

Preparation and characterization of a new organic–inorganic nano-composite poly-*o*-toluidine Th(IV) phosphate: Its analytical applications as cation-exchanger and in making ion-selective electrode

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Abstract

An organic–inorganic hybrid poly-*o*-toluidine Th(IV) phosphate was chemically synthesized by mixing *ortho*-toluidine into the gel of Th(IV) phosphate in different mixing volume ratios, concentration of inorganic reactant with a fixed mixing volume ratios of organic polymer. The physico-chemical characterization was carried out by elemental analysis, TEM, SEM, XRD, FTIR and simultaneous TGA–DTA studies. The ion-exchange capacity, chemical stability, effect of eluant concentration, elution behavior and pH titration studies were also carried out to understand the ion-exchange capabilities. The distribution studies revealed that the cation-exchange material is highly selective for Hg²⁺, which is an important environmental pollutant. Due to selective nature of the cation-exchanger ion-selective membrane electrode was fabricated for the determination of Hg(II) ions in solutions. The analytical utility of this electrode was established by employing it as an indicator electrode in electrometric titrations. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Organic–inorganic hybrid, a new class of materials is attractive for the creating high performance or high functional polymeric behaviors that are expected to provide many possibilities. Hybrid can be used to modify organic polymeric material or to modify inorganic materials that exhibit very different properties from their original component. The inorganic ion-exchange materials besides other advantages are important in being more stable to high temperature and radiation field than the organic ones [1]. In order to obtain a combination of these advantages associated with polymeric and inorganic materials as ion-exchangers, attempts have been made to develop polymeric-inorganic composite ion-exchangers by incorporation of organic monomers in the inorganic matrix [2]. Few such excellent ion-exchange materials have been developed in our laboratory and successfully being used in chromatographic techniques [3–5]. An inorganic precipitate ion-exchanger based on

organic polymeric matrix must be an interesting material, as it should possess the mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion-exchanger regarding its selectivity for some particular metal ions [6–12]. It was therefore considered to synthesize such hybrid ion-exchangers with a good ion-exchange capacity, high stability, reproducibility and selectivity for heavy metal ions, indicating its useful environmental application.

Mercury is responsible for causing poisoning through water, food and smoking. Mercury contamination in drinking water inhibits the function of certain enzymes necessary for the formation of haem in bone marrow, the pigment that combines with protein to form haemoglobin. Its vapor, on inhalation, enters the brain through the blood stream and causes severe damage to the central nervous system. Inorganic mercuric compounds mainly attack liver and kidney. Mercuric chloride is corrosive and, when ingested, precipitates proteins of the mucous membrane causing ashen appearance of the mouth, pharynx and gastric mucus. Organic mercurial are the most toxic substances; the CH₃Hg⁺ can pass through the placental barrier and enter the foetal tissues. Hg(II) is therefore a potential pollutant in the environment. Heavy metal ion removal from

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waters has been the subject of extensive technological research [13].

The ion-exchange membranes obtained by embedding ion-exchangers as electroactive materials in a polymer binder, i.e. PVC, has been extensively used as potentiometric sensors, i.e. ion sensors, chemical sensors or more commonly ion-selective electrodes. In our present studies attempt has been made to obtain a new heterogeneous precipitate based membrane electrode by using the poly-*o*-toluidine Th(IV) phosphate, a nano-composite cation-exchanger as an electroactive material for the determination of Hg(II) ion present in the sample solution.

2. Experimental

2.1. Reagents and instruments

The main reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E-Merck and Qualigens (India Ltd., used as received). All other reagents and chemicals were of analytical grade. Following instruments were used during present research work: a FTIR spectrophotometer (Perkin-Elmer, USA, model Spectrum-BX); digital pH-meter (Elico Li-10, India); X-ray diffractometer—Phillips (Holland), model PW 1148/89; UV/VIS spectrophotometer—Elico, model EI 301E; a thermal analyzer—V2.2A DuPont 9900; an elemental analyzer—Elementary Vario EL III, Carlo-Erba, model 1108; a digital potentiometer (Equiptronics EQ 609, India); accuracy ± 0.1 mV with a saturated calomel electrode as reference electrode; an electronic balance (digital, Sartorius-210S, Japan) and an automatic temperature controlled water bath incubator shaker—Elcon (India) were used.

