

A SENSITIVE ELECTROCHEMICAL SENSOR BASED ON GOLD NANOPARTICLES DROPLET DEPOSITION ON GLASSY CARBON ELECTRODE FOR BISPHENOL A DETECTION

Hoda Ezoji¹, Mostafa Rahimnejad^{1*}, Maryam Asghary²

¹Biofuel & Renewable Energy Research Center, Faculty of Chemical Engineering, Babol Noshirvani University of Technology, Babol, Iran

²Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran
Rahimnejad_mostafa@yahoo.com

Article received 13.4.2016; Revised 12.6.2016; Accepted 18.6.2016

ABSTRACT

A convenient, rapid and extremely sensitive electrochemically detection of bisphenol A (BPA) was proposed in phosphate buffer (pH =7) on a gold nanoparticles modified glassy carbon electrode (GNs/GCE). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were applied for characterization of GNs/GCE. Differential pulse voltammetry (DPV) was employed for measuring BPA. The studies exhibited lower over potentials, improved current response, high reproducibility and lower detection limit at the GNs/GCE versus the bare electrode. Therefore, GNs displays excellent electroactivity toward BPA. Within the concentration range of 1×10^{-8} to 6×10^{-6} M. The fabricated electrochemical sensor demonstrated linear response to BPA with the detection limit of (1.5×10^{-9} M).

KEYWORDS: Bisphenol A, Gold nanoparticles, Electrochemical sensor, Cyclic voltammetry, Glassy carbon electrode.

INTRODUCTION

BPA is one of the serious industrial waste chemicals. It is known as an environmental endocrine disruptor and carcinogen due to its estrogenic activity (Kinnberg & Toft, 2003; Van Ginkel, Hassan, & Oh, 2010; Yin, Cui, Ai, Fan, & Zhu, 2010). So, BPA has been known as a hazard to human health, because of its undesirable effect on sperm quality and its ability to increase cancer rate. In addition, BPA found to cause diverse pleiotropic actions and reduce immune functions (Steinmetz et al., 1998; L. Zhou, Wang, Li, & Li, 2014). Moreover, it can badly affects wildlife. BPA is widely used in many industrial applications including producing polycarbonate (PC), and epoxy resins. Thus, it is the main component in manufacturing of nursing bottles, food can linings, beverage containers, medical devices for dentistry (Brede, Fjeldal, Skjevraak, & Herikstad, 2003; Kawamura, Sano, & Yamada, 1999; Poorahong et al., 2012). As has been reported, BPA can enter the food from packaging materials and may be eaten by humans (Krishnan, Stathis, Permuth, Tokes, & Feldman, 1993; Olea et al., 1996). Therefore developing a sensitive and rapid monitoring to measure the levels of BPA should be considered as our first priority.

So far, various analytical techniques have been tried to detect BPA. These include enzyme-linked immunosorbent assay (ELISA)(Kim et al., 2007; Zhao, Li, Guo, Zhang, & Chang, 2002), liquid chromatography-mass spectrometry (LC-MS) (Sambe, Hoshina, Hosoya, & Haginaka, 2006), gas chromatography-mass spectrometry (GC-MS) (Cunha & Fernandes, 2010; Gatidou, Thomaidis, Stasinakis, & Lekkas, 2007), fluorescence (Molina-García, Fernández-de Córdova, & Ruiz-Medina, 2012) and high pressure liquid chromatography (HPLC) (Wen, Zhou, Xu, Jin, & Feng, 2006). These approaches are very sensitive and selective, they present accurate identification and low limit of detection. On the other hand, they are expensive and time-consuming, they need advanced and complicated instruments and so often there should be operators to use these instruments properly(Chen, Zhang, Cai, Rao, & Long, 2014; Yin, Zhou, et al., 2010; W. Zhou, Sun, Zhou, Yang, & Yang, 2014). Accordingly, nowadays electrochemical sensors are of most interest due to their reliability, low cost, fast response, time saving, simple operation, good selectivity, cheap instruments, real-time and high sensitivity detection compared to other methods.

BPA with the molecular structure as shown in Figure 1 is electrochemically active because of its hydroxyphenyl groups. As a result it can be oxidized at different electrodes (Chauke, Matemadombo, & Nyokong, 2010; Dempsey, Diamond, & Collier, 2004; Portaccio et al., 2010). However fouling effects often causes poor responses at bare electrodes. Thus, in order to overcome this problem, it is essential to modify electrodes by means of materials having electrocatalytic activity, good conductivity and high stability (Raj & Ohsaka, 2001; Shahrokhian, Hamzehloei, Thaghani, & Mousavi, 2004).

