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Research

Preparation of magnetic imprinted polymer nanoparticle carbon paste electrode for determination of valproic acid

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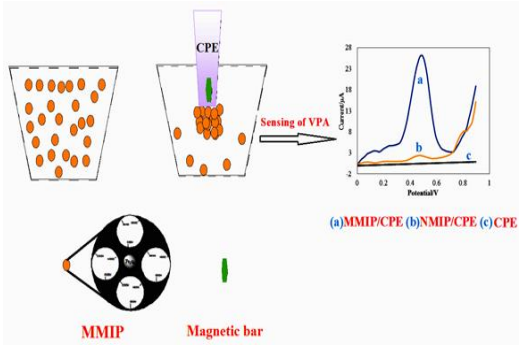
Abstract

In this work, the modified carbon paste electrode was prepared by the nano-sized magnetic molecularly imprinted polymer (MMIP) and utilized for electrochemical determination of valproic acid. The synthesized nano-MMIP was characterized by scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FT-IR). The resulted nano-sized compound was suspended in 0.1 M HCl and then collected on the surface of a carbon paste electrode via a permanent magnet, which was situated within the carbon paste electrode. The electrochemical performance of the valproic acid sensor was investigated by cyclic voltammetry and differential pulse voltammetry techniques. All parameters influencing the electrode performance, including pH, the amount of MMIP, and the immersion time, were evaluated and optimized. Under the optimal condition, the sensor showed a dynamic linear concentration range of 0.5 nM–150.0 µM with a detection limit of 0.16 nM.



Keywords: *Carbon paste electrode, Molecularly imprinted polymer, Valproic acid, Differential pulse voltammetry.*

Introduction

In order to have a constant development of more efficient drugs and control the quality of pharmaceutical preparations, drug analysis seems crucial. Moreover, the detection of drugs in biological fluids is important for pharmacokinetic studies and the clarification of therapeutic and toxic effects. Valproic acid (VPA; 2-propylpentanoic acid) is a C8- branched carboxylic acid and an anti-epileptic drug widely used for the treatment of seizure disorders.[1,2] It is one of the rampant antiepileptic drugs in different regions of the world, and it can be administered as either monotherapy or a part of polytherapy regimens comprising several antiepileptic drugs. Common antiepileptic drugs prescribed together with VPA in polytherapy include carbamazepine, topiramate, phenytoin, and lamotrigine.[3,4] Monitoring of VPA levels in patient serum or plasma is essential when there are changes in VPA dose, concomitant medication or clinical condition of patient.[5] Many analytical approaches have been used in determination of VPA. Gas chromatography,[6-8] liquid chromatography,[9-11] and capillary electrophoresis[12-14] are the main reported techniques for its determination. Electrochemical methods with their advantages of higher sensitivity, lower cost, and less interference by non-electroactive substances are preferable to the determination of VPA. During recent years there has been an increasing interest in the modification of electrode's surface with a molecularly imprinted polymer (MIP) to enhance selectivity.[15]

MIPs are synthetic materials with artificially generated recognition sites able to specifically rebind a target molecule in preference to other closely related compounds. MIP is a technique, in which a template is employed in order to facilitate recognition site formation during polymerization process. The subsequent removal of the template permits the recognition to occur in the spaces vacated by the template agents. This technique has attracted great interest because of its high selectivity (in terms of size, shape, and functionality) for target molecules.[16] MIPs have also features of easy preparation, low cost, high mechanical, and chemical stability.[17] Several polymer preparation methods have been developed such as bulk polymerization,[18-21] membrane polymerization,[22,23] precipitation polymerization,[24-26] and surface-grafting polymerization.[27-29] Magnetic separation technology, in which polymers are prepared by fabricating the MIP on the surface of a magnetic substrate, has received considerable attention in recent years for its superior characteristics such as small size, magnetic susceptibility, and functional modifications in various fields such as extraction, magnetic separation, catalysis, and

