Chapter III

Conducting membrane for electrochemical dye degradation and arsenic detection/removal
Chapter III: Conducting membrane detection and removal

3.1. Polymer electrolyte membrane (PEM) for dye degradation

Various types of synthetic dyes are manufactured for widespread sectors such as fabric, leather, paper and food industries, in developing country like India [1-7]. Removal of dye from wastewater was studied by physicochemical flocculation [8], nanofiltration (NF) [9, 10], micellar enhanced (UF) [11], and adsorption on suitable adsorbents [12-14]. UF and NF methods are used for dye removal, their reduced the membrane flux and durability make them unsuitable [10,15]. Adsorptions of dyestuffs using variety of adsorbents still have significant limitations of either desorption or disposal of colour adsorbed material. Chemicals such as hypochlorite, ozone and hydrogen peroxide in the presence of UV light or hydrogen peroxide with Fe$^{2+}$ (Fenton’s reagent) were used for pre-treatment of dye-bearing wastewater [16-18]. The electrochemical processes have advantages since in situ formation oxy-halide free radicals during water splitting in presence of salt [19-21]. These radicals are unstable intermediates, and act as oxidizing agent for dye degradation [22,23]. But, operational difficulties for electrochemical methods such as chlorine-tolerant PEM obstructed the practical applications.

Perfluorosulfonic acid PEM such as Nafion has been considered as reference for fuel cell and electro-membrane processes, because of its high conductivity and oxidative stability in harassed conditions of chloro-alkali [24-27]. However, there is much interest in alternative chlorine tolerant PEM because high cost of Nafion membrane [27,28]. For developing cost effective, fluorine-free PEMs with comparable properties to Nafion, sulfonated aromatic polymers such as poly(ether sulfone) (PES) were successfully proposed [29-32]. Engineering thermoplastics showed excellent stabilities (mechanical, chemical and thermal) [32,33]. PES is a better chlorine resistance material because main chain consists aromatic rings and chemically strong bonding between carbon, sulfur and oxygen [34]. Additionally, this material does not have any chlorine sensitive linkage. Thus, there is an urgent requirement to develop chlorine resistant, cost effective and highly stable PEM for complete dye degradation (about 100% dye removal) and recovery of NaOH as by product based on the principles of chloro-alkali process

Therefore in this chapter, we investigate an electrochemical dye degradation method with advantages of water splitting products (H$^+$ and OH$^-$) and by-product recovery. Eosin B degradation efficiency for developed PEM was compared with Nafion® 117
membrane, which suggested commercial viability of the process with high current efficiency, low energy consumption and cost.

3.1.1. Materials and membrane preparation

PES (3500) was received from Udel. Eosin B dye (4’,5’-Dibromo- 2’,7’ dinitrofluorescein di sodium salt, colour index: 45400), chloroform, chlorosulfonic acid, methanol, and dimethylformamide (AR grade) were obtained from S.D fine Chemicals, India, and were used without any further purification. Double distilled water was used in all experiments. Sulfonation of PES was carried out as reported earlier [29], using chlorosulfonic acid in chloroform under stirring at 0 °C for 30 min. The precipitated polymer was filtered, washed with distilled water until only a trace of acid remained and dried under vacuum for 12 h at 50 °C. For the membrane preparation, sulfonate poly (ether sulfone) (SPS) was dissolved in dimethylformamide (20% w/v) to obtain a homogeneous solution under constant stirring. Resultant viscous solution was cast in form of thin film of desired thickness on a clean glass plate after proper degassing and dried under IR lamps followed at 70 °C for 12 h. SPS membranes were conditioned in 0.10 M HCl and 0.10 M NaOH solutions alternatively several times and then equilibrated with the experimental solution before subjected to physicochemical and electrochemical studies [35-37].

3.1.2. Electrochemical reactor for dye degradation

![Flow diagram of the experimental setup of EMR.](image-url)

Fig. 3.1.1. Flow diagram of the experimental setup of EMR.
Chapter III: Conducting membrane detection and removal

Schematic diagram of electrochemical reactor employed for dye degradation is depicted in Fig. 3.1.1. Electrochemical reactor was made of PTFE and divided into an anode compartment (AC) and cathode compartment (CC) by PEM (8.0×10^{-3}m^2). Two peristaltic pumps were used to move each stream, while an adjustable dc power supply (model L 1285, Aplab, Mumbai, India) was used to apply constant potential gradient. Two 1.5mm thick expanded TiO_2 sheets, coated with triple precious metal (titanium–ruthenium–platinum) with 6.0µm thickness, were obtained from Titanium Tantalum products (TITAN, India) and used as electrodes. Two storage tanks and pumps were used for continuous feeding into AC and CC with 0.006m^3/h flow rate, to create high turbulence in both compartments of the reactor. Experiments were conducted in batch mode, i.e., the same volume of solution was recirculated in the respective compartments. Magnetic stirrers were used to ensure the complete mixing of the solution in storage tanks. The whole setup was placed at room temperature (30 °C). Initially, a known volume of water was fed through the CC, while eosin B solution was recirculated through AC. Under the influence of applied potential, Na^+ migrated from AC towards CC through developed PEM and formed NaOH. The pH values of AC and CC were recorded as function of time using pH sensor in both compartments. NaOH concentration in the CC was also monitored regularly. In all cases, equal volumes of AC and CC were taken to study the feasibility of the separation process.

Build-up of NaOH concentration in CC was determined by acid-base titration using phenolphthalein indicator. The dye concentrations were analyzed by UV-Vis spectrometry at maximum wavelength (\(\lambda_{\text{max}} = 517\) nm) using calibration curve (Fig. 3.1.2) and eosin B removal was obtained following equation [38]:

\[
\text{Eosin removal (\%)} = 1 - \frac{C_t}{C_0} \times 100 \quad (3.1.1)
\]

![Fig. 3.1.2. Standard curve of eosin B at wavelength of 517 nm.](image-url)
where \( C_t \) and \( C_0 \) were the concentration of dye at reaction time \( t \) and \( 0 \), respectively.

### 3.1.3. Result and discussion for dye degradation using polyelectrolyte membrane

#### 3.1.3.1. Membrane properties

Extent of sulfonation, evaluated by \(^1\)H NMR spectra, was found about 62.0% [29]. Sulfonation of PES was also confirmed by FTIR-ATR spectra (Fig. 3.1.3). The peaks at 1580 and 1486 cm\(^{-1}\) are attributed to vibration of aromatic ring skeleton [39]. The characteristic absorption band for the aromatic sulfone group appears at 1151 cm\(^{-1}\) and the peak for aryl oxide appears at 1104 cm\(^{-1}\) [40]. Two absorption peaks at 1078 and 1022 cm\(^{-1}\) were characteristic of aromatic \( \text{SO}_3^- \) stretching vibrations. The physicochemical and electrochemical properties of SPS membrane are presented in Table 3.1.1.

