

## ELECTROCHEMICAL BEHAVIOR AND DETERMINATION OF ARSENIC (III) FROM WATER USING AG-DOPED –ZEOLITE-CARBON NANOTUBES COMPOSITE ELECTRODE

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### ABSTRACT

The electrochemical behavior of Arsenic (III) from water was investigated using Ag-doped–synthetic zeolite-carbon nanotubes composite electrode envisaging its determination in the aqueous solution. The electrocatalytic oxidation of arsenic in acidic medium at Ag-doped –synthetic zeolite-carbon nanotubes composite electrode (Ag-ZCNT) was investigated by cyclic voltammetry, with different practical working pretreatment applications.

### INTRODUCTION

Arsenic occurs in the natural environmental in the earth’s crust, in soil, rocks and minerals. It exists in four oxidation states e.g. arsenate (+V), arsenite (+III), arsenic (0), and arsine (–III) [1]. Arsenic has been used widely in pigments, insecticides and herbicides, glass manufacture and veterinary chemicals [2]. Arsenic is highly toxic to both plants and animals and chronic exposure to arsenic can cause a variety of adverse health problems [3].

A wide variety of methods to determine arsenic have been used, many based on spectrometry methods [4]. However, the methods based on these techniques are time-consuming and requires expensive instrumentations and complicated procedure [5].

Electrochemical detection techniques provide an attractive alternative to determine arsenic and arsenic compounds at low concentrations and due to low-cost instrumentation, simple operation and rapid analysis time.

Different electrodes, such as mercury, [6], gold, [7], platinum [8] silver, [9] were used to detect arsenic by voltammetric techniques. However, there are often problems associated with arsenic voltammetry at such electrodes, due to the potential toxicity of Hg electrode, or general limitations for the sensitivity and selectivity of the other electrodes. These problems may be solved by using metallic nanoparticles nanotubes modified electrodes, which can enhance the electrocatalytic activity and selectivity towards the oxidative detection of arsenic.

This work aimed to describe the electrochemical behavior of arsenic on the composite electrode and the determination of Ag-doped–synthetic zeolite-carbon nanotubes composite electrode. The electroanalytical parameters for the detection of arsenic in 0.09 M Na<sub>2</sub>SO<sub>4</sub> and 0.01 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte were determined by cyclic voltammetry (CV).

### MATERIALS and METHODS

#### *Materials*

The epoxy resin used in the study was Araldite®LY5052/ Aradur®5052 purchased from Huntsman Advanced Materials, Switzerland. Multiwall carbon nanotubes (CNT) synthesized by catalytic carbon vapour deposition were produced by Nanocyl<sup>TM</sup>, Belgium. A-type synthetic zeolite was prepared using natural zeolite from Mirsid, Romania, with 68% wt.

clinoptilolite as a silicon source and sodium aluminate as aluminium source, and Ag-doped synthetic zeolite was obtained by ion-exchange process.

#### *Preparation of Ag-ZCNT composite electrodes*

The dispersion of MWCNT in tetrahydrofuran, 99.9% (THF, Sigma Aldrich) was achieved by ultrasonication using a Cole-Parmer® 750-Watt Ultrasonic Processor for about 10 min prior to mixing with the polymer resin. After the sonication process, the solution of MWCNT/THF was sonicated again with epoxy resin to obtain a more homogeneous mixture. An effective method, two roll mill (TRM) of achieving high levels of dispersion and distribution was used to prepare the Ag-ZCNT composite electrode. The ratio between the components was chosen to reach 20-weight percent (w/w) content of CNT, 20-weight percent (w/w) content of silver-doped synthetic zeolite. During processing the temperature was kept constant at 70°C, the mixing speed was maintained at 10 and 20 rpm for about 40 min. Then the zeolite doped with Ag was mixed with CNT and after then the curing agent (weight ratio of epoxy resin:curing agent was 100:38) was added to MWCNT. The mixture was then poured into PVC tubes and cured in a vacuum oven at 80°C for 24h, after which it was left to cool down at room temperature. Prior to use, the working electrode was gradually cleaned, first polished with abrasive paper and then on a felt-polishing pad by using 0.3 µm alumina powder (Metrohm, Switzerland) in distilled water for 5 minutes and rinsing with distilled water.