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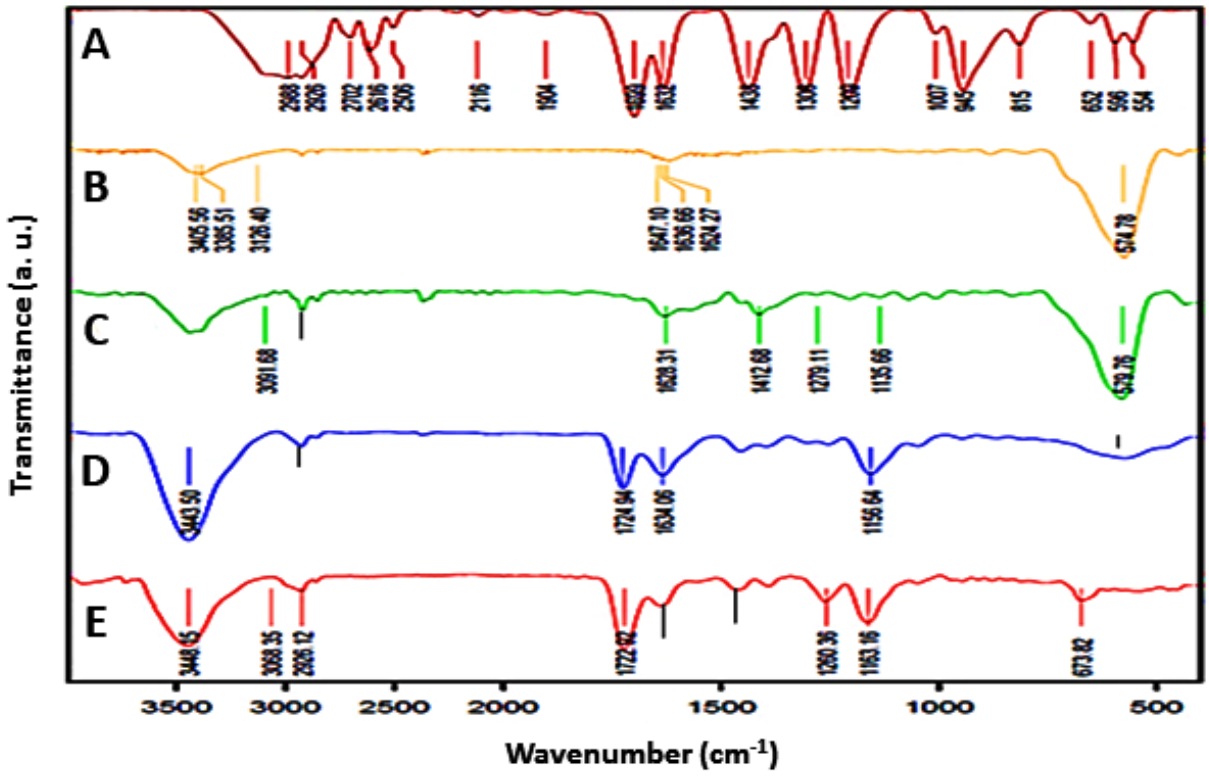

Figure 1. *FT-IR spectrums of* ***(A)*** *metacrylic acid,* ***(B)*** *magnetic nanoparticles,* ***(C)*** *magnetic nanoparticles modified with MMA,* ***(D)*** *magnetic nanoparticles modified with NIP, and* ***(E)*** *magnetic nanoparticles modified with MIP.*

sensors.[30-35] Magnetic nanoparticles carbon paste (CP) electrode, which was accomplished by either incorporation of the magnetic nanoparticles into carbon paste electrode or their attachment to the CP electrode surface via a permanent magnet, was deposited inside the CP electrode.[36-39] However, the combination of MMIP nanoparticles with a CP electrode has not been widely reported.

Herein, we synthesized the VPA–imprinted magnetic nanoparticles and by using synthesized nano–MMIP, modified CP electrode was constructed. The fabricated electrochemical sensor was successfully employed to detect the concentration of VPA. In the literature review, no report was found on the fabrication and application of the MMIP/CP for the detection of VPA concentrations.