**Table 3.1.1.** Physicochemical and electrochemical properties of the PEM.

<table>
<thead>
<tr>
<th>Property</th>
<th>SPS</th>
<th>Nafton® 117</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (μm)</td>
<td>150</td>
<td>195</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>13.6</td>
<td>36.0</td>
</tr>
<tr>
<td>Ion-exchange capacity (meqvt/g of dry membrane)</td>
<td>1.20</td>
<td>0.90</td>
</tr>
<tr>
<td>Counter-ion transport number ((i^-))</td>
<td>0.95</td>
<td>0.98</td>
</tr>
<tr>
<td>Membrane conductivity (mS/cm)</td>
<td>20.0</td>
<td>95.6</td>
</tr>
</tbody>
</table>

Membrane exhibited good water content, ion-exchange capacity and counter-ion transport numbers in the membrane phase and high specific membrane conductivity. Furthermore, properties of SPS membrane were comparable with the best-known cation-exchange membrane [41]. Also excellent chemical and mechanical stabilities of these membranes are attractive features for their applicability in the electro-membrane
Chapter III: Conducting membrane ....................... detection and removal

processes. SEM images of SPS membrane showed uniform, dense and homogeneous surface [29].

For EMR, knowledge on membrane conductivity in equilibration with actual operating conditions is an essential parameter. Membrane conductivity data \( (k^m) \) for SPS membrane in equilibration with eosin B and NaCl solutions of different concentrations (10-100 ppm) is presented in Fig. 3.1.4. \( k^m \) values depended on ionic strength of equilibrating solution, and increased initially with concentration (eosin B and NaCl) before attending limiting value (beyond 30 ppm). This observation may be attributed to comparatively low dissociation and ionic strength of eosin B solution. However, comparable membrane conductivities under both operating conditions (eosin B or NaCl) revealed the membrane suitability for an EMR.

3.1.3.2. Membrane stability

Membrane thermal stability was assessed by thermogravimetric curve (Fig. 3.1.5) which showed three steps weight loss. The first weight loss appeared at 70-140 °C due to absorbed water. The degradation of the sulfonic acid group was observed between 270 and 440 °C. The third weight loss at about 448 °C was assigned to decomposition of the polymer backbone [42]. These data indicated of SPS membrane is thermally stable.
Chapter III: Conducting membrane ..................... detection and removal

The chlorine tolerant nature of prepared SPS membrane was assessed in comparison with Nafion® 117 membrane in terms of percentage in weight loss and IEC loss for definite time intervals. Formation of oxy radicals during electrochemical water splitting in the presence of halide ion occurred AC, which may attack on hydrogen containing bonds of PEM. Thus, developed PEM should be highly chlorine tolerant in nature. Resultant data are presented in Fig. 3.1.6 (A,B). It is obvious that both membranes (SPS and Nafion® 117) lost about 5-6% IEC after 24 h treatment of membranes. Progressively, loss in IEC and weight attained limiting values. Furthermore, for SPS membrane, weight loss was slightly higher than Nafion® 117 membrane, while latter showed comparatively high IEC loss. The membrane degradation occurred chemically as a result of oxy-chloride free radical (•OCl) attack on the polymer chain in the vicinity of hydrophilic domains [37]. IEC is measure of functional group concentration in the membrane matrix, and high for SPS membrane (1.20 mequiv./g) in comparison with membrane (Table 3.1.1). Thus, because of more hydrophilic nature of SPS membrane than Nafion®117, IEC loss was comparatively high under chlorine stability test (Fig. 3.1.6). Moreover, chlorine tolerant nature for both (SPS and Nafion® 117) was same and these membranes showed their potential applications under chlorine environment.

![Graph A](image1)

![Graph B](image2)

Fig. 3.1.6. Comparison of percentage loss in (A) weight and (B) IEC for SPS and Nafion® 117 membrane after treatment in 5% aq. NaOCl solution at 80 °C for different time intervals.
3.1.3.3. Electrochemical eosin B degradation

Most dye contains NaCl as the major constituent, thus electrochemical degradation is easy in absence of supporting electrolytes [43,44]. Generally, dye molecule is electrochemically inactive and anode changes occur because oxidation of water/Cl\(^{-}\) to O\(_2\)/Cl\(_2\). Chlorine gas is robust oxidizing agent and dissolves in water (HOCl), which is instable in acidic solution (pKa = 7.4). HOCl immediately dissociates and formation of OCl\(^{-}\) is responsible for dye degradation. Thus, basic or neural pH conditions are more favorable for dye degradation. Principle of EMR used for eosin B degradation was based on electro-electrodialysis as presented in Fig. 3.1.7.

In AC, eosin B degraded by chloride/hypochlorite mediated oxidation [45]. Degradation was effected by O\(_2\)/OCl\(^{-}\) generation at anode, and migration of H\(^{+}\)/Na\(^{+}\) from AC through SPS membrane (CEM) towards cathode. This leads formation of NaOH in CC using OH\(^{-}\) formed due to reductive water splitting [43,44]. Moreover, eosin B degradation process depends on the initial eosin B dye concentration and oxidizing strength of anode (active species concentration).

Electro-active species produced at electrodes exhibited peak type responses in cyclic voltammetry because exchange of electron during anodic- and cathodic-potential scans. Dye degradation occurred due to anodic oxidative process and by-product produced because of cathodic reductive process. Fig. 3.1.8 shows the cyclic voltammetry responses of 0.1 M NaCl before and after addition of eosin B at different potential scan rates.
Chapter III: Conducting membrane ..................... detection and removal

after the addition of dye effluent (1 ml) with 3 h time interval at a glassy carbon electrode in the potential range of 1.5 to -1.5 V. Saturated calomel electrode (SCE) was used as reference electrode. Electrode responses under both cases were identical (Fig. 3.1.8 (a,b)). However, at cathodic potentials (-1.0 and -0.5 V), considerable reduction in anodic current was observed, which further decreased with dye concentration and revealed dye adsorption on anode surface prior to decomposition. Large anodic current maybe attributed to the displacement of chlorine and oxygen from the NaCl with or without the simultaneous dye decomposition.

The FTIR spectra for eosin B solution before (0 h) and after the electrochemical treatment for 1 and 2 h are shown in Fig. 3.1.9. Considerable changes were observed in the regions 1000–1700 cm\(^{-1}\) and 2000–3000 cm\(^{-1}\). Absorption bands for untreated eosin B (0 h) at 1420–1335 cm\(^{-1}\) and 1260–1180 cm\(^{-1}\) aroused due to C–O symmetric stretch and the combination of the C–O stretching with O–H bending [46-49]. In case of electrochemically treated dye (1 and 2 h), disappearance of these bands indicated oxidation of corresponding groups. Similarly, bands at 2950, 2850, 2525 cm\(^{-1}\) for untreated eosin B aroused due to aromatic ring, but after electrochemical degradation, these bands were disappeared due to degradation of aromatic ring. Also, presence of peak at about 505–760 cm\(^{-1}\) confirmed C-Cl stretching, while peak at 1645 cm\(^{-1}\) (C-C stretch, diene conjugated group) was slightly reduced because of reduction in eosin B concentration. This overall change in the IR spectra can be explained by completely degradation of organic compounds and formation of chlorinated dienes [50].

