto 300 °C, and retained 60% of its initial ion exchange capacity. This may be due to the binding of poly-*o*-toluidine polymer part with inorganic counterpart ZrPB. The water loss, decomposition and conversion of material into oxide form may be responsible for decrease in ion exchange capacity after 300 °C.

Distribution Studies

The synthesized composite ion exchanger i.e. PTD-ZrPB was explored for separation of metal ions, on the basis of their distribution studies. The selectivity order of adsorption for various metal ions on PTD-ZrPB composite ion exchanger was observed as Hg^{2+} (198.3) > Mn^{2+} (103.2) > Ba^{2+} (100.3) > Co^{2+} (42.8) > Pb^{2+} (37) > Ni^{2+} (36.6) > K^+ (32.4)> Fe^{3+} (23.6) >Cd^{2+} (23) > Cr^{3+} (21.7). These results clearly indicated that the proposed composite ion exchanger is selective for Hg^{2+} ions. Hence, the present work was carried out to use the proposed composite ion exchanger for fabrication of Hg^{2+} ion selective electrode. One of the main parameters before using an ion exchange membrane as ion selective electrode is its physiochemical characterization [22]. Various properties like thickness, swelling, water content and porosity of the membrane were investigated and reported in **Table 3**. It is evident from **Table 3** that among the prepared membranes, PTD-ZrPB composite membrane M-2 has comparatively higher ion exchange capacity, water content and minimum thickness. Therefore, it was selected for fabrication of ion selective electrode.

Table 3. Characteristics of PTD-ZrPB cation exchange membrane

Membrane	Thickness (mm)	Water Content (%)	Porosity	Na^+ ion exchange Capacity (meq/g)
M-1	0.64	18.4	1.9×10^{-3}	0.23
M-2	0.62	20.1	5.7×10^{-3}	0.27
M-3	0.73	17.4	1.1×10^{-3}	0.21

Response Time and Life Span of Membrane Electrode

The response time of PTD-ZrPB membrane was observed to be 6 seconds (**Fig. 6**). The working period of this ion selective electrode was six months and it worked without any change in response time and detection limit. After this period, the electrode response does not remain reproducible and stable. The slope of the calibration curve decreases sharply.

Slope and Detection Limit

The potential response of PTD-ZrPB membrane was measured for different concentrations of Hg (II) ion solutions. EMF values were plotted against log of activities of Hg (II) ions (**Fig. 7**). The reproduction of results is very important factor for successful operation of an electrode. Thus, the experiments were repeated five times to check and confirm the reproducibility of this electrode system. The electrode showed a linear response in the concentration range 1×10^{-7} M to 1×10^{-1} M, with an average slope of 28.0 mV per decade change in concentration. The limit of detection was calculated according to IUPAC recommendations [23], from intersection of the two extrapolated linear portions of the curve, and was found to be 2.05×10^{-8} M for Hg (II) ions.

Effect of Internal Solution Concentration

As observed from **Fig. 8**, a change in internal solution concentration does not have any significant effect on the response of proposed electrode, as reported by Ganjali et al. [24]. However, a small change in the intercept of the curve is observed.

Effect of non-aqueous Solvents

In most of the real life problems, the sample under investigation may be contaminated with non-aqueous solvents. So, the proposed sensor was investigated in partially non-aqueous media using methanol and acetone mixed with water. As observed from **Table 4**, the addition of non-aqueous solvents did not have any significant effect on the slope of curve and the lower detection limit. Hence, the proposed mercury electrode can be safely used in partially non-aqueous solutions also.