Experimental

Material and reagents

All solutions were freshly prepared with double distilled water. VPA and graphite powder were purchased from Fluka (Buchs, Switzerland). Metacrylic acid (MAA), ethylene glycol diamethacrylate (EGDMA), $FeCl_3.6H_2O$ and all of the other reagents were of analytical grade and obtained from Merck (Darmstadt, Germany). Phosphate buffer (PB, 0.1 M) was prepared by mixing the stock solution of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4, and the pH was adjusted by NaOH or HCl. All electrochemical experiments were carried out at a room temperature.

Apparatus

Electrochemical studies such as cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a µ-AUTOLAB electrochemical system type III and FRA2 board computer controlled Potentiostat/Galvanostat (Eco–Chemie, Switzerland) driven with NOVA software in conjunction with a conventional three electrode system. A classical three-electrode system was used for all measurements; a MMIP-modified carbon paste electrode as the working electrode, an Ag/AgCl (KCl, 3.0 M) as the reference electrode and a platinum (Pt) wire as the auxiliary electrode were used. Scanning electron microscopic (SEM) images of the modified surfaces were acquired using a Vega–Tesacn electron microscope. The infrared spectra were recorded on VERTEX 70 FT–IR spectrometer in the range of 400–4000 cm^{-1} using KBr pellets.

Preparation of magnetic nanoparticles

For the production of magnetic nanoparticles a mixture of 10.0 mL of $FeCl_3.6H_2O$ solution (1.0 M) and 2.5 mL of $FeSO_4.7H_2O$ solution (2.0 M) was gently added to 120.0 mL of NH_3 solution (0.7 M) within 30 minute under nitrogen atmosphere. The solution was stirred mechanically during synthesis stage. After 24 h stirring, the precipitate was isolated by magnetic force. To remove unreacted chemicals the precipitate was washed three times with water then diluted with 150 mL doubly distilled water.

Preparation of modified magnetic nanoparticle

To produce the magnetic VPA–imprinted polymer, the surface of the previously produced magnetic nanoparticles was first modified with MAA. To do this, 0.5 gr of magnetic nanoparticles was solved in 10.0 mL acetonitrile by ultrasonicating. Then, 2 mL of MAA was added to the mixture and shaken for 24 h. After that, the precipitant was separated from the solution and cooled be used at the next stage.

Table 1. *Comparison of the performances of various methodes for the determination of valproate.*

Method	linear range	Detection limit	Ref.
Sol–gel sensor	1.0–50.0 mM	5.0 µM	[43]
RP[a]–HPLC	50–100 µg/mL	0.8 µg/mL	[44]
Solid–state valproate ion–selective	40.0 µM–0.4 M	10.0 µM	[45]
GC[b]	50.0–100.0 mg/L	8.0 µg/mL	[46]
Electrochemical sensor	0.5 nM–150.0 µM	0.16 nM	This work

[a] RP: Revers Phase
[b] GC: Gas Chromatography

Preparation of magnetic VPA-imprinted polymer

In order to prepare the magnetic VPA-imprinted polymer, 0.7 g of 2, 2′-azobisisobutyronitrile (AIBN) was dispersed in 10.0 mL acetonitrile which has been mixed with 1.0 mmol of VPA, 1.6 mL MAA, and 2.5 mL EGDMA. The prepared mixture was added to 0.9 g of magnetic modified nanoparticles which dispersed in 20.0 mL acetonitrile by ultrasonicating for 10 minutes. Then, it was put in a water bath fixed at 60 ˚C. After the completion of the polymerization reaction (24 h), the magnetic MIP was separated by external magnet and washed several times with ethanol to remove template from MMIP. The Preparing of the non-imprinted polymer (NIP) is similar to the MIP, but the template was not present in the polymerization media.

Preparation of the magnetic CP electrode

To prepare the magnetic CP electrode, 80.0 mg graphite powder and 50.0 µL paraffin oil were mixed. Then a plastic tube with 3 cm depth and a given surface area was filled with the prepared CP and a magnetic bar was put in the 0.05 cm depth of the tube. The filled tube with CP was connected to the copper wire for electrical connection. Before each measurement, the surface of the modified electrode was smoothed on a paper sheet to produce a thin layer. In the following the prepared electrode was immersed in the solution of 40.0 mg/mL MMIP for 10.0 minutes. In this step MMIP by the magnetic force adsorbed to the surface of the CP electrode. The prepared electrode was denoted as MMIP/CPE.