3.1.3.4. Effect of operating conditions on dye degradation in EMR

Rate of dye degradation was found to be affected by applied potential, dye concentration and feed flow rate [51]. Fig. 3.1.10 (A) shows variation of eosin B removal
Chapter III: Conducting membrane ..................... detection and removal

under different applied potential for 50 ppm eosin B in feed at 40 ml/min. Eosin B concentration was monitored by absorbance spectra before and after degradation at 517 nm band. With time and applied potential, dye removal was enhanced during electrolysis. About 95% eosin B degradation was achieved for its 50 ppm concentration in AC (40 ml/min flow rate) after 180 min electrochemical treatment at 12.0 V applied potential.

Effect of dye concentration on its degradation was also investigated (10-100 ppm) at 12.0V applied potential with 40 ml/min flow rate and relevant results are presented in Fig. 3.1.10 (B). Rate of change of dye concentration was relatively fast at high concentration under similar experimental conditions. It revealed about 95% degradation of eosin B (40 ml/min flow rate) after 180 min at 12.0 V. Fig. 3.1.10 (C) showed influence of feed flow rate or turbulence (AC) during oxidative degradation of eosin. These data revealed that high applied potential, dye concentration and low feed flow rate are required for fast and efficient degradation process. Further, these parameters also depended on EMR flow pattern and membrane as

Fig. 3.1.10. Removal of eosin B concentration under different conditions (A) variation of applied potential at 50ppm eosin B and 40 ml/min flow rate; (B) variation of eosin B concentration at 12.0 V applied potential and 40 ml/min flow rate ; (C) variation of feed flow rate at 12.0 V applied potential and 50 ppm eosin B.

Fig. 3.1.11. Variation of pH of AC and CC with time during degradation of eosin B (50 ppm) at 8.0 V (solid line) and 10.0 V (dotted line) applied potential.
well as electrode area. Thus complete optimization of these parameters is essential for an efficient process. Under optimum conditions about 95-98% degradation was observed during 180 min, which can be further enhanced with increase in applied potential or membrane area. Further, production of NaOH also followed the same pattern as change in the dye concentration (Fig. 3.1.11). It was observed that oxidative degradation of 1.0 ppm of dye produced about 2.0 ppm of NaOH. This observation also confirmed the electrochemical dye degradation mechanism and formation of NaOH as by-product in CC. Also, it was observed change in the both compartments (AC and CC) were dependent on the operation condition employed (e.g., voltages, dye concentration, electrolysis time and flow rate) [52].

The changes in absorbance characteristics of dye effluent were investigated over a wide wavelength interval during the electrochemical process and the results for different hour electrolysis are presented in Fig. 3.1.12. The spectra showed maximum absorbance at 517 nm band in the visible region. This peak gradually suppressed after the electrolysis with time interval. This result confirmed complete dye degradation. Inset Fig. 3.1.12, also confirmed degradation of eosin B after 3 h of electrochemical treatment.

3.1.3.5. Kinetic study for dye degradation

The rate constants were calculated by pseudo-first order kinetic models [52]. The first order expression given as:

$$\log(C_e - C_t) = \log C_e - \frac{k_1 \cdot t}{2.303} \quad (3.1.2)$$

[91]
Chapter III: Conducting membrane detection and removal

$C_e$ is the concentration of dye at equilibrium, and $C_t$ is the concentration of dye at time $t$. $k_1$, first order rate constant, was estimated from the slope of $\log (C_e - C_t)$ vs $t$ linear plots at different concentrations (Fig. 3.1.13) and presented along with correlation coefficient ($R^2$) in (Table 3.1.2). Data showed slope value (first order constant) slightly lowered with dye concentration which revealed that, oxidative dye degradation process followed pseudo first order kinetics.

**Table 3.1.2.** Pseudo-first order kinetics constants, correlation coefficients ($R^2$) for the dye degradation process.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Pseudo-first order kinetics</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.0077</td>
<td>0.9991</td>
</tr>
<tr>
<td>20</td>
<td>0.0073</td>
<td>0.9977</td>
</tr>
<tr>
<td>50</td>
<td>0.0069</td>
<td>0.9927</td>
</tr>
</tbody>
</table>

3.1.3.6. Current efficiency and energy consumption for EMR

The energy consumption ($W$) and current efficiency ($CE$) are important parameter to assess the feasibility of an electrochemical process. $W$ (kWh/kg) for degradation of eosin may be obtained as follows:

$$W (\text{kWh/kg}) = \int_0^t \frac{V I dt}{m} \quad (3.1.3)$$

where $V$ is the applied potential (volt), $I$ is the current, $t$ is the time allowed for the electrochemical process, and $m$ is the weight of dye (eosin). The overall current efficiency ($CE$) was defined as the fraction of Coulombs utilized for the water splitting and electro-migration of ions:
Chapter III: Conducting membrane detection and removal

\[ CE(\%) = \frac{m n F}{M Q} \times 100 \] (3.1.4)

where \( F \) is the Faraday constant, \( M \) is the molecular weight of eosin, \( n \) is the stoichiometric number (\( n = 1 \) in this case) and \( Q \) is the electric quantity passed (Coulombs; \( A s \)).

![Graph comparing energy consumption and CE for SPS and Nafion® 117 PEM](image)

**Fig. 3.1.14.** Comparison of: (A) Energy consumption (W); and (B) CE, in EMR using SPS or Nafion® 117 PEM during eosin B degradation at 12.0 V applied potential, 50 ppm eosin B concentration and 40 ml/min AC feed flow rate.

Fig. 3.1.14 (A,B) shows W and CE values for EMR with SPS or Nafion® 117 PEM, for degradation of 50 ppm eosin B (initial feed of AC) at 12.0 V constant applied potential and 40 ml/min AC feed flow rate. In case of SPS PEM, 97% degradation of eosin B was achieved with 92% CE corresponding to 4.97 kWh/kg of energy consumption. While for Nafion® 117 PEM, same extent of eosin B degradation (97%), was observed with 76.6% CE and 3.94 kWh/kg of energy consumption. Low energy consumption was exhibited by Nafion® 117 PEM in EMR, which may be explained on the basis of high proton conductivity and electro-osmotic drag of solvent. SPS and Nafion® 117 membrane showed conductivity 20.2 and 95.6 mS/cm, respectively (Table 3.1.1). Thus, high potential drop across SPS membrane was mainly responsible for relatively high energy consumption under comparable experimental conditions. This process involved simple procedure and also generated NaOH as a by-product. Environmental advantages such as reduced emission of gaseous species and reduced disposal of liquid effluent during the process of development were also realized.
Chapter III: Conducting membrane detection and removal

3.1.4. Conclusions for electrochemical dye degradation using polymer electrolyte membrane (PEM)

In summary, SPS membrane, derived from controlled sulphonation of PES under completely optimized environment, exhibited good physicochemical properties, conductivity, stabilities and tolerance to chlorine (oxy-chloride free radicals) under experimental conditions of EMR used for dye (eosin B) degradation. All properties and chlorine tolerance nature of SPS membrane were comparable to commercially used Nafion® 117 membrane. The efficiency of SPS PEM was also evaluated for electrochemical dye degradation in EMR to compare with Nafion®117 PEM.