Table 4. Response characteristics of Hg (II) selective electrode in partially non aqueous media

Non Aqueous Solvent	Volume of Solvent (v/v %)	Slope (mV/decade)	Measuring range (M)
Acetone	5	27.0	1×10^{-7} to 1×10^{-1}
	10	27.5	1×10^{-7} to 1×10^{-1}
	15	27.5	1×10^{-7} to 1×10^{-1}
	20	27.0	1×10^{-7} to 1×10^{-1}
Ethanol	5	27.5	1×10^{-7} to 1×10^{-1}
	10	28.0	1×10^{-7} to 1×10^{-1}
	15	26.5	1×10^{-7} to 1×10^{-1}
	20	27.0	1×10^{-7} to 1×10^{-1}

Effect of pH

As shown in **Fig. 9**, the electrode potential of the proposed sensor remains almost constant over the pH range 2.5 to 10.0. At pH lower than 2.5, the electrode potential increases, which might be the result of membrane response to both the hydronium ions and Hg (II) ions, while the sharp decrease in electrode potential above pH 10.0 may be due to precipitation of Hg (II) as $Hg(OH)_2$.

Potentiometric Titrations

The proposed membrane electrode was employed as an indicator electrode in the potentiometric titration of Hg (II) ion solution against EDTA solution, to explore its analytical utility. 10 mL of 1.0×10^{-3} M Hg (II) solution was taken in a 50.0 mL beaker and titrated against 1.0×10^{-2} M EDTA solution. As shown in **Fig. 10**, the addition of EDTA caused a regular decrease in electrode potential due to complexation of mercury (II) ions with EDTA that resulted in decrease of free mercury ion concentration.

Selectivity Coefficient Studies

The potentiometric selectivity coefficients ($K_{a,B}^{Pot}$) of proposed electrode for Hg^{2+} ions relative to other interfering ions are given in **Table 5**. The electrode preferentially responds to primary ion if the value of $K_{a,B}^{Pot} < 1$. It is quite evident from selectivity coefficient values that the proposed electrode is highly selective for Hg^{2+} ions in presence of interfering ions.

Table 5. The selectivity coefficients ($K_{a,B}^{Pot}$) of PTD-ZrPB membrane electrode for different interfering ions

Interfering ion (B)	$K_{a,B}^{Pot}$	Interfering ion (B)	$K_{a,B}^{Pot}$
K^+	0.64×10^{-1}	Mn^{2+}	0.3×10^{-3}
Co^{2+}	0.24×10^{-3}	Ni^{2+}	0.63×10^{-3}
Mg^{2+}	0.12×10^{-3}	Pb^{2+}	0.18×10^{-3}
Ca^{2+}	0.34×10^{-2}	Fe^{3+}	0.12×10^{-2}
Al^{3+}	0.23×10^{-3}	Ba^{2+}	0.37×10^{-3}
Cu^{2+}	0.30×10^{-3}	Cd^{2+}	0.22×10^{-3}

The response characteristics of proposed PTD-ZrPB electrode have been compared with some of the reported sensors for Hg (II) determination (**Table 6**). The proposed sensor exhibits comparable linear range (1×10^{-7} M to 1×10^{-1} M), lower detection limit (7.08×10^{-8} M), better working pH range and response time in comparison to other reported electrodes for Hg (II) determination. The proposed electrode can also be used satisfactorily in partially non-aqueous media, whereas none of the other reported electrodes was used in non-aqueous media. The life time of the proposed sensor is also longer compared to other reported sensors.

Table 6. Comparison of response characteristics of proposed PTD-ZrPB electrode and other reported mercury selective electrodes

References	**Linear Response (M)**	**Low detection limit (M)**	**Slope mV/decade**	**Slope in the presence of non-aqueous solvent**	**pH range**	**Response time (Seconds)**
25	$3.2 \text{ x } 10^{-7}$-$3.2 \text{ x} 10^{-4}$	$1.5 \text{ x } 10^{-7}$	58.8	-----	3.8-7.8	-----
11c	$5.0 \text{ x } 10^{-7}$-$7.0 \text{ x} 10^{-2}$	-----	30.0	-----	1.0 - 3.5	<10
26	$1.8 \text{ x} 10^{-6}$- $1.0 \text{ x} 10^{-1}$	$1.0 \text{ x } 10^{-6}$	29.0	-----	1.0-3.0	30
27	$1.0 \text{ x } 10^{-6}$-$1 \text{ x } 10^{-2}$	$1.0 \text{ x } 10^{-6}$	27.8	-----	1.0-6.0	20

