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Full Paper

Cobalt Ferrite Nanoparticles Modified Carbon Paste Miniaturized Electrode with Enhanced Sensitivity for Electrochemical Sensing of Donepezil Hydrochloride

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Abstract- A nanocomposite miniaturized electrode modified with cobalt ferrite nanoparticles ($CoFe_2O_4$ NPs) was used for determination of donepezil (DON) in presence of memantine HCl. The voltammetric results indicate that $CoFe_2O_4$ NPs can remarkably enhance electrocatalytic activity toward the oxidation of donepezil in buffer solution. Scanning electrochemical microscopy (SEM) and transmission electron microscopy (TEM) were used for characterization of $CoFe_2O_4$ NPs and the modified electrode surface. Characteristics of the electrochemical responses of the modified electrode toward donopezil were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV). Experimental parameters including preconcentration time, scan rate and pulse height were optimized for high sensitivity. An *In-situe* electrochemical cleaning step was proposed for regeneration of the initial surface conditions of the electrode between measurements. The electrocatalytic oxidation current of donepezil was found to have a linear relation to concentration over the range from 5 to ≤ 20 µM by the DPV method. The average recovery of DON in Aricept tablet was 97.49 with a %RSD <0.5%. The modified electrode can be applied to the determination of DON in tablets and urine samples with satisfactory results.

Keywords- Miniaturized carbon paste electrode, Cobalt ferrite nanoparticles, DPV, Donepezil, Pharmaceutical formulation, Clinical samples

1. INTRODUCTION

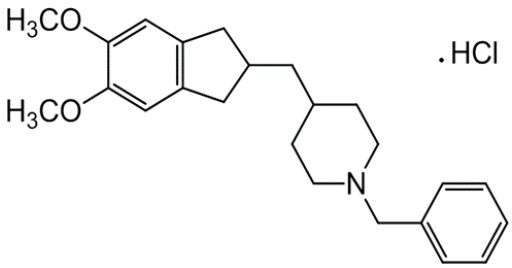
Donepezil (DON) (Figure 1) is a reversible inhibitor of acetylcholinesterase enzyme which is prescribed for treatment of Alzheimer's disease [1]. Donepezil over doses causes difficult sleeping, muscle cramps and anorexia [2]. Due to this great pharmacological importance there has been a great demand for fast reliable procedures for the assay of DON in pharmaceutical formulation.

Therefore, different analytical methods were proposed for the assay of DON either in pharmaceutical products or in biological fluids involving HPLC [3-7], capillary electrophoresis [8] potentiometric ion selective electrodes [9] and voltammetric methods [10-12]. Even though the proposed methods have been successfully used for the assay of DON, each has its drawbacks as well. The HPLC methods are time and solvent consuming and the capillary electrophoresis require expensive instrumentations which is not available in most laboratories of routine analysis. The potentiometric ion selective electrodes are cost effective and can be used in turbid solution. However, this technique requires special skills and has been so far not applicable for routine analysis of pharmaceutical compounds. Although voltammetric methods would be an alternative fast, precise and accurate for analysis of DON, the proposed methods, unfortunately, have not provided a satisfactory remedy to the problem of electrode fouling during the measurements. Such problem has a great influence on the accuracy of the measurements.

Recently, magnetic nanoparticles (MNPs) have attracted a growing interest in the development and fabrication of sensors and biosensors. MNPs exhibit the best performance at sizes of 10–20 nm due to supermagnetism, which makes them especially suitable when looking for a fast response, large surface area and high mass transference [13]. Among MNPs, cubic-spinel-structure cobalt ferrite ($CoFe_2O_4$) has been widely studied because of its being inexpensive to produce, excellent chemical stability, high electromagnetic performance, mechanical hardness, biocompatible, environmentally safe and promising catalytic activity [14-16]. Several groups have reported the preparation and properties of magnetic materials for electroanalytical application for determination of biologicaly important compounds. For example,a glassy carbon electrode modified with Fe_3O_4 magnetic nanoparticles was used for voltammetric determination of nimesulide [17]. A nano-scaled γ–Fe_2O_3 catalysts supported on multi-walled carbon nanotubes was employed for the electrochemical detection of detection of dopamine [18]. Moreover, glassy carbon electrodes modified either with carbon-coated nickel [19] or $CoFe_2O_4$ [20] magnetic nanoparticles were used for the determination acetaminophen and paracetamol, respectively.