In this light our aim is to prepare a desirable electrochemical sensor having high sensitivity and good stability for detection of BPA based on GNs/GC electrode. The peak current of BPA oxidation is significantly heightened at the surface of GNs/GCE in comparison to bare GCE. The CV and DPV results highlighting that gold nanoparticles are efficient sensing materials for determination of BPA.

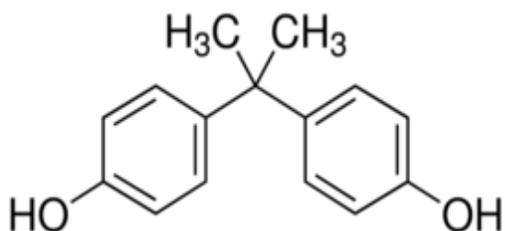


Figure 1. chemical structure of bisphenol A

MATERIALS AND METHODS

Reagents: BPA was supplied from Sigma Aldrich, K_2HPO_4 and KH_2PO_4 were used for preparation of phosphate buffer solution, and $HAuCl_4$ and sodium citrate supplied by Merck. All of the materials were applied without extra purification. The phosphate buffer solution was made of 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4 stock solution. Stock solutions of ($1 \times 10^{-2} M$) BPA were prepared by dissolving the chemical in to methanol (HPLC grade) and then stored at $4^\circ C$ in the dark. All other solutions were provided using deionized water.

Analysis: The electrochemical techniques were performed using a potentiostat/galvanostat (IVIUM TECHNOLOGY-VERTEX). A traditional three-electrode system was employed to carry out all electrochemical experiments: $Ag|AgCl$ was utilized as reference electrode.

Auxiliary and working electrodes were Pt and glassy carbon, respectively. Field emission scanning electron microscope (FESEM) was performed using a Mira 3-XMU field emission SEM with an acceleration potential of 15 kV.

Synthesis of gold nanoparticles: For preparation of colloidal gold nanoparticles as the first step, 100 ml of 0.01% $HAuCl_4$ solution should be heating up to boiling, afterward 2.5 ml solution made by sodium citrate (1%) should be combined with the boiling $HAuCl_4$ and the mixed solution should be maintained at boiling point for 10 minutes, and after that it should be stirred for another 10 minutes in the absence of heat. The resulting solution should be stored at $4^\circ C$ in dark. By using this method, a 17 nm diameter gold nanoparticles will be obtained.

Preparation of the BPA electrochemical sensor: Firstly the surface of bare GCE was mechanically polished with alumina slurry ($0.05 \mu m$) on a cloth pad and then rinsed ultrasonically in absolute ethanol and double distilled deionized water for a few minutes.

To prepare the modified electrode using a microinjector $5 \mu l$ of gold nanoparticles was dropped on to the smoothed prepared GCE surface and finally dried at $25^\circ C$.

RESULTS AND DISCUSSION

Characterizing of gold nanoparticles: The morphology of GNs have been investigated by FESEM and the images were operated at 15KV. As can be seen in Figure 2, the synthesized GNs were uniform and spherical in shape with their size ranging from 10 to 25 nm.

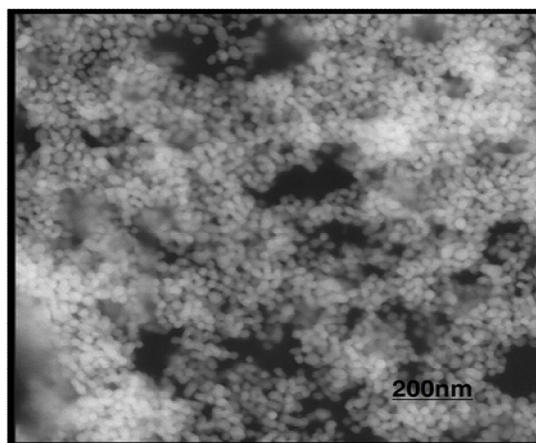


Figure- 2: FESEM image of Nano gold on the GC electrode surface

Electrochemical characterization of BPA:

According to pervious reports (Ntsendwana, Mamba, Sampath, & Arotiba, 2012) the peak current was found to be higher at neutral medium (pH=7). Voltammetric behaviors of 1×10^{-4} M BPA at bare and GNs modified GCE in phosphate buffer (0.1M, pH=7) were studied using CV and its results were shown in Figure3. According to the curves, electrochemical behavior of BPA at both electrodes is a quite irreversible reaction.