Preparation of real samples

Some human blood serum samples were ordered from a local clinical laboratory and were stored frozen before use. In order to obtain the proper sample, methanol (2.0 mL) was added to 1.5 mL of serum sample for protein separation. After the vortexing the serum sample for 2 min, the precipitated proteins were separated by centrifugation (5 min at 5000 rpm). Afterwards, the serum sample was diluted 5 times with HCl (0.1 M) and different concentrations of VPA were spiked to the diluted serum sample. The standard addition method was used for the determination of VPA in serum samples

Results and discussion

FT-IR study

To prepare the MMIP, the surface of Fe_3O_4 nanoparticles was modified with methacrylic acid. In this stage the methacrylic acid has been attached to the MNPs surface using –COOH groups through covalent bonds. Subsequently, the valproate has been supported on the modified nanoparticles which form a polymeric layer on the nanoparticles.

Figure 1A shows the FT–IR spectrum of MAA that was specified with broad band at 2500–3500 cm^{-1} indicates acidic O–H groups, the peak at 1632 cm^{-1} indicates stretching of C=O and the peaks that appear at 1438 and 1699 cm^{-1} reveal C=C stretching vibrations.

Figure 1B shows the FT–IR spectrum of Fe_3O_4 nanoparticles. The peak at 574 cm^{-1} can be attributed to the Fe–O stretching vibrations and the broad band at 3200–3389 cm^{-1} was the characteristic of O–H stretching vibration of Fe–OH or the absorbed H_2O on the surface of MNPs. The peak at 1620 cm^{-1} indicates the physical absorption of H_2O on iron oxide.[40-42]

Figure 1C shows the FT–IR spectrum of Fe_3O_4 nanoparticle modified with MAA. The peak at 579 cm^{-1} exhibited vibrations of Fe–O band and the peaks in 1413 and 1629 cm^{-1} indicates C=C stretching vibrations. Furthermore, the peak at 2926 cm^{-1} is related to C–H stretching vibration. The immobilized MMA on the surface of MNPs was characterized by stretching vibration at 1629 cm^{-1} and refers to C=O stretching which was shifted to lower frequency from

Table 2. *The effect of interfering compounds on the recovery of 100 nM, of valproate (n=4).*

Interfering compounds	Concentration of interfering compounds (mM)	Recovery(%)
captopril	1.0	99.5 ± 0.2
mefenamic acid	1.0	98.7 ± 0.3
pantoprazole	1.0	99.8 ± 0.3
ascorbic acid	1.0	99.3 ± 0.1
uric acid	1.0	99.1 ± 0.2
cadmium	1.0	100.1 ± 0.2
copper	1.0	98.8 ± 0.1
potassium	1.0	100.2 ± 0.3

1699 cm^{-1} to 1629 cm^{-1}. All of these results reveal that the surface of Fe_3O_4 nanoparticles is successfully modified with MMA.

Figure 1D shows the FT–IR spectrum of NIP–Fe_3O_4. The peaks at 1454 and 1634 cm^{-1} indicate C=C stretching vibrations. The peaks at 2928 and 1724 cm^{-1} indicates C–H and C=O stretching vibrations, respectively. Furthermore the peak at 573–700 cm^{-1} indicates vibrations of Fe–O, respectively.

Figure 1E shows the FT–IR spectrum of MIP–Fe_3O_4. The comparison of MIP and NIP spectrum shows that the two spectrums are not very different. The peaks that are evident in the spectrum, the 3448 cm^{-1} indicates O–H or H_2O which exist on the surface of Fe_3O_4. The peak at 2926 cm^{-1} indicates C–H stretching vibrations. The peak at 1722 cm^{-1} indicates the C=O stretching vibrations. The peaks at 1461 and 1638 cm^{-1} indicate C=C.