2.2. Preparation of reagents

Thorium nitrate $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and phosphoric acid, H_3PO_4 solutions of different molarities were prepared in 1 M HNO_3 and demineralised water (DMW), respectively.

2.3. Preparation of poly-*o*-toluidine Th(IV) phosphate composite

2.3.1. Synthesis of poly-*o*-toluidine

The polymerization of the monomer *ortho*-toluidine was initiated by the addition of oxidizing agent, i.e. ammonium persulphate in 1:1 ratio under constant stirring at room temperature for 2 h [14]. After 2 h a brown colored poly-*o*-toluidine polymer was obtained.

2.3.2. Synthesis of thorium(IV) phosphate

The method of preparation of the inorganic precipitate of Th(IV) phosphate ion-exchanger was very similar to that of Alberti and Constantino with slight modification [15] by mixing a solution of 0.1 M $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ prepared in 1 M HNO_3 at the flow rate at 0.5 ml min^{-1} to a solution of H_3PO_4 in different molarities. Constant string was done during mixing using a magnetic stirrer at a temperature of 85°C , white gel type slurries

were obtained. After digestion of the mixture for several hours, it was cooled to room temperature in each case.

2.3.3. Synthesis of poly-*o*-toluidine Th(IV) phosphate

The composite cation-exchanger was prepared by the sol-gel mixing of poly-*o*-toluidine an organic polymer into the inorganic precipitate of thorium(IV) phosphate. In this process, when the gels of poly-*o*-toluidine were added to the white inorganic precipitate of thorium(IV) phosphate with a constant stirring, the resultant mixture was turned slowly into brown colored slurries. The resultant brown colored slurries were kept for 24 h at room temperature.

Now, the poly-*o*-toluidine based composite cation-exchanger gels were filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of ammonium persulphate. The washed gels were dried over P_4O_{10} at 30°C in an oven. The dried products were immersed in DMW to obtain small granules. They were converted to the H^+ form by keeping it in 1 M HNO_3 solution for 24 h with occasionally shaking intermittently replacing the supernatant liquid. The excess acid was removed after several washing with DMW. The material was finally dried at 40°C and sieving to obtain particles of particular size range ($\sim 125 \mu\text{m}$). Hence, a number of poly-*o*-toluidine thorium(IV) phosphate nano-composite cation-exchanger samples were prepared and on the basis of Na^+ exchange capacity (i.e.c.), percent of yield and physical appearance, sample S-3 was selected for further studies.

2.4. Ion-exchange capacity (i.e.c.)

The ion-exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation-exchanger was determined by standard column process. One gram of the dry cation-exchanger sample S-3 in the H^+ -form was taken into a glass column having an internal diameter (i.d.) ~ 1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. One molar alkali and alkaline earth metal nitrates as eluants were used to elute the H^+ ions completely from the cation-exchange column, maintaining a very slow flow rate ($\sim 0.5 \text{ ml min}^{-1}$). The effluent was titrated against a standard 0.1 M NaOH using phenolphthalein indicator.

2.5. Effect of eluant concentration

To find out the optimum concentration of the eluant for complete elution of H^+ ions, a fixed volume (250 ml) of sodium nitrate (NaNO_3) solutions of varying molar concentration were passed through a column containing 1 g of the exchanger in the H^+ -form with a flow rate of $\sim 0.5 \text{ ml min}^{-1}$. The effluent was titrated against a standard alkali solution of 0.1 M NaOH for the H^+ ions eluted out. A maximum elution was observed with the concentration of 1.6 M NaNO_3 as indicated in Fig. 1.

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