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Screen-printed Electrodes Modified with Magnetic Core–Shell Nanoparticles Film for the Development of a Sensor for Imipramine Detection

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Abstract- In the present study, a novel electrochemical sensor involving magnetic core shell nanoparticles (MCSNP) was developed for the detection of imipramine. The screen-printed electrode (SPE) with several advantages, including low cost, versatility and miniaturization was employed. On the other hand, the magnetic core shell nanoparticles were casted on the surface of SPE to obtain MCSNP/SPE. The proposed nanosensor has excellent performance such as high sensitivity and analytical application in real samples. The combination of MCSNP with the SPE is favorable for amplifying electrochemical signals. Under optimized conditions, square wave voltammetry exhibited linear dynamic ranges from 1.0×10^{-6}– 2.0×10^{-4} M with detection limit of 1.8×10^{-7} M.

Keywords- Imipramine determination, Magnetic core shell nanoparticles, Screen-printed electrode

1. INTRODUCTION

Nowadays, certain pharmaceuticals are attracting attention as a potentially-new class of water pollutants. These compounds that are synthetically-manufactured produce highly-toxic chemicals that not only affect the health of human beings but also potentially compromise the health of aquatic organisms [1,2]. Tricyclic antidepressants (TCAs) are one of the groups of

these drugs that are used as the reference for the treatment of psychiatric disorders, mainly, major depressions [3]. Imipramine is 10, 11 dihydro-N,N-dimethyl-5Hdibenz[b,f]azepine-5-propanamine and is often referred to as tricyclic antidepressant [4]. Studies have indicated that the efficacy of this drug in alleviating depression at night is due to the enhancement of noradrenergic activity through the blockage of norepinephrine reuptake in blocking peripheral and central noradrenergic system [5]. Apart from its therapeutic effect it may cause negative side effects such as: convulsions, parasthesia, hallucinations, delusions, tachycardia or arythmia [6]. Therefore, choosing the proper therapeutic dose is one of the most important elements of a treatment. Therefore, measurement of these compounds in water, especially, wastewater of pharmaceutical factories, can be important for a variety of purposes such as prevention of the entrance of these drugs into the environment [7].

A survey of the literature reveals that there are various methods available for the determination of imipramine including spectrophotometry [8], spectrofluorimetry [9], potentiometry with an ion-selective electrode [10], voltammetry [11], amperometry [12], liquid chromatography [13], capillary electrophoresis [14], atomic absorption spectrometry [15] and chemiluminescence [16]. Electrochemical methods are more desirable than other techniques because they are convenient and low cost.

The screen-printed electrodes (SPEs) have been designed especially for miniaturization of electrochemical analytical systems [17]. SPEs are highly-versatile, easy to use, cost-effective analytical tools, also suitable to miniaturization [18]. Furthermore, a screen printed electrode avoids the cleaning process, unlike conventional electrodes such as a glassy carbon electrode (GCE) [19].

In order to improve their electrochemical performance, SPEs have been modified with nano sized materials [20-22]. The modified electrode has good electro catalytic activity, sensitivity, and selectivity; it has also a low detection limit compared to unmodified electrodes [23–26]. Nanostructures modified electrodes have been adopted as a promising way to facilitate the direct electron transfer of biomolecules [27-35].

From both fundamental and industrial points of view, many different synthetic procedures have been developed for the preparation of metal nanoparticles (NPs). Nanoscale materials are attractive targets because, due to their large surface-to-volume ratio, they exhibit properties that can be significantly different from those of bulk materials [36].

Various nanomaterials for the modification of electrode surfaces, response signal enhancement, increased sensitivity and better reproducibility have been reportedin recent years [37-48]. More recently, magnetic nanoparticles (MNPs) have received increasing attention in virtue of their high surface-to-volume ratios -that enables a high density of chemical to bind- and their excellent magnetic properties, which allow the direct capture and easy separation and concentration of targets in complex samples in an external magnetic field [49].

In the present work, we synthesized magnetic core-shell manganese ferrite nanoparticles (MCSNP) [50] and screen printed electrodes were modified with MCSNP. To the best of our knowledge, no study has been reported so far on the determination of imipramine by using magnetic core-shell manganese ferrite nanoparticles -screen printed electrodes (MCSNP/SPE).

2. EXPERIMENTAL

2.1. Apparatus and Chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System software. Screen printed electrodes were purchased from Italsens Co. A Metrohm 710 pH meter was used for pH measurements.

Imipramine hydrochloride and all the other reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany). The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–9.0. Magnetic core-shell manganese ferrite nanoparticles were synthesized in our laboratory as reported previously [51].