Morphologies study

Figure 2 shows the SEM images of magnetic nanoparticles (A), magnetic nanoparticles modified with MAA (B) and MMIP (C). As it can be seen the average diameter of synthesized magnetic nanoparticles are in the range of 20 to 50 nm, with a regular spherical shape. After the imprinting process, the surface of the synthesized polymers was rough and porous. The differences in surface characteristics suggest the magnetic nanoparticles were successfully coated with a polymer layer.

Electrochemical behavior of valproate on the modified carbon paste electrode

The preliminary study on the electrochemical behavior of valproate in PB solution (pH=1.0) on the modified carbon paste electrode was performed by cyclic voltammetry in the potential range from 0.0 to +1.0 V (*vs*. Ag/AgCl). As it can be seen, an oxidation peak at around +0.5 V with cathodic peak at around +0.4 V on the reverse scan was observed (Figure 3A). This oxidation peak was selected as an analytical response for the determination of valproate.

Figure 3B shows the DPVs of (a) bare carbon paste (CP), (b) MMIP/CP, and (c) MNIP/CP electrodes in supporting electrolyte containing 100.0 nM VPA. In the following determination and measuring of valproate carried out by the using of DPV technique. As shown in Figure 3B the resulting peak current at the MMIP modified electrode was sharper and stronger than that of the electrode modified with the NIP, revealing the existence of selective binding sites involved in the MMIP. Thus, the MIP as a selective recognition element was used in the fabrication of the sensor.

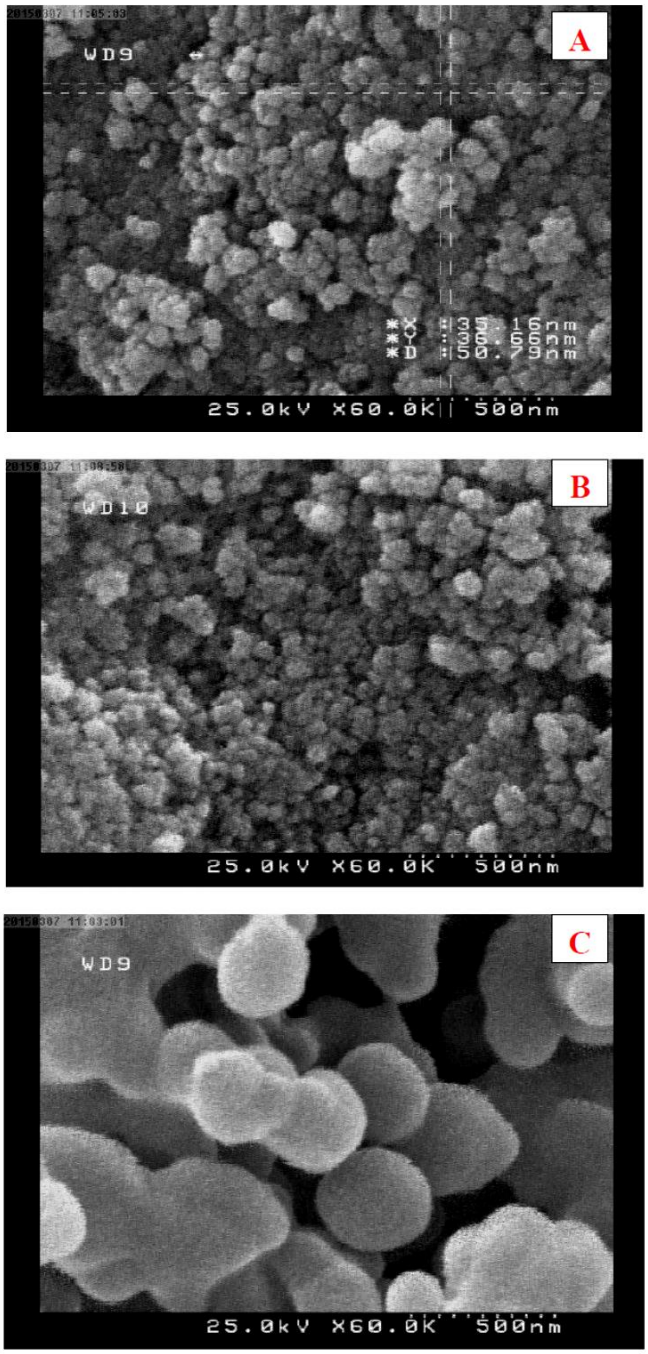

Figure 2. *SEM images of* ***(A)*** *magnetic nanoparticles, magnetic nanoparticles modified with* ***(B)*** *MAA and* ***(C)*** *MMIP.*

