Chapter 6
Preparation and Characterization of Alumina-based Polyacrylonitrile Nano Composite as an Anion-exchanger: Its Electroanalytical Application as AsO$_4^{3-}$ Ion-selective Membrane Electrode
Chapter 6

6.1 Introduction.

Detection of the metal is one of the great interests in analytical chemistry and different methods have been employed for detection, such as atomic absorption spectrophotometry, ICPMS and others, but the use of ion selective electrode has attracted much attention for the detection of the particular metal ion in presence of other metal ions. It is considered as versatile analytical tool and recommended widely for quick, easy to use, non-destructive and allow accurate determination of chemical species at relatively low level. The rapid growth in use of ion selective electrode has led to a search for suitable materials that can be used for preparation of sensitive and selective ion-sensors, chemical sensors or more commonly ion-selective electrodes (ISEs). There is continuous research work going for the synthesis of ions selective membrane electrodes for determination of heavy metal ions such as Cu(II), Pb(II), Th(IV), Hg(II), Cd(II) and Ni(II) [1-6]. Significant number of ionophores including crown ethers, cryptands, aza-crowns and thiocompounds and ion exchangers have been exploited for fabrication of poly(vinyl chloride) (PVC) membrane electrodes for series of alkali, alkaline earth, transition and heavy metal ions [7-12]. The development of synthetic ion exchange membranes reported by Juda [13] in 1949 and Juda and Mc Rae [14] in 1950 stimulated both commercial and academic interest in such membranes and the related membranes. Ion exchange membranes are now widely used for membrane electrolysis, solid polymer electrolyte and fuel cell storage batteries as well as electrochemical separations which includes diffusion dialysis, electro dialysis and electro-deionization etc [15-18]. In recent years, a new kind of material, the organic-inorganic hybrid has been extensively investigated because of the ability to combine the best properties of both organic and inorganic components [19-21]. Due to restricted commercial application of anion exchangers, these are less common as compare to cation exchangers. However in some electro analytical processes, such as electrochemical sensors and electro catalysis anion exchange organic inorganic membranes are highly desirable [22, 23, 24].
The present work reports the synthesis of polyvinylchloride (PVC) based ion selective electrode using alumina based anion exchanger. The composite material shows good selectivity for arsenic as determined by the Volhard thiocyanate method on the basis of which arsenic ion selective membrane electrode have been developed using the present anion exchanger. The selectivity of any ion selective sensor is clearly one of its most important characteristic, as this property often determines whether a sensor may be used reliably in the target sample [25]. Arsenic is a naturally occurring element, widely distributed in the earth’s crust and a common contaminant of drinking water, exposure to arsenic can cause a variety of adverse health effects, including dermal changes, respiratory, cardiovascular and carcinogenic effects. In the present research work we have developed a very simple technique of determining arsenic in trace amounts by using ion selective membrane electrode prepared by the anion exchanger as well as by using arsenom at discussed below. This chapter presents not only the importance of the material in the determination of arsenic but also its use as an electro active material.

6.2 Experimental

6.2.1 Reagents and Instruments

The main reagents i.e Polyacrylonitrile (PAN), Aluminium oxide (Al₂O₃) and Tetrahydrofuran (CH₂)₄O (THF) were used for the synthesis of the material and obtained from CDH, E-merck, and Qualigens (India Ltd., used as received). All other reagents and chemicals were of analytical grade. The following instruments were used during present research work: A Fourier Transform Infra Red (FTIR) spectrophotometer (Perkin Elmer, USA, model Spectrum-BX); digital pH meter (Elico Li-10, India); model PW 1148/8; an electronic balance (digital, Sartorius-21OS, Japan); Elemental analyzer — Elementary Vario EL III, Carlo-Erba, model 1108; A scanning electron microscope — LEO 435 VP (Australia): Arsenic Analyzer.

6.2.2 Synthesis of Anion Exchanger

Many samples of the anion exchanger have been prepared by dissolving different amount of polyacrylonitrile in THF and in this mixture different amounts of alumina were added with constant stirring for two hours. Leave the mixture for 24 hrs, and then pour the mixture in distilled water with constant stirring. A semi fibrous type material was obtained. Wash the fiber with deminaralize water (DMW) and dry them.
6.2.3 Ion Exchange Behavior

6.2.3.1 Ion Exchange Capacity of Cl\(^-\) ion

The dried fibers were converted into Cl\(^-\) form by keeping them in 1M NaCl for one day, and then the material was washed with DMW to remove excess Cl\(^-\). The material was again dried in an oven at \(\sim 45^\circ\text{C}\) and placed in 1M Na\(_2\)SO\(_4\) solution for 24 hrs. The supernatant liquid was titrated with 0.5 M AgNO\(_3\) solution using 1% 2-7 dichlorofluorocene indicator. Pink color ppt shows the presence of AgCl.

\[
\text{XCl}^- + \text{Na}_2\text{SO}_4 \xrightarrow{\text{Ion Exchange}} 2\text{NaCl} + X\text{SO}_4^{2-}
\]

Where X is the exchanger phase.

