

Electrochemical behavior of Morphine at the surface of magnetic core shell manganese Ferrite nanoparticles modified screen printed electrode and its determination in real samples

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Abstract

In the present work, a new sensor for morphine (MO) measurement, based on modification of screen-printed carbon electrode (SPE) by using magnetic core shell manganese ferrite nanoparticles was reported. The electrochemical behaviour of MO was investigated in phosphate buffer solution (pH 7.0) by voltammetry. The electrochemical response of the modified electrode toward morphine was studied by means of cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CHA). The modified electrode displayed a decrease in the overpotential (ca. 80 mV) and an obvious increase in the peak current was observed compared to the non-modified SPE. The results indicated that modified screen-printed electrode enhanced electrocatalytic activity towards the oxidation of MO. Under the optimized conditions the calibration curve for MO was linear from 0.1 – 600.0 μM and the detection limit based on $3S_b/m$ was 0.02 μM . The application of the proposed method in analysis of real sample was also evaluated and satisfactory results were obtained.

Keywords: Magnetic Core Shell Nanoparticles; Modified Electrode; Morphine Determination; Screen-Printed Carbon Electrode; Voltammetry.

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INTRODUCTION

Morphine (MO, IUPAC name: (5 α , 6 α)-7, 8-didehydro-4, 5-epoxy-17-methylmorphinan-3, 6-diol) is a strong opioid used for the treatment of moderate to severe pain. Morphine, a phenolic compound is an alkaloid, which can cause disruption in the central nervous system, is frequently used to relieve severe pain in patients, especially that undergoing surgical procedure [1]. However, its use is associated with adverse effects including sedation, nausea, constipation, respiratory depression, and development of tolerance as well as dependence [2]. On the other hand, it is toxic in excess and when abused. Thus, the development

of convenient, rapid and sensitive analytical methods for the determination of MO in human urine samples, has gained great importance. The most common analytical techniques currently used include high-performance liquid chromatography [3], gas chromatography [4], electrophoresis with electrochemical detection [5], chemiluminescence [6], radioimmunoassay [7], sequential injection analysis [8], surface plasmon resonance [9], and electrochemical methods [10-20].

Electrochemical methods are generally fast and economical in trace analysis. Compared with other analytical techniques, electrochemical analysis has the advantages of simplicity and high sensitivity [20]. The use of bare unmodified

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electrodes as an electrochemical sensors for morphine detection has a number of limitations such as low sensitivity and reproducibility, slow electron transfer reactions, low stability over a wide range of solution compositions and high overpotential at which the electron transfer process occurs and some of them are not sensitive enough for real sample analysis. The chemical modification of inert substrate electrodes with redox active thin films offers significant advantages in the design and development of electrochemical sensors. Different modified electrodes have been used for electrooxidation of morphine [21, 22].

Nanomaterials, because of their unique properties, have been extensively developed. Nanoparticles can act as conduction centers facilitating the transfer of electrons and provide great catalytic surface areas [23-27]. Among them, nanosized metal particle modified electrodes have emerged as a promising alternative for the electroanalysis of organic and inorganic compounds [28-31]. Metal nanoparticles have some distinct advantages such as higher mass transport, lower influence of the solution resistance, low detection limit, and better signal-to noise ratio over the conventional macroelectrodes [32-35].

The development of screen-printed electrodes (SPEs) has become a major revolution in the construction of electrochemical sensors/biosensors [36]. The SPEs have been designed especially for miniaturization of electrochemical analytical systems [37]. SPEs are highly-versatile, easy to use, cost-effective analytical tools, and also suitable to miniaturization [38]. Furthermore, a SPE avoids the cleaning process, unlike conventional electrodes such as a GCE [39].

In the present work, we synthesized magnetic core-shell manganese ferrite nanoparticles (MCSNP) [40] and screen printed carbon electrodes were modified with MCSNP. To the best of our knowledge, no study has been reported so far on the determination of morphine by using MCSNP/SPCE.

EXPERIMENTAL

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. The screen-printed electrode (DropSens, DRP-C110, Spain) consists of three main parts which are a counter electrode, a silver pseudo-reference electrode and a working electrode. A Metrohm 710 pH meter was used for pH measurements.

Morphine hydrochloride and all the other reagents were analytical grade and obtained from Merck (Darmstadt, Germany). The phosphate buffer solutions (PBS) were prepared from orthophosphoric acid and its salts in the pH range of 2.0-9.0.

Synthesis of MCSNP

Magnetic core-shell manganese ferrite nanoparticles were synthesized in our laboratory as reported previously [40]. Briefly, 4.90 g manganese nitrate and 13.4 g iron nitrate was dissolved in 50 mL distilled water and added to an aqueous solution of 4.2 g NaOH in 70 mL distilled water and 3 mL ethylene diamine. This solution was heated to 85 °C for 1 h to achieve complete chelation. The precipitate was filtered, dried 10 h at 80 °C, and calcined in an alumina crucible at 500 °C for 1 h, starting from 30 °C with a heating rate of 10 °C min⁻¹.

