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Determination of Cu^{2+} in aqueous solution using a polyindole–tin(IV) molybdophosphate conductive nanocomposite ion-selective membrane electrode

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ABSTRACT

Polyindole–tin (IV) molybdophosphate (PIn-SMP), an organic-inorganic nanocomposite ion exchanger, was synthesized by a sol-gel process and exhibited excellent ion exchange capacity (2.1 meq g^{-1}). A heterogeneous ion exchange membrane of PIn-SMP (ion exchange capacity 0.95 meq g^{-1}) was also prepared by a solution casting method. The materials were characterized by various instrumental methods, such as scanning electron microscopy, transmission electron microscopy, Fourier transform IR spectroscopy, and thermogravimetric analysis. PIn-SMP exhibits high electrical conductivity (6.1×10^{-2} S/cm) and is stable up to 120 °C under ambient conditions. A Cu^{2+}-selective membrane electrode was fabricated, and its linear working range (1.8×10^{-7}–1.0×10^{-1} M), response time (20 s), Nernstian slope (24.07 mV dec^{-1}), and working pH range (4–7) were calculated. Moreover, it was used as an indicator electrode in the potentiometric titration of Cu^{2+}.

1. Introduction

Copper is one of the essential elements for vital biological processes in the human body; however, it becomes toxic at elevated levels, causing vomiting, diarrhea, nausea, gastrointestinal distress, liver damage, and kidney disease. Its widespread use in industrial, agricultural, and domestic activities makes it a significant heavy metal pollutant in the environment. To monitor trace amounts of copper in environmental samples, various instrumental methods are used, such as inductively coupled plasma mass spectrometry [1], atomic absorption spectrometry [2], anodic stripping voltammetry [3], high-performance liquid chromatography [4], modified carbon electrode [5], colorimetric detection [6,7], and adsorption [8]. However, these methods are not suitable for analysis of a large number of environmental samples as they are time-consuming, are too expensive, and require pretreatment procedures.

In recent years, the development of efficient and inexpensive copper-selective electrodes [9–20] and other metal ion–selective electrodes [21–33] has been noteworthy as these provide simple, accurate, and fast results. Since most of them lack high selectivity, a wide concentration range, a short response time, a low detection limit, a Nernstian response, and reproducibility, efforts are still being made to improve the quality of copper-selective electrodes. One area of improvement in designing the electrode is the use of a mechanically strong and dimensionally stable heterogeneous ion exchange membrane with better ion exchange capacity (IEC), electrochemical properties, and selectivity for a particular ion. This can be achieved by use of a good conductive nanocomposite ion exchange material that exhibits high affinity for a particular ion to prepare the membrane. Consequently, a number of ion-selective electrodes based on a heterogeneous ion exchange membrane have been reported in the literature [9], but very few conductive nanocomposite ionomeric materials used in making ion exchangers have been reported [34,35].

In the present study, polyindole was used to prepare nanocomposite ionomeric material to fabricate a Cu^{2+}-selective membrane electrode for the estimation of copper in aqueous samples, since polyindole is a better conductor than polyaniline, polypyrrole, polycarbazole, polythiophene, polyanisidine, etc., which we used in our previous studies [36–40]. Polyindole–tin (IV) molybdophosphate (PIn-SMP) was synthesized by incorporation of tin (IV) molybdophosphate (SMP) in the polymer matrix of the organic polymer polyindole to obtain a quick response of exchangeable ions as a result of its greater conductivity. The linear concentration range, working pH range, and response time were investigated to evaluate the performance of the membrane electrode. The heterogeneous membrane used in the fabrication of the Cu^{2+}-selective membrane electrode was prepared by a solution casting method using conductive nanocomposite ion exchange material with polyvinyl chloride (PVC) serving as a binder.

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2. Materials and methods

2.1. Chemicals, reagents, and instruments

Stannic chloride pentahydrate ($SnCl_4·5HO_2$), pure sodium molybdate ($Na_2MoO_4·2H_2O$), and ortho-phosphoric acid (H_3PO_4) was purchased from CDH, Indole (C_8H_7N) was purchased from HiMedia (India), ferric chloride, *N*,*N*-dimethyacetamide, and chloroform (AR grade) were acquired from Qualigens, and ethylenediaminetetraacetic acid (EDTA) was purchased from E. Merck (India) Ltd. All other chemicals were of analytical grade and were used as received. The following instruments were used: a scanning electron microscope with an energy-dispersive X-ray (EDX) analyzer (LEO 435-VF, JEOL, Japan); a transmission electron microscope (JEM-2100, JEOL); a Fourier transform IR (FTIR) spectrophotometer (PerkinElmer); a thermal analyzer (DTA)-2.2 A (model 9900, DuPont, USA); a DFP-RM-200 (research model) four-probe setup (SES Instruments, Roorkee, India); a digital potentiometer (Q 609, Equiptronics, India); and an atomic absorption spectrophotometer (model GBC 902, Australia).

2.2. Synthesis of PIn-SMP and its membrane

SMP was prepared by the mixing of stannic chloride and sodium molybdate with ortho-phosphoric acid in different volume ratios at room temperature (about 25 °C) as given in Table S1.