2.2. Preparation of the Electrode

The bare screen-printed electrode was coated with MCSNP as follows. A stock solution of MCSNP in 1 mL aqueous solution was prepared by dispersing 1 mg MCSNP with ultrasonication for 1 h, and a 2 µL aliquot of the MCSNP/H_2O suspension solution was casted on the carbon working electrodes, waiting until the solvent was evaporated in room temperature.

2.3. Preparation of Real Samples

Ten tablets of imipramine (labeled 25 mg per each tablet) were completely ground and homogenized; 200 mg of this powder was accurately weighed and dissolved with ultrasonication in 10 mL of water. Finally the mixture was filtered and the clear filtrate was transferred into a 25 mL volumetric flask and diluted to the mark using 0.1 mol L^{-1} PBS pH 7. Finally, a suitable volume of the resultant solution was transfer to electrochemical cell and the resulting solution was used for the analysis of imipramine. The sample was spiked with different amounts of imipramine and contents were analyzed by using the standard addition method in order to prevent any matrix effect. The amount of unknown imipramine in the tablet can be detected by extrapolating the plot.

Urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 15 min at 2000 rpm. The supernatant was filtered out using a

0.45 µm filter. Then, different volume of the solution was transferred into a 25 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The diluted urine sample was spiked with different amounts of imipramine. The imipramine contents were analyzed by the proposed method using the standard addition method in order to prevent any matrix effect.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of imipramine at the surface MCSNP/SPE

The electrochemical behavior of imipramine is dependent on the pH value of the aqueous solution. Therefore, pH optimization of the solution seems to be necessary in order to obtain the best results for electrooxidation of imipramine. Thus the electrochemical behaviors of imipramine were studied in 0.1 M PBS in different pH values (2.0–9.0) at the surface of MCSNP/SPE by voltammetry. It was found that the electro-oxidation of imipramine at the surface of MCSNP/SPE was more favored under neutral conditions than in acidic or basic medium. Thus, the pH 7.0 was chosen as the optimum pH for electro-oxidation of imipramine at the surface of MCSNP/SPE.

Fig. 1 depicts the CV responses for the electro-oxidation of 25.0 µM imipramine at an unmodified SPE (curve a) and MCSNP/SPE (curve b). The peak potential due to the oxidation of imipramine occurs at 515 mV, which is about 95 mV more negative than that of unmodified SPE.

Also, MCSNP/SPE shows much higher anodic peak current for the oxidation of imipramine compared to unmodified SPE, indicating that the modification of unmodified SPE with MCSNP has significantly improved the performance of the electrode toward imipramine oxidation.

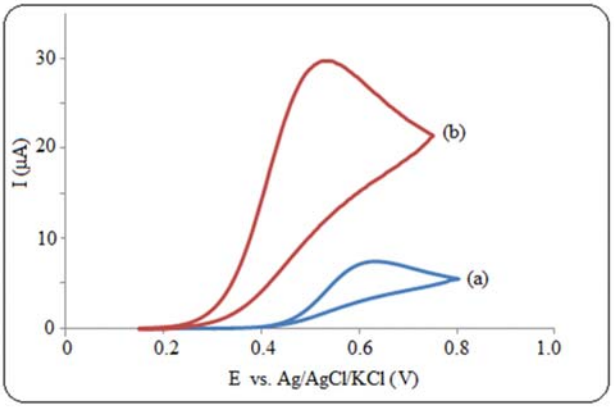

Fig. 1. Voltammograms of (a) unmodified SPE and (b) MCSNP/SPE in the presence of 25.0 µM imipramine at pH 7 (at 50 mV s^{-1})

3.2. Effect of Scan Rate

The effect of potential scan rates on the oxidation current of imipramine (Fig. 2) has been studied. The results showed that increasing in the potential scan rate induced an increase in the peak current. In addition, the oxidation processes are diffusion controlled as deduced from the linear dependence of the anodic peak current (I_p) on the square root of the potential scan rate ($\nu^{1/2}$).

Tafel plot was drawn from data of the rising part of the current voltage curve recorded at scan rate of 50 mVs^{-1} for imipramine (Fig. 3).

This part of voltammogram, known as Tafel region, is affected by electron transfer kinetics between substrate (imipramine) and MCSNP/SPE. Tafel slope of 0.1336 V was obtained which agree well with the involvement of one electron in the rate determining step of the electrode process [51] assuming charge transfer coefficients, α=0.56 for imipramine.