28	1.0×10^{-7}-1×10^{-1}	1.0×10^{-7}	21.0	-----	4.0-8.0	30
29	5.0×10^{-7}-1.0×10^{-2}	1.0×10^{-7}	29.7	-----	3.0	15
30	2.0×10^{-6}-1.0×10^{-1}	8.0×10^{-7}	29.2	-----	1.3-2.9.	10
Present Work	1.0×10^{-7}-1.0×10^{-1}	7.08×10^{-8}	28.0	27.5	2.5-10.0	6

Analytical Application

The calibrated electrode was successfully employed for Hg(II) ion estimation in tap water, CFL unit waste water and thermometer unit waste. The results obtained were found to be in good agreement with those determined by other standard analytical techniques (AAS and mercury analyser) and were found to be in good agreement (**Table 7**). These results confirmed the practical utility of the proposed electrode for estimation of Hg (II) ions in real life samples.

Table 7. Comparison of analytical results of water samples using proposed PTD-ZrPB membrane electrode with AAS and mercury analyser techniques

Sample Description	**Concentration of Hg (II) Ions in ppmas Estimated by**		
	AAS method (SD)	**Mercury Analyzer (SD)**	**Proposed Method (SD)**
Double distilled water	ND	ND	ND
CFL	0.51 (±0.035)	0.51(±0.038)	0.49 (±0.043)
Thermometer	38.27 (±0.017)	38.3(±0.020)	37.98 (±0.035)

ND - Not Detected, SD - Standard Deviation

Conclusion: In summary, poly-*o*-toluidine-ZrPB nanocomposite ion exchanger has been successfully used as an electro-active material for fabrication of Hg (II) ion selective membrane electrode. The prepared sensor shows pretty good detection ability towards Hg^{2+} ions in comparison to alkali, alkaline earth, transition and even some heavy metal ions. The electrode shows near Nernstian response over a wide concentration range (1×10^{-7} M - 1×10^{-1} M) with a slope of 28.0 mV decade^{-1}. The interesting features of the proposed sensor include low limit of detection (7.08×10^{-8} M), fast response time of 6 s and a long life time of 6 months. The potential response of the proposed sensor is found to be constant in the pH range 2.5-10.0. The promising results in the potentiometric titration of Hg (II) ions with EDTA solution and Hg (II) ion estimation in tap water, CFL unit waste water and thermometer unit waste, confirmed the practical utility of the proposed electrode.

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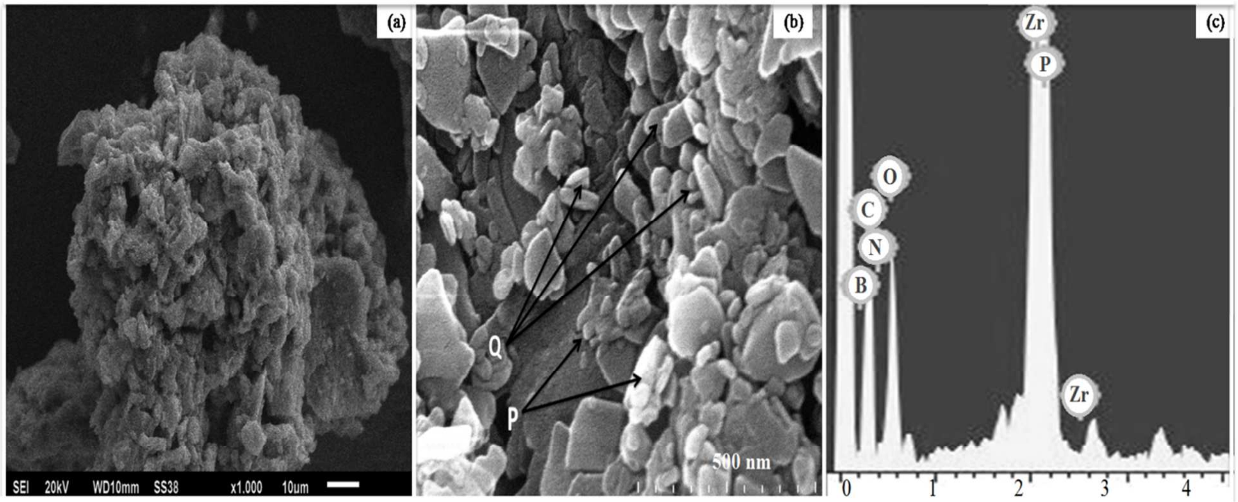