EMR process showed 97% degradation of eosin B against 92% CE and 4.97 kWh/kg of eosin B removed energy consumption, with SPS PEM. While for Nafion® 117 PEM showed 76.6% CE and 3.94 kWh/kg of eosin B removed energy consumption for same extent of eosin B degradation (97%) under optimum operating conditions. Furthermore, the eosin B removal efficiency was dependent on feed dye concentration, applied potential and flow rate. Developed process avoids any other chemicals and production of NaOH as byproduct is an attractive feature. At the same time environmental advantages are realized such as reduced emission of gaseous species and reduced disposal of liquid effluent during the process development. Moreover, developed reactor can be efficiently used for the degradation of other dye effluent. Depending on the polymer stabilities and properties, SPS membrane also can be tailored for specific separation purposes by electrodialysis, because of its high chlorine tolerance, stabilities, conductivity and counter-ion transport number.

3.2. Silver nanoparticles-chitosan composite thin film for arsenic (As^{3+}) detection/removal

Arsenic contamination of ground water is a world-wide serious problem encountered in several countries (India, Bangladesh, Taiwan, Argentina, Vietnam and United States) as it can affect the safety of drinking water [53]. As^{3+} is thought to be more toxic than As^{5+}, due to its reactions with enzymes in human metabolism [54]. This causes many diseases such as skin lesions, keratosis, lung cancer, bladder cancer, etc [55-58]. U.S. Environmental Protection Agency (USEPA) recommended 2-20 ppb arsenic level, while WHO guideline recommends less than 10 ppb of arsenic contamination in
drinking water. Thus, the availability of a cheap and environmental friendly tool for detecting arsenic contamination level in ground water samples is of great importance from the eco-toxicological point of view [59].

Inductively coupled plasma mass spectrometry (ICP-MS), electro-spray MS (ES-MS) coupled to chromatography (HPLC, GC) and atomic absorption/fluorescence spectroscopy (AAS/AFS) techniques, are commonly used to determine arsenic [60,61]. However, these techniques are expensive and the need for sample storage and transport is an obstacle speciation studies [62]. Because of this, we have explored the possibility to determine As\(^{3+}\) in water by anodic stripping voltammetry. Reported procedure has great potential for on-site environmental monitoring due to its favorable portability, suitability for automation, short analysis time, low power consumption, and inexpensive equipment [63]. Stripping voltammetry at gold or mercury electrode is generally employed for the detection of As\(^{3+}\) [64-67]. Mercury drop is not adapted for on-site analysis, although it has been used [68]. Gold has been used on-site [66,67,69] but it is expensive. Thus alternative methods that combine simplicity, sensitivity, stability and low price are urgently needed to meet the growing demands for on-site environmental monitoring of As\(^{3+}\) [69].

Nanomaterials of different shapes, sizes, and compositions, have found broad applications in analytical methods [70-72]. Among these materials, metallic nanoparticles are of great interest due to their important properties and multiple applications. Metal nanoparticle-modified electrodes show dramatically enhanced sensitivity due to their large specific surface area and high surface free energy. However, interference from other metals, formation of intermetallic compounds and peak overlap, are serious problems for stripping voltammetry sensors [73].

Different metals and metal compounds, such as cobalt oxide, gold, and platinum nanoparticle-modified GCEs were demonstrated to be suitable for As\(^{3+}\) detection [74-77]. But, low efficiency, interferences of other metal ions and high cost of these electrodes hindered their commercial exploitation [26-28]. Simm et al. demonstrated that a bulk silver electrode in combination with ultrasound could be used for As\(^{3+}\) detection in HNO\(_3\) media [78,81], but copper seriously interfered because it formed intermetallic compounds with arsenic. Silver nanoparticles (AgNPs) are a good material for electrochemical
sensors and represent a good substrate for the preparation of chemically modified electrodes [82]. But, no report has been available regarding the use of AgNPs as electrochemical sensor for arsenic detection. For metal ions adsorption, chitosan (CT) is a suitable biopolymer as host matrix because of its film-forming ability, good adhesion to electrode surfaces, high water permeability, non-toxicity, biocompatibility, high mechanical strength and susceptibility to chemical modifications [83]. Hydrophilic surface of CT due to presence of reactive amino and hydroxyl functional groups also indicate its applicability for developing electrochemical sensors and biosensors [84, 85]. Moreover, CT was extensively studied for the removal of metal and metalloids due to its hydrophilic nature (presence of a large number of hydroxyl and amino groups) and presence of adsorption sites, along with its non-toxicity, biocompatibility, and biodegradability [86]. Reports for As$^{3+}$ removal by CT-based adsorbents are available [86-89]. The mechanism involved in the removal of arsenic through adsorption on molybdate-impregnated chitosan beads is an ion-exchange precipitation between the impregnated metal and arsenate ions [86].

Herein, we report the modified GCE with AgNPs embedded in a thin-film CT matrix. The electrode was found to be sensitive and selective allowing the detection of As$^{3+}$ in groundwater, without any interference from major ions. High active surface area and the strong adsorptive capability were found to provide a long linear range. The diffusion of As$^{3+}$ within the AgNPs/CT membrane was also explored.

### 3.2.1. Materials

Chitosan (CT) (high molecular weight and $\geq$75% of degree of deacetylation) was obtained from Sigma-Aldrich. All other reagents such as NaAsO$_2$, AgNO$_3$, HNO$_3$ and hydrazine hydrate (35%, v/v) etc (AR grade) were obtained from S.D. fine Chemicals, India and used without any further purification. Double distilled water was used for all experimental purpose. As$^{3+}$ stock solution (1 ppm) was prepared with NaAsO$_2$ dissolved in 1.0 M HNO$_3$. (Caution! NaAsO$_2$ is highly toxic; proper care must be taken in handling).

### 3.2.2. Preparation of AgNPs/CT modified electrode
Chapter III: Conducting membrane detection and removal

Stock solution of CT (0.5 wt %) was prepared in 0.1 M acetic acid. Undissolved materials were filtered (Whatman filter paper, pore size: 11 μm), and solution pH was adjusted at 5.1 via careful additions of concentration of NaOH under vigorous stirring.

For the synthesis of Ag nanoparticles (AgNPs), 10 ml of 30 mM AgNO₃ were added to 10 ml of 5mg/ml CT stock solution under stirring (30 min) at room temperature. Then, 1 μl of hydrazine hydrate (35%, v/v) was added to the resulting mixture. The mixture was kept under constant stirring at 60 °C for 3 h. Material was obtained by centrifugation and washed couple of times with water. The purified sample was dispersed in water (10 cm³) and used for characterization.

