



# Fabrication of efficient and selective total arsenic sensor using the hybrid materials modified carbon paste electrodes



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## ABSTRACT

The aim of this communication is to develop a robust electro-analytical tool for low level detection of total arsenic from aqueous solutions at neutral pH conditions. Hybrid materials were obtained using the natural clay. Further, the carbon paste electrode (CPE) was modified with the hybrid materials and employed in the detection of total arsenic(V). The arsenic(V) was detected prior to chemically reduced to As(III). pH dependence electrochemical behavior of reduced arsenic(V) was obtained at a wide range of pH 2.0 to 10.0. A characteristic reduction peak for arsenic was obtained using the hybrid materials-modified CPE at an applied potential of around 0.8 V. Concentration dependence studies were conducted for the arsenic(V) by increasing the arsenic(V) concentration from 5.0 to 40.0 µg/L. A significant increase in the reductive current was measured around potential 0.80 V using the modified CPEs. Regression line was obtained between the studied concentration of arsenic(V) and cathodic peak current values. Further, the detection limit (DL) and quantification limit (QL) was obtained for the arsenic(V) using hybrid materials modified CPEs. The DL values were found to be 2.214, 1.502 and 1.408 µg/L for the materials BCH (HDTMA-loaded bentonite), LCH (HDTMA-loaded local clay) and LCAH (aluminium pillared-HDTMA-loaded local clay)-modified CPEs, respectively. The ten-fold excess of several interfering ions (Cd(II), Pb(II), Cu(II), Mn(II), Fe(III), EDTA, glycine and PO<sub>4</sub><sup>3-</sup>) were studied in the detection of As(V). Similarly, the tap water was spiked with the arsenic(V) and separately studied for the detection of arsenic(V) from aqueous solutions.

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## 1. Introduction

Arsenic contamination of ground water is a serious environmental concern which poses a serious health hazard to millions of people around the globe as well affect greatly the world economy at a larger extent [1–3]. Arsenic exposure for a longer duration eventually causes lung, skin, bladder and kidney cancer [4–5]. Moreover, the inorganic arsenic which is highly toxic to living being is recognized as Group I carcinogen [6–7]. Inorganic arsenic often exists as +3 (arsenite) and +5 (arsenate) oxidation states within the terrestrial environment. Among these two oxidation states the +3 state is reportedly more toxic than the +5 oxidation state hence, poses sever environmental threats [8–10]. The drinking water standard as prescribed by the WHO (World Health Organization) is revised to 10 ppb (~10 µg/L) for total arsenic in drinking water. This is even adopted by many of the developing/developed countries and forced to develop useful analytical method to detect arsenic at very low level to maintain the existing water standards of arsenic. Further, the societal need is onsite and reliable detection/monitoring of arsenic from aqueous solution. Therefore, easy, robust and

reliable analytical methods are greatly demanded by many developed and developing nations where the large section of human being greatly affected with arsenic poisoning because of drinking the arsenic contaminated ground water.

The *in situ* detection of arsenic using the electrochemical devices is, therefore, an attractive and promising method which provides the required limit of detection and easy operations. Majority of the electrochemical methods were suggested with the modification of working electrodes using newer Nano or hybrid materials to improve the electrochemical signals for arsenic detection. This enhances the detection limit of arsenic with an enhanced selectivity. Therefore, the materials are found to be useful in terms of suitability and even the device possesses potential use in real matrix analysis. Fluorine doped cadmium oxide (F-doped CdO) thin film was obtained onto the glass substrate using the spray technique. The modified electrode was employed in the detection of arsenic(III) which gave a reduction and oxidation peaks at –0.10 and 0.05 V (vs Ag|AgCl), respectively. The method provides the detection limit of  $4.55 \times 10^{-3}$  ppb with an analytical sensitivity of  $5.747 \times 10^{-3}$  µA ppb<sup>-1</sup> [1]. Cyclic voltammetric study was conducted using the Au-Fe<sub>3</sub>O<sub>4</sub> Nanonocomposite modified glassy carbon electrode for arsenic(III) detection [11]. In a line ibuprofen gold Nanoflowers/Nanostructures (Ibu-AuPNFs/Ibu-AuNSs) was synthesized

