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Hg (II) Selective Electrode based on Poly-O-Toluidine Tin-Zirconium (IV) Molybdophosphate Nano-Composite

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Abstract

Present work deals with the fabrication and potentiometric studies of a novel Hg (II) ion selective electrode based on nano-composite poly-o-toluidine tin-zirconium (IV) molybdophosphate. The synthesized material was characterized through the instrumental techniques viz. FT-IR, FE-SEM, TEM, XRD and TG/DTA. The higher IEC (2.40 meq/g) and selectivity for mercuric ions, prove its best candidature for the fabrication of a Hg (II) ion selective electrode. The designed electrode follows the Nernstion response over a wide concentration range (1×10–7 M to 1×10–1 M) and pH (2.5 to 8.0) with a slop of 24.82 mV/decade. The response time of proposed electrode was observed to be 16 seconds and it can be used effectively at least for four months without any measurable change in its potential response.

Keywords: Organic-Inorganic Composite Material; PTD/Snzrmop; Ion Selective Electrode; Response Time; Potentiometric Titrations

Introduction

Though the term 'heavy metals' is less precisely defined. But more often, the term is simply used to indicate metals that are toxic. Among the various heavy metals Hg proved to be the most toxic because of its rapid methylation in the aquatic environment by some bacteria. Its poisoning may lead to diseases like: Hunter-Russell syndrome, Acrodynia and Minamata, mercury poisoning may also cause a permanent damage to brain and kidney, Mercury poisoning can cause brain damage to the fetus and can lead to a condition called Erethism characterized by jerking, irritability, mental and emotional disturbance. The main sources of mercury emission are, burning of fossil fuels, processing of thermometers, batteries, ores, dental amalgam, pesticides, etc. The elevated level of Hg and other heavy metals in the local water stream is a major concern for public. According to WHO the permissible limit for mercury in drinking water is >0.0005 mg/L [1-3].

Methods

Reagents and instruments

The chemical reagents and solvents used in this study were of analytical reagent grade and used as received, without any further purification. Some important reagents used are, zirconium oxychloride, stannic chloride, sodium molybdate, sodium dihydrogen phosphate, o-toluidine, potassium persulphate, disodium salt of ethylene diamine tetra acetic acid (EDTA), epoxy resin, mercuric nitrate etc.

Synthesis of ptd/snzrmop nano-composite ion exchanger

The nano-composite poly-o-toluidine tin-zirconium (IV) molybdophosphate was prepared by the sol-gel method, by the incorporation of green gel of poly-o-toluidine into the white precipitates of SnZrMoP with constant stirring at room temperature.

Ion exchange capacity

The ion exchange capacity was determined by the standard column process by making the use of glass wool supported column. The hydrogen ions were eluted with NaNO3 solution and titrated against a standard solution of sodium hydroxide (0.1M) using phenolphthalein as indicator. The IEC of nano-composite was calculated with the help of the following.

Characterization techniques

The common analytical techniques viz. FT-IR, Powder XRD, FE-SEM, HR-TEM, and EDX spectroscopy were employed to study the morphology, topography, elemental composition and particle size of nano-composite ion exchanger. TG/DTA studies were performed to investigate the thermal behavior of nano-composite ion exchanger.

Distribution studies

The distribution coefficients (Kd) of various metal ions on the nano-composite were determined in different solvent systems to investigate the selective nature of nano-composite ion exchanger.

Fabrication of PTD/SnZrMoP nano-composite based Ion Exchange Membrane (IEM)

Nano-composite based heterogeneous ion exchange membrane was prepared by solution casting technique. The nano-composite sample with high ion exchange capacity was used for the synthesis of IEM. The material was ground into a fine powder form and then mixed with epoxy resin. The prepared slurry was mixed thoroughly for the even mixing of nano-composite in the binding material. After even mixing the slurry was spread into two folds of parchment paper [2]. A pressure of 2.0 kg cm-2 was applied over the glass slabs for 24 h. As the parchment membrane is non-sticky in nature and thus can be easily removed. The smooth sheet of fabricated membrane, was cut with the help of a sharp edge knife into circular discs of about 18 mm diameter. The membrane discs which have good surface qualities were selected for further investigations.

Physical characterization of synthesized Ion Exchange Membrane (IEM)

The fabricated membranes were tested for the parameters like, membrane water content, thickness, swelling, porosity, Ion exchange capacity etc. after the conditioning of the membrane. The effect of resin ratio loaded on the physical properties of the membrane was also investigated.