Obviously, in comparison to bare GCE, a considerable enhancement can be observed in the

electrochemical response to the oxidation peak current of BPA at GNs/GCE. As is clear, a significant improvement in surface properties of electrode can be seen because of increasing the conductivity of the electrode by gold nanoparticles. Also, it demonstrates the electrocatalytic activity of GNs toward the oxidation of BPA because of the facile electron transfer of GNs and their remarkable conductivity and specific surface area.

The bare and GNs/GCE electrode exhibit the oxidation peak current of around $1.099 \mu\text{A}$ and $1.437 \mu\text{A}$ around 0.6V for BPA respectively.

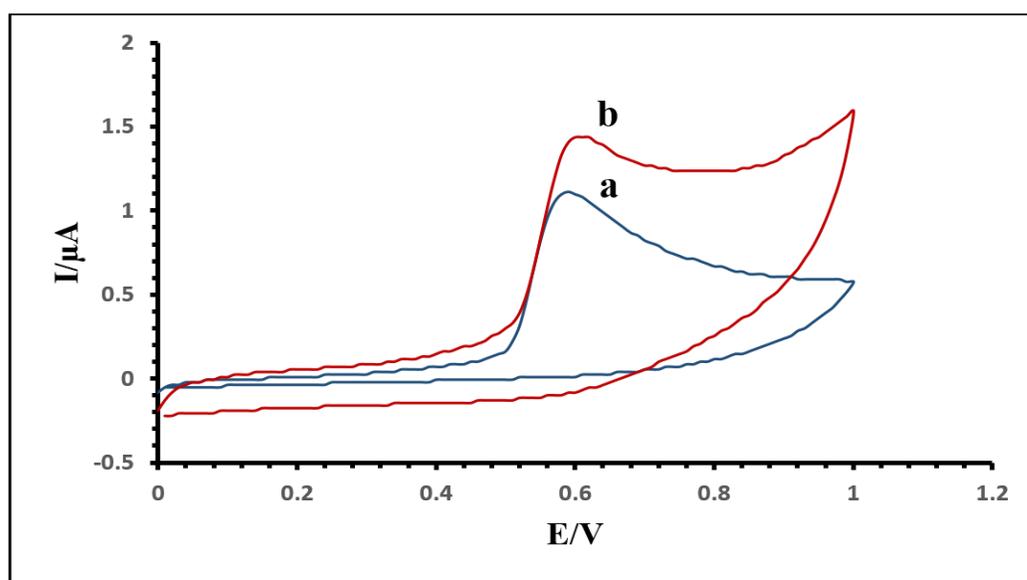


Figure-3: Cyclic voltammograms of 1×10^{-4} M BPA (a) at bare GCE and (b) 1×10^{-4} M BPA at GNs/GCE

Electrochemical characterization of GNs/GCE

The investigation of the structure and electrochemical properties of GNs/GCE were carried out using CV and electrochemical impedance spectroscopy (EIS) techniques in potassium ferricyanide as a redox probe (Figure 4).

Figure 4A, displays the cyclic voltammograms of $\text{K}_3\text{Fe}(\text{CN})_6$ at bare and gold nanoparticles modified GCE. The peak current was improved distinctly from $11.75 \mu\text{A}$ at bare electrode to $6.524 \mu\text{A}$ at GNs modified GCE. Furthermore, the peak to peak separation (ΔE_p) was obtained as 0.13 for bare GCE and it increased slightly at

GNs/GCE. The results show that the GNs can enhance the conductivity and sensitivity of the glassy carbon electrode.

For complementary information about the modified GC electrode, EIS was employed (Figure 4B). The curve a shows the Nyquist diagram of EIS at bare GCE and curve b is the Nyquist plot of GNs/GCE. Electron transfer resistance (R_{et}) was found to be 8317 for bare GCE and 6533 for GNs/GCE. Thus the resistance value of the GNs/GCE decreased drastically versus the bare GCE. Accordingly from the EIS, it can be concluded that the GNs modified GCE can efficiently improve the electron transfer rate.