For the preparation of AgNPs/CT modified electrode, glassy carbon electrode (GCE) was polished (with 0.3 and 0.05 μm alumina slurries), washed with deionized water and acetone thoroughly, and sonicated in deionized water for 1 min. The electrode was then transferred to the electrochemical cell for the activation by cycling (between -0.15 and 1.30 V) in 0.5 M H₂SO₄ solution, until a stable profile was obtained. A 10 µl amount of AgNPs/CT suspension solution was dropped on clean GCE and dried under an IR lamp. Also, AgNPs/CT containing different concentrations of AgNO₃ (10, 70, 100 and 200 mM, respectively) were prepared with the same synthetic route pattern. Differential pulse anodic stripping voltammetry (DPASV) experiments for As³⁺ detection, were carried out in 1.0 M HNO₃ (supporting electrolyte), using -0.60 V deposition potential for 120 s (deposition time), 10 s rest period, with the following differential pulse parameters: modulation amplitude, 200 mV; modulation time, 50 ms; scan rate, 10 mV/s; step potential, 5 mV. After analysis of As³⁺, the electrode was cleaned as previously described.

3.2.3. Diffusion studies for As³⁺ removal

0.5 wt% of CT (dissolved in 0.1 M acetic acid, un-dissolved materials was filtered, and solution pH was adjusted to 5.1 using 10 mM NaOH) was added to poly vinyl alcohol (PVA) solution (3.0 wt% in distilled water) under stirred conditions. 10 ml of AgNO₃ solution (30 mM) was further added at room temperature. The resulting highly viscous white colored gel was transformed into thin film on a cleaned glass plate and first dried under IR lamps at ambient temperature before being placed under vacuum at 60°C for 24 h. The thin films of desired thicknesses were then soaked in hydrazine hydrate
Chapter III: Conducting membrane ..................... detection and removal

(35%, v/v) for 3h. Film thickness was maintained by using casting blades. Resultant membrane was stored in double distilled water for further characterizations.

![Diagram](image)

**Fig. 3.2.1.** Schematic representation of diffusion cell combined with As$^{3+}$ sensor.

Diffusion studies were performed in a two-compartment diffusion cell, equipped with an As$^{3+}$ sensor placed in each compartment (Fig. 3.2.1). Both compartments were well stirred and separated by a circular membrane piece (20.0 cm$^2$). The feed compartment was initially fed with As$^{3+}$ solution of known concentration, while distilled water was initially fed through the permeate compartment. Two peristaltic pumps were used to feed each compartment, separately. In permeate and feed compartment, As$^{3+}$ concentration was regularly monitored by prepared electrochemical sensor with respect to time one after another. Geometric characteristics of the cell can be grouped into a constant “$\delta$”, which may be called as cell constant, and estimated by [90]:

$$\delta = \frac{A}{T} \left( \frac{1}{V_1} + \frac{1}{V_2} \right)$$  \hspace{1cm} (3.2.1)

where $A$ is effective membrane area (20.00 cm$^2$), $T$ the membrane thickness (0.015 cm), $V_1$ and $V_2$ are the volume of solutions used in compartments 1 and 2 (100 cm$^3$).

From Fick’s second law for diffusion can be written as:

[98]


Chapter III: Conducting membrane ..................... detection and removal

\[ \frac{\partial C^2}{C^1 - C^2} = \delta D \partial t \quad (3.2.2) \]

Under boundary conditions, \( t = 0 \) to \( t = f \), integration of Eq. (3.2.2) is:

\[ \int_{t}^{f} \frac{\partial C^2}{C^1 - C^2} = \delta D \int \partial t \quad (3.2.3) \]

Finally:

\[ \ln \left( \frac{C^1_f - C^2_f}{C^1_i - C^2_i} \right) = -\delta D t \quad (3.2.4) \]

where \( C \) is the final concentration or initial concentration in the compartment 1 or 2 (super and subscripts are \( i \), initial; \( f \), final; 1, compartment 1; 2, compartment 2), \( t \) is diffusion time. Diffusion coefficients (D) were evaluated by Eq. (3.2.4).

3.2.4. Results and discussions for As\(^{3+}\) detection and removal

3.2.4.1 Characterization of AgNPs/CT

![Fig. 3.2.2](image)

**Fig. 3.2.2.** (A) FTIR and (B) Uv-Vis Spectra of: a) CT, b) 10 mM of AgNO\(_3\) containing AgNPs/CT, and c) 70 mM of AgNO\(_3\) containing AgNPs/CT.

FTIR measurements were performed to identify possible interactions between silver ions and chitosan molecules, which could be accountable for the reduction of silver ions and stabilizing silver nanoparticles. FTIR spectra of the CT and AgNPs/CT samples are included in Fig. 3.2.2. Although there was the possibility of overlapping between N-H and O-H stretching vibrations, strong broad band at 3300-3500 cm\(^{-1}\) (peak 1, curve a) is
Chapter III: Conducting membrane ..................... detection and removal

characteristic of the N-H stretching vibration. In this band region, significant decrease in transmittance indicates effect on N-H vibration due to attached AgNPs [91]. N-H bending vibration bands (peak 2, curve b and c) (at about 1560 cm\(^{-1}\)) were shifted to 1578 and 1570.8 cm\(^{-1}\), accompanied by a gradual decrease in intensity with increased silver concentrations. Thus, attachment of silver to nitrogen atoms was responsible for reduced vibration intensity of the N-H bond due to the molecule weight becoming heavier after silver binding. All changes in the transmittances related to the bonds with N atoms reveal that nitrogen atoms in the chitosan are binding sites for silver. It is notable that AgNPs/chitosan samples showed a new band at 1760 cm\(^{-1}\) (curve b, peak 2) corresponding to carbonyl stretch vibrations in ketones, aldehydes and carboxylic acids [92]. Presence of peak at 1760 cm\(^{-1}\) in AgNPs/CT samples, confirmed reduction of silver ions coupled with oxidation of the hydroxyl groups (chitosan molecular and/or its hydrolyzates). Further, band at 1250-1350cm\(^{-1}\) (Peak 4 and 5) corresponds to O-H bending vibrations, and their disappearance for AgNPs/CT samples, may be due to a reduced interaction between silver ions and hydroxyl group. For AgNPs, conduction and valence band lie very close, in which electrons move freely. These free electrons are responsible for surface plasmon resonance (SPR) absorption band [93,94], due to their collective oscillation in resonance with the light wave [95]. UV-Vis absorption spectra of AgNPs/CT solutions showed the characteristic surface plasmon resonance (SPR) band of AgNPs centered at about 420 nm (Fig. 3.2.2 (B)). From the UV-Vis absorption spectra, it was evidenced that as the silver ions concentration increased, there was a progressive enhancement in the intensity of the SPR band for AgNPs. Thus, increased content of AgNPs yielded high absorbance features [96, 97].