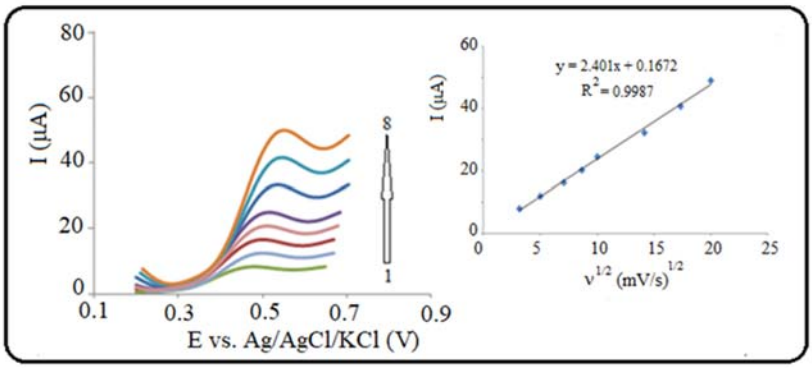

Fig. 2. LSVs of MCSNP/SPE in 0.1 M PBS (pH 7.0) containing 10.0 µM imipramine at various scan rates; numbers 1-8 correspond to 10, 25, 50, 75, 100, 200, 300 and 400 mV s^{-1}, respectively. Inset: Variation of anodic peak current *vs*. square root of scan rate

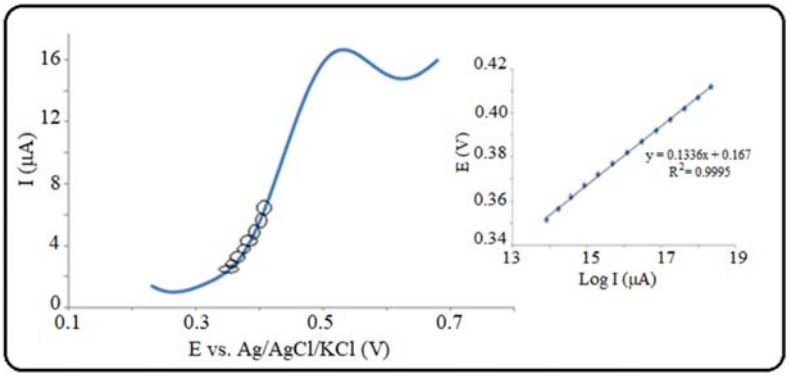

Fig. 3. Tafel plot derived from LSV of MCSNP/SPE in 0.1 M PBS (pH 7.0) containing 10.0 µM imipramine at scan rate of 50 mV/s

3.3. Chronoamperometric Measurements

Chronoamperometric measurement of imipramine at MCSNP/SPE was carried out by setting the working electrode potential at 0.6 V *vs*. Ag/AgCl/KCl (3.0 M) for the various concentrations of imipramine (Fig. 4) and in PBS (pH 7.0). For electroactive materials (imipramine) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation [51]:

$$I = nFAD^{1/2} C_b \pi^{-1/2} t^{-1/2} \quad (1)$$

where D and C_b are the diffusion coefficient (cm^2 s^{-1}) and the bulk concentration (mol cm^{-3}), respectively. Experimental plots of I *vs*. $t^{-1/2}$ were employed, with the best fits for different concentrations of imipramine (Fig. 4a). The slope of the resulting straight lines was then plotted *vs*. imipramine (Fig. 4b) concentrations. From the resulting slope and Cottrell equation the mean value of the D was found to be 2.6×10^{-6} cm^2/s for imipramine.

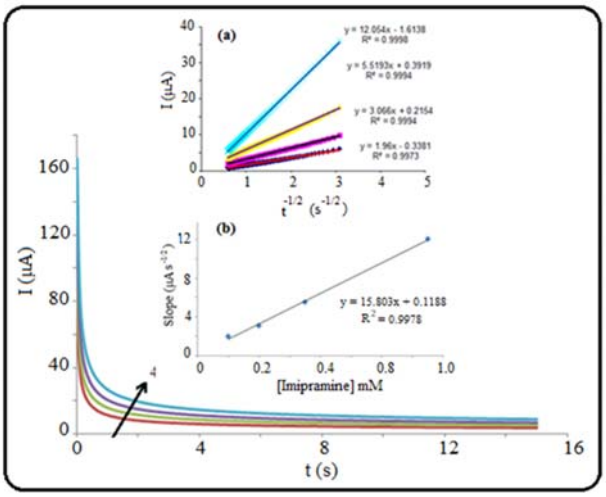

Fig. 4. Chronoamperograms obtained at MCSNP/SPE in 0.1 M PBS (pH 7.0) for different concentration of imipramine. The numbers 1–4 correspond to 0.1, 0.2, 0.25 and 0.75 mM of imipramine. Insets: Plots of I *vs*. $t^{-1/2}$ obtained from chronoamperograms 1–4 (a), and Plot of the slope of the straight lines against imipramine concentration (b)

3.4. Calibration plots and limits of detection

The electro-oxidation peak current of imipramine at the surface of the MCSNP/SPE can be used for determination of imipramine in solution. Since, square wave voltammetry (SWV) has the advantage of an increase in sensitivity and better characteristics for analytical applications, therefore, SWV experiments were performed using MCSNP/SPE in 0.1 M PBS containing various concentrations of imipramine (Fig. 5). The results show the

electrocatalytic peak currents of imipramine oxidation at the surface of MCSNP/SPE was linearly dependent on the imipramine concentrations, over the range of 1.0×10^{-6}–2.0×10^{-4} M (with a correlation coefficient of 0.9959) and the detection limit (3s) was obtained 1.8×10^{-7} M. These values are comparable with values reported by other research groups for determination of imipramine (Table 1).