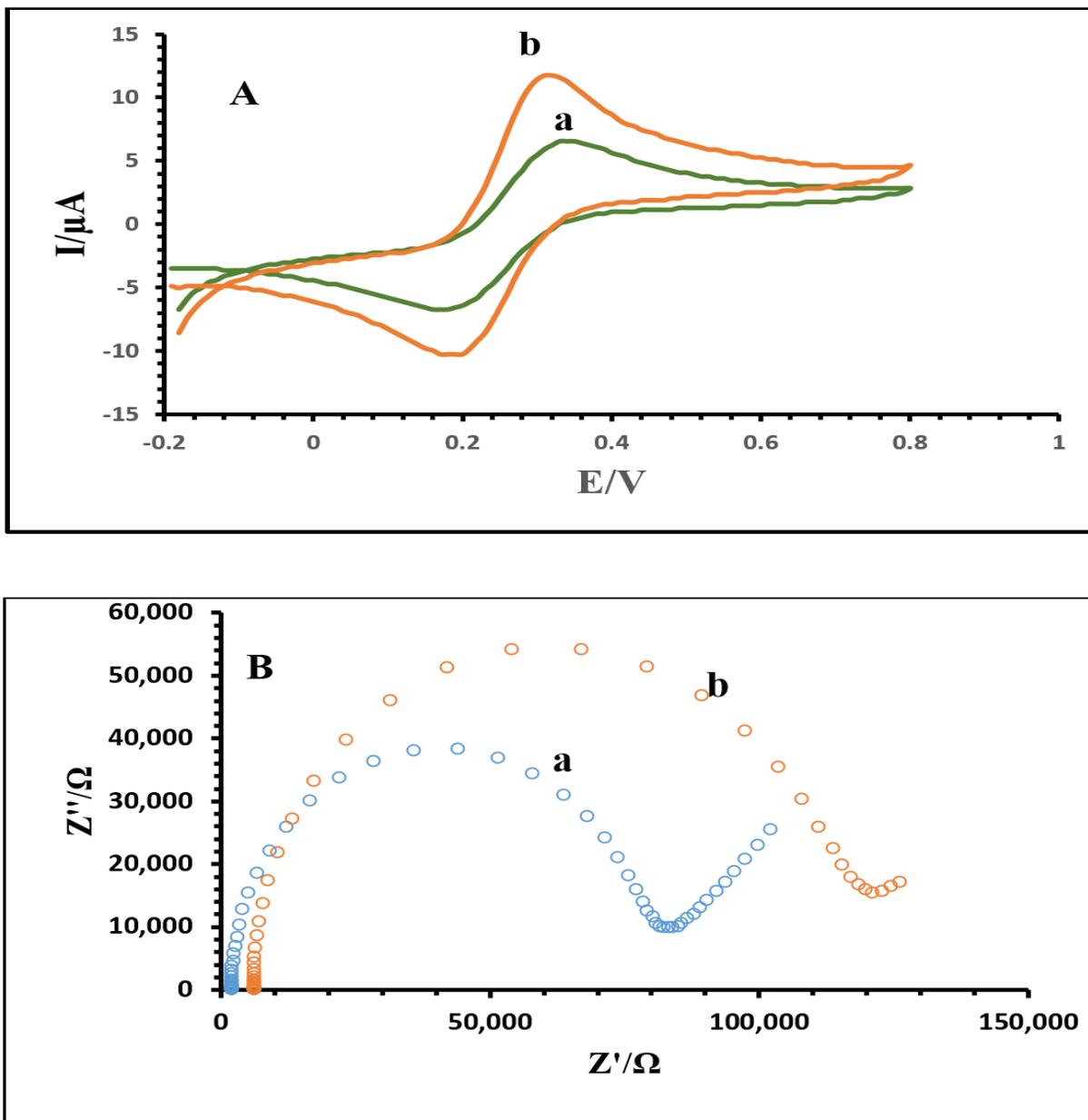


Figure -4: CVs (A) and EIS (B) of bare GC electrode (a) and GNs/GC electrode (b) in the solution of 5mM ferrocyanide (1:1) including 0.1MKCl. (For CV scan rate: 50mVs^{-1} , for EIS: frequency range of 0.1 to 10^5 Hz at OCP of 0.18 V).