6.2.3.2 Ion Exchange Capacity of Arsenic (V) by Volhard Thiocyanate Method.

The dried fibers sample (S-5) were converted into AsO\(_4^{3-}\) form by keeping them in 0.1 M solution of sodium arsenate for one day, then the material was washed with DMW to remove excess AsO\(_4^{3-}\). The material was again dried in an oven at \(\sim 45^\circ\text{C}\) and placed in 0.1M NaCl solution for 24 hrs. Exchange of AsO\(_4^{3-}\) by Cl\(^-\) takes place as shown below.

\[
\text{X} \text{AsO}_4^{3-} + \text{Na}^+\text{Cl}^- \xrightarrow{\text{Ion Exchange}} \text{XCl}^- + \text{Na}^+ \text{AsO}_4^{3-}
\]

Add 0.5 M AgNO\(_3\) to the supernatant liquid. In this case to the filterate obtained after exchange of AsO\(_4^{3-}\) with Cl\(^-\) ions, add 0.5 M AgNO\(_3\), white colour ppt will appear by keeping the solution in dark. Wash the ppt and add 20 ml HNO\(_3\) (Conc), then make upto100 ml with DMW. The solution was titrated with 0.1N KSCN using ammonium ferric alum indicator (2-3 drops). Brick red color ppt shows the presence of arsenic and the arsenic ion exchange capacity of selected sample (S-5) was found to be 0.8 meq/g. The results were also checked by arsenic analyzer.
6.3 Chemical Composition

The chemical composition also plays an important role in the elucidation of molecular structure of the ion-exchangers. The composition of the material can be determined either by gravimetrically or spectrophotometrically. With the help of these methods, we can determine the percentage of metals or groups present in the ion-exchangers. Carbon, Hydrogen, Nitrogen and Oxygen contents of the anion exchanger were determined by elemental analysis.

6.4 Characterization of the Material

The nature, particle size, morphology, thermal stability and the functional groups present in the prepared composite material have been characterized by using TEM, SEM, XRD, FTIR and TGA-DTA techniques.

6.5 Membrane Preparation

Anion exchange membrane of alumina based anion exchanger was prepared by the same method reported for various cation exchangers. To find out the optimum membrane composition, different amounts of the composite material was grounded to a fine powder and mixed thoroughly with fixed amount (200 mg) of PVC, dissolved in 10 ml tetrahydrofuran. The resultant slurries were poured to cast in a glass tube having 10 cm in length and 5 mm in diameter. These glass tubes were left for slow evaporation for several hours. In this way three master membranes of different thickness were obtained.

6.5.1 Characterization of Membranes

Physico-chemical characterization is important to understand the performance of the membrane. Thus some parameters such as porosity, water content, swelling, thickness, etc were determined [26-29].

6.5.1.1 Water Content (% Total Wet Weight)

Firstly the membranes were soaked into water to elute diffusible salt, blotted quickly with Whatmann filter paper to remove surface moisture and immediately weighed. These were
further dried to a constant weight in a vacuum over $P_2O_5$ for 24 hrs. The water content (total wet weight) was calculated as:

$$\% \text{ Total wet weight} = \frac{W_w - W_d}{W_w} \times 100$$

Where $W_w =$ weight of the soaked/wet membrane and $W_d =$ weight of the dry membrane.

**6.5.1.2 Porosity**

Porosity ($\varepsilon$) was determined as the volume of water incorporated in the cavities per unit membrane volume from the water content data:

$$Porosity = \frac{W_w - W_d}{W_w \rho_o LA}$$

Where $W_w$ and $W_d$ are weight of wet/soaked membrane, $\rho_o$ is the density of water while $A$ and $L$ are the area and thickness of the membrane.

**6.5.1.3 Thickness and Swelling**

The thickness of the membrane was measured by taking the average thickness of the membrane by using screw gauze. Swelling is measured as the difference between the average thickness of the membrane equilibrated with 1 molL$^{-1}$ NaCl for 24 hrs and the dry membrane.