In the present work, a new miniaturized carbon paste electrode (CPE), modified with very small sized $CoFe_2O_4$ nanoparticles ($CoFe_2O_4$ NPs) is constructed and used for the sensitive electrochemical determination of DON using differential pulse voltammetry (DPV). Due to the excellent electric conductivity of $CoFe_2O_4$ NPs/CPE, the fabricated sensor showed

excellent electrocatalytic activity toward DON. The sensor exhibited selectivity and acceptable reproducibility, and could be used for the determination of DON in urine samples.



Scheme 1. Molecular structure of donepezil HCl; Mol. Wt: 415.95

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

Donepezil HCl drug substance (98%) was obtained from EUG Pharma, 6th industrial zone, 6 October City, Egypt. Aricept tablets (5 mg of donepezil HCl per tablet) were obtained from Pfizer, Cairo, Egypt. Boric acid was purchased from Elnasr Pharmaceutical Chemicals Co. (Abou Zaabal, Egypt). Phosphoric acid was obtained from Fisher Scientific. Acetic acid was purchased from Loba Chemie PVT Ltd (Mumbai, India). Paraffin oil and graphite powder were purchased from Sigma-Aldrich and were used as received. Britton-Robinson buffer (B-R buffer) 0.04 M was prepared by mixing phosphoric, acetic and boric acids and the pH was adjusted by NaOH to the desired pH value. Solutions of reacting materials were prepared in deionized water provided by a Milli-Q water purification system. All Glassware were washed with aqua regia (HCl:HNO_3=3:1 (v/v)) and then rinsed with Milli-Q water. Cobalt (II) chloride hexahydrate (≥99%), Iron (III) chloride hexahydrate (analytical grade) and aqueous tetramethylammonium hydroxide (TMAOH, 25%) were purchased from Sigma-Aldrich.

2.2. Apparatus

Voltammetric measurements were performed using SP-150 potentiostat (BioLogic Science Instrument, France) provided with EC-Lab for windows v 11.02 software. A platinum wire was employed as the auxiliary electrode. The cell potentials were measured with respect to Ag/AgCl (3.0 M NaCl) reference electrode. A Cyberscan 500 digital (Eutech Instruments, USA) pH meter with a glass combination electrode was used for the pH adjustment. All the electrochemical experiments were performed at an ambient temperature. TEM images were performed using a JEOL 200 CX (Akishima, Tokyo, Japan) at 200 kV.

The SEM measurements were carried out using Quanta 250 FEG scanning electron microscope (FEI company, Netherlands).

2.3. Prepared Solutions

Stock standard solution of DON, (1×10^{-2} mol/L), was prepared by transferring 41.6 mg in 10-mL volumetric flask, and dissolved in suitable amount of water, then the volume was completed with the same solvent. The working standard solutions of DON (5.0×10^{-6}–2.0×10^{-5} mol/L) were prepared by suitable dilution from stock standard (1.0×10^{-2} mol/L).

2.4. Preparation of Cobalt ferrite nanoparticles ($CoFe_2O_4$ NPs)

Cobalt ferrite nanoparticles ($CoFe_2O_4$ NPs) were synthesized in facile way using a wet chemical method and described as follow: In a typical synthesis, 2.378 g of $CoCl_2\cdot6H_2O$ was dissolved in a solution of 5.0 ml of 8% HCl, and 5.406 g of $FeCl_3\cdot6H_2O$ was dissolved in 40 ml of water. The two solutions were heated at 60° C, mixed, and then quickly added to 100-150 ml of 1.0 M TMAOH solution (pH 11-12) at 90-100° C with vigorous stirring. A black precipitate formed immediately, and stirring was continued for 2 h at 90-100° C. After that time, the reaction mixture was cooled to room temperature, and the precipitate was magnetically separated, washed with water several times, and dried in a hot air oven at 50 °C for 3 h. The synthesized $CoFe_2O_4$ NPs were characterized by transmission electron microscopy (TEM) and X-Ray diffractometery (XRD). In an attempt to eliminate any toxicity comes from organic chemicals, stabilizing and capping agents are avoided in the preparation of recommended NPs.