Effect of scan rate: Scan rate effect on electrochemical oxidation behavior of BPA was studied using CV technique in 1×10^{-4} M BPA solution (Figure 5A). This method provides further information about the process of BPA oxidation at GNs/GCE. As shown in Figure 5 the peak current of oxidation enhanced proportionally by rising of the scan rate and also, the relationship between scan rate and peak current was linear (Figure 5B). It can be seen that the oxidation of

BPA at GNs/GCE is an adsorption-controlled process. In addition, the linear relation was governed between E_p and $\log v$ according to the equation 1, as shown in Figure 5C. The electron transfer coefficient (α) was achieved 0.622 by equation 2:

$$E_p = 0.5308 + 0.0392 \log v \quad (1)$$

$$b = 2.303RT/n(1-\alpha)F \quad (2)$$

Where α is transfer coefficient, n is total electrons transferred, R , T and F are attributed to gas constant, the absolute temperature and the faraday constant respectively.

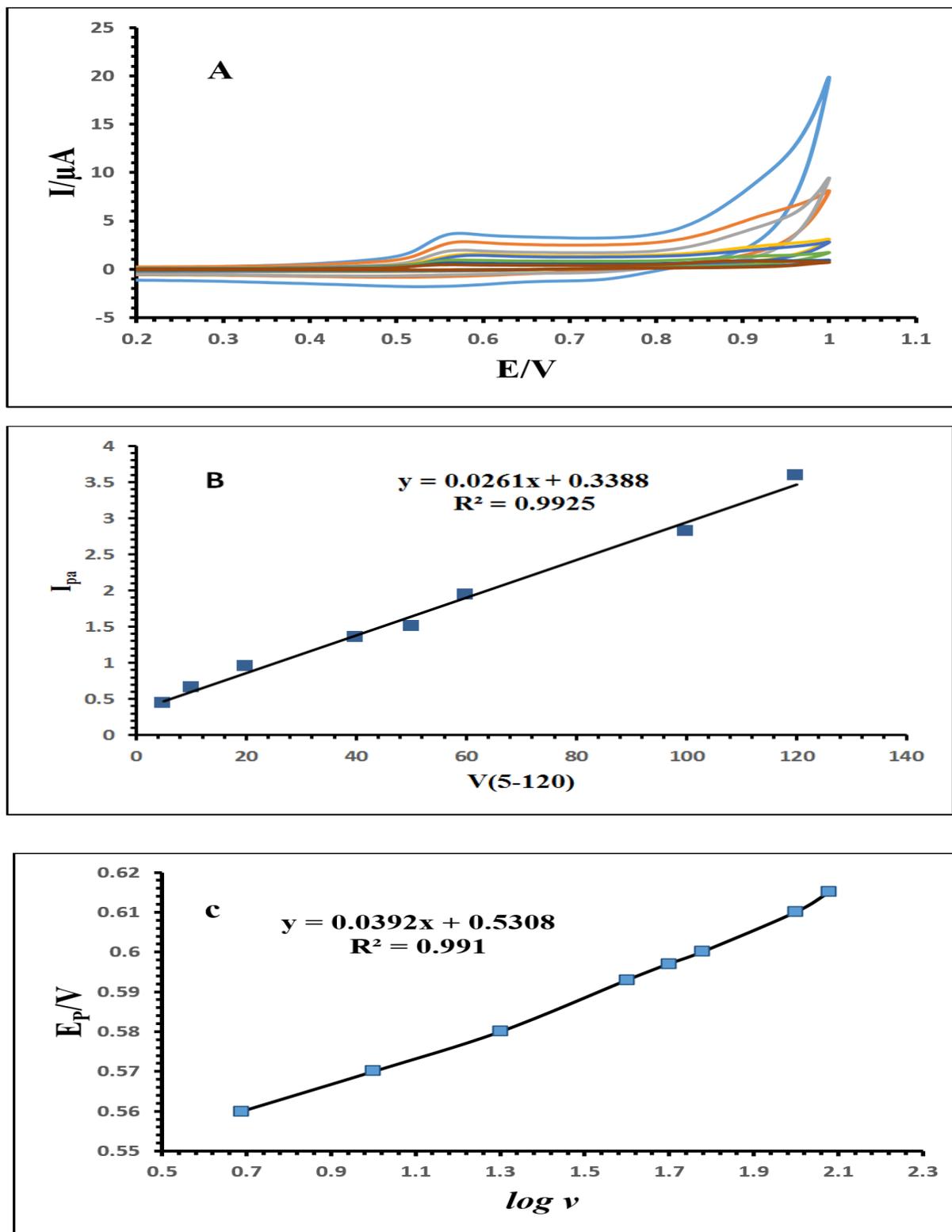


Figure-5: (A) CVs for BPA ($1 \times 10^{-4} \text{ M}$) at GNs/GC electrode in various scan rates (5, 10, 20, 40, 50, 60, 100, 120). (B) Dependency of peak current on the scan rate. (C) The relation between E_p and $\log v$