Water content: The membrane was equilibrated in DMW for 24 h to elute the diffusible salts present in the membrane. After the complete removal of surface water noted down the weight of water soaked wet membrane, and in the next successive step the wet membrane was dried under vacuum condition at the temperature of 60 ˚C until a constant weight is obtained. The weigh difference of dry and wet membrane was evaluated. The percentage water content of IEM can be calculated by the use of following [4].

Thickness and swelling: Screw gauge is used to find out the average thickness of the membrane, whereas the swelling property of the fabricated membrane was determined by noting down the difference between the average thickness of dry membrane and membrane equilibrated in 1 M NaCl for 24 h.

Porosity: It is the property used to estimate exchange behavior and mechanical strength of fabricated membrane. Porosity (ε) is regarded as the volume of water incorporated in the cavities per unit membrane volume and calculated from the following relation:

Ion exchange capacity: The ion exchange capacity of heterogeneous, homemade, H+ ion saturated, ion exchange membrane was calculated through the batch process.

Fabrication of ion-selective electrode

All the fabricated membranes were tested for the properties like: thickness, water content, porosity, IEC, swelling, etc., and the membrane which have the best ion exchange capacity and greater physical strength was used to fabricate the ISE. The membrane was cut into a disc shape and afterward fixed at the bottom of a Pyrex glass tube (of outer diameter 1.6 cm and inner diameter 0.8 cm) with the epoxy resin, the whole assembly was allowed to dry for 24 h at room temperature. Fabricated electrode was then equilibrated with Hg(NO3)2 (0.1 M) for 7 days. The glass tube was filled 3/4 with 0.1 M Hg(NO3)2 solution. To make the electrical contact a saturated calomel electrode was inserted in the tube and another calomel electrode was inserted in the test solution. The potentiometric measurements were made by using following cell assembly [5].

Characterization of Ion Selective Electrode (ISE)

The following parameters are generally evaluated to characterize an ion selective electrode:

Response time: The response time for ISE was determined by making the use of two standard solutions of Hg(NO3)2, the electrode was first inserted in the solution of molar concentration 1×10-3 M, and in next consecutive step the electrode is immediately shifted to another solution of molar concentration 5×10-3 M. The first electrode potential value was recorded at zero interval and the next at the interval of 5 seconds. The recorded electrode potential was plotted as a function of time. The time interval at which the electrode potential attains a constant value is known as the response time of the electrode.

Slope and detection limit: Potential measurements were made for the series of standard solutions of Hg(NO3)2 in the range of 1×10-10 M to 1×10-1 M, prepared by the dilution of stock solution, as described by IUPAC the commission for analytical nomenclature. The recorded values of electrode potential were plotted against the log of the activities of analyte solution. The reproducibility of the system was verified by plotting the calibration curves thrice. All the measurements were performed by keeping the internal solution concentration fix at 5 × 10-2 M. After the completion of the process the electrode kept [6].

Effect of change in internal solution concentration: The response of proposed electrode was also investigated by changing the concentration of solution filled inside tube of ISE. The concentrations of internal solutions of Hg(NO3)2 were kept The value of electrode potential obtained was plotted against the log of concentration analyte solution.

Effect of partially non-aqueous medium: The effect of partially non-aqueous medium containing acetone or ethanol mixed with water on the response of the proposed sensor was also investigated by varying the concentration

Effect of pH: For this study of proposed electrode a series of solutions were prepared by adjusting the pH between 1-13, by adding a few drops of 0.1 M HCl or 0.1 M NaOH solution as required, during these investigations the concentration of Hg(NO3)2 solution was kept constant in the test solution.

Selectivity coefficients: Potentiometric selectivity coefficient (K_(A,B)^Pot), measure the response of the proposed electrode towards the primary ions in the presence of other interfering ions. Fixed interference method (FIM) was used to find out the value of selectivity coefficients . In this process the concentration of interfering ions was maintained 1×10−4 M. According to this method, a calibration curve has to be plotted by varying the primary ion concentrations in a fixed background concentration of interfering ions. The linear calibration curve of the electrode, which is the function of the activity of the primary ions, even in the presence of other interfering ions, should be extrapolated until at the lower detection limit. The selectivity coefficients were calculated from these two extrapolated linear segments of the calibration curve by making the use of the following [7].

Storage and lifetime of electrode: The electrode is stored in distilled water when not in use. For the further use the electrode is first activated, by keeping it immersed in the respective metal ion solution (0.1 M) for two hours. The electrode is washed thoroughly with distilled water, before every use. The lifetime of the electrode was tested by testing the variation in its slop and response time for the interval of 15, 30, 60, 90 and 120 days. It is expected that there should not be any significant variation in the response of the proposed electrode.