Fig. 1. SEM images of PTD-ZrPB composite at (a) 1000 X and (b) 1,50,000X; (c) EDX of PTD-ZrPB

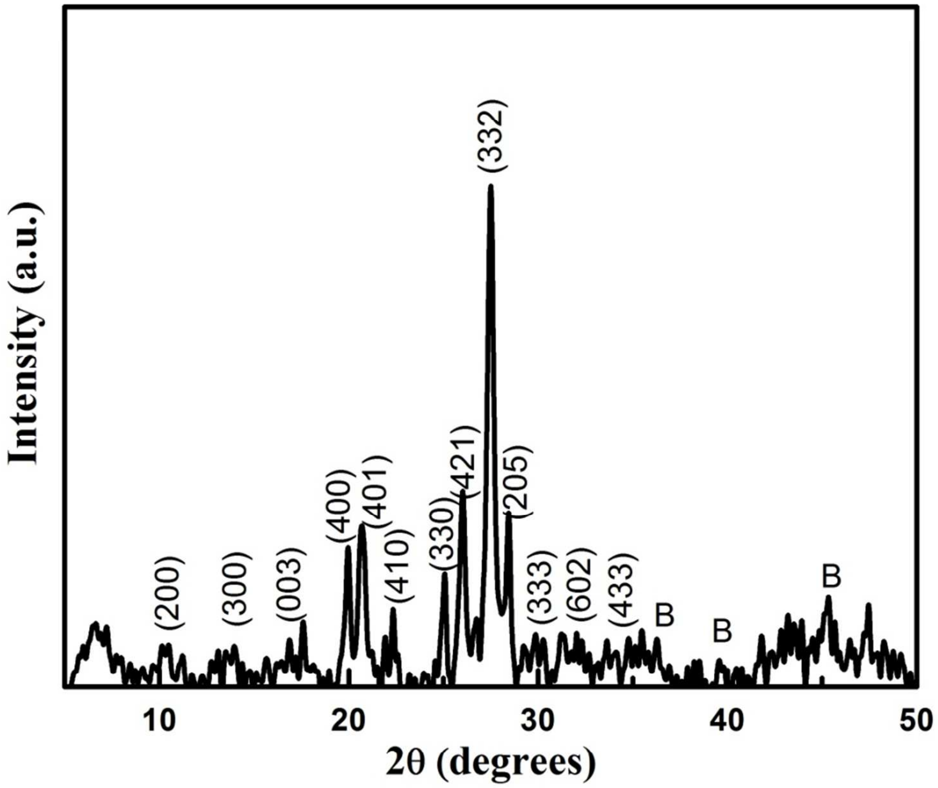

Fig. 2. X-ray diffraction pattern of PTD-ZrPB composite