Determination of detection limit: Figure 6 displays the DPVs of BPA at the GNs/ GC electrode over concentration in the range of 1×10^{-8} to 6×10^{-6} M. In the mentioned range, the peak

current is commensurate with the concentration of BPA and a linear relationship with the correlation coefficient of (0.9874), was obtained for BPA according to the equation 3:

$$i_p = 6.0086 \mu\text{A L mol}^{-1} \times [\text{BPA}] + 1.607 \quad (3)$$

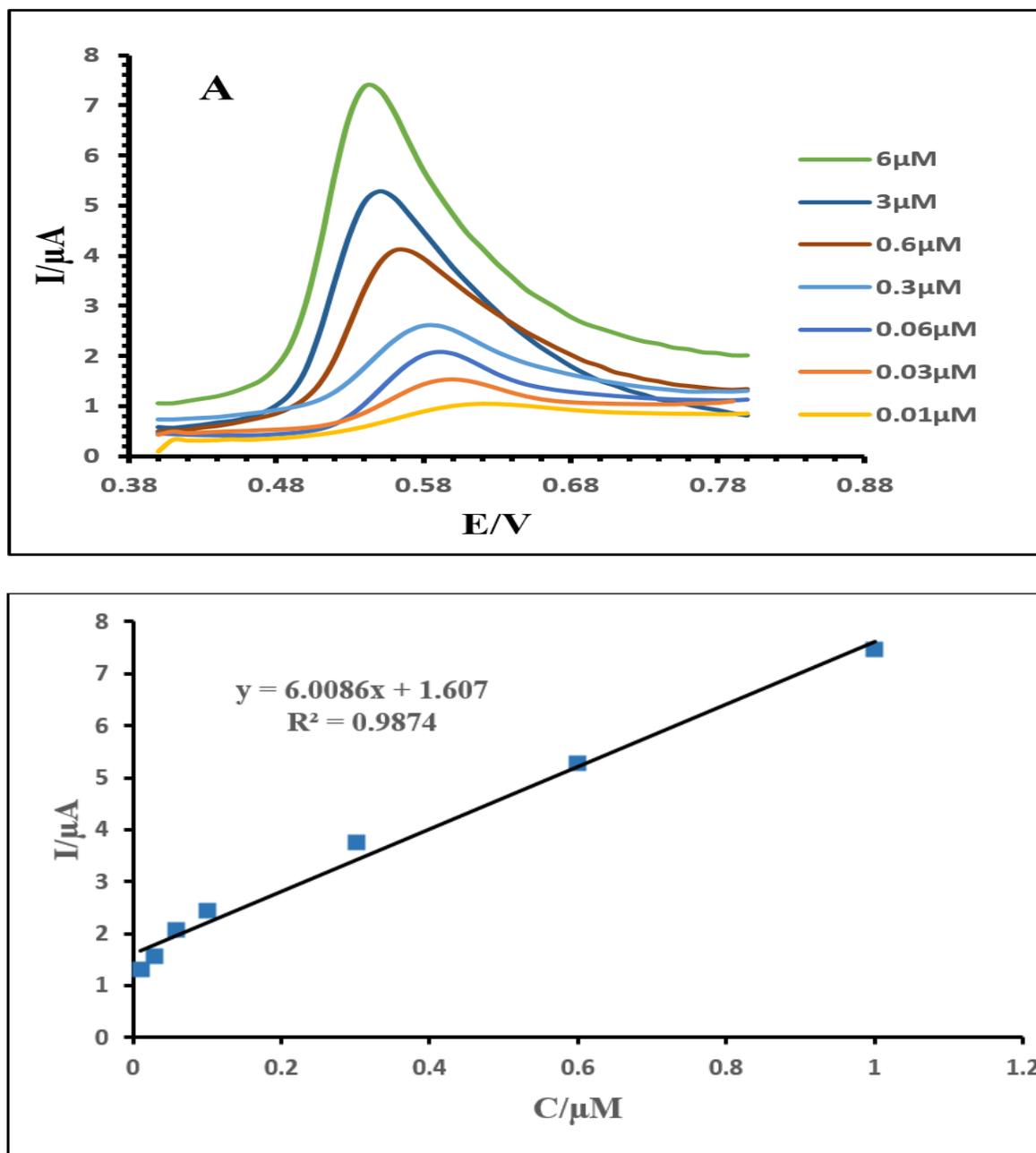


Figure -6: (A) Voltammograms of BPA at various concentrations and (B) BPA calibration curve. (In the concentration range of 1×10^{-8} to 6×10^{-6} M. The BPA lowest limit of detection using this method was attained as low as (1.5×10^{-9} M).

CONCLUSION

This study proposed not only a convenient but a rapid and authentic electrochemical sensor using GNs/GCE for detecting and measuring BPA. Compared to the bare electrode, at the surface of GNs/GCE an increase in the peak current of oxidation and negative shift of the peak potential of BPA was observed. Due to the high selectivity, low detection limit, wide linear range, reproducibility of the gold nanoparticles modified glassy carbon electrode and the satisfactory results of this method, it could be applied for the determination of Bisphenol A in real sample.

REFERENCES

- Brede, C., Fjeldal, P., Skjevraak, I. and Herikstad, H., Increased migration levels of bisphenol A from polycarbonate baby bottles after dishwashing, boiling and brushing. *Food Additives and Contaminants* **20**(7): 684-689 (2003).
- Chauke, V., Matemadombo, F. and Nyokong, T., Remarkable sensitivity for detection of bisphenol A on a gold electrode modified with nickel tetraamino phthalocyanine containing Ni–O–Ni bridges. *Journal of Hazardous Materials* **178**(1): 180-186 (2010).
- Chen, H., Zhang, Z., Cai, R., Rao, W. and Long, F. Molecularly imprinted electrochemical sensor based on nickel nanoparticles-graphene nanocomposites modified electrode for determination of tetrabromobisphenol A. *Electrochimica Acta* **117**: 385-392(2014).
- Cunha, S. and Fernandes, J., Quantification of free and total bisphenol A and bisphenol B in human urine by dispersive liquid–liquid microextraction (DLLME) and heart-cutting multidimensional gas chromatography–mass spectrometry (MD–GC/MS). *Talanta* **83**(1): 117-125 (2010).