Table 3. *Determination of valproate in human blood serum (n=3).*

Sample	Added (nM)	Founded (nM)	RSD(%)	Recovery(%)
Sample 1	50.0	51.92	2.14	103.8
Sample 2	100.0	102.81	3.13	102.8

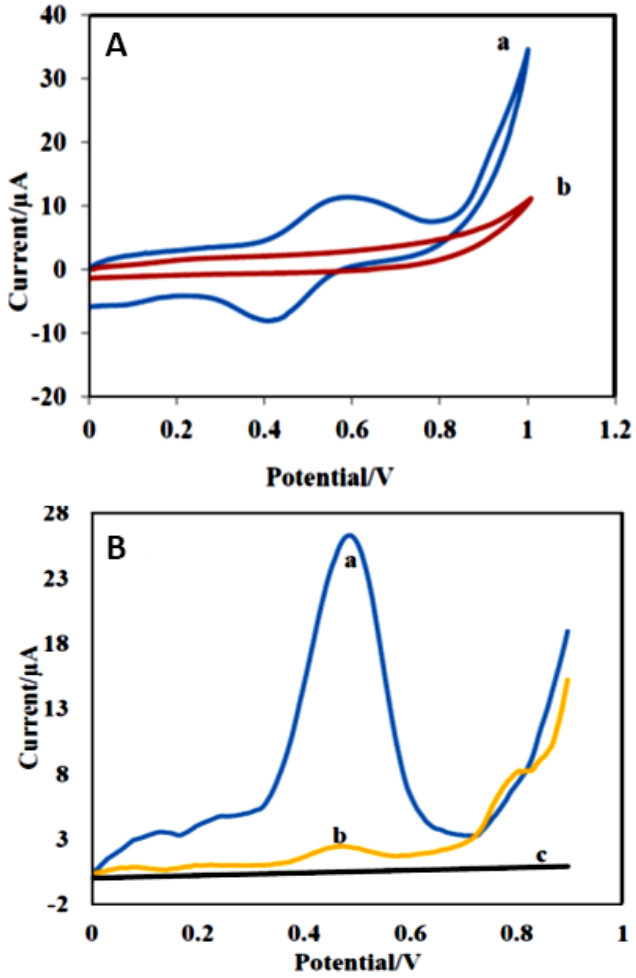

Figure 3. (A) *CVs recorded in pH = 1.0 containing 10.0 µM VPA for (a) MMIP/CPE and (b) bare CP electrode, scan rate: 50 mVs^{-1}.* ***(B)*** *DPV recorded for (a) MMIP/CPE, (b) NIP/CPE, and (c) bare CPE in pH = 1.0 containing 100.0 nM VPA.*

Effect of the MMIP amount and immersion time

The effect of the amount of MMIP on the properties of the resulting modified electrode was examined by DPV technique (Figure 4A). The inset of Figure 4A shows that the oxidation current for 50.0 nM VPA increased gradually with increasing MMIP amount in the range 3–20 mg and decreased when the MMIP amount is higher than 20 mg. The increasing of MMIP amount provides more binding sites for stabilization of the VPA on the surface of the electrode which in turn increases the signals. After 20 mg, with increase of the MMIP amount to 40 mg the oxidation current of the VPA decreases. This shows that the surface of the electrode has saturated with the increasing of MMIP, therefore, the oxidation current has decreased. So, 20 mg was used as the best amount of MMIP in all of the following experiments.