**6.5.2 Fabrication of Ion-Selective Membrane Electrode**

The membranes as obtained by the above procedure was cut in the shape of disc and mounted at the lower end of a Pyrex glass tube (o.d. 1.6 cm, i.d. 0.8) using PVC as adhesive. Finally the assembly was allowed to dry in air for 24 hrs. These were then equilibrated with 0.1 molL$^{-1}$ AsO$_4^{3-}$ solution for 5-7 days. The glass tube was filled 3/4 with 0.1 molL$^{-1}$ AsO$_4^{3-}$ solution, then a saturated calomel electrode was inserted in the tube for electrical contact and another calomel electrode was immersed in a beaker containing the test solution of varying concentration of AsO$_4^{3-}$: keeping the level of inner filling solution higher than the level of the test solution to avoid any reverse diffusion of the electrolyte. Following parameters were evaluated to study the characteristics of the electrode such as lower detection limit, electrode response curve, response time and working pH range.
6.5.2.1 Electrode Response or Membrane Potential

To determine the electrode response, a series of standard solutions of varying concentrations were prepared by gradual dilution of the stock solution. External electrode and ion selective membrane electrode are plugged in digital potentiometer and the potentials were recorded.

Potential measurement was plotted against selected concentration of the respective ion in aqueous solution using the electrode assembly. The response of the membrane electrode have been also checked in a series of aqueous solutions of 50-100 ppb and the concentration of an unknown solution was determined by using the calibration plot. The result was also confirmed by the arsenomat and the calibration graphs were plotted three times to check the reproducibility of the system.

6.5.2.2 Effect of pH

A series of solutions of varying pH range, 1-11 were prepared. Keeping the concentration of the relevant ion constant (1x10^{-2} molL^{-1}). The value of electrode potential at each pH was recorded and was plotted against pH.

6.5.2.3 The Response Time

The method of determining response time in the present work is being outlined as follows:
The electrode is first dipped in a 1 × 10^{-3} molL^{-1} solution of the ion concerned and immediately shifted to another solution of 1 × 10^{-2} molL^{-1} ion concentration of the same ion (10 fold higher concentration). The potential of the solution was read at zero second; just after dipping of the electrode in the second solution and subsequently recorded at the intervals of 5 sec. The potentials were then plotted vs. the time. The time during which the potentials attain constant value represents the response time of the electrode.
6.5.2.4 Selectivity Coefficient of Interfering Anions

The selectivity of the electrode towards arsenic ions over sulphate and chloride ion was determined using a mixed solution method [30]. A specified amount of the interfering (M\text{\textsuperscript{n-}}) ions (1×10\textsuperscript{-2} M) were added to varying concentrations (1×10\textsuperscript{-1} – 1×10\textsuperscript{-11} mol L\textsuperscript{-1}) of AsO\textsubscript{4}\textsuperscript{3-} and the potentials were recorded.

6.6 Determination of arsenic in Industrial waste effluents:

In the present research work AsO\textsubscript{4}\textsuperscript{3-} was determined from industrial waste effluents collected from different areas of Aligarh City.

6.7 Result and Discussion.

Different samples of Alumina based Polyacrylonitrile nano composite have been prepared by a very simple technique as described above in (section 6.2.2). Among them sample (S-5) Table 6.1 was chosen for further studies due to its better ion exchange capacity and reproducible behavior. In order to check the reproducibility of prepared composite, it was synthesized five times under identical condition of concentration of reagents, mixing ratio and drying temperature. The composition and ion exchange capacity of each product were examined. The average and standard deviation of the ion exchange capacity was found to be 1.2 meq/g ± 0.02%. The percent composition of C, H, N, O, and Al, in the material were found to be 22.5, 3.2, 2.2, 34.5, 38.6 and the molar ratios were found to be 20.77: 35.1: 1: 24:16.6 respectively. A tentative structure of the composite can be proposed as below in which binding of polymer with inorganic part may be through unshared pair of electrons on Nitrogen:

\[ (\text{C}–\text{C}≡\text{N})–\text{Al}_2\text{O}_3 \]

The anion exchange material was characterized by SEM, TEM, FTIR and TGA-DTA, studies. TEM micrographs shows that the particles size of the synthesized composite material lies in nano range 80-97 nm (Fig.6.1) which proves that the proposed anion-exchanger is a nano-composite.
Table 6.1 Conditions of preparation and the ion-exchange capacity of Alumina based anion exchanger

<table>
<thead>
<tr>
<th>S. No</th>
<th>Polyacrylonitrile (gm)</th>
<th>Tetrahydrofuran (ml)</th>
<th>Aluminium oxide (gm)</th>
<th>Stirring time (hr)</th>
<th>Ion exchange capacity (meq/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>40</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
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<tr>
<td>2</td>
<td>1</td>
<td>80</td>
<td>1</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>20</td>
<td>0.2</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>20</td>
<td>0.2</td>
<td>2</td>
<td>0.52</td>
</tr>
<tr>
<td>5</td>
<td>0.2</td>
<td>20</td>
<td>0.4</td>
<td>2</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
<td>20</td>
<td>0.2</td>
<td>2</td>
<td>0.9</td>
</tr>
</tbody>
</table>
**Fig. 6.1** TEM Micrographs of Alumina based Polyacrylonitrile nano composite anion exchanger.