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and hence screen printed electrode (SPE) was obtained. The SPE was subjected for the arsenic(III) detection using the cyclic voltammetric studies. Results indicated that the lower detection limit (LDL) of arsenic(III) was achieved as low as 0.018 ppb with the relative standard deviation (RSD) of 1.9% for  $n = 15$ . The method is selective enough since various water samples viz., tap water, drinking water, Indus river water, and ground water were analyzed and compared with the standard method [12]. Bismuth modified exfoliated graphite (EG-Bi) electrode was fabricated and employed in the development of arsenic(III) sensor using the square wave anodic stripping voltammetry [13]. Interesting to observe that the EG-Bi electrode showed a detection limit of arsenic(III) to 5  $\mu\text{g/L}$  and it was not effected even in presence of several interfering cations except Cu(II). A recent study enabled the As(III) and total arsenic detection henceforth the As(V) detection using the anodic stripping chronopotentiometry (ASCP) in an electrochemical flow-through cell with an Au wire as the working electrode [14]. The method avoids the reduction of As(V) to As(III) and then its detection. Moreover, the limits of detection were found to be 0.42 mg/L for As(III) and 0.55 mg/L for As(V) recorded at the deposition potentials of 350 mV and 1600 mV, respectively. The gold electrode was coated with the slurry of graphene oxide (GO) and L-leucine prepared in 5 wt% nafion solution (Au/GO/Leucine/Nafion) [4]. The cyclic voltammetric studies revealed that the sensitivity of determination was obtained as  $\sim 30 \mu\text{A/ppm/cm}$  having the lowest detection limit of 0.5 ppm. An interesting study indicated that the integrated sound source ('sonotrode' low frequency 250 Hz) with square wave anodic stripping voltammetry enabled to enhance the sensitivity of arsenic detection by 50 times and caused to reduce the limit of detection by 2 orders of magnitude [15].

On the other hand, arsenate(V) was found relatively stable and electrically inactive species hence; difficult to detect electrochemically [16–17]. The detection of As(V) was carried out reducing arsenic(V) to As(III) by chemical or electrochemical means and then total arsenic was detected electrochemically [18]. In an effort the As(V) was reduced in presence of mannitol and perchlorate solution and co-precipitated with copper followed by the voltammetric determination by further reduction to  $\text{AsH}_3$  ( $\text{As}(-3)$ ) using the hanging mercury drop electrode. The method provided the limit of detection for As(V) to 4.4  $\mu\text{g/L}$  [16]. As(V) was chemically reduced to As(III) using the  $\alpha$ -cysteine in presence of  $\text{N}_2\text{H}_4 \cdot \text{HCl}$  at 80 °C. Further, the gold plated carbon paste electrode was employed in a constant current stripping analysis. The detection limit of As(III) and As(V) were found to be 2.0 and 0.5 ppb, respectively whereas method showed no interferences in presence of Cu(II) [19]. Similarly, the As(V) was reduced to the As(III) using the dithionite and the total arsenic was detected at the sub ppb level using the cathodic stripping voltammetry with HDME (hanging mercury electrode) and in presence of Cu(II) [20]. Similarly, the inorganic As(V) was reduced to As(III) chemically using the cysteine and hydrazine at 80 °C and then it was detected at low level at the gold nano-electrode ensembles under stripping square wave voltammetry. The method could provide a detection limit as low as 5 ng/L (65 pM) after 3 min of preconcentration and at  $-0.4 \text{ V}$  applied potential [18]. A manganese-coated gold micro wire electrode was introduced in the direct detection of As(V) from sea water at natural pH conditions. The mechanism is proposed that the Mn reduces the As(V) to As(III) further, the three electron electrochemical reduction of As(III) to As(0) occurs that enables an electrochemical detection of total arsenic. The detection limit of arsenic is found to be 0.2 nM AsV at a deposition time of 180 s [21]. Arsenic is deposited onto the gold electrode at acidic conditions and detected using the differential pulse anodic stripping voltammetry. The As(III) is detected directly whereas the As(V) was reduced to As(III) by the gaseous  $\text{SO}_2$  and hence, the total arsenic is detected electrochemically. The detection limit was found to be  $\text{Ca } 0.2 \mu\text{g/L As}$  at a deposition time of 4 min [22]. As(III) was electrochemically oxidized to As(V) using the platinum nanoparticles modified glassy carbon electrode under the cyclic voltammetry and linear sweep voltammetry and the detection of As was unaffected in presence of Cu(II). The LOD of As detection was