- Dempsey, E., Diamond, D. and Collier, A., Development of a biosensor for endocrine disrupting compounds based on tyrosinase entrapped within a poly (thionine) film. *Biosensors and Bioelectronics* **20**(2): 367-377(2004).
- Gatidou, G., Thomaidis, N. S., Stasinakis, A. S. and Lekkas, T. D., Simultaneous determination of the endocrine disrupting compounds nonylphenol, nonylphenol ethoxylates, triclosan and bisphenol A in wastewater and sewage sludge by gas chromatography–mass spectrometry. *Journal of Chromatography A*, **1138**(1): 32-41(2007).
- Kawamura, Y., Sano, H. and Yamada, T., Migration of bisphenol A from can coatings to drinks. *Journal of the Food Hygienic Society of Japan (Japan)* (1999).
- Kim, A., Li, C.-R., Jin, C.-F., Lee, K. W., Lee, S.-H., Shon, K.-J., . . Shim, Y.-B., A sensitive and reliable quantification method for bisphenol A based on modified competitive ELISA method. *Chemosphere* **68**(7): 1204-1209 (2007).
- Kinnberg, K. and Toft, G., Effects of estrogenic and antiandrogenic compounds on the testis structure of the adult guppy (*Poecilia reticulata*). *Ecotoxicology and environmental safety* **54**(1): 16-24(2003).
- Krishnan, A. V., Stathis, P., Permuth, S. F., Tokes, L. and Feldman, D., Bisphenol-A: an estrogenic substance is released from polycarbonate flasks during autoclaving. *Endocrinology* **132**(6): 2279-2286(1993).
- Molina-García, L., Fernández-de Córdova, M. L. and Ruiz-Medina, A., Analysis of Bisphenol A in milk by using a multicommutated fluorimetric sensor. *Talanta* **96**: 195-201(2012).
- Ntsendwana, B., Mamba, B., Sampath, S. and Arotiba, O., Electrochemical detection of bisphenol A using graphene-modified glassy carbon electrode. *Int J Electrochem Sci.* **7**(4): 3501-3512(2012).
- Olea, N., Pulgar, R., Pérez, P., Olea-Serrano, F., Rivas, A., Novillo-Fertrell, A., . . . Sonnenschein, C., Estrogenicity of resin-based composites and sealants used in dentistry. *Environmental Health Perspectives* **104**(3): 298(1996).
- Poorahong, S., Thammakhet, C., Thavarungkul, P., Limbut, W., Numnuam, A. and Kanatharana, P., Amperometric sensor for detection of bisphenol A using pencil graphite electrode modified with polyaniline nanorods and multiwalled carbon nanotubes. *Microchimica Acta* **176**(1-2): 91-99 (2012).