#### *Electrochemical measurements*

The electrochemical performance of this electrode was studied by cyclic voltammetry (CV). An electrochemical pre-treatment by three repetitive cyclings from 0 V to +1.0 V vs. SCE in 0.1 M in 0.09M Na<sub>2</sub>SO<sub>4</sub> and 0.01M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte was performed. All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, a platinum counter electrode, and the composite working electrode.

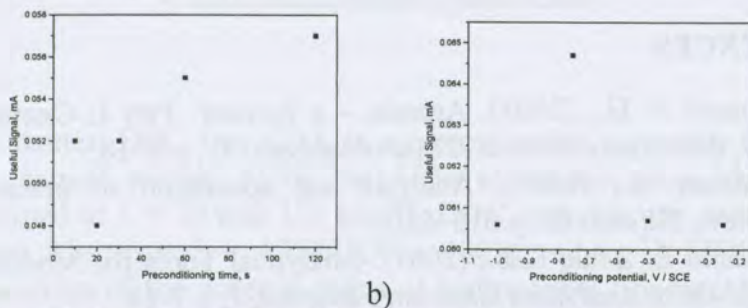
## RESULTS

#### *Voltammetric determination*

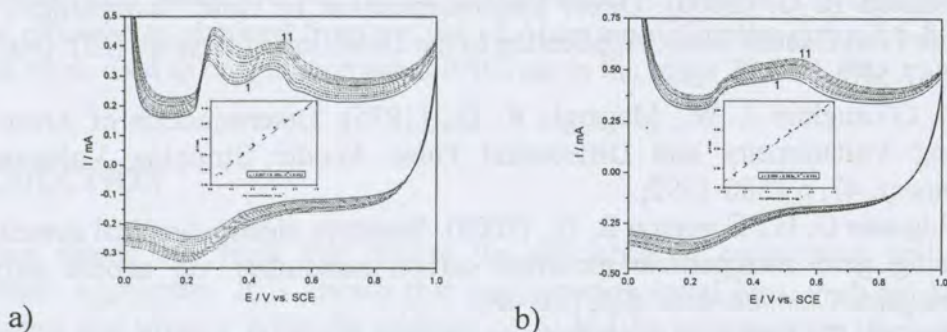
To examine the ability of the Ag-ZCNT composite electrode as a tool in arsenic determination in aqueous solutions, an initial test of this electrode were carried out by cyclic voltammograms in 0.09 M Na<sub>2</sub>SO<sub>4</sub> and 0.01 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte solution in 1 mgL<sup>-1</sup> As (III), in potential range of 0 to 1.0 V/SCE, scan rate of 50 mV/s with a preconditioning step that consisted in a reduction process of As (III), which was chosen at -0.5 V/SCE in according with the literature [9]. Without this preconditioning step no signal corresponding to arsenic presence was found (the results are not shown here). The presence of arsenic led to increasing oxidation current starting with the potential value of about +0.2 V/SCE and the best signal was found at the potential value of about +0.5 V/SCE, which was selected for arsenic determination. To determine the optimum working conditions for arsenic determination, the potential value of -0.5 V/SCE was applied at different conditioning time, i.e., 10, 20, 30, 60 and 120s. Based on the results presented in Fig 1a, the optimum preconditioning time of 60 s was selected. Also, different potential values, i.e., of -0.25, -0.5,

-0.75, and -1.0 V/SCE were applied at a preconditioning time of 60s, and the results are shown in Fig. 1b. Based on these results, the further measurements were performed at the potential values of -0.5V/SCE for 60s, and -0.75V/SCE for 60s.

Fig. 2 (a) and (b) show the cyclic voltammograms of Ag-ZCNT composite electrode at various As(III) concentrations ranged from 0.1 to 1 mgL<sup>-1</sup> (curves 2-11), in 0.09 M Na<sub>2</sub>SO<sub>4</sub> and 0.01 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte solution, within potential range of 0 to 1.0 V/SCE, at the scan rate of 50 mV/s with preconditioning potential value of -0.5V/SCE for 60s, and respective, -0.75V/SCE for 60s.



**Fig. 1.** The useful signals corresponding to 1 mgL<sup>-1</sup> arsenic determined by cyclic voltammograms of Ag-ZCNT composite electrode in 0.09 M Na<sub>2</sub>SO<sub>4</sub> and 0.01 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte solution in, with a preconditioning of electrode at -0.5V/SCE at deposition time of 10, 20, 30, 60 and 120s, (a), and with a preconditioning time of 60s at the potential values of -0.25, -0.5, -0.75, and -1.0 V/SCE (b)



**Fig. 2.a-** Cyclic voltammograms at Ag-ZCNT composite electrode in 0.09 M Na<sub>2</sub>SO<sub>4</sub> and 0.01 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte (1) and in the presence of 0.1-1 mgL<sup>-1</sup> arsenic (curves 2-11); potential scan rate: 0.05 Vs<sup>-1</sup>; potential range: 0 to +1.0 V/SCE, with preconditioning at -0.5V/SCE for 60 s. Inset: The calibration plot of the currents recorded at E= +0.50 V/SCE vs. arsenic concentration. **b-** Cyclic voltammograms at Ag-ZCNT composite electrode in 0.09 M Na<sub>2</sub>SO<sub>4</sub> and 0.01 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte (1) and in the presence of 0.1- 1 mgL<sup>-1</sup> arsenic (curves 2- 11); potential scan rate: 0.05 Vs<sup>-1</sup>; potential range: 0 to +1.0 V/SCE, with preconditioning at -0.75V/SCE for 60 s. Inset: The calibration plot of the currents recorded at E= +0.50 V/SCE vs. arsenic concentration.

## CONCLUSIONS

The silver-doped synthetic zeolite-multiwalled carbon nanotube-epoxy (Ag-ZCNT) composite electrode showed a good electrocatalytic behavior for arsenic oxidation in 0.09 M Na<sub>2</sub>SO<sub>4</sub> and 0.01 M H<sub>2</sub>SO<sub>4</sub> supporting electrolyte but only with a preconditioning step

imposed for arsenic reduction, which requires stripping voltammetric analysis method applying. Even if for both preconditioning potential values of -0.5 and -0.75V/SCE for 60 s the linear dependence of anodic peak current versus arsenic concentration was found, the best sensitivity for arsenic determination was found at the potential value of -0.5V/SCE, which was selected as optimum one. The electrocatalytic behavior of this electrode against arsenic oxidation together with easy preparation and regeneration by a simple polishing of the electrode surface, give it a potential for the practical quantitative determination of arsenic in real samples.

## LIST OF REFERENCES

- [1] Bissen M., Frimmel F. H., (2003). Arsenic – a Review. Part I: Occurrence, Toxicity, Speciation, Mobility, *Acta hydrochimica et hydrobiologica*. 31, p 9–18;
- [2] Munoz E., Palmero S., (2005). Analysis and speciation of arsenic by stripping potentiometry: a review, *Talanta* 65, p 613–620;
- [3] Luong J.H.T., Majid E., Male K.B., (2007). Analytical Tools for Monitoring Arsenic in the Environment. *The Open Analytical Chemistry Journal*, 1, p 7-14.
- [4] Matoušek T., Hernández-Zavala A., Svobod M., Langrová L., Adair B. M., Drobná Z., Thomas D. J., Stýblo M., Dědina J., (2008). Oxidation state specific generation of arsines from methylated arsenicals based on L-cysteine treatment in buffered media for speciation analysis by hydride generation-automated cryotrapping-gas chromatography-atomic absorption spectrometry with the multiatomize, *Spectrochimica Acta Part B* 63, p 396–406;
- [5] X. Dai, Compton R. G. (2006). Direct Electrodeposition of Gold Nanoparticles onto Indium Tin Oxide Film Coated Glass: Application to the Detection of Arsenic (III) *Analytical Sciences*. 22, p 567-570;
- [6] Forsberg G., O’Laughlin J. W., Megargle R. G., (1975). Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry, *Analytical Chemistry*. 47, p 1586-1592;
- [7] Xiao L., Wildgoose G. G., Compton R. G., (2008). Sensitive electrochemical detection of arsenic (III) using gold nanoparticle modified carbon nanotubes via anodic stripping voltammetry, *Analytica Chimica Acta*. 620, p 44-49;
- [8] Shin S.H., Hong H.G., (2010). Anodic Stripping Voltammetric Detection of Arsenic (III) at Platinum-Iron (III) Nanoparticle Modified Carbon Nanotube on Glassy Carbon Electrode, *Bulletin of the Korean Chemical Society* 31, p 3077-3083;
- [9] Simm A. O., Banks C. E., Compton R. G., (2005). The Electrochemical Detection of Arsenic (III) at a Silver Electrode, *Electroanalysis* 17, p 1727 – 1733.

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