

Full Paper

Electrochemical Grafting by Reduction of 4-Methylaminobenzenediazonium Salt at GC, Au and Pt Electrode: Investigation of Sensitivity Against Phenol by Cyclic Voltammetry

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Abstract- The aim of this study is to modify a glassy carbon, gold and platinum electrode with 4-methylaminobenzenediazonium salt (MABDAS) to evaluate the possible application on the detection of phenol by cyclic voltammetry (CV). Diazonium salt was reduced electrochemically and covalently electro-grafted onto GC, Au and Pt electrodes surface to form modified electrodes in non-aqueous media. The electrode surfaces were modified with MABDAS in acetonitrile (CH₃CN). MAB modified GC (MAB/GC) electrode was used for the phenol determination in aqueous media. The effect of pH on the electrochemical behavior of the modified GC electrode was investigated for the phenol detection.

Key words- Cyclic Voltammetry, Modified Electrode, Surface Characterization, Synthesis of Diazonium Salt

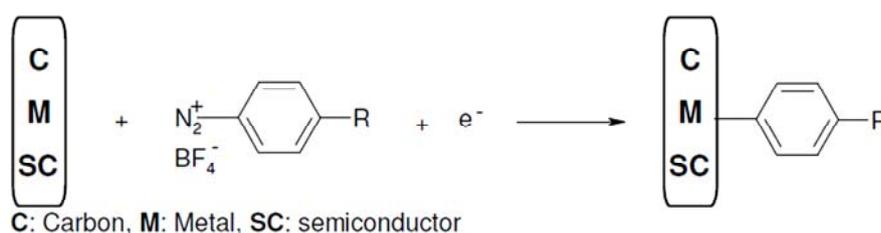
1. INTRODUCTION

Electrode modification is an important part of the electrochemical studies and has been heavily used for two decades. After the optimum conditions are set the modification can be

performed by the electrochemical oxidation (amine and alcohol oxidation etc.) or electrochemical reduction (diazonium reduction etc.) [1-4]. The electrochemical reduction of diazonium salts, first developed by Pinson et al. [5], begins to become one of the trendiest electrochemical methods to reach this aim. Indeed the electrochemical grafting of aryl diazonium is a very versatile method.

A diazonium salt ArN_2^+ ($c \approx 1$ to 10 mM) dissolved in a non-aqueous media with a supporting electrolyte ($\text{CH}_3\text{CN} + 0.1$ M NBu_4BF_4) or in acidic aqueous media [6] (for example 0.1 M H_2SO_4) is reduced, using the surface to be modified as a cathode. The potential of this cathode is set with the help of a potentiostat at the potential of the voltammetric peak of diazonium or at more cathodic (more negative) potential for a variable period of time (seconds to minutes). After thorough rinsing of the electrode in an ultrasonic bath in order to remove any chemical which could be only weakly adsorbed, it is possible to observe the aryl group bonded to the surface by the different methods described hereafter. Diazonium salts ($\text{BF}_4^- \text{N}_2\text{Ar}$) are easily and rapidly prepared in one step from a wide range of aromatic amines many of which are commercially available. The synthetic methods are well established and standard procedures can be found in practical organic chemistry textbooks. Tetrafluoroborates are particularly advisable as they are stable and there is no risk of explosion. The half life of solutions in non-aqueous or acidic media is of the order of five days but diazonium salts are not stable in aqueous solution above $\text{pH} \approx 2-3$ [7].

The modification of surfaces by electrochemical reduction of diazonium salts can be summarized on carbon [8], metal [9] or semiconductor [10] as shown in Scheme 1. The binding of aryl groups to carbon electrodes is likely a two-step process. The first step involves the electrochemical reduction of the diazonium salt to generate aryl radicals. This is followed by the reaction of the radicals with the carbon surface.



Scheme 1. Modification of solid electrode surfaces with diazonium reduction method

Phenolic compounds represent a large group of biological molecules with a variety of functions in plant growth, development, and defence. These compounds are a class of chemical compounds consisting of a hydroxyl functional group ($-\text{OH}$) attached to an aromatic hydrocarbon group, with a ring structure like that of benzene. They are also related to the groups of hormones, vitamins, amino acids and antioxidants [11]. These molecules are

a large group of pollutants in industrial effluents and, due to their low degradability by conventional effluent treatment, even at low concentrations they present toxicity and bioaccumulation problems [12]. Phenolic pollutants come from plastic, oil, food, coal, etc., industries, which frequently discharged them in effluent wastes. Due to the carcinogenic risk for humans, methods for phenol detection are highly relevant in environmental sciences [13].

Various analytic methods have been developed and used for the determination of phenol. Such methods include spectrophotometric [14], chromatographic [15] and electrochemical methods [16]. Particularly, electrochemical methods are very convenient to the analysis of this kind of organic compounds [17, 18]. Electrochemical methods have great potential for environmental monitoring because of its inherent advantages such as fast response speed, ease of miniaturization, low cost, timesaving, high sensitivity, excellent selectivity, low background current, low equipment, chemical inertness and minimum sample pretreatment required prior to analysis. To determine quantitatively phenols in a variety of media, films have been applied on several types of electrodes, such as gold, platinum, glassy carbon and graphite [19].

The purpose of this study is to modify the GC, Au and Pt surface by the electrochemical reduction of MABDAS in CH₃CN containing 100 mM NBu₄BF₄, to characterize modified electrodes by CV and EIS, and to evaluate the possible application on the detection of phenol by CV.

2. EXPERIMENTAL SECTION

2.1. Chemicals

In all experiments, ultrapure water with a resistance of 18.3 MΩ cm (Millipore Milli-Q purification system, Millipore Corp. Bedford, MA, USA) was used for preparation of aqueous solutions, the cleaning of glassware and polishing of the electrodes. All chemicals of reagent grade were used as received. 4-methylbenzene-1,2-diamine (MBDA), tetrabutylammonium tetrafluoroborate (NBu₄BF₄), CH₃CN, and phenol were obtained from Fluka (Buchs SG, Switzerland), Riedel de Haën (Seelze, Germany) or Sigma-Aldrich (Buchs SG, Switzerland) chemical companies.