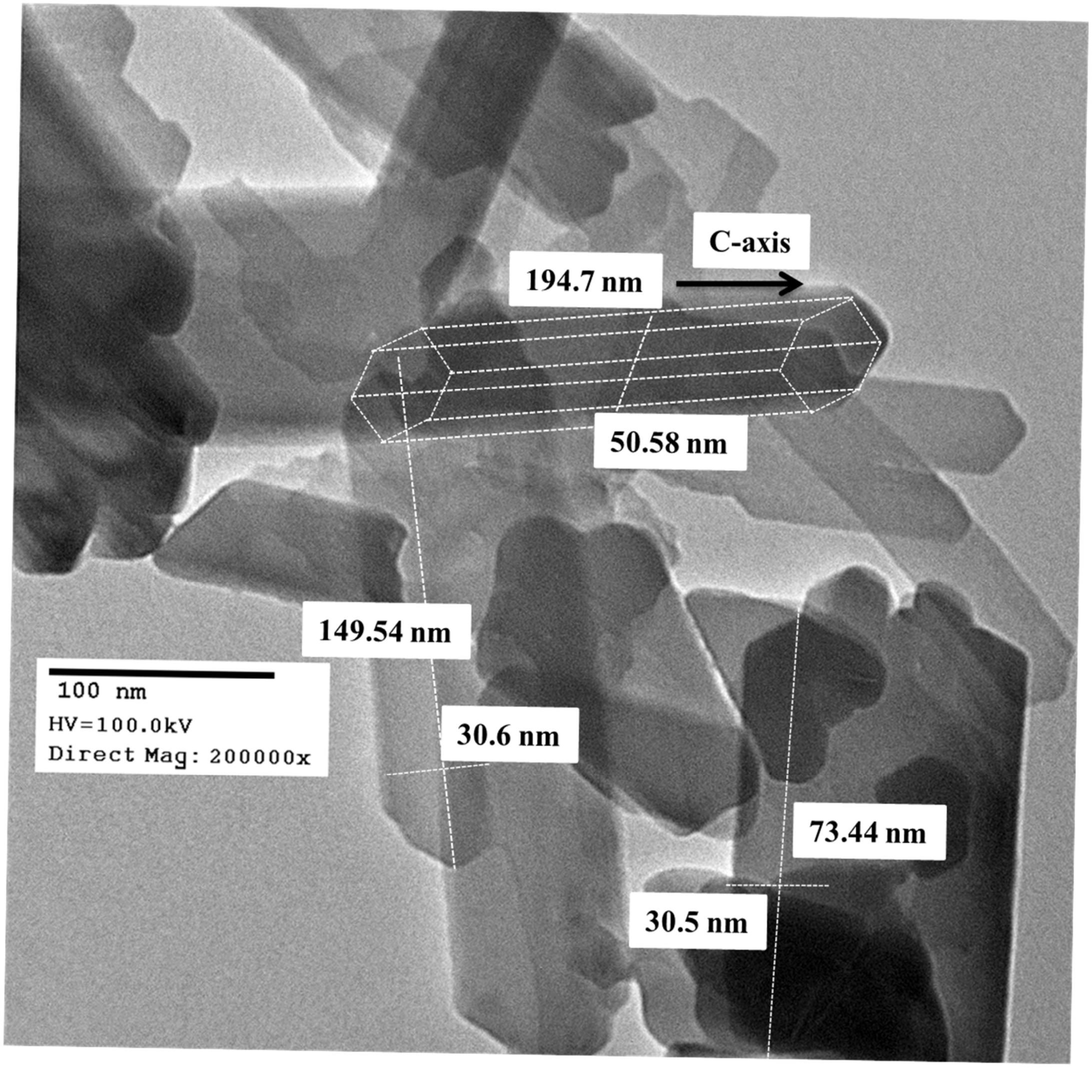

Fig. 3. TEM image of PTD-ZrPB composite

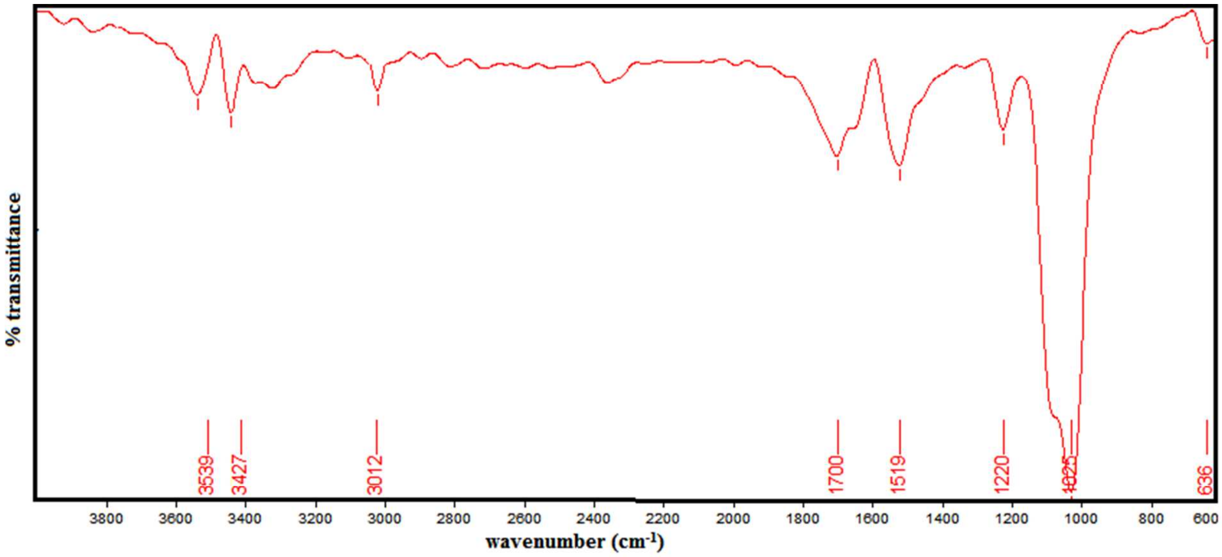

Fig. 4. FTIR spectrum of PTD-ZrPB composite


M-1 M-2 M-3

Fig. 5. Images of PTD-ZrPB composite membranes