The effect of the immersion time of CP electrode in MMIP solution was also studied as a function of time, in the 4–15 min interval (Figure 4B). The results showed that the peak current increased by increasing the immersion time until 10 min, while for immersion times longer than 10 min, the changes in the current intensity is insignificant (inset of Figure 4B). Therefor, 10 min is selected as the best time for the immersion of electrode in MMIP solution.

The effect of supporting electrolyte

In order to investigate the effect of supporting electrolyte on the electrochemical behavior of VPA at the modified electrode, the effect of supporting electrolyte on the oxidation peak current was investigated by DPV. Various electrolytes such as HCl, sodium nitrate, and sodium acetate were tested as a supporting electrolyte. On the basis of the achieved results of these tested electrolytes, 0.1 M HCl gave the best response and was selected as a suitable electrolyte for all of the electrochemical experiments (Figure 5A).

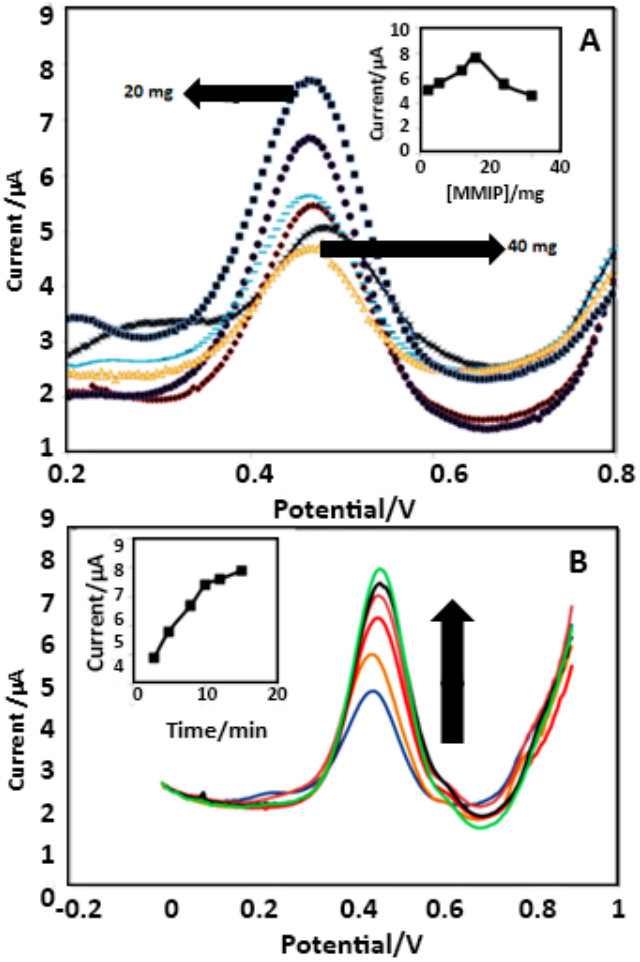

Figure 4. (A) *DPV recorded for 50.0 nM VPA at MMIP/CPE in pH = 1.0 at various amounts of MIP (3 to 40 mg) in modification stage of electrode. The inset shows the plot of DPV response versus amount of MIP.* ***(B)*** *DPV recorded for MMIP/CPE at various immersion times (3 to 15 min) in valproate solution. The inset shows the plot of DPV response versus immersion time.*

Analytical characteristics

In order to demonstrate the determination sensitivity, DPV was used to record the oxidation peak currents of VPA at the modified electrode. Figure 5B shows the DPV response of the sensor to various concentration of VPA into the PB. It can be seen that an increase in valproate concentration is accompanied by an increase in oxidation peak current. The plots of the currents vs. VPA concentration are shown in insets of Figure 5B. Linear ranges of 0.5 nM–150.0 µM were obtained for VPA determination. The linear regression equation was expressed as:

$$Ip(\mu A) = 0.2922[VPA](nM) + 0.0606 \quad (1)$$

with the correlation coefficient of 0.9951. The lower detection limit, C_m, was obtained using the equation

$$C_m=3s_{bl}/m \quad (2)$$

where s_{bl} is the standard deviation of the blank response (µA) and m is the slope of the calibration plots. In this experiment the sensitivity and detection limit were estimated 0.29 µA/nM and 0.16 nM, respectively.