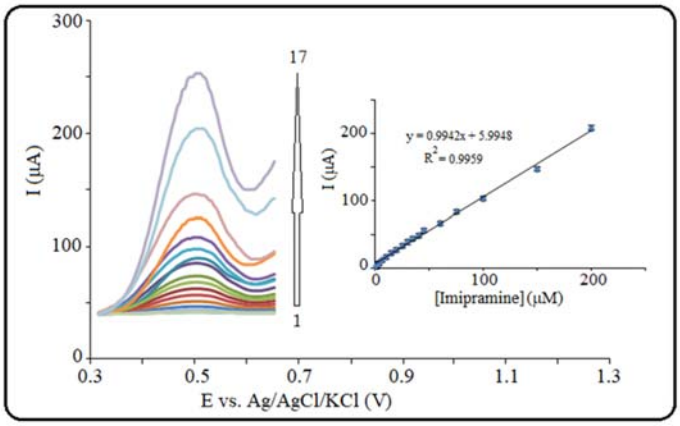

Fig. 5. SWVs of MCSNP/SPE in 0.1 M PBS (pH 7.0) containing different concentrations of imipramine (1.0, 2.0, 4.0, 6.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 60.0, 75.0, 100.0, 150.0 and 200.0 μM) Inset: The plot of the peak current as a function of imipramine concentration in the range of 1-200 μM

Table 1. Comparison of some characteristics of the different methods for the determination of imipramine

Method	**Modifier**	**Detection limit (M)**	**Linear dynamic range (M)**	**Ref.**
electrochemical sensor	Au nanoparticles with a thin molecularly imprinted film	1×10^{-9}	5×10^{-6}- 1×10^{-3}	[52]
DNA-based electrochemical biosensor	DNA	5×10^{-10}	5×10^{-9}-5×10^{-8}	[53]
Flow-injection pulse amperometric detection	------	4.2×10^{-7}	1×10^{-6}–1.0×10^{-4}	[54]
capillary electrophoresis with electro-chemiluminescence detection	------	5×10^{-9}	1×10^{-7}-5×10^{-6}	[55]
electrochemical sensor	magnetic core–shell nanoparticles	1.8×10^{-7}	1.0×10^{-6} – 2.0×10^{-4}	This Work

3.5. Real Sample Analysis

Finally, MCSNP/SPE was applied for determination of imipramine in imipramine tablet, and urine samples. For this purpose, the determination of imipramine in the real samples was carried out by using standard addition method to prevent any matrix effects. The results are shown in Table 2. Also, the recovery of imipramine from samples spiked with known amounts of imipramine was studied. The results were showed that, the added imipramine was quantitatively recovered from the real samples. These results demonstrate the applicability of the MCSNP/SPE for determination of imipramine in the real samples. Also, the reproducibility of the method was demonstrated by the mean relative standard deviation (RSD).

The amount of imipramine in tablet was found to be 24.7 mg per each tablet. It was found that there is no significant difference between the result obtained by the MCSNP/SPE and the nominal value on the tablet label (25.0 mg). The t-test was applied to the results and showed that there was no significant difference at the 95% confidence level.

Table 2. The application of MCSNP/SPE for determination of imipramine in real samples (n=5)

Sample	Spiked (µM)	Found (µM)	Recovery (%)	R.S.D. (%)
Imipramine tablet	0	14.7	---	2.8
	5.0	19.8	102.0	2.3
	10.0	24.6	99.0	3.3
	20.0	34.9	101.0	2.1
Urine	0	ND[a]	---	---
	5.0	4.9	98.0	3.2
	10.0	10.2	102.0	2.7
	20.0	19.7	98.5	2.2

[a] Not detected

4. CONCLUSION

In this work, employing magnetic core shell nanoparticles as modifier in modification of SPEs, a novel sensor has been developed that provides a sensitive method for the determination of imipramine. The proposed protocol demonstrated herein a novel, simple, portable, inexpensive and easy-to-use fabrication method for the measurement of imipramine concentration in tablet and urine samples with good analytical performance. Due to the unique properties of magnetic core shell nanoparticles, the sensor exhibited remarkable electrochemical activity toward the oxidation of imipramine. Under optimized conditions,

square wave voltammetry exhibited linear dynamic ranges from 1–200 μM with detection limit of 0.18 μM.

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