2.5. Preparation of miniaturized $CoFe_2O_4$ NPs modified carbon paste electrode

The carbon paste was prepared by mixing the previously synthesized $CoFe_2O_4$ NPs (25.0 mg) with paraffin oil (0.25 mL) in a small beaker; the mixture was sonicated for 30 min. The graphite powder (475 mg) was added and the mixture was well mixed in a mortar. The tapered end (id:300 µm) of a pulled glass capillary served as electrode tip. For the internal contact a copper wire was cannulated inside the capillary until it reached 2 mm bellow the tapered end. The tip was filled with the paste by pressing it against the paste.

2.6. Transmission electron microscope (TEM)

A droplet of the sample was placed on a copper grid and allowed to dry before being examined in the transmission electron microscope. The TEM images were analyzed using the Image-Pro Plus and Gatan Digital Micrograph program (Yubinbango103-0027 Nihonbashi, Chuo-ku, Tokyo, Japan).

2.7. Powder XRD analysis

Powder X-ray diffraction (XRD) patterns were recorded for $CoFe_2O_4$ nanoparticles prepared sample with a PANalytical: X'Pert PRO diffractometer using Cu Kα radiation source for investigation of the crystalline structure and phase transition.

2.8. Electrode Pre-treatment

After mounting the working electrode into the electrochemical cell, characterization of the electrodes was performed. For surface activation, the working electrode was cycled from 0 to +1.5 V *vs*. Ag/AgCl reference electrode until a stable cyclic voltammogram was observed in 0.04 M B-R buffer (pH 7) electrolyte solutions (i.e., approx. 15 cycles).

2.9. Recommended Procedure

After mounting the working electrode into the electrochemical cell, the modified electrode was cycled in the potential range from 0 to 1.5 V with a scan rate of 100 mVs^{-1} in B-R buffer of pH 7.0 for several times (i.e., approx. 15 cycles) until a stable response was achieved. Subsequently, a proper amount of DON was added and the cyclic voltammograms were recorded from 0 to 1.5 V at a scan rate of 100 mVs^{-1}. For DPV procedure, aliquots from studied drug were transferred from stock standard solution using a micropipette into a series of 10-mL volumetric flasks to cover the concentration range from 5.0×10^{-6}–2.0×10^{-5} mol/L. The volume was completed to the mark with B-R buffer of pH 7.0 and the DPV were recorded for each concentration.

2.10. Analytical application

Twenty tablets of Aricept tablets (5 mg/tablet) were finely powdered in a mortar and an accurately weighed amount of the powder equivalent to 41.6 mg of donepezil hydrochloride was transferred into a10-mL measuring flask and dissolved in 5.0 mL bidistilled water. The solution was sonicated for 3 min and the flask was completed to mark with bidistilled water to obtain final concentration 1.0×10^{-2} mol/L. The amount of DON in tablets was determined by the standard addition method.

In case of urine samples, drug-free human urine was obtained from a healthy volunteer who has never treated with donepezil. We diluted 1 mL urine sample to 100 mL with distilled water. Then, 1.0 mL of the diluted urine sample was diluted to 10 mL with B-R buffer pH 7. The solution was spiked with different concentration of DON. The concentration of spiked samples is calculated by the standard addition method.