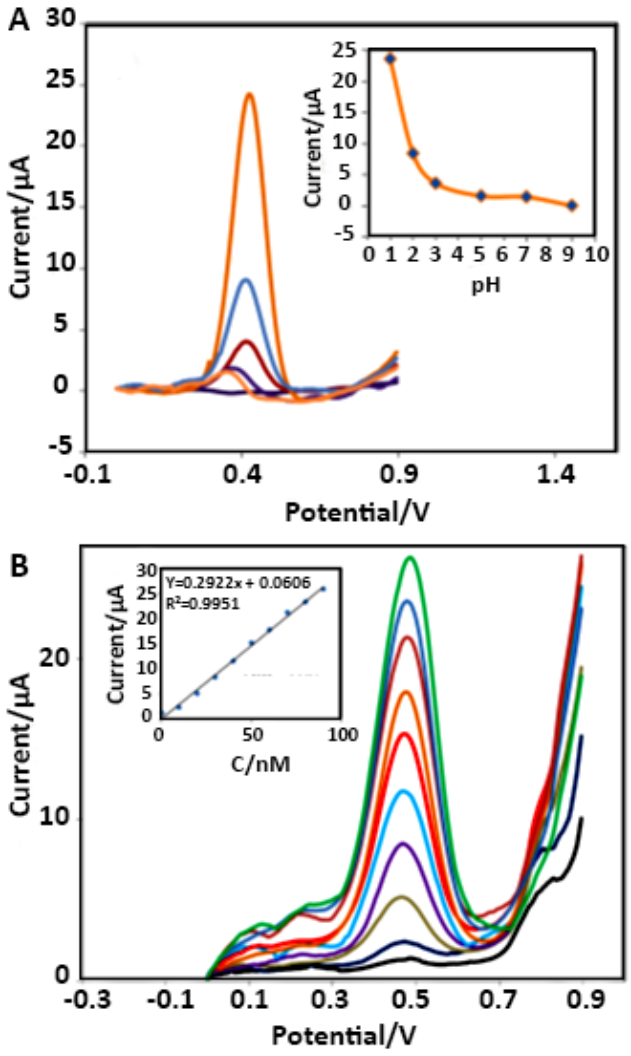

Figure 5. (A) *DPV recorded for MMIP/CPE in supporting electrolyte at various pH values (1, 2, 3, 5, 7 and 9). The inset shows the plot of DPV response versus pH values.* ***(B)*** *DPV recorded for MMIP/CPE in pH = 1.0 at various concentrations of VPA (0.5 to 90.0 nM). The inset shows the plot of DPV response versus VPA concentration.*

In Table 1, the performance of the developed method is compared with other methods used for valproate determination. As it is obvious, the performance of the MMIP sensor is superior to the reported methods in terms of the linear range and detection limit.

The Interference effect

To investigate the selectivity of the modified CP electrode, the possible interferents, namely, captopril, mefenamic acid, pantoprazole, ascorbic acid (AA), uric acid (UA), cadmium (Cd^{2+}), copper (Cu^{2+}), and potassium (K^{+}) were examined. As a general rule, if the relative error in the determination was controlled at approximately ±5% that it could be considered to have no interference. The interfering effect of 1.0 mM of each interferon compared to 100.0 nM VPA was evaluated. The results were shown in the Table 2. It can be seen that a very good selectivity is achieved.

The Application in Real sample analysis

To illustrate feasibility of the proposed sensor in practical analysis, MMIP/CP electrode was used to detect VPA concentration in human blood serum sample solutions by using DPV technique under optimized conditions. Each sample was measured in triplicate. The results are summarized in Table 3. The recovery values are 102.8 to 103.8%, thereby validating the usefulness of the MMIP/CP electrode for practical analysis.

Conclusion

In this work, a novel electrochemical sensor for the selective and sensitive voltammetry determination of valproate was constructed. The developed sensor has a good performances such as low detection limit and wide linear. One of the advantageous of MMIP/CP electrode is easy to fabricate.

Acknowledgment

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