Potentiometric titrations

The analytical importance of fabricated ISE can be established by using it as an indicator electrode for the potentiometric estimation of Hg (II) ions in a test solution against EDTA as titrant. The electrode potential value should be plotted against the volume of EDTA solution used. The practical utilization of the ISE was also proved through its use in the potentiometric estimation of Hg (II) ions in the water samples collected from different industrial units.

Quantitative estimation of Hg (II) ions from industrial effluents: As an environmental application, the proposed electrode was also used for the potentiometric estimation of Hg (II) ions in the water samples collected from different industrial units. For this study the effluent samples were collected from, CFL manufacturing unit Ambala (India), thermometer manufacturing unit Ambala (India) and thermal power plant effluents Roop Nagar India). All the samples were first filtered out to remove all the suspended impurities and then neutralized. The color producing substances were removed by adsorption on charcoal. In the first attempt Hg (II) ions in the test samples were estimated through the simple complexometric titrations by making the use of PAN-(1-(2-Pyridylazo)-2-naphthol) indicator and a buffer solution of pH ≈ 3. Then the same titrations were performed by the use of fabricated Hg (II) ion selective electrode based on nano-composite PTD/SnZrMoP as an indicator electrode. The experiment was repeated thrice to check the validity of proposed electrode.

Quantitative separation of Hg (II) ions from the water samples collected from different Industrial effluents on the column PTD/SnZrMoP nano-composite ion exchanger

The effluent samples were collected from: CFL unit waste water and thermometer unit waste and thermal power plant effluents. After purification and neutralization a fixed volume of the samples collected from different industrial units was passed through the glass wool supported columns of PTD/SnZrMoP at a flow rate of 0.5 ml min−1.. The effluent were collected and recycled thrice. The metal ions were eluted with 1.0 M HNO3 solution.

Results

Physio-chemical properties of nano-composite PTD/SnZrMoP

The present work includes various aspects of the novel, Hg (II) ion selective electrode based on nano-composite cation exchanger poly-o-toluidine tin-zirconium (IV) molybdophosphate. The nano-composite material was synthesized through the sol-gel technique which is a less time consuming, and cost effective technique for the synthesis of nano-particles. The nano-composite was synthesized through the mixing of green organic gel of poly-o-toluidine into the precipitates of tetravalent metal acid salt SnZrMoP with two anions and two cations. The conditions of synthesis were optimized by varying the mixing volume ratios of the reactants and sample K-5 was observed to possess the maximum ion exchange capacity (2.40 meq/g) and was selected for further studies [8-10].

Physio-chemical properties of the membrane based on nano-composite PTD/SnZrMoP

On the basis of ion exchange capacity sample K-5 was considered best for the synthesis of ion exchange membrane. For the optimization of the membrane material, the epoxy resin and nano-composite PTD/SnZrMoP were mixed in ratios, 1:9, 2:8, 3:7 and 4:6 (w/w). All these fabricated membranes were tested for the properties like: thickness, water content, porosity, IEC, swelling, etc., and the best membrane is considered one which should have high value of IEC and higher strength. It can be observed from that the membrane M-3 has been considered fit for further studies due to its better IEC, moderate thickness and moderate porosity. The higher ion exchange capacity of membrane M-3 may be due to the proper distribution of resin particles in the binder phase [10].

Electrode Characteristics

The fabricated electrode was tested for various parameters like response time, the slope of the calibration curve, lower detection limit, linear response concentration range, effective pH range etc. The following observation were obtained from the investigation of these studies: the response time of ion selective electrode was evaluated as a function of time. The response time of Hg (II) ISE based on nano-composite was observed to be 16 seconds [11-14].

Conclusion

The present study is based on the fabrication, characterization and applications of Hg (II) ion selective electrode based on nano-composite PTD/SnZrMoP. The response time of the proposed electrode has been observed to be 16 second, which is less than the response time of most of the reported electrodes. The other positivity of the proposed electrode is that it can be used most effectively even in non aqueous solvents. Whereas none of other reported electrode was used in non aqueous solvents. The slope of the electrode is Non-Nernation and its lower detection limit is 3.55×10-8 M. The electrode follows the Nernation response over a wide concentration range. As an analytical application the electrode was used for the potentiometric estimate the Hg (II) ions in the industrial effluents. Thus the nano-composite cation exchanger PTD/SnZrMoP can find a place in various industries dealing with separation processes.

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