XRD profile of AgNPs/CT (Fig. 3.2.3) showed peaks at 20 = 38.21\(^{\circ}\), 44.42\(^{\circ}\), and 64.58 \(^{\circ}\) due to the Bragg
Chapter III: Conducting membrane ..................... detection and removal

reflections corresponding to the [111], [200] and [220] sets of lattice planes. This may be indexed based on the fcc structure of silver present in its composite [98]. Moreover, interplanar distance (d-spacing) of the nanocomposites was measured by Bragg’s equation; the d_{[111]} and d_{[200]} of nanocomposites were 0.125 nm and 0.110 nm, respectively.

The surface morphology of the AgNPs/CT film was examined by SEM and TEM techniques. SEM image (Fig. 3.2.4., image A) of pristine chitosan confirmed a porous and spongy like structure. SEM image of AgNPs/CT (image B) showed unevenly distributed silver cubic nanoparticles on the surface of chitosan. Unevenly distributed nanoparticles with large agglomeration were also observed.

![Fig. 3.2.4. SEM images of: A) CT, and B) AgNPs/CT. TEM images of: (C) 30 mM AgNO₃ containing AgNPs/CT (high magnification) and (D) 30 mM AgNO₃ containing AgNPs/CT (low magnification), (E) SAED picture of the AgNPs/CT and (F) EDX spectra for AgNPs/CT (Cu peak aroused due to sample holder).](image)

TEM analysis showed silver nanoparticles (few nanometers sized) in AgNPs/CT sample. Unevenly distribution of silver nanoparticles (less than 10 nm sized) is visible in Fig. 3.2.4(C,D). Furthermore, thick and bright spots in Fig. 3.2.4 (E) (due to electron diffraction of silver particles) also suggested the presence of nano-sized particles. It seems that the presence of chitosan led to the aggregation of AgNPs, may be due to the
complexation between Ag\(^+\) species and functional groups of the CT matrix [99]. Selected area electron diffraction (SAED) images showed circular rings of silver nanoparticles, which were identified as [111], [200] and [220] planes of Ag\(^0\) in fcc arrangement [98]. The d spacing of the [111] and [200] planes were 0.135 nm and 0.116 nm, respectively, also supported by XRD. In EDX spectrum of sample, Cu peak aroused from Cu sample holder (Fig. 3.2.4 (F)).

3.2.4.2 Electrochemical behavior of As\(^{3+}\) at nanostructure electrode

Differential pulse voltammograms were recorded from -0.30 to 0.40 V for the determination of arsenic by ASV with various electrodes in 1.0 M HNO\(_3\), using the conditions reported in section 2.3. No obvious stripping peak was obtained for 100 ppb As\(^{3+}\) at CT/GCE (Fig. 3.2.5) Under similar conditions, a stripping peak was observed when AgNPs are present within the CT matrix (as seen in Fig 3.2.5) for 100 mM and 30 mM AgNO\(_3\) respectively. The combined presence of AgNPs and the conductivity of the CT matrix thus provide a 3D network for the reduction of As\(^{3+}\) to As\(^0\) during the deposition step. Stripping peaks are only obtained in presence of AgNPs showing that the reduction of As\(^{3+}\) to As\(^0\) occurs at the silver surface. This results in an increase in stripping peak currents. It is clear that As\(^{3+}\) were selectively deposited on the AgNPs array, while no response was observed for modified electrode without AgNPs. To explain the high sensitivity of As\(^{3+}\) detection, the following hypothesis can be formulated. Chitosan (CT) has been identified as effective adsorbent during electrochemical detection of metals and As\(^{4+}\) [100]. The presence of amino and hydroxyl functional groups were responsible for large hydrophilic surface area, and thus high adsorption capacity. The presence of functional groups on CT matrix is responsible for adsorption of As\(^{3+}\). Adsorbed As\(^{3+}\) reduced to (As\(^0\)) at -0.60 V
deposition potential, while CT is good adsorbent for As\(^{3+}\), but deposition potential enhanced the accumulation of the As\(^{3+}\). No peak current was observed for As\(^{3+}\) at the electrode, for varying the deposition times at open potential. Thus, more electro-active sites for As\(^{3+}\) accumulation on AgNPs/CT modified GCE were available. Accordingly, this enhanced current response for stripping analysis. In this paper, we focus on the use of AgNPs/CT composite because of its strong adsorption capability for As\(^{3+}\).

3.2.4.3. Influencing factors for As\(^{3+}\) detection

In principle, combined accumulation and reduction process prior to actual stripping detection enhances the sensitivity and selectivity for the determination of metal ions and other elements. In this work, As\(^{3+}\) accumulated by chemical pre-concentration and its subsequent stripping voltammetric estimation may be explained as described below (Fig. 3.2.6). During pre-concentration, As\(^{3+}\) is adsorbed onto the AgNPs/CT modified electrode surface [101], then it was reduced (Eq. 3.2.5) and deposited on the electrode under cathodic potentiostatic conditions (-0.60 V) for 120 s. Under un-stirred condition, quiescence time (10 s) was allowed for equilibration. The differential pulse scan was carried out from -0.30 – 0.40 V. The As\(^{3+}\)stripping peak (Eq. 3.2.6) was recorded at 0.125 V± 0.006 V and its intensity measured using the peak area. The standard additions method was used to calibrate the DPASV sensitivity and to check the linearity of response along with to measure unknown concentrations.

![Schematic presentation of AgNPs/CT arsenic interaction and stripping out on modified GCE.](image)

**Fig. 3.2.6.** Schematic presentation of AgNPs/CT arsenic interaction and stripping out on modified GCE.

\[
\begin{align*}
\text{Deposition:} & \quad \text{As}^{3+} + 3e^- \rightarrow \text{As}^0 \quad (3.2.5) \\
\text{Stripping:} & \quad \text{As}^0 \rightarrow \text{As}^{3+} + 3e^- \quad (3.2.6)
\end{align*}
\]
Chapter III: Conducting membrane ................. detection and removal

Nanoparticles play important roles for modified electrode’s performance, thus effect of AgNO₃ content in composite was investigated (Fig. 3.2.7(A)). It can be seen that the As³⁺ peak current increased with AgNO₃ content in composite, because of large specific surface area and high surface free energy, which facilitated As³⁺ detection [102, 103]. Maximum current response (I_p) value was obtained for 30 mM of AgNO₃ containing composite modified GCE. Further, I_p reduced steadily because of more agglomerated AgNPs present in CT matrix.

![Graph A](image1)

**Fig. 3.2.7.** Effect of: (A) AgNO₃ content, and (B) deposition time on the stripping peak current at AgNPs/CT/GC electrode in 1.0 M HNO₃ containing 100 ppb As³⁺. Deposition potential: -0.60 V for 120 s, rest period: 10 s.