found to be 2.1 ppb [23]. The other studies indicate that the EDTA stabilizes the arsenic speciation and also eliminates the interferences of manganese and iron for arsenic(III) detection using the cathodic stripping voltammetry. Further, the total arsenic was determined after acidification at pH 1.0 using the anodic stripping voltammetry [24].

Therefore, the present communication is an attempt to exploit the use of hybrid materials in the modification of carbon paste electrode and hence, the modified CPEs are employed in the low level detection of reduced arsenic(V) from aqueous solutions at natural pH conditions. The real matrix analysis in the detection of arsenic(V) is further studied for greater applicability of the method.

## 2. Experimental

### 2.1. Materials

Hexadecyl trimethyl ammonium bromide (HDTMA), carbon powder (Glassy Spherical Powder 2–12  $\mu\text{m}$ ) and titanium wire (0.81 mm) were obtained from Sigma-Aldrich, USA. Paraffin oil, sodium arsenate dibasic heptahydrate AR (98.5% Purity), ethylene diamine tetraacetic acid (EDTA) and glycine were purchased from the HiMedia Chemicals, India. Cadmium nitrate, copper sulphate, lead nitrate and potassium chloride were procured from the Merck, India. Ferric nitrate was obtained from Loba Chemie, India and aluminium trichloride was obtained from the Fisher Scientific, India. Bentonite and local was collected from the Bhuj, Gujarat and Phullen, Champai district, Mizoram, India, respectively. Cation exchange capacities (CEC) of bentonite and local clay was found to be 69.35 and 46.38 meq/100 g of bentonite and local clay, respectively [25]. The deionized water was further purified (18 M $\Omega$ -cm) using a Millipore water purification system (Milli-Q+).

A Potentiostat/Galvanostat (BioLogic Science Instruments, France, Model: SP 50) was used for electrochemical measurements. The electrochemical data was then analyzed using the ECLab® computer software. Ag|AgCl (Saturated) and platinum electrodes were used as reference and supporting electrodes in the cell assembly. Carbon paste electrode (CPE) was further modified with the hybrid material was used as working electrode.

### 2.2. Methodology

The clay samples viz., bentonite (B) and local clay (LC) were loaded with the hexadecyl trimethyl ammonium chloride (HDTMA) by the wet cation exchange process and named as BH and LCH, respectively [26]. Local clay was also pillared with aluminium and then loaded with the HDTMA as to obtain the inorgano-organo-clay sample (LCAH) [27]. The hybrid materials were characterized by the FE-SEM (Field Emission Scanning Electron Microscopy), FT-IR (Fourier Transform InfraRed), XRF (X-ray Fluorescence Spectrometer) and XRD (X-ray Diffraction) analyses and detailed elsewhere [26–27].

### 2.3. Reduction of As(V)

As(V) was reduced to As(III) using an excess of sodium dithionite solution [20]. The 1.0 mg/L As(V) solution was prepared using 0.1 mol/L KCl solution and then added requisite amount of sodium dithionite to make the dithionite concentration of 0.5 mol/L. The solution mixture was stirred for 30 min in  $\text{N}_2$  atmosphere. This could enable to reduce the As(V) to As(III) in aqueous solution. Further, the stock solution was diluted to the required concentration using the 1.0 mol/L of KCl solution.

### 2.4. Electrochemical analysis

The reduced arsenic(V) solution (50.0 mL) having known concentration was taken into the electrochemical cell. The pH of this solution was pre-adjusted using the 0.1 M  $\text{HNO}_3$  and 0.2 M NaOH solutions

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