Two gram manganese ferrite nanoparticle and 4 mL (3-aminopropyl) trimethoxy silane were poured into 20 mL of a mixture of water, ethanol and Triton X-114 (6 : 3 : 1) and mixed for 24 h at 25 °C. The precipitated magnetic core-shell nanoparticles were filtered (Whatman Glass Microfiber Filter, 0.7 μm, 4.7 cm), washed with deionized water, and dried 8 h at 80 °C.

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. Then, 2 μL of the MCSNP/H₂O suspension solution was casted on the carbon working electrodes, waiting until the solvent was evaporated in room temperature.

The electrochemical behavior of MO is dependent on the amount of the suspension solution. Therefore, in order to obtain the best results for electrooxidation of MO, optimization of the amount of the suspension solution is necessary. The results are shown in Fig. 1 and showed that the best results are obtained using 2 μL of the MCSNP/H₂O suspension solution.

Preparation of Real Samples

The MO ampule was prepared by the appropriate dilution with 0.1 M PBS solution (pH 7.0) and directly used for determination of MO. Finally, a suitable volume of the resultant solutions were transfer to the electrochemical cell and the resulting solution was used for the analysis of MO.

Urine samples were stored in a refrigerator immediately after collection. 20 milliliters of the sample was centrifuged for 10 min at 3000 rpm. The supernatant was filtered out using a 0.45 μm filter. Then, 20 mL of the solution was transferred into a 50 mL volumetric flask and diluted to the mark with PBS (pH 7.0). The diluted urine sample was spiked with different amounts of MO. The MO contents were analyzed by the proposed method using the standard addition method in order to prevent any matrix effect.

The samples were spiked with different amounts of MO and contents were analyzed by using the standard addition method in order to prevent any

matrix effect. The amount of unknown MO in the MO ampule can be detected by extrapolating the plot.

RESULTS AND DISCUSSION

Characterization of MCSNP

SEM is an important tool to characterize the surface morphology and is useful to determine the particle shape and size distribution of the nanoparticles. The SEM of MCSNP is shown in Fig. 2 and showed that MCSNP has relatively homogenous particle ($\geq 100\text{ nm}$).

The functional groups of MCSNP were studied by FTIR (Fig. 3). The absorption peaks around 3450 cm^{-1} and $500\text{-}600$ are due to the O–H stretching vibration and metal–oxygen vibration, respectively. The band at and 1025 cm^{-1} is attributed to stretching vibration of Si–O–Metal [41].

The absorption peaks around 3435 , 2927 , 2864 , 1560 , and 1120 cm^{-1} are due to the N–H stretching vibration, $-\text{CH}_2-$ asymmetric vibration,

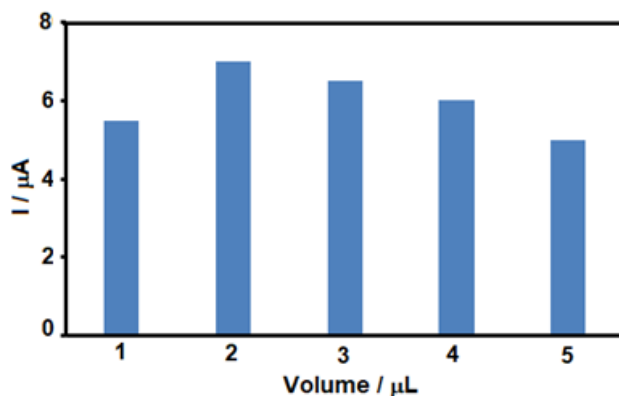


Fig. 1. Effect of suspension solution amount on the response of modified electrode in the presence of $200.0\text{ }\mu\text{M}$ MO in 0.1 mol L^{-1} PBS (pH= 7.0).

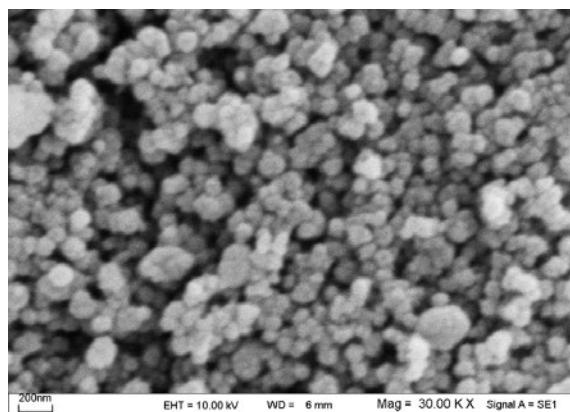


Fig. 2. SEM image of MCSNP.



-CH₂- symmetric vibration, C-N (amine) bending vibration, and C-N stretch (aliphatic amine), respectively [41].

Electrochemical behavior of MO at the surface MCSNP/SPCE

The electrochemical behavior of MO is dependent on the pH value of the aqueous solution. Therefore, in order to obtain the best results for electrooxidation of MO, optimization of the pH is necessary. For this purpose, the

electrochemical behavior of MO was studied in 0.1 M PBS in different pH values (3.0–9.0) at the surface of MCSNP/SPCE by voltammetry. It was found that the electrooxidation of MO at the surface of MCSNP/SPCE was more favored under neutral conditions