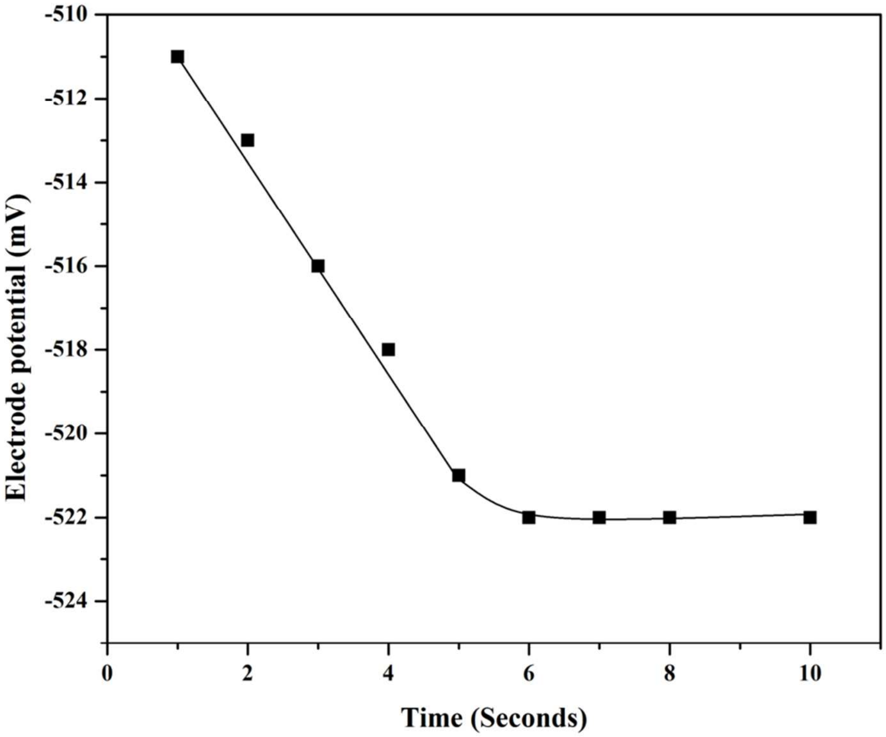

Fig. 6. Response time of PTD-ZrPB cation exchange membrane

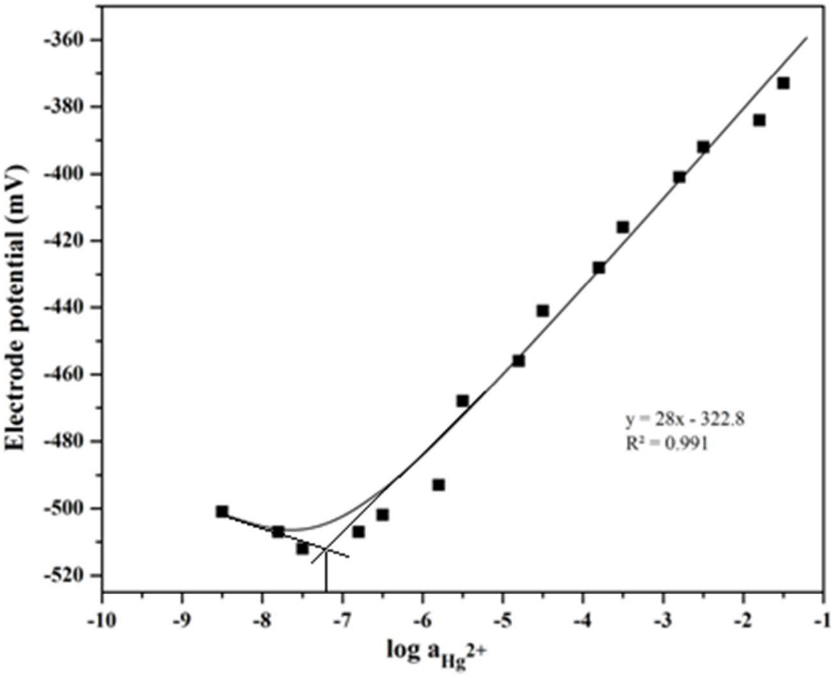

Fig. 7. Calibration curve of proposed Hg (II) selective electrode based on PTD-ZrPB composite

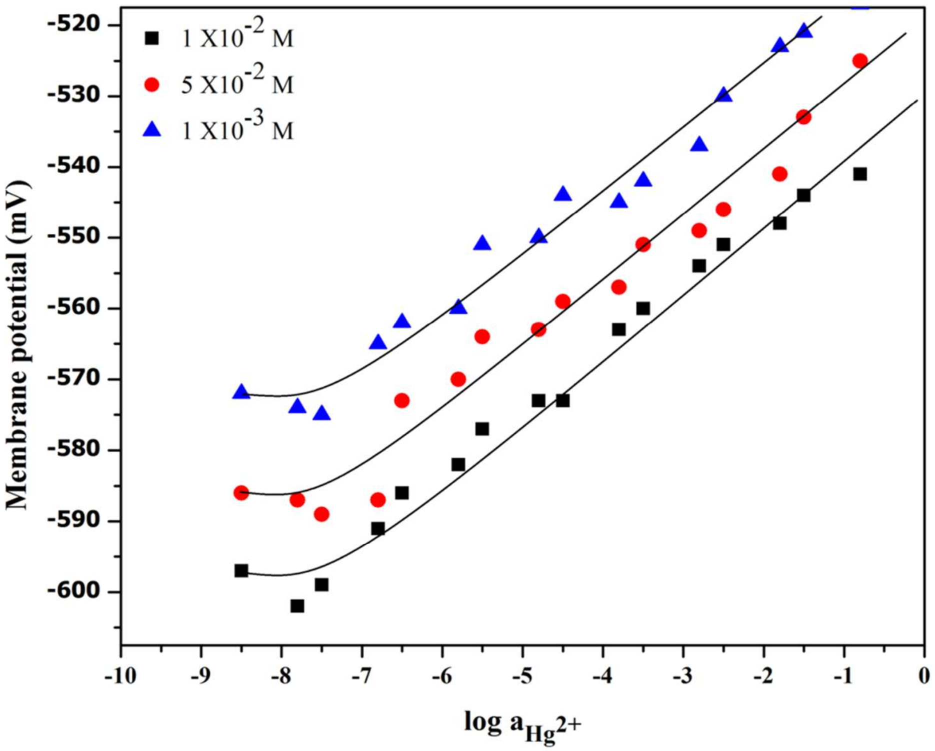

Fig. 8. Calibration curves of PTD-ZrPB membrane electrode using different concentrations of internal solution