3. RESULTS AND DISCUSSION

3.1. Characterization of the as-synthesized $CoFe_2O_4$ NPs

The $CoFe_2O_4$ NPs were prepared by co-precipitation of Co and Fe precursors in a basic medium. The TEM image in Fig. 1a reveals that the $CoFe_2O_4$ NPs prepared with TMAOH are nearly spherical, with good size distributions and average particle sizes ranging from 5.0 to 9.0 nm. The TEM micrograph shows smaller sizes than those prepared by coprecipitation with NaOH (18 nm) and that probably as a result of improvement in the solubility product constant of the corresponding divalent metal hydroxides [21,22].

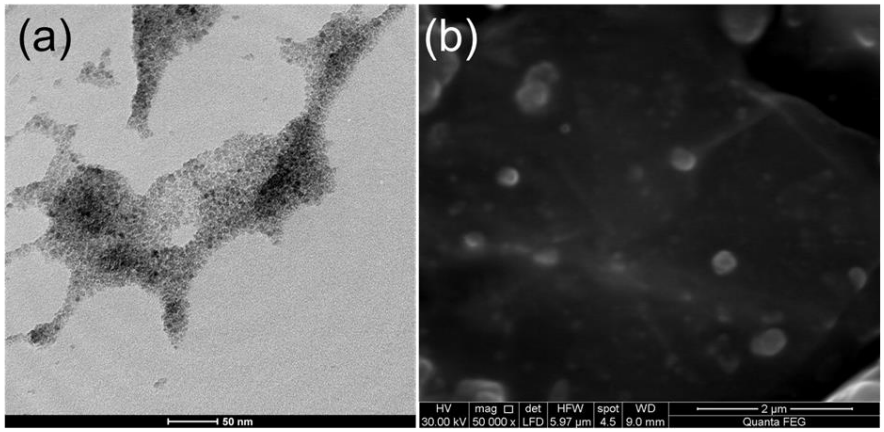


Fig. 1. (a) Transmission electron microscopy (TEM) image of $CoFe_2O_4$ NPs prepared using Co and Fe precursors in basic medium, spherical in shape with approximately size 7.0 nm, and (b) Scanning electrochemical microscopy (SEM) micrograph of a carbon paste modified with 5% $CoFe_2O_4$ NPs.

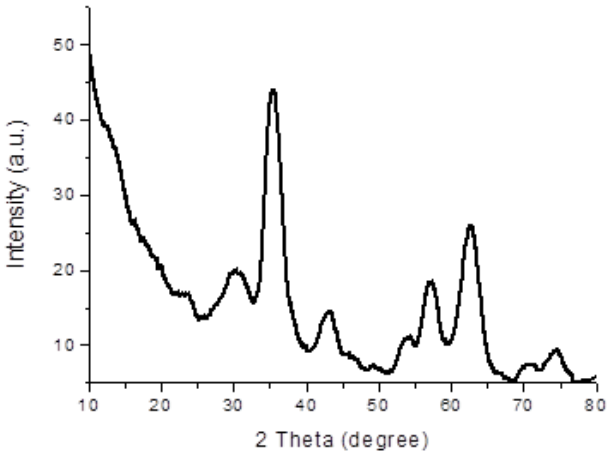


Fig. 2. X-ray diffraction (XRD) pattern of cubic $CoFe_2O_4$ nanoparticles prepared by coprecipitation of Co and Fe precursors in basic medium

XRD experiment was performed to identify the crystallographic structure of the prepared $CoFe_2O_4$ NPs. The XRD pattern (Fig. 2) shows that the as-prepared material consisted entirely of nano-crystalline $CoFe_2O_4$ NPs and coincides with the standard data of the cubic Co ferrite phase with the Fd3m space group (JCPDS no. 22-1086) [23].

The pattern revealed peaks of low intensities and observed at 2θ values corresponding to the crystal plane of cubic $CoFe_2O_4$: ~30.06° (220), ~35.45° (311), ~37.28° (222), ~43.47° (400), ~53.89° (422), ~57.16° (511), ~62.73° (440), ~65.70° (531) and ~70.79° (620). The low intensities of the reflection peaks of the XRD pattern indicate the small size of the crystallite particles.