The scanning electron microphotographs of Polyacrylonitrile (a), Aluminium oxide (b) and anion exchange material (c) are given in **Fig. 6.2** It is clear from the photographs that after binding of organic polymer, polyacrylonitrile with Aluminium oxide morphology has been changed which indicates the formation of organic-inorganic composite anion exchanger.
Fig. 6.2 SEM photographs of Polyacrylonitrile film (a), Alumina (b), Alumina based Polyacrylonitrile nano composite anion exchanger (c).
The TGA curve Fig. 6.3 shows three distinct weight losses which are mirrored by the exothermic peaks on the DTA curve. In order of increasing temperature ranges, weight loss is caused by initial water losses up to 250 °C, gaseous hydrocarbon release from 250-350 °C and a gradual weight loss from 350-400 °C may be due to the decomposition of metal oxides. A smooth horizontal section on TGA curve represents the complete formation of oxide form of the material.

**Fig.6.3** Simultaneous TGA-DTA curves of Alumina based Polyacrylonitrile nano composite anion exchanger.

FTIR is a very useful tool to detect the existence of functional groups present in the composite material. A small peak at around 600 cm\(^{-1}\) is a characteristic of metal oxygen bond and a sharp peak at around 2245 cm\(^{-1}\) may be due to the presence of cyanide group. **Fig. 6.4** Abroad band at ~3421 cm\(^{-1}\) is due to N-H stretching mode. The band at 1250 cm\(^{-1}\) is attributed to a plane bending vibration of C-H.
Fig. 6.4 FTIR spectra of Polyacrylonitrile (a), Alumina (b), Alumina based Polyacrylonitrile nano composite anion exchanger (c).
Sensitivity and selectivity of the ion-selective electrodes depend upon the nature of electro-active material, membrane composition and physico-chemical properties of the membranes employed. A series of the composite anion exchange membranes were prepared with different amounts of the composite and fixed amount (200 mg) of PVC, the membrane. M-2 was selected to check the mechanical stability, surface uniformity, materials distribution, cracks and thickness, etc. The results are summarized in Table 6.2.

**Table 6.2** Characterization of alumina based polyacrylonitrile nano composite anion exchanger membranes.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Thickness of the membrane (mm)</th>
<th>Water content as % weight of wet membrane</th>
<th>Porosity</th>
<th>Swelling of % weight of wet membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>0.22</td>
<td>2.01</td>
<td>0.0007</td>
<td>0.05</td>
</tr>
<tr>
<td>M-2</td>
<td><strong>0.28</strong></td>
<td><strong>2.2</strong></td>
<td><strong>0.0004</strong></td>
<td><strong>0.03</strong></td>
</tr>
<tr>
<td>M-3</td>
<td>0.3</td>
<td>2.2</td>
<td>0.0003</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The heterogeneous precipitate AsO$_4^{3-}$ ion selective membrane electrode obtained from the anion exchange composite material gives linear response in the range $1 \times 10^{-1}$ molL$^{-1}$ to $1 \times 10^{-6}$ molL$^{-1}$, also shows same response in the backward direction. Fig.6.5. The mechanism can be discussed as follows.

The Alumina based polyacrylonitrile membranes carry positive charge of Aluminum which are fixed on the matrix of the polymer. Therefore they exclude all cations and are permeable to anions only. Thus the selectivity of anion exchanger membrane results from the exclusion of cations (co-ions) from membrane phase and permits transfer of anions (counter ions). The concentration of mobile anion is higher in the solution then in ion exchange membrane. Thus the concentration gradients are established between the membrane and the solution. This gradient acts as driving force for the mobile cations to move into the solution and mobile anions to move into the membrane.

Because of electro neutrality conditions, the permeation of cations into the solution and anions into the ion exchanger membrane leads to a counter-acting space charge due to
uncompensated ions and an equilibrium is established between the attempts of diffusion on one side and the establishment of an electrical potential difference on the other. Thus electrical potential difference between an ion exchanger membrane and adjacent salt solution can be measured.