2.2. Electrochemical equipment and apparatus

Electrochemical measurements were performed with GAMRY Reference PCI4/750 series Potentiostat/Galvanostat/ZRA from GAMRY Instruments (PA, USA), using a standard cell with three electrodes. The working electrodes were a GC electrode BAS (Bioanalytical Systems, West Lafayette, IN, USA) model MF-2012 (3.0 mm dia.), a Au electrode BAS model MF-2014 (1.6 mm dia.) and a Pt electrode BAS model MF-2013 (1.6 mm dia.). The reference electrodes a Ag/Ag⁺ (10 mM AgNO₃) (BAS Model MF-2042) for non-aqueous

media and a Ag/AgCl/3 M KCl (BAS Model MF-2063) for aqueous media were used. Pt wire (BAS Model MW-1032) was used as counter electrode. Solutions were thoroughly deoxygenated by purging with purified argon gas (99.99%) for 10 min prior to the electrochemical experiments. Argon blanket was maintained over the solutions to supply an inert atmosphere during electrochemical measurements. All electrochemical experiments were carried out inside a BAS model C3 cell stand (IN, USA) at room temperature. In all experiments, the electrodes were kept in CH₃CN when they were not in use. Jenway 3010 pH meter (Staffordshire, UK) was used for the measurement of pH values. The CV technique was applied with PHE200 Physical Electrochemistry software (PA, USA), EIS was applied with EIS300 Electrochemical Impedance Spectroscopy software (PA, USA).

2.3. Electrode preparation and modification

The GC electrode, geometric area of the former was 0.071 cm² and O-ring delimited area of the latter was 3.0 mm dia., surfaces were prepared for the experiments by polishing to gain a mirror-like appearance, first with fine wet emery papers (grain size 4000) and then with 1.0 μm and 0.3 μm alumina slurry on micro cloth pads (Buehler, USA). After the initial polishing, the GC electrodes were resurfaced with 0.05 μm alumina slurry. First, in the following order, the GC electrodes were sonicated both in an ultrasonic water bath (Bandelin RK 100, Germany), and then in 1:1 (v/v) isopropyl alcohol (IPA) and CH₃CN (IPA+CH₃CN) mixture for 5 min [20]. In all experiments, the electrodes were kept in CH₃CN when they were not in use. Electrode surfaces were sonicated with CH₃CN before and after each treatment.

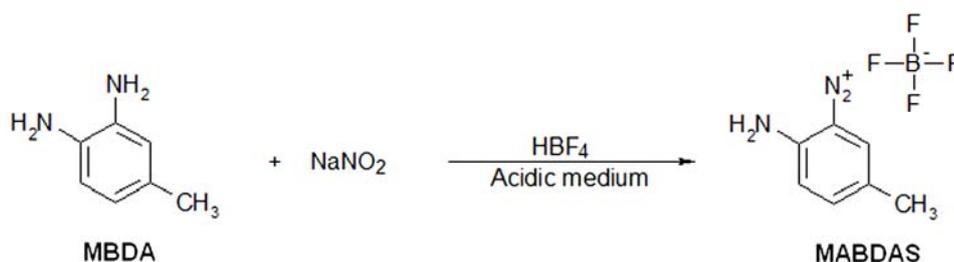
The gold electrode (1.6 mm dia.) was prepared to remove the oxide and other functionalities by polishing first with fine wet emery papers (Buehler with grain size of 4000) and then with 1.0 μm, 0.3 μm and 0.05 μm alumina slurry made from aluminium suspension solution on a Buehler polishing microcloth. After removal of trace alumina from the surface by rinsing with water and brief cleaning in ultrasonic water bath with water then an IPA+CH₃CN mixture purified over activated carbon, the gold electrode was rinsed with CH₃CN to remove any physisorbed and unreacted materials from the electrode surface. The gold slide (i.e. gold coated SF10) substrates were first cleaned by repeated rinsing with deionized water and CH₃CN. They were then further cleaned with a mixture of NH₃ (25%, v/v), H₂O₂ (30%, v/v), and ultrapure water having a volume ratio of 1:1:5 at a temperature of 70 °C for 20 min [21]. The cleaned gold surfaces were rinsed with CH₃CN to remove any physisorbed materials from the electrode surface prior to modification.

The size of Pt working electrode was 1.6 mm dia. Prior to the surface modification, the platinum electrode was polished on a polishing cloth with wet alumina powders, starting with 0.3 μm particle size and then with finer grades down to 0.05 μm. It was then rinsed with ultrapure water and sonicated for 5 min [22].

Cleaned GC, Au and Pt electrodes were then dipped into the 1 mM MABDAS solution and derivatized by CV scanning from -100 mV to -1300 mV at a 100 mV s^{-1} scan rate with 10 cycles.

2.4. Synthesis of 4-methylaminobenzene diazonium tetrafluoroborate salt

4-methylaminobenzene diazonium tetrafluoroborate salt was prepared using the method of literatures [23, 24]. MBDA (0.5 g, 0.0041 mol) was mixed with HBF_4 (48%, 10 mL). The suspension was cooled to room temperature and transferred into a salt-ice bath ($\approx -10 \text{ }^\circ\text{C}$). With vigorous stirring, sodium nitrite (1.45 g, 0.021 mol) was added in dropwise over 30 min as a saturated solution in water. Then the solution was allowed to warm to room temperature, the reaction mixture was vacuum filtered. The product was re-crystallized by dissolving in cold ($0 \text{ }^\circ\text{C}$) CH_3CN followed by slow addition of cold anhydrous diethyl ether to recover the diazonium tetrafluoroborate salt (Scheme 2). Diazonium salts should be stored in a freezer and generally should be used within 2 month of synthesis. Older diazonium salts may be re-crystallized before use. Diazonium salt solutions should be used within several hours of preparation and are quite sensitive to heat.



Scheme 2. Synthesis mechanism of 4-methylaminobenzene diazonium tetrafluoroborate salt

3. RESULTS AND DISCUSSION

3.1. Modification of GC, Pt and Au electrodes

In this study, after the synthesized of diazonium salt, the diazonium salt was also analyzed electrochemically. The electrochemical and spectrochemical properties on MAB modified GC, Au and Pt electrode surfaces were investigated. For this purpose, first the GC electrode surface was modified by using a solution of 1 mM MABDAS, in a non-aqueous media, in CH_3CN containing 100 mM NBu_4BF_4 . Modification was performed in the range from -100 mV to -1300 mV at 100 mV s^{-1} scan rate with 10 cycles (Fig. 1A).

At GC electrodes, the voltammogram exhibits a broad reduction peak on the first cycle at $E_{\text{pc}} = -1085.4 \text{ mV}$ and -1227.7 mV on GC electrode, respectively. This peak was no more observed on subsequent cycles. This electrochemical behaviour is closely similar to those performed with various substituted diazonium salts [25, 26] and is consistent with the

grafting of a diazonium salt on the electrode surface. Only three reduction cycles are sufficient to get the grafting of an organic layer leading to the passivation of the electrode surface, since only capacitive current is observed after ten voltammetric scans.

A gold sensor electrode surface was modified in non-aqueous media by an electrochemical diazonium reduction modification method. By scanning from -100 mV to -1300 mV, the diazonium salt was reduced electrochemically and reacted with the polished Au electrode surface to form a compact film using 100 mV s^{-1} scan rate with 10 cycles (Fig. 1B).

Cyclic voltammetric experiments performed with a Pt working electrode did not show any significant reduction peak and did not modified the electrode surface when the working electrode potential was scanned between -100 mV and -1300 mV by using a solution of 1 mM MABDAS in CH_3CN containing 100 mM NBu_4BF_4 at 100 mV s^{-1} scan rate with 10 cycles (Fig. 1C).

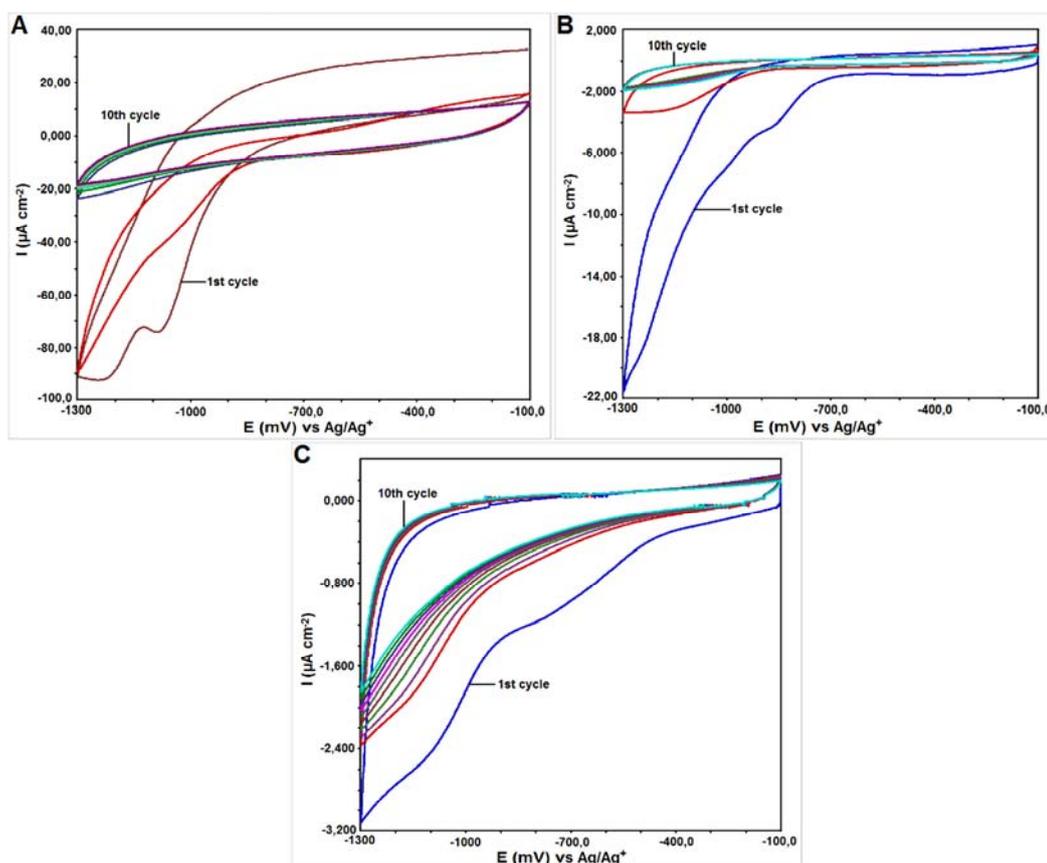


Fig. 1. Ten cyclic voltammetric scans recorded with **A)** a GC working electrode, **B)** a Au working electrode and **C)** a Pt working electrode at 100 mV s^{-1} scan rate in CH_3CN containing 100 mM NBu_4BF_4

3.2. Characterization of GC, Pt and Au electrodes

CV is a very essential technique for evaluating the blocking property of the organic-coated electrodes using diffusion controlled redox couples as probes. Surface characterizations after the modification process were carried out by CV in non-aqueous media and aqueous media. In the characterizations with CV, 1 mM ferrocene redox probe (*vs.* Ag/Ag⁺ (10 mM AgNO₃)) solution in 100 mM NBu₄BF₄ was performed between -200 mV to +400 mV potential range using 100 mV s⁻¹ scan rate in non-aqueous media and shown in Fig. 2. Ferrocene is not blocked on the MAB modified electrode surfaces.

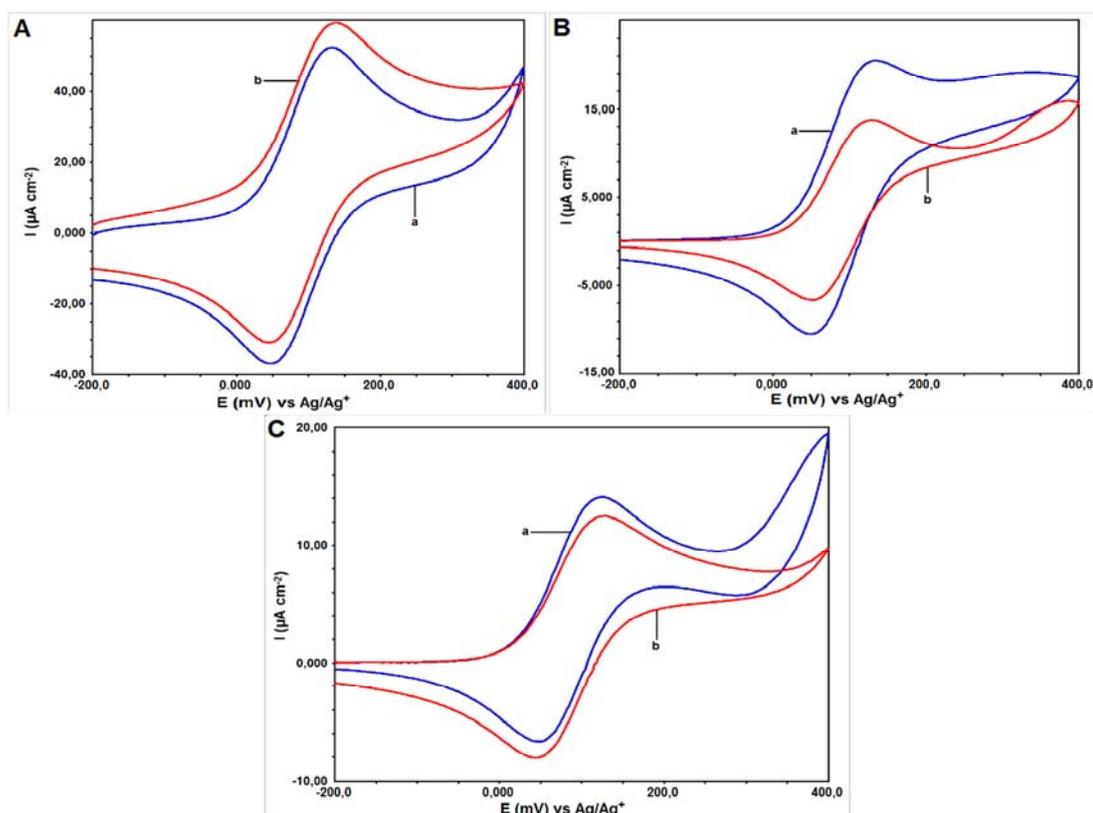


Fig. 2. Overlaying cyclic voltammograms for different solution media 1 mM ferrocene redox probe solution *vs.* Ag/Ag⁺ (10 mM AgNO₃) in MeCN +100 mM NBu₄BF₄ with **A)** a GC working electrode, **B)** a Au working electrode and **C)** a Pt working electrode at 100 mV s⁻¹ scan rate (**a**, bare; **b**, modified surface)

MAB modified electrode surfaces were characterized with potassium ferricyanide, Fe(CN)₆³⁻, (in BR buffer containing 0.1 M KCl, pH 2) redox probe at bare and MAB modified electrode surfaces (*vs.* Ag/AgCl/3 M KCl) the potential range from +500 mV to -100 mV at a 100 mV s⁻¹ scan rate were used in aqueous media (Fig. 3B). Ferricyanide is not blocked on the MAB modified electrode surfaces.

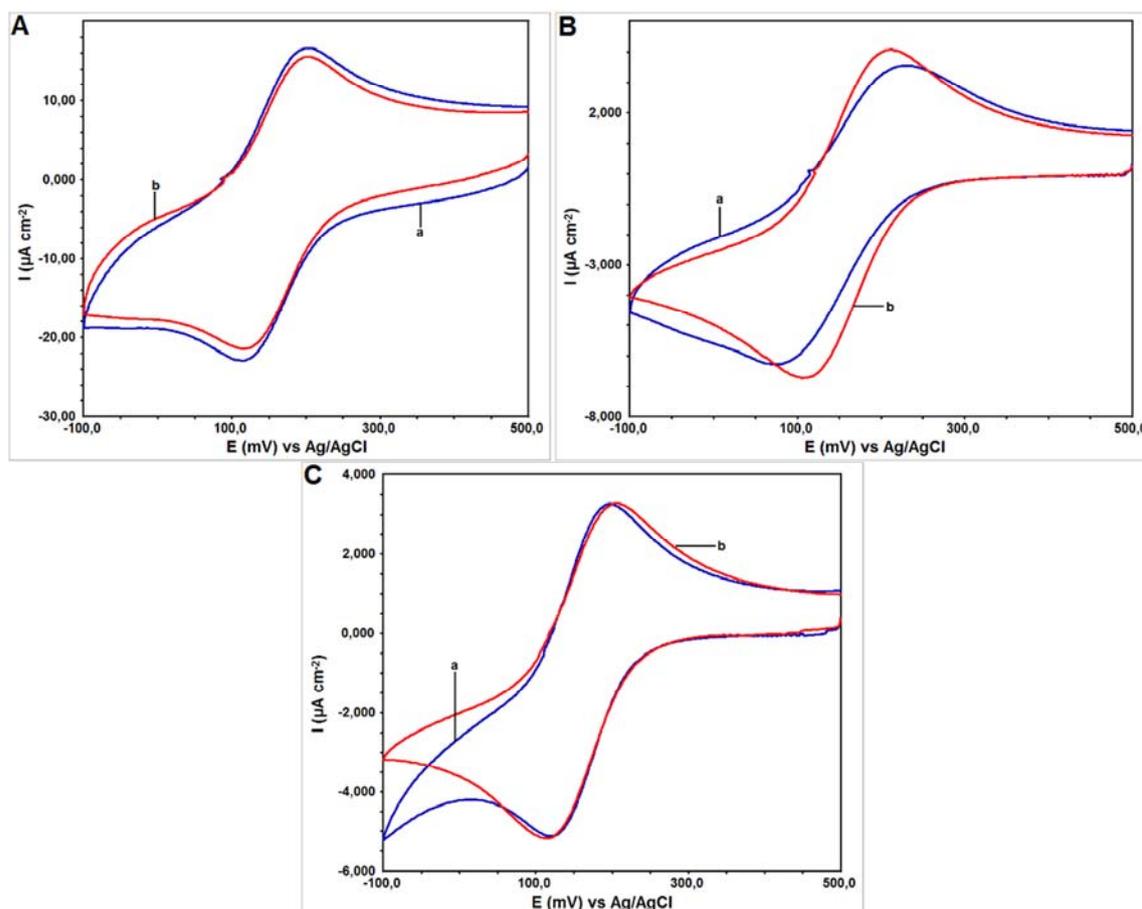


Fig. 3. 1 mM $\text{Fe}(\text{CN})_6^{3-}$ redox probe solution vs. Ag/AgCl/3 M KCl reference electrode in BR buffer solution, pH= 2, **A)** a GC working electrode, **B)** a Au working electrode and **C)** a Pt working electrode at 100 mV s^{-1} scan rate (**a**, bare; **b**, modified surface)

EIS is a suitable technique for investigation of surface properties. It is capable of giving useful data about defects/holes of the modified surface, the kinetics and mechanism of the surface formation processes, surface coverage, and so forth [27]. Methodology used with this technique is always based on a comparison of the results that obtained with the unmodified and modified electrode surfaces. This case was supported by the results of the EIS obtained by using 10 mV potential and a mixture of 1 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ at 100.000 Hz and 0.05 Hz. The EIS graphs obtained after modifications in non-aqueous media of electrode surface are given in Fig. 4.

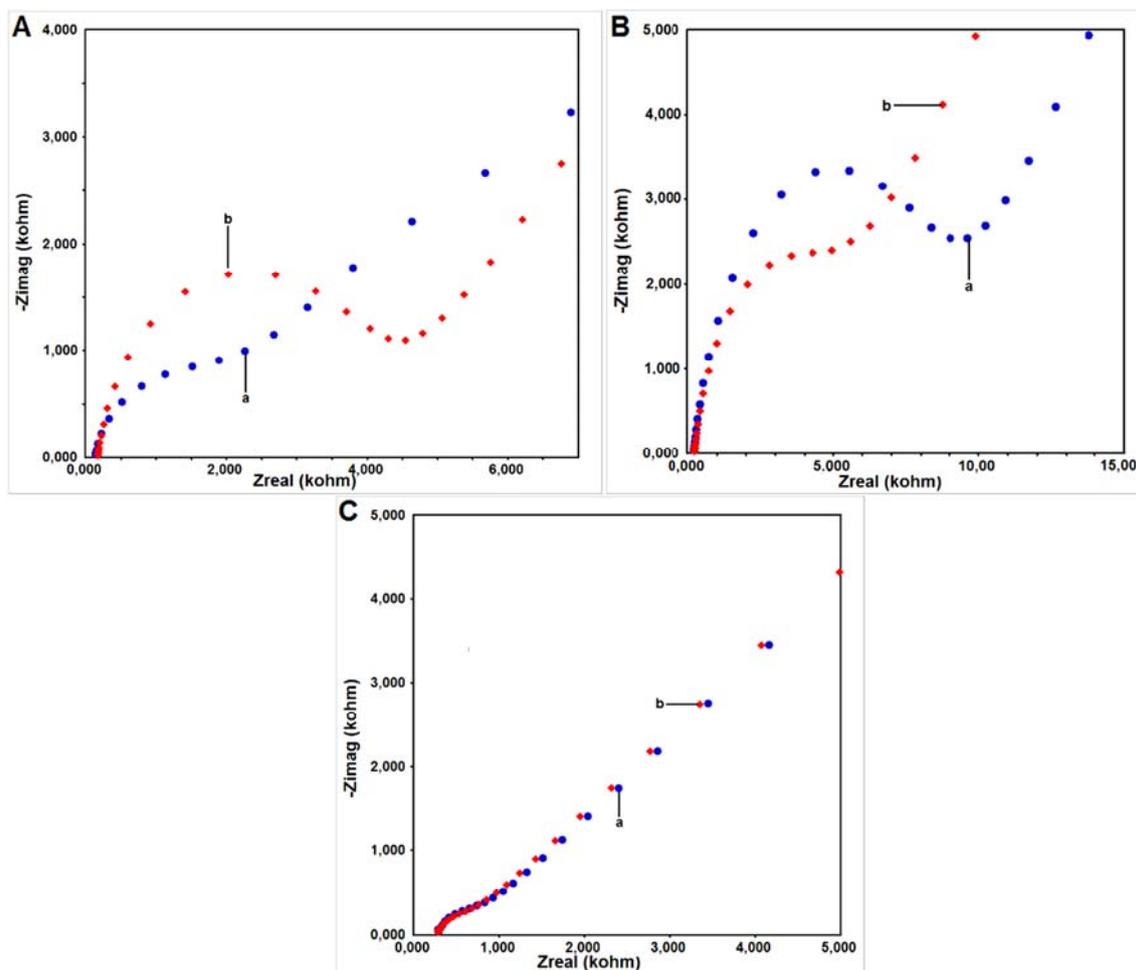


Fig. 4. Nyquist plots for electrochemical impedance spectra of 1 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple solution in 0.1 M KCl at the frequency range of 100.000–0.05 Hz at 10 mV wave amplitude **A)** a GC working electrode, **B)** a Au working electrode and **C)** a Pt working electrode (**a**, bare; **b**, modified surface)

According to the data obtained from the characterization procedures, an interpretation was done over the fact that MAB molecules in non-aqueous media are grafted on the GC, Au and Pt electrode surfaces. EIS is a valuable method to monitor the impedance changes of the electrode surface during the modification process. The semicircle diameters of Nyquist plot reflects the electron transfer resistance (Ret), which is from the electron transfer of the redox probe $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ solution. Fig. 4A showed the EIS of bare GC and MAB modified GC electrodes. On the traditional GC the value of Ret was got as 2378 Ω . After GC electrode surface was modified MAB molecule, the value of Ret was increased to 4523 Ω . Fig. 4B showed the EIS of bare Au and MAB modified Au electrodes. The value of Ret was got as 9973 Ω . After Au electrode surface was modified MAB molecule, the value of Ret was decreased to 5980 Ω . Fig. 4C showed the EIS of bare Pt and MAB modified Pt electrodes. No difference was observed when Nyquist plots of bare Pt and MAB modified Pt surfaces were

overlayed. As it can be seen from Fig. 1/C, 2/C and 3/C, MAB molecule completely does not bind to Pt electrode surface. For this reason, MAB modified Pt surface cannot be used in the phenol determination. Initially, both Au and GC surfaces were thought to be used in phenol determination but preliminary studies on Au electrode surface showed that this surface was not suitable for phenol determination.

Therefore, with MDA/GC electrode surface, the electrode surface obtained from the non-aqueous media in the application was used. Since the surface allows to the electron transfer by showing little resistance, MDA/GC surface has been thought to be suitable for the sensitivity determination of chosen flavonoid derivatives.

3.3. Effect of scan rate

The effect of scan rate on GC surface with a single cycle at the potential range from -100 mV to -1300 mV using 1 mM MABDAS solution was investigated using cyclic voltammetry at scan rates $\nu = 10, 25, 50, 100, 200, 300, 500$ and 1000 mV s^{-1} . Overlaying cyclic voltammograms of different scan rate with a GC working electrode is shown in Fig. 5A. That the $\log I_p$ - $\log \nu$ graphic drawn by using the peak currents from the obtained voltammograms is linear (Fig. 5B). The linearity is expected for diffusion-controlled processes.

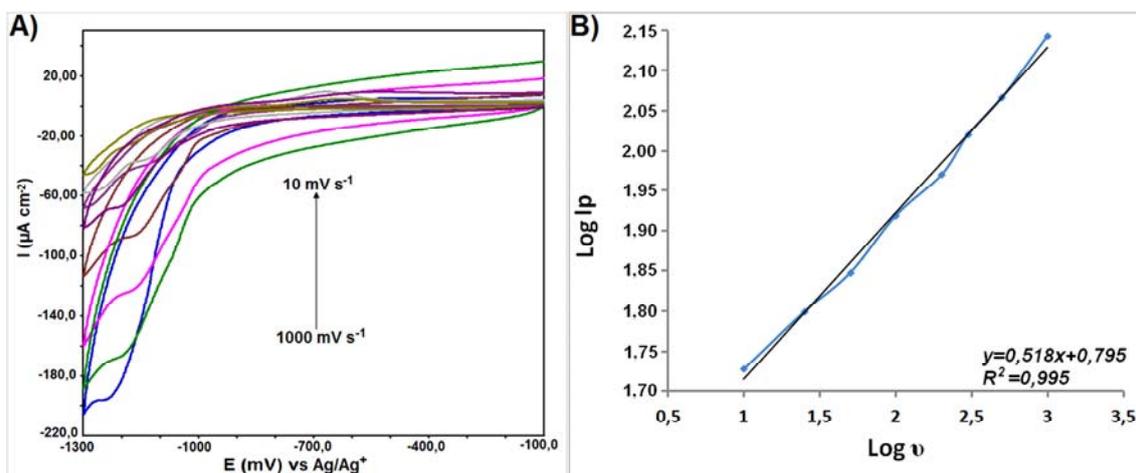


Fig. 5. A) Overlaying cyclic voltammograms of different scan rate for 10, 25, 50, 100, 200, 300, 500 and 1000 mV s^{-1} with a GC working electrode. B) Plot of logarithm of peak current versus logarithm of scan rate dependence of the cyclic voltammetric response at a modified GC electrode

3.4. Effect of pH

The effect of pH on the electrochemical behavior of the modified electrode was investigated. For the determination of optimum pH value for the binding of phenol to MAB

modified GC electrode surface, different BR buffer solutions (pH 2, 4, 6, 8, 10 and 12) were used to prepare 1 mM phenol solutions. Phenol was binded to MAB modified surface in the 0.0 mV and +1100 mV potential ranges using 100 mV s^{-1} scan rate with 10 cycles in the prepared solutions at different pH. The overlaid voltammograms of this study for the first cycle are given in Fig. 6. From the Fig. 6, the most stable and sensitive signals was observed at pH 10 and this value was chosen as optimum pH in this study.

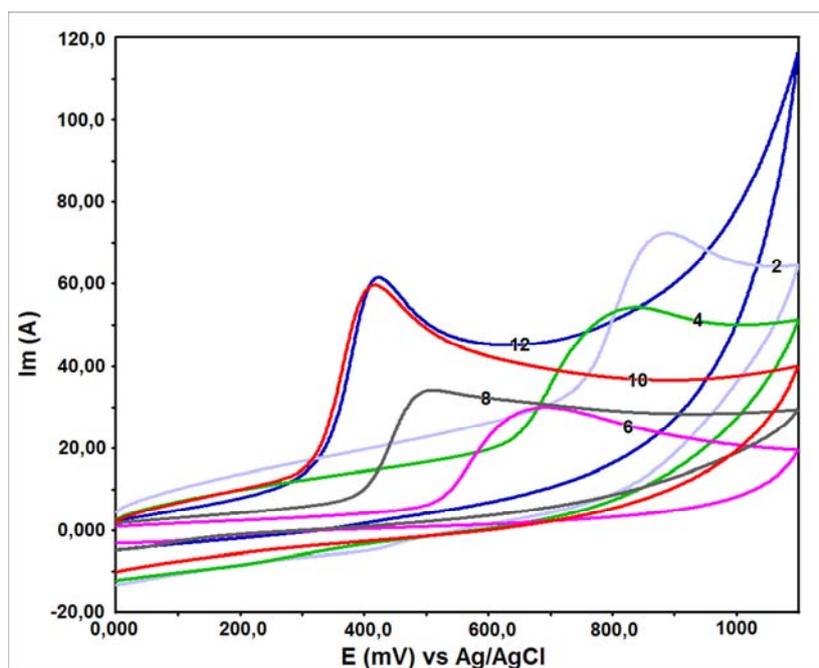


Fig. 6. An overlaying voltammograms for phenol binding to MAB modified GC surface at different pH 2-12

3.5. Investigation of phenol determination using MAB/GC sensor electrode

After the evaluation of modification voltammograms, given in Fig. 1, and characterization studies, given in Fig. 2, 3, 4, the modification onto the GC surface was found to be more stable. Both modification voltammograms and characterization studies results clearly show that the molecule is not modified onto the Pt working electrode. To determine the optimum pH value 1 mM phenol solution in BR buffer solution at different pH values (2, 4, 6, 8, 10 and 12) was used. For this purpose GC surface was modified using 1 mM MABDAS in CH_3CN containing 100 mM NBu_4BF_4 . Phenol binded to the electrode surface from 0.0 mV to +1100 mV potential range using 100 mV s^{-1} scan rate with 10 cycles. When the first cycles of phenol voltammograms at different pH values were overlayed in Fig. 6, pH 10 and 12 was found to be the optimum values. However pH 12 was accepted as the optimum pH value due to the higher peak current comparing to binding peak value.

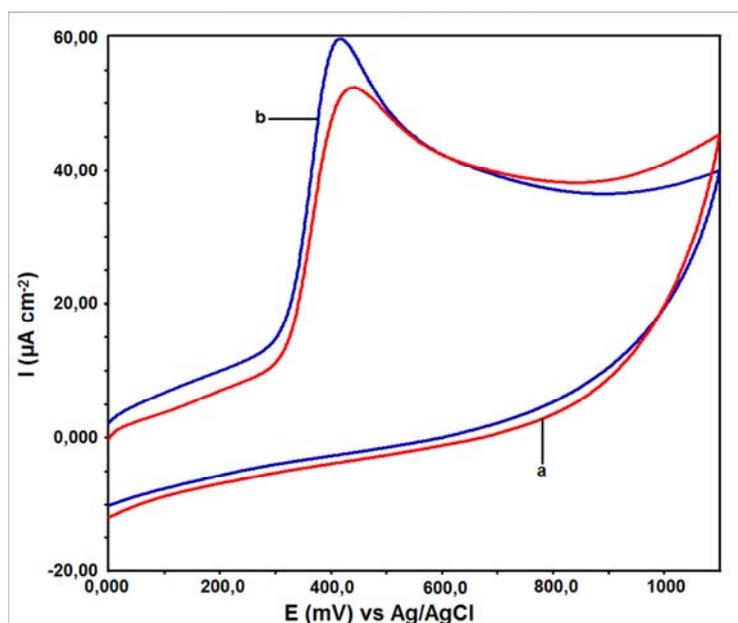


Fig. 7. The phenol modification voltammograms both **a)** bare GC and **b)** MAB modified GC in BR buffer solution at pH 10, 0.0 V and +1.1 V potential range, 100 mV s^{-1} scan rate

At optimum pH value, electrochemical behaviors of 1 mM phenol solution on bare GC and MAB/GC electrode surface were investigated. Fig. 7 is the overlaid voltammograms of phenol binding to the bare GC and MAB/GC electrode surface. This figure show that phenol binds to both electrode surfaces at the same potential but the peak current is higher in the case of binding to the MAB/GC electrode surface. This case proves that MAB/GC electrode surface can be effectively used in the quantitative determination of phenol. The results of characterization studies of phenol binding has been given together with the characterization results of bare GC, MAB/GC and MAB/GC-Ph in Fig. 8 to make a better comparison among them. From the characterization studies by CV are given in ferrocene (Fig. 8A) and ferricyanide (Fig. 8B) redox probes, we can conclude that the phenol binded MAB/GC electrode surface does not allow to electron transfer process.

This is a clear indication of phenol phenol binding to electrode surface successfully. This case was strongly supported by ferricyanide test in aqueous media because the modification of phenol to MAB/GC electrode surface was carried out in aqueous media. Besides when Nyquist plots obtained from impedance tests done by using EIS technique, were overlaid (Fig. 8C), one can easily see that the modified surface does not allow to electron transfer.

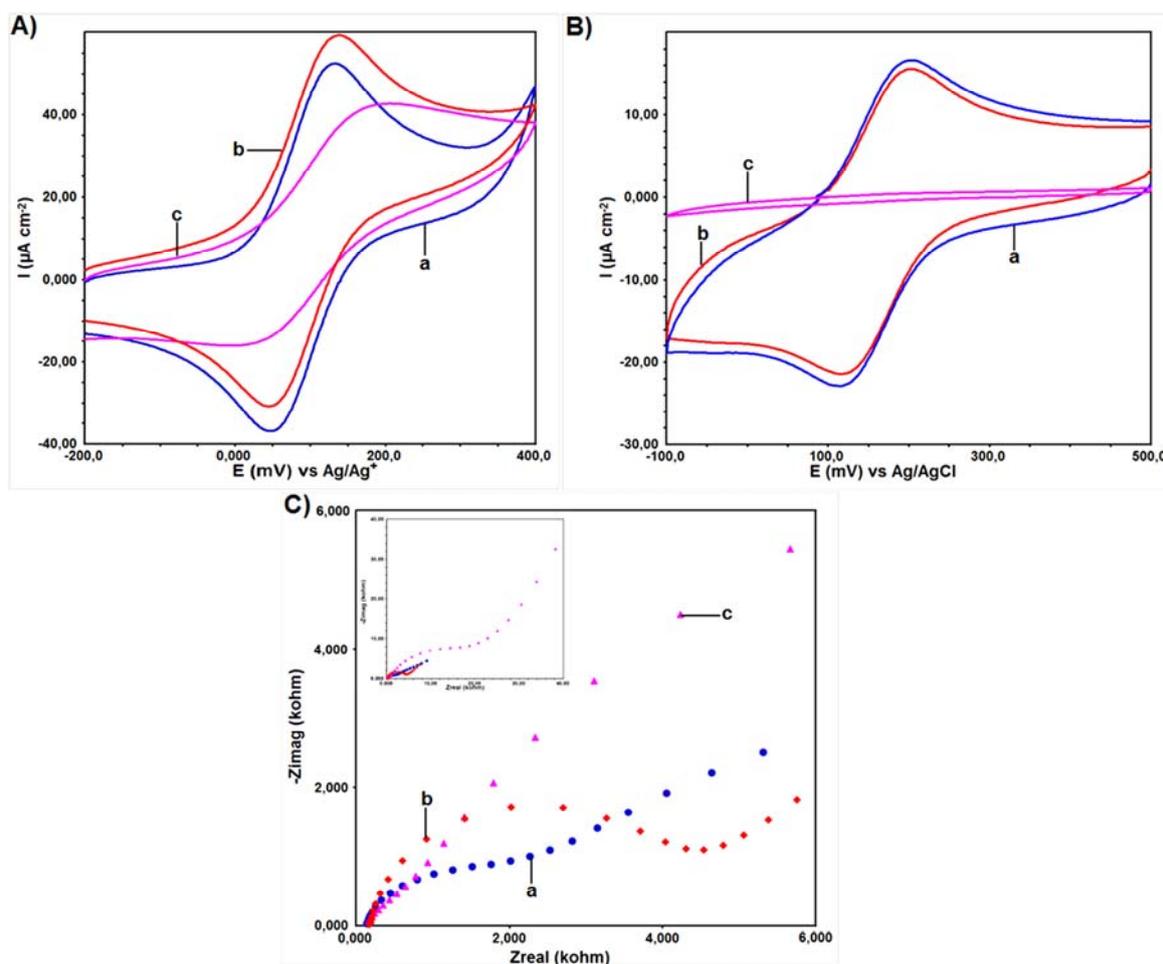


Fig. 8. Overlaying cyclic voltammograms for different solution media **A)** 1 mM ferrocene redox probe solution vs. Ag/Ag^+ (10 mM AgNO_3) in $\text{CH}_3\text{CN} + 0.1 \text{ M NBu}_4\text{BF}_4$ using 100 mV s^{-1} scan rate **B)** 1 mM $\text{Fe}(\text{CN})_6^{3-}$ redox probe solution vs. $\text{Ag}/\text{AgCl}/3 \text{ M KCl}$ reference electrode in BR buffer solution, $\text{pH}=2$ using 100 mV s^{-1} scan rate. **C)** Nyquist plot for electrochemical impedance spectra of 1 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ redox couple solution in 0.1 M KCl at the frequency range of 100.000–0.05 Hz at 10 mV wave amplitude. (a, bare GC; b, MAB/GC; c, MAB/GC-phenol)

4. CONCLUSIONS

Recently, quantitative determination of phenol in various media by electrochemical method gained quite importance due to the low detection limit, small amount of sample use, reliable results and speed of the method. For this cause, various chemical sensors are being prepared and phenol is being determined by electrochemical technique. In this study, first MABDAS was synthesized and then electrochemical properties of this molecule have been investigated on the GC, Au and Pt working electrode. After we decided that we could use MAB/GC electrode surface for phenol determination, phenol has been successfully binded to

MAB/GC electrode surface at pH 10 and then the surface characterization studies have been performed. By this study we clearly proved that this developed sensor electrode can be used for the quantitative phenol determination. The following step will be the quantitatively determination of phenol in various media.

REFERENCES

- [1] D. Zielinska, and B. Pierozynski, *J. Electroanal. Chem.* 625 (2009) 149.
- [2] G. Jin, Y. Zhang, and W. Cheng, *Sens. Actuators B Chem.* 107 (2005) 528.
- [3] H. Yao, Y. Sun, X. Lin, Y. Tang, and L. Huang, *Electrochim. Acta* 52 (2007) 6165.
- [4] H. Zhao, Y. Zhang, and Z. Yuan, *Anal. Chim. Acta* 441 (2001) 117.
- [5] S. Griveau, D. Mercier, C. Vautrin-UI, and A. Chausse, *Electrochem. Commun.* 9 (2007) 2768.
- [6] M. Delamar, G. Désarmot, O. Fagebaume, R. Hitmi, J. Pinson, and J. M. Savéant, *Carbon*. 35 (1997) 801.
- [7] J. Pinson, and F. Podvorica, *Chem. Soc. Rev.* 34 (2005) 429.
- [8] P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, and J. M. Savéant, *J. Am. Chem. Soc.* 119 (1997) 201.
- [9] A. Adenier, M. C. Bernard, M. M. Chehimi, E. Cabet-Deliry, B. Desbat, O. Fagebaume, J. Pinson, and F. Podvorica, *J. Am. Chem. Soc.* 123 (2001) 4541.
- [10] C. H. de Villeneuve, J. Pinson, M. C. Bernard, and P. Allongue, *J. Phys. Chem. B* 101 (1997) 2415.
- [11] E. T. Denisov, and I. B. Afanasev, *Chemistry of antioxidants in oxidation and antioxidants in organic chemistry and biology*, CRC Press, Taylor & Francis Group 6000 Broken Sound Parkway NW (2005).
- [12] J. L. N. Xavier, E. Ortega, J. Z. Ferreira, A. M. Bernardes, and V. Pérez-Herranz, *Int. J. Electrochem. Sci.* 6 (2011) 622.
- [13] L. Fernandez, C. Borrás, and H. Carrero, *Electrochim. Acta* 52 (2006) 872.
- [14] W. Frenzel, and S. Krekler, *Anal. Chim. Acta* 310 (1995) 437.
- [15] O. Jauregui, and M. T. Galceran, *Anal. Chim. Acta* 340 (1997) 191.
- [16] I. E. Mülazımođlu, and E. Yılmaz, *Desalination* 256 (2010) 64.
- [17] D. C. Jonson, J. Feng, and L. L. Houk, *Electrochim. Acta* 46 (2000) 323.
- [18] G. Saracco, L. Solarino, R. Aigotti, V. Specchia, and M. Maja, *Electrochim. Acta* 46 (2000) 373.
- [19] İ. E. Mülazımođlu, A. Demir Mülazımođlu, and E. Yılmaz, *Desalination* 268 (2011) 227.
- [20] A. D. Mülazımođlu, İ. E. Mülazımođlu, and E. Yılmaz, *Rev. Anal. Chem.*, DOI 10.1515/revac.2011.151 (2012).

- [21] Z. Üstündağ, M. O. Çağlayan, R. Güzel, E. Pişkin, and A. O. Solak, *Analyst* 136 (2011) 1464.
- [22] N. Daud, N. A. Yusof, T. W. Tee, and A. H. Abdullah, *Int. J. Electrochem. Sci.* 7 (2012) 175.
- [23] C. Saby, B. Ortiz, G. Y. Champagne, and D. Belanger, *Langmuir* 13 (1997) 6805.
- [24] A. O. Solak, L. R. Eichorst, W. J. Clark, and R. L. McCreery, *Anal. Chem.* 75 (2003) 296.
- [25] T. Basova, A. Hassan, F. Yuksel, A. G. Gürek, and V. Ahsen, *Sens. Actuators B* 150 (2010) 523.
- [26] A. Nabok, A. Tsargorodskaya, F. Davis, and S. P. J. Higson, *Biosens. Bioelectron.* 23 (2007) 377.
- [27] M. S. Xu, M. F. Luo, X. H. Xing, and H. Z. Chen, *Food Bioprod. Process* 84 (2006) 237.