3.2. Electrochemical behavior of DON at NPs modified carbon paste electrode

Fig. 1 b shows the SEM of $CoFe_2O_4$ NPs modified carbon paste. The picture shows $CoFe_2O_4$ NPs with variable size (≤100 nm). It seems that some of $CoFe_2O_4$ NPs agglomerated in the carbon paste matrix. DON exhibited an oxidation peak at 0.9 V after adsorptive preconcentration of donepezil at a bare and $CoFe_2O_4$ NPs-modified carbon paste electrodes (Figure 3). The electrochemical oxidation process is irreversible as no reduction peak was observed in the reverse CV scan over the potential range from 0 to 1.5 V. Note, the magnitude of the oxidation peak current was enhanced when $CoFe_2O_4$ NPs were incorporated into the carbon paste, this would be explained by the electroactivity of $CoFe_2O_4$ NPs towards the oxidation of donepezil in buffer pH 7.0.

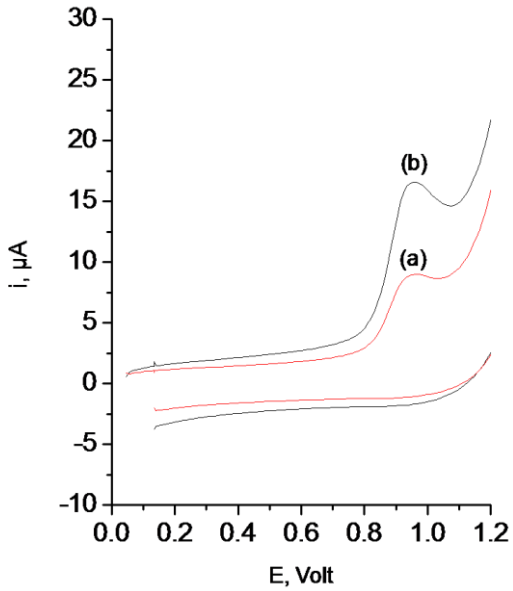


Fig. 3. Cyclic voltammogram of (a) a bare and (b) modified carbon paste electrodes of 1×10^{-5} mol/L donepezil HCl in Britton Robinson buffer pH 7

3.3. EIS characterization of the modified electrode

EIS spectra were recorded over the frequency range from 50 kHz to 10 kHz in 1 mM $[Fe(CN)_6]^{-3/-4}$. The EIS results are displayed in complex impedance plots (Fig. 4). The electrochemical impedance (*Z*) is represented as a vector in the complex plain. The frequency decreases from left to right along the real *Z* axis. The solution and electrode parameters are determined from this plot by fitting a circle through the points that represent the electrode-solution interphase. The R_s is independent of the electrode type and was found to equal 66 Ω, whereas, the charge transfer resistance was greatly reduced from 1005 Ω for the bare carbon paste electrode to 473 Ω for the $CoFe_2O_4$ NPs modified paste.