Deposition of As³⁺ on 30 mM of AgNO₃ containing AgNPs/CT/GCE under optimized conditions (deposition potential: -0.6 V, rest period: 10 s, electrolyte: 1.0 M HNO₃) was carried out by DPASV for different deposition times (1-10 min) (Fig. 3.2.7(B)). Area of stripping peak (i.e. sensitivity) increased with deposition time due to increased amount of arsenic on AgNPs/CT modified GCE. Response of the modified electrode for As³⁺ (100 ppb) increased rapidly up to 2 min deposition time and then increased gradually because of limited active sites. Increasing the deposition time improved the sensitivity and can be used to monitor low concentration levels [104]. Although the linear range was reduced, 2 min deposition time was considered for subsequent experiments.
Stripping peak current depends on the supporting electrolyte, and different electrolytes (HCl, HNO₃ and H₂SO₄) were investigated separately to determine the optimum conditions for As³⁺ detection by cyclic voltammetry (Fig. 3.2.8). When HCl (1.0 M) was used as a supporting electrolyte, silver oxidation was observed at 0 V (possible formation of AgCl at the AgNPs surface) which strongly interfered with the As³⁺ signal [66,78]. Also, in the H₂SO₄ media, more energy is required for dissociation, because of the bulky nature of the sulfate ion. To eliminate the possibility of AgCl formation and bulkier ion effect, HNO₃ (1.0 M) was used as supporting electrolyte. Different concentrations of HNO₃ (0.1 M, 0.5 M, 1.0 M and 2.0 M) were explored for As³⁺ detection, and sensitivity increased with concentration. A concentration of 1.0 M was found as the best compromise between sensitivity and reproducibility. Thus, further experiments were performed using HNO₃ (1.0 M) as supporting electrolyte.

Fig. 3.2.9(A) shows the DPASV current response of As³⁺ with varied concentrations at -0.6 V deposition potential in 1.0 M HNO₃. Upon each addition of As³⁺, current response increased prominently, peak potential slightly changed. Concentration calibration plots were obtained at 2 min deposition time (Fig. 3.2.9(B)). The detection limit was calculated by previously reported method [80].
Chapter III: Conducting membrane detection and removal

Fig. 3.2.9. (A) DPASV response of the AgNPs/CT/GCE for As$^{3+}$ in 1.0 M HNO$_3$: (a) 0, (b) 10 ppb (c) 20 ppb, (d) 30 ppb, (e) 40 ppb, (f) 50 ppb, (g) 70 ppb, (h) 90 ppb and (i) 100 ppb and (B) the corresponding calibration plot. Other conditions are similar to Fig. 3.

For three repeated measurements, sensitivity and detection limit (LOD) of the sensor were estimated as 0.3089 $\mu$A/ppb and 1.20 ppb (16.2 nM, S/N=3), respectively. The calibration plot was obtained from the DPASV analysis for As$^{3+}$ (Fig. 3.2.9(B)), by standard addition method. The equation of calibration graph for As$^{3+}$ is: $Y = 0.309 \times + 0.063$ ($\alpha=0.05, \ n=10, \ R^2=0.998$). Although the peak potential slightly varied, the peak intensities varied linearly with As$^{3+}$ concentrations in the range 10-100 ppb (Fig. 3.2.9).

3.2.4.4. Simultaneous detection of As$^{3+}$ and Cu$^{2+}$

Fig. 3.2.10. (A) DPASV response for simultaneous detection of As$^{3+}$ and Cu$^{2+}$ using AgNPs/CT/GCE in 1.0 M HNO$_3$. Concentration of the analytes: (a-i) 0-100 ppb and (B) the corresponding calibration plot for detection of As$^{3+}$ and Cu$^{2+}$.
Selective detection of As\textsuperscript{3+} in natural water samples is a challenging task, because of co-deposition of other metals (present in the water) and stripping off under the experimental condition used for the detection of As\textsuperscript{3+}. Particularly, Cu\textsuperscript{2+} is a main interference in the detection of As\textsuperscript{3+}, and reduced the sensitivity of target ions. Fig. 3.2.10 shows detection of As\textsuperscript{3+} at variation of Cu\textsuperscript{2+} concentration on the modified electrode. Two well-defined peaks were observed for As\textsuperscript{3+} and Cu\textsuperscript{2+} at 0.100 V and 0.300 V, respectively. In this case, Cu\textsuperscript{2+} did not interfere during As\textsuperscript{3+} detection. Thus, As\textsuperscript{3+} may be detected in presence of Cu\textsuperscript{2+}, which confirmed suitability of reported nanostructured electrode for sensitive and selective detection of arsenic at ppb level.

The calibration plot was obtained from the DPASV analysis for As\textsuperscript{3+} and Cu\textsuperscript{2+} (Fig. 3.2.10(B)), by using the standard addition method. The equation of calibration graph for each metal was:

\begin{align*}
\text{As}\textsuperscript{3+}: & \quad Y = 0.3887 X + 3.76 \quad (\alpha=0.05, \; n=10, \; R^2=0.975) \\
\text{Cu}\textsuperscript{2+}: & \quad Y = 0.2979 X - 1.28 \quad (\alpha=0.05, \; n=10, \; R^2=0.992)
\end{align*}

Careful conditioning of electrode is necessary to improve its quality and reproducibility. Stability tests were performed with the investigated electrode to determine the precision of the measurements. First 20 consecutive cycles were carried out for As\textsuperscript{3+} (50 ppb) detection using HNO\textsubscript{3} (1.0 M), as supporting electrolyte. The peak current decreased slowly with each successive cycle, and first 10 cycles showed 1.2% relative standard deviation. After 20\textsuperscript{th} cycle, the peak current was decreased by 12%. The modified electrode was stored in closed vessel and its stability was examined after 15 days, with 98% reproducibility. Long-term stability of these electrodes was attributed to nanostructured film and its preparation methodology [105].

3.2.4.5. Analysis of As\textsuperscript{3+} in the presence of interferences

In ground water samples, high amount of chloride or sulfate salt of Na\textsuperscript{+}, Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions are present. Thus, performance of nanostructured electrode for detection of As\textsuperscript{3+} was checked in presence of interfering substances (NaCl, CaCl\textsubscript{2}, and MgCl\textsubscript{2}) (Fig. 3.2.11). The effect on As\textsuperscript{3+} peak current caused by the interfering ions was small up to 30 ppm (NaCl, CaCl\textsubscript{2}, and MgCl\textsubscript{2}) and then it’s increased, causing a rise in peak current and negative potential shift by 10 mV due to the formation of AgCl on the electrode surface [85]. Up to 1000 ppm of sulfate ions containing salt (Na\textsubscript{2}SO\textsubscript{4}, MgSO\textsubscript{4} and CaSO\textsubscript{4}) did not
Chapter III: Conducting membrane ..................... detection and removal

influence the As\(^{3+}\) signal (Fig. 3.2.11B). Thus, the developed electrode showed good performance for As\(^{3+}\) detection in the presence of interfering substances at the above-mentioned levels [83]. As\(^{5+}\) is always present together with As\(^{3+}\) in natural water [54]. Detection of As\(^{5+}\) in acidic condition is difficult because of its oxidized state [66]. We performed the As\(^{3+}\) (10 ppb) experiments after addition of As\(^{5+}\) (10 ppb) and recorded the increase in peak current at 0.125 V. This indicated interference of As\(^{5+}\) during detection of As\(^{3+}\). In the presence of As\(^{5+}\), As\(^{3+}\) cannot be determined. Only total arsenic can be quantified after chemically reducing As\(^{5+}\) to As\(^{3+}\).