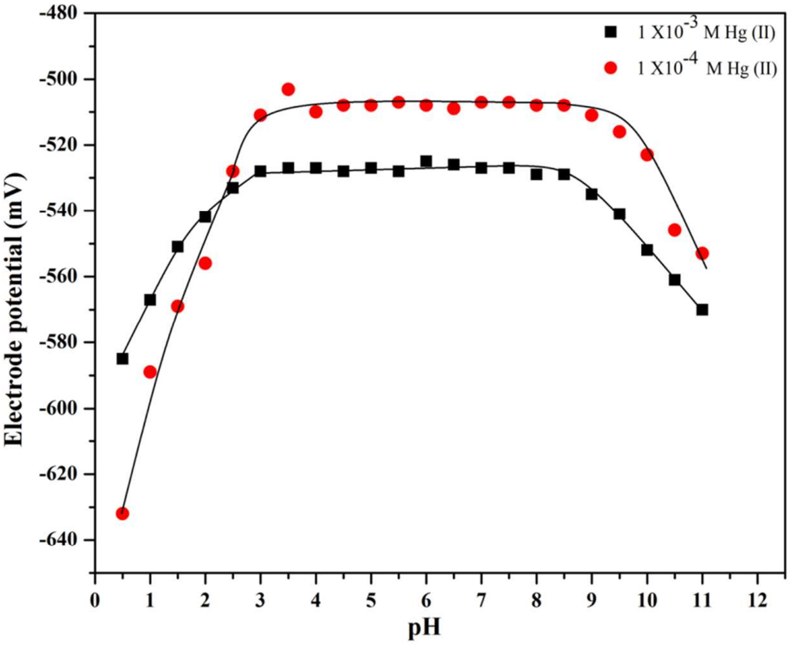

Fig. 9. Electrode potential responses of PTD-ZrPB electrode using solutions of different pH values

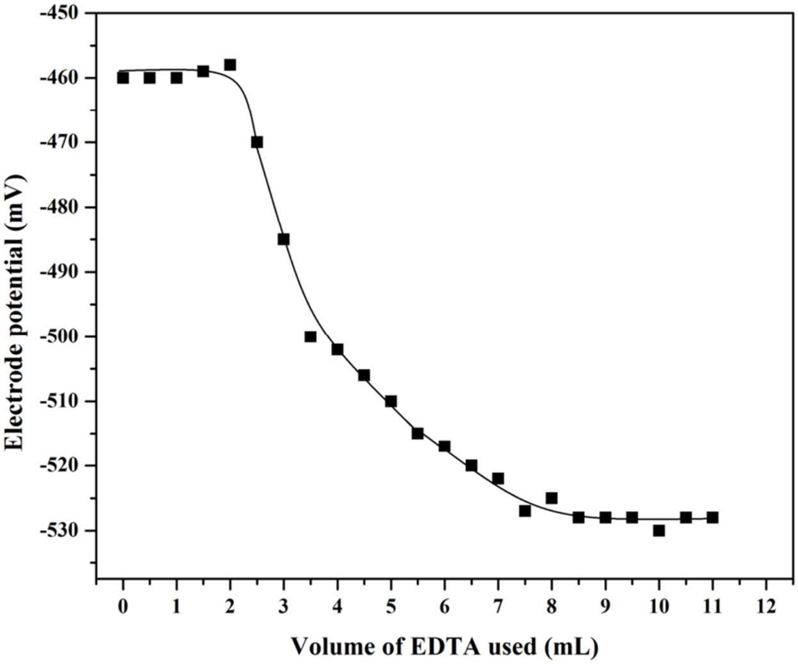

Fig. 10. Potentiometric titration of Hg (II) ions against EDTA solution with PTD-ZrPB membrane electrode