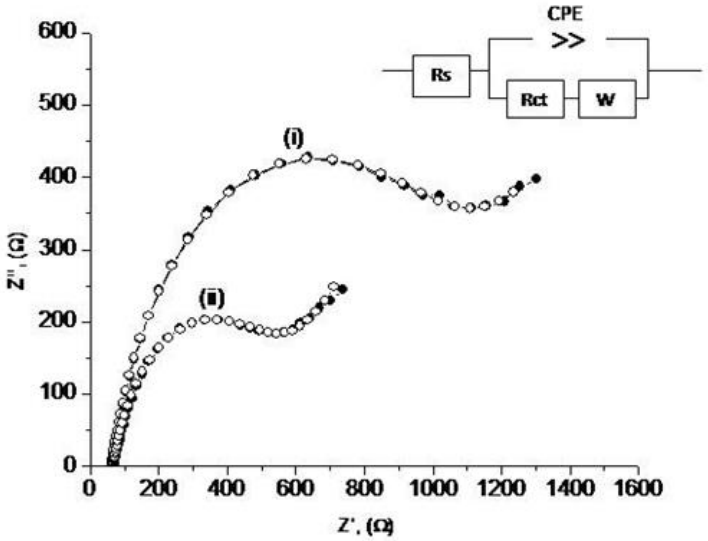


Fig. 4. Nyquist plots of a bare (i) and $CoFe_2O_4$ modified (ii) carbon paste electrodes. The experiment was carried out in 5 mM $[Fe(CN)_6]^{3-/4-}$, +210 mV *vs*. Ag/AgCl, perturbation amplitude: 5 mV pp, frequency range: 50 kHz to 10Hz). The inset is the Randels equivalent circuit. The charge transfer resistance at the bare electrode is 1005 Ω and at the modified electrode is 473 Ω. The open symbols are the fitted values

3.4. Regeneration of the electrode surface

The positive potential applied to obtain the anodic peak (close to 1 V) tend to affect the surface of the electrode by generating oxidizing surface groups, leading to insufficient sensitivity for DON after a number of measurements. To keep the sensitivity of the carbon paste electrode stable, a potential of -500-mV was applied for 20 s in the measurement solution. This step effectively regenerated the same initial surface of the carbon paste before each subsequent measurement. Reproducibility of the peak height was typically 1-2% with this cleaning step (data not shown).

3.5. Dynamics of Adsorption

It was observed that the peak current diminish in the second CV cycles. Additionally, when the electrode was immersed in a DON solution for 1 min and washed with bidistilled water and moved to a DON free solution, an oxidation peak was observed even when a new reference electrode which was never been in contact with DON solution was used. Therefore, we had to study the effect of the adsorption time on the peak current. A practical advantage of drug adsorption at the electrode surface is that, it can be used for preconcentration of DON, thus amplifying the signal that might be too small to detect.

The peak current of the cyclic voltammograms revealed exponential saturation of the electrode surface with a time constant about 5 min. (y=19.04 -12.44 exp (-x/5.2)); this equals to 93% saturation. Thus, 6 min preconcentration time lead to 96% completion of the adsorption process. Note, small errors in this period will not affect significantly the results due to the relatively small slope of the dynamic saturation curve at *t*=6 min. Figure 5 shows the effect of the preconcentration time on the peak current. Surface coverage and, therefore, sensitivity can be increased by using longer preconcentration period. However, shorter time can be used; 1 min results in 60% completion of the adsorption process.

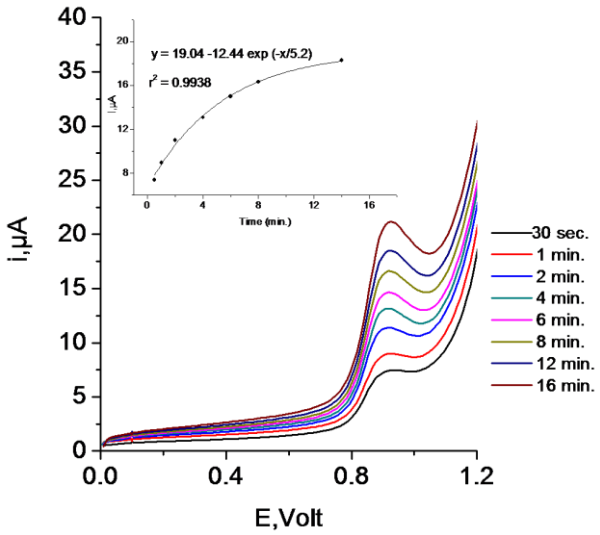


Fig. 5. Forward scans of cyclic voltammograms showing the effect of preconcentration time on the sensitivity of the electrode, the experiment was carried out under stirring

3.6. Effect of scan rate

It has been reported that voltammetric curve recorded at the CPE is controlled by both adsorption and diffusion of the analyte in the paste phase and in the solution phase (i.e diffusion towards the electrode surface at the electrode-solution interface [24]. The effect of the potential scan rate was studied using the CV technique. The peak potential was shifted to more positive with increasing the scan rate which confirms the irreversibility of the oxidation

process. Plotting the peak current *vs* the square root of the scan rate produced a linear curve ($y=1.34\ \nu^{1/2}$ (mV/s)–3.7, $r^2=0.9983$); indicating that the diffusion process dominates the adsorption process.

3.7. Working pH range

To determine the optimum pH value for the electrochemical detection of DON at modified $CoFe_2O_4$ NPs modified electrode, CV was recorded in solutions with a pH range from 2.0 to 7.0 in 1.0×10^{-4} mol/L DON (Figure 6). The oxidation peak of DON showed distinct pH dependence and shifted to lower potentials with increasing pH values, which means that the voltammetric behavior of DON is a process of proton transfer. Plotting $E_{1/2}$ *vs*. pH showed a linear response ($E_{1/2}=1.28$ - 0.061 pH, $r^2=0.993$) with a slope of 61 mV/pH (Figure 6, inset). Therefore, the detection of DON was performed at a pH of 7.0 in B-R buffer solutions (DON pKa=8.5), Similar peak current was observed in phosphate buffer pH 7. Interestingly, memantine HCl, another active ingredient drug, showed no electrochemical activity at the electrode surface under the same experimental conditions including the potential window and the working pH.

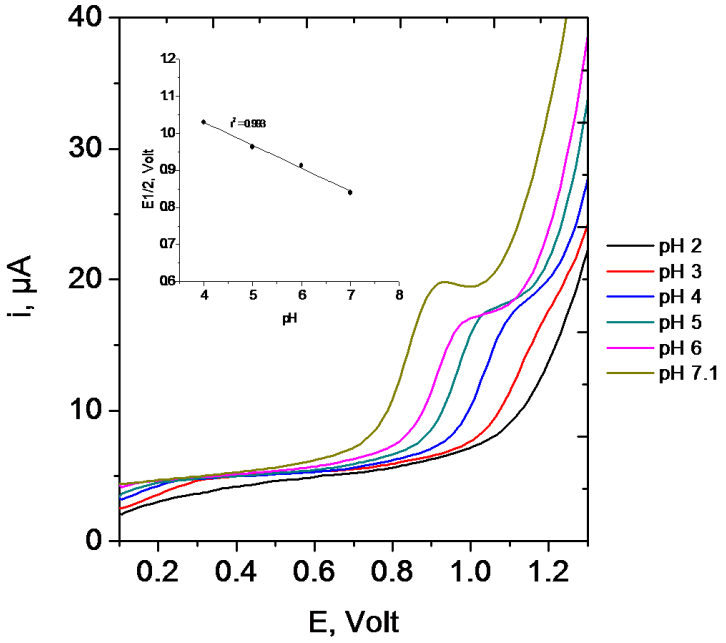


Fig. 6. Forward scans of cyclic voltammograms recorded in 1.0×10^{-4} mol/L DON at different pH values using A $CoFe_2O_4$ modified carbon baste miniaturized electrode; scan rate of 100 mV s. Note: The peak potential is shifted towards negative potential with increasing the pH. A well-shaped with high peak current is observed at pH 7

3.8. DPV for determination of DON

We proposed a DPV protocol with optimized pulse height and scan rate. We observed that the sensitivity was improved when the pulse height was 100 mV and the scan rate was 250 mV/s. Therefore, all subsequent DPV studies were performed under these conditions. Plotting the height of the DPV *vs*. the concentration of DON produced a linear calibration graph over the concentration range from 5.0×10^{-6}–2.0×10^{-5} mol/L DON (r^2=0.995). The DPV calibration graph is shown in Figure 7.