![Graph](image)

**Fig. 3.2.11.** Sensing of As\(^{3+}\) (30 ppb) at AgNPs/CT/GCE with changes in peak currents in the presence of various interferents (A and B) (metal salts, surfactant and EDTA).

Organic materials such as EDTA and surfactants can interfere due to complexation effects [106] and to competitive adsorption onto the electrode surface respectively. Thus, influence of surfactant and EDTA on voltammetric As\(^{3+}\) signal was also studied (Fig. 3.2.11(A,B)). The presence of EDTA up to 500 ppm was found to be no significant effect on As\(^{3+}\) detection, whereas above 500 ppm EDTA showed considerable interference with As\(^{3+}\) detection (Fig. 3.2.11(B)). Surfactant effects were tested by addition of the Triton-X-100 (non-ionic surfactant) and the SDS (anionic surfactant); no effect was caused by 10 ppm of Triton-X-100 and SDS. Due to complex formation between As\(^{3+}\) and EDTA, sulphate, or chloride ions, it was easily adsorbed on the electrode and reduced to As\(^0\). Thus, the As\(^{3+}\) peak intensity increased in the presence of EDTA, sulphate, or chloride ions. These results revealed that the modified electrode was suitable for the determination
Chapter III: Conducting membrane ..................... detection and removal

of As\(^{3+}\) in the presence of these kinds of organic materials when present at the mentioned levels [107].

AgNPs/CT modified GCE was used to detect arsenic in different samples obtained from ground water of Ranaghat, Nadia district (West Bengal, India) and Bhavnagar (Gujarat, India) (Fig. 3.2.12). The samples (10 ml) were added with 1.0 M HNO\(_3\) for detection of arsenic by standard addition method [76]. The measurements were performed three times. 12.3 ppb of As\(^{3+}\) was detected in samples of Ranaghat, while As\(^{3+}\) was below the detection limit in the samples received from Bhavnagar. Thus, a known quantity of 19 ppb of As\(^{3+}\) was added in Bhavnagar water sample; the value found was 18.5 ppb. These samples were analyzed with a Metrohm 797 VA, Autolab, voltammetric metal analyzer and 3.0% error was observed compared with proposed method [108,109]. This observation validates the suitability of As\(^{3+}\) detection in water samples.

Table 3.2.1 Comparison of different metal-nanoparticles modified electrodes for arsenic detection

<table>
<thead>
<tr>
<th>Modified electrode</th>
<th>Linear range</th>
<th>LOD (ppb)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtNPs/GCE</td>
<td>0.075- 3.75 ppm</td>
<td>2.00</td>
<td>[77]</td>
</tr>
<tr>
<td>Ir/BDDE</td>
<td>0.007-7.40 ppm</td>
<td>1.50</td>
<td>[80]</td>
</tr>
<tr>
<td>Au electrode</td>
<td>0.148–1.48 ppm</td>
<td>4.50</td>
<td>[111]</td>
</tr>
<tr>
<td>I(_2) generated BDDE</td>
<td>0.74– 4.44 ppm</td>
<td>8.25</td>
<td>[112]</td>
</tr>
<tr>
<td>AgNPs/CT/GCE</td>
<td>10- 100 ppb</td>
<td>1.20</td>
<td>this work</td>
</tr>
</tbody>
</table>
Chapter III: Conducting membrane ..................... detection and removal

Developed sensor showed lower detection limits than previously reported sensor based on nanoparticles (Table 3.2.1) [77, 80, 110, 111]. The above studies of modified electrode revealed high sensitivity, low detection limit and fast response time, etc properties of AgNPs/CT arsenic sensor, because of synergetic effects of silver nanoparticles and chitosan, which greatly increased the sensitivity towards As\textsuperscript{3+}.  

3.2.4.6. Diffusion coefficients of As\textsuperscript{3+}

Prepared AgNPs/CT film showed good affinity for As\textsuperscript{3+}, thus this membrane was used for As\textsuperscript{3+} removal by diffusion experiments. In the two-compartments diffusion cell (separated by AgNPs/CT membrane), As\textsuperscript{3+} solution of known concentration (10-75 ppb) was passed in feed compartment, while water was initially passed through permeate compartment. As\textsuperscript{3+} concentrations were regularly monitored (Fig. 3.2.13). The results show a decrease of arsenic in the feed compartment and a corresponding increase in the permeate compartment, confirming that AgNPs/CT membrane is suitable for As\textsuperscript{3+} removal [112].

![Fig. 3.2.13](image)

Fig. 3.2.13. (A) Diffusion coefficient values across AgNPs/CT membrane as function of different concentrations of As\textsuperscript{3+} and (B) Variation of As\textsuperscript{3+} concentration in permeates side with time, for different As\textsuperscript{3+} feed compartment (solid line: feed compartment, dotted line: permeated compartment).

Diffusion coefficient of As\textsuperscript{3+} across AgNPs/CT membrane was evaluated by Eq. (3.2.4) (Fig. 3.2.13). Diffusion coefficient values for As\textsuperscript{3+} 6 to 8 fold with increase in concentration. Our research group is working on detailed and systematic studies and kinetics of As\textsuperscript{3+} removal by AgNPs/CT membrane by filtration method.
Chapter III: Conducting membrane ..................... detection and removal

3.2.5. Conclusions for As$^{3+}$ detection and removal

AgNPs/CT/GCE was developed for detection of As$^{3+}$ by stripping analysis in water, based on synergistic properties combining AgNPs and chitosan (i.e., high active surface area and strong adsorptive capability). Reported electrode was successfully used for detecting As$^{3+}$ in the presence of other interfering species, as in case of natural water samples, without any exchange of medium or electrode activation. AgNPs/CT/GCE electrode showed individual well-defined voltammetric peaks for As$^{3+}$ and Cu$^{2+}$. The reported electrode (AgNPs/CT/GCE) has good sensitivity and it is suitable for the electrochemical detection of As$^{3+}$ in natural water samples with 10-100 ppb linear range and 1.2 ppb limit of detection (LOD). During detection of As$^{3+}$, As$^{5+}$ interfered. In the presence of As$^{5+}$, As$^{3+}$ can be determined as total arsenic and can be quantified after reducing As$^{5+}$ to As$^{3+}$. Diffusion coefficient values of As$^{3+}$ across AgNPs/CT membrane showed suitability of the membrane for As$^{3+}$ removal.

References

Chapter III: Conducting membrane ..................... detection and removal


Chapter III: Conducting membrane detection and removal


[113]
Chapter III: Conducting membrane ..................... detection and removal


[114]
Chapter III: Conducting membrane ..................... detection and removal


Chapter III: Conducting membrane detection and removal