- Portaccio, M., Di Tuoro, D., Arduini, F., Lepore, M., Mita, D., Diano, N., . . . Moscone, D., A thionine-modified carbon paste amperometric biosensor for catechol and bisphenol A determination. *Biosensors and Bioelectronics* **25**(9): 2003-2008 (2010).
- Raj, C. R. and Ohsaka, T., Electroanalysis of ascorbate and dopamine at a gold electrode modified with a positively charged self-assembled monolayer. *Journal of Electroanalytical Chemistry* **496**(1): 44-49 (2001).
- Sambe, H., Hoshina, K., Hosoya, K. and Haginaka, J., Simultaneous determination of bisphenol A and its halogenated derivatives in river water by combination of isotope imprinting and liquid chromatography-mass spectrometry. *Journal of Chromatography A* **1134** (1): 16-23 (2006).
- Shahrokhian, S., Hamzehloei, A., Thaghani, A. and Mousavi, S. R., Electrocatalytic Oxidation of 2-Thiouracil and 2-Thiobarbituric Acid at a Carbon-Paste Electrode Modified with Cobalt Phthalocyanine. *Electroanalysis*, **16**(11): 915-921 (2004).
- Steinmetz, R., Mitchner, N. A., Grant, A., Allen, D. L., Bigsby, R. M. and Ben-Jonathan, N., The xenoestrogen Bisphenol A induces growth, differentiation, and c-fos gene expression in the female reproductive tract 1. *Endocrinology* **139**(6): 2741-2747 (1998).
- Van Ginkel, S. W., Hassan, S. H. and Oh, S.-E., Detecting endocrine disrupting compounds in water using sulfur-oxidizing bacteria. *Chemosphere* **81**(2): 294-297 (2010).
- Wen, Y., Zhou, B.-S., Xu, Y., Jin, S.-W. and Feng, Y.-Q., Analysis of estrogens in environmental waters using polymer monolith in-polyether ether ketone tube solid-phase microextraction combined with high-performance liquid chromatography. *Journal of Chromatography A* **1133**(1): 21-28 (2006).
- Yin, H., Cui, L., Ai, S., Fan, H. and Zhu, L., Electrochemical determination of bisphenol A at Mg-Al-CO₃ layered double hydroxide modified glassy carbon electrode. *Electrochimica Acta* **55**(3): 603-610 (2010).
- Yin, H., Zhou, Y., Ai, S., Han, R., Tang, T. and Zhu, L., Electrochemical behavior of bisphenol A at glassy carbon electrode modified with gold nanoparticles, silk fibroin and PAMAM dendrimers. *Microchimica Acta* **170**(1-2): 99-105(2010).
- Zhao, M.-P., Li, Y.-Z., Guo, Z.-Q., Zhang, X.-X. and Chang, W.-B., A new competitive enzyme-linked immunosorbent assay (ELISA) for determination of estrogenic bisphenols. *Talanta* **57**(6): 1205-1210 (2002).
- Zhou, L., Wang, J., Li, D. and Li, Y., An electrochemical aptasensor based on gold nanoparticles dotted graphene modified glassy carbon electrode for label-free detection of bisphenol A in milk samples. *Food chemistry* **162**: 34-40(2014).
- Zhou, W., Sun, C., Zhou, Y., Yang, X. and Yang, W., A facial electrochemical approach to determinate bisphenol A based on graphene-hypercrosslinked resin MN202 composite. *Food chemistry* **158**: 81-87 (2014).