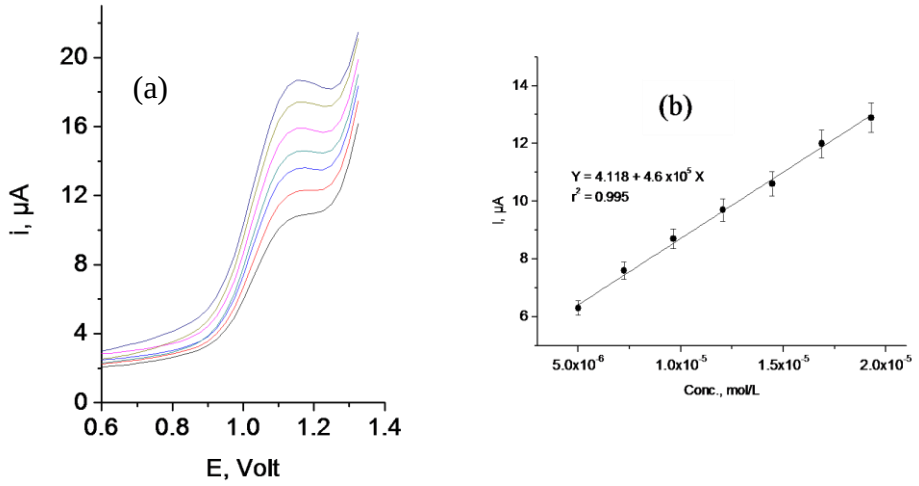


Fig. 7. a) Calibration curve using the height Δ ip against E of anodic DPV peaks at 1.1 mV. Peak heights were determined graphically and plotted against the concentration; b) The corresponding differential pulse voltammograms recorded in a potential range from 0 to +1.4 V *vs*. Ag/AgCl in 0.04 M Britton Robinson buffer (pH=7) with different DON concentrations (5.0–20.0 µmol) at a $CoFe_2O_4$ modified carbon paste miniaturized electrode

3.9. Analytical application

The proposed analytical procedure was applied for determination DON in pharmaceutical tablets (5 mg per tablet) and spiked urine samples. The average recovery at three different concentrations (3.0, 5.0 and 7.9 µg/mL) was within 97.49%±1.5 indicating a satisfactory accuracy of the method. On the other hand, the lower %RSD (<0.5%) refers to the high precision of the method. The results are summarized in Table 1.

In case of urine samples, the average recovery of 5.0 µg/mL was >98.00% with a relative standard deviation <1.00% (Table 1).

3.10. Specificity

Specificity was proved by comparing the voltammograms of the pharmaceutical preparation to that of the pure form, they were found similar. This proves that the method is specific and no interference from the tablet excipients

.

Table 1. Accuracy and precision of the DPV method for determination of DON in tablets and Urine samples

	Conc. (µg/ml)	**Found (µg/mL)**	**%Recovery**	**RSD**
Aricept Tablet	3.0	2.96 ± 0.134	98.94	0.34
	5.0	4.86 ± 0.085	97.42	0.21
	7.9	7.60 ± 0.304	96.11	0.34
Urine	5.0	4.95± 0.275	99.09	0.44
	7.9	7.80 ± 0.51	98.73	0.62

Statistical comparison between the proposed and the official methods was performed showing no significant difference between the two methods (Table 2).

Table 2. Statistical analysis of the results obtained by the proposed DPV and official methods for the determination DON in their pure form

Item	**DPV**	**Official method[a]**
Mean	99.89	99.77
S.D.	0.498	0.464
Variance	0.248	0.215
n	7	6
Student's t test	0.285 (2.201)[b]	
F test	1.153 (4.950)[b]	

[a]HPLC method (official) [37]; octyldisylil silica gel column (5 µm) (15 mm x 4.6 mm i.d.), mobile phase: (buffer: acetonitrile) 65:35, flow rate: 1.4 mL/min, UV detection: 271 nm; [b]Values in parentheses are the corresponding tab. values for t and F at (p = 0.05).

4. CONCLUSION

In this work, we successfully determined DON at a miniaturized carbon baste electrode. With an electrocatalytic effect due to cobalt ferrite nanoparticles and adsorptive preconcentration of DON on the electrode surface, significant signal enhancement was achieved compared to the usual diffusion current-based methodology. Such combination of

electrocatalytic of the nanoparticles and adsorptive effects is unique for miniaturized carbon paste electrodes. The electrode was used for determination of DON in pharmaceutical products and clinical samples with high accuracy and precision.

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