The precipitate was filtered, washed, and dried to a fine powder. PIn-SMP composite ion exchange material was synthesized by a sol-gel method [41]. A calculated amount of indole was dissolved in 100 mL chloroform in a round-bottom flask. Then 1.5 M $FeCl_3$ in chloroform was prepared in a separate beaker and was slowly added to the flask, and the mixture was stirred for 6 h for complete polymerization of indole at room temperature of about 25 °C [42]. Freshly prepared SMP was added slowly to the flask, and stirring continued for another 12 h. Finally the mixture was filtered, washed, dried, and ground to a fine powder. The preparation conditions and details are given in Table 1.

The heterogeneous ion exchange membrane was prepared by a solution casting method. The composite PIn-SMP as the ion exchange material and PVC as a binder were mixed in various mixing ratios in tetrahydrofuran in a beaker with a magnetic stirrer for 12 h to make a thick homogeneous mixture. The mixture was cast onto a clean glass plate and kept at room temperature until it was dry. Then it was peeled off and washed with distilled water, dried, and used for further studies. The preparation conditions are given in Table 2.

2.3. Ion exchange capacity

The IEC of SMP and PIn-SMP composite was calculated by a column method. First, the ion exchange material was kept in 1 M HNO_3 for 24 h to convert it to the H^+ form. Then it was filtered, washed with demineralized water (DMW) to remove excess acid, and dried in an oven at 40 °C. A glass column of internal diameter approximately 1 cm containing glass wool (bed length approximately 1.5 cm) was packed with 1 g of exchanger. The H^+ ions were eluted from the column by use of 1 M $NaNO_3$ at a flow rate of 0.5 mL min^{-1}. The eluate was collected and titrated against 0.1 M NaOH standard solution with phenolphthalein as the indicator.

To calculate the IEC of the membrane, first it was cut into a 3 cm × 3 cm piece and dipped in 1 M HNO_3 for 24 h to convert it to the H^+ form. Then it was taken out and rinsed with DMW and dried at room temperature. It was kept in 1 M $NaNO_3$ for 24 h, and was intermittently shaken to elute H^+ ions from the membrane. Finally, the eluate was titrated against 0.1 M NaOH standard solution with phenolphthalein as the indicator.

Table 1
Conditions for the preparation of and ion exchange capacity (IEC) of polyindole (PIn)–tin (IV) molybdophosphate (SMP) cation exchange composite.

Sample	Fixed mixing volume ratio (v/v/v)			Na^+ IEC (meq g^{-1})
	PIn	SMP	$FeCl_3$	
C-1	1	1	1 (1.0 M)	1.8
C-2	1	2	1 (1.5 M)	2.0
C-3	1	1	2 (1.5 M)	1.9
C-4	2	3	1 (2.0 M)	2.1
C-5	2	1	2 (2.0 M)	1.8

Table 2
Conditions for the preparation of and the ion exchange capacity (IEC) of the polyindole–tin (IV) molybdophosphate heterogeneous ion exchange membrane.

Membrane	PVC (g)	Composite (g)	THF (mL)	Stirring time (h)	IEC (meq g^{-1})
M-1	0.30	0.20	50	24	0.60
M-2	0.25	0.20	50	24	0.70
M-3	0.20	0.20	50	24	0.95
M-4	0.20	0.10	50	24	0.60
M-5	0.15	0.20	50	24	0.65

PVC, polyvinyl chloride; THF, tetrahydrofuran.

2.4. Distribution coefficient (K_d values)

The distribution study was done by the batch method by equilibration of the metal ions (Ni^{2+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}) between different solvents (HCl, HNO_3, H_2SO_4, CH_3OH, etc.) and the composite ion exchanger to determine the distribution coefficients [43]. The suspension in a conical flask containing 0.005 M metal ion solution and 2 g ion exchanger was agitated for 24 h with intermittent shaking to ensure the complete distribution of metal ions between the aqueous phase (solvent) and the solid phase (exchanger). The metal ion concentration was determined by titration with EDTA. K_d was calculated by the following equation:

$$K_d = \left(\frac{I-F}{F}\right) \times \frac{V}{M}\ (\mathrm{mL\ g^{-1}}), \tag{1}$$

where *I* is the initial amount of metal ion in the aqueous phase, *F* is the final amount of metal ion in the aqueous phase, *V* is the volume of the solution (mL), and *M* is the amount of cation exchanger (g). The details are given in Table 3.

2.5. Characterization of PIn-SMP nanocomposite ion exchanger and its membrane

The nanocomposite ion exchanger and the heterogeneous ion exchange membrane were characterized by various instrumental methods. To observe the surface microstructure and chemical composition of the materials, a scanning electron microscope with an EDX analyzer (LEO 435-VF, JEOL, Japan) was used with an accelerating voltage of 20 kV in secondary electron imaging mode at a working distance of 12 mm. The particle size of the material was observed by transmission electron microscopy (TEM; JEM-2100, JEOL) by the coating of the sample with gold and use of a higher accelerating voltage of 200.0 kV at a resolution of 30,000. The thermal stability of the samples was checked by a thermal analyzer (DTA)-2.2 A (model 9900, DuPont, USA) by heating of the samples at 20 °C min^{-1} from 0 to 600 °C in a nitrogen atmosphere. The functional groups present in the sample were identified by FTIR spectroscopy in the original form by the KBr disk method in the range from 400 to 4000 cm^{-1} at room temperature.