The limit of detection is determined from the intersection of the two extrapolated segments of the calibration graph, was found to be $1 \times 10^{-6}$ molL$^{-1}$, and thus the working concentration range is found to be $1 \times 10^{-1}$ molL$^{-1}$ to $1 \times 10^{-6}$ molL$^{-1}$ for AsO$_4^{3-}$ ions. Suitable concentrations were chosen for sloping portion of the linear curve (forward direction) and the slope value is found to be 26.5 mV while for the linear curve (backward direction) the slope value is found to be 25mV.

![Figure 6.5](image)

**Fig.6.5** Calibration curve of alumina based polyacrylonitrile nano composite anion exchange membrane electrode in aqueous solutions of AsO$_4^{3-}$ (Con in molL$^{-1}$)

Another important factor is the promptness of the response of the ion-selective electrode. The average response time is defined as the time required for the electrode to reach a stable potential after successive immersion of the electrode in different AsO$_4^{3-}$ ion solutions each having a 10-fold difference in concentration. The response time in contact with $1 \times 10^{-2}$ molL$^{-1}$ AsO$_4^{3-}$ ion solution was determined and the results are shown in **Fig 6.6**. It is clear from the figure, that the response time of the membrane is ~35 s. pH effect on the potential response of the electrode were measured for a fixed ($1 \times 10^{-2}$ molL$^{-1}$) concentration of AsO$_4^{3-}$ ions in
different pH values. It was observed that the electrode potential is very unstable upto 7 pH while it remains unchanged within the pH range 8.0-11.0 **Fig 6.7**, known as working pH range for the electrode. It indicates that electrode is working in alkaline medium.

**Fig.6.6** Time response curve of alumina based polyacrylonitrile nano composite anion exchanger membrane electrode.

**Fig.6.7** Effect of pH on the potential response of the alumina based Polyacrylonitrile nano composite anion exchange membrane electrode at $1 \times 10^{-2}$ molL$^{-1}$ AsO$_4^{3-}$ concentration.
The selectivity coefficients of sulphate and chloride for the $\text{AsO}_4^{3-}$ selective anion exchanger membrane electrode were determined by the mixed solution method [30]. It is observed from Table 6.3 that sulphate and chloride ions interfere to a very little extent. Thus the results revealed that the electrode is selective for $\text{AsO}_4^{3-}$ in presence of interfering anions.

Table 6.3  Selectivity coefficient values for $\text{AsO}_4^{3-}$ selective anion exchanger membrane electrodes

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Interfering ions (M$^{n-}$)</th>
<th>Selectivity coefficient values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl$^-$</td>
<td>$1.72 \times 10^{-2}$</td>
</tr>
<tr>
<td>2</td>
<td>$\text{SO}_4^{2-}$</td>
<td>$2.2 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

The determination of arsenic is a very important section of this research work, as arsenic is a very toxic pollutant in the environment causing serious health hazards. It was found that our electrode also gives response in a series of 50-100 ppb solutions and with the help of calibration plot Fig. 6.8 the concentration of an unknown solution was found to be 75 ppb while by using the arsenomat the concentration of the same unknown solution was found to be 65 ppb. The results are very close to each other and the difference can be considered as negligible because the concentrations are in ppb range.
Fig. 6.8 Calibration curve of alumina based Polyacrylonitrile nano composite anion exchange membrane electrode in ppb aqueous solutions of $\text{AsO}_3^{3-}$

The content of arsenic was also determined in various industrial waste effluents collected from different areas of Aligarh city. The electrode was found to give a response in the range of 350 to 359 mV in these samples also the same samples were tested by the arsenomat and the content of arsenic found are also given in Table 6.4 Thus from the calibration plot Fig. 6.8 it is clear that the concentration of $\text{AsO}_3^{3-}$ in different samples of water are below 50ppb.

Table 6.4 Content of Arsenic in different areas of Aligarh city determined by Arsenic analyzer and Alumina based polyacrylonitrile anion exchanger membrane electrode.

<table>
<thead>
<tr>
<th>Areas of Aligarh city</th>
<th>Content of Arsenic ($\mu$g/L)</th>
<th>Potentiometric Value (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kasimpur</td>
<td>5.5</td>
<td>359</td>
</tr>
<tr>
<td>Firdous Nagar</td>
<td>4.3</td>
<td>357</td>
</tr>
<tr>
<td>Gyansarover</td>
<td>4.5</td>
<td>357</td>
</tr>
<tr>
<td>Janakpuri</td>
<td>3.95</td>
<td>354</td>
</tr>
<tr>
<td>Vikram Colony</td>
<td>3.69</td>
<td>350</td>
</tr>
<tr>
<td>Mahendar Nagar</td>
<td>4.00</td>
<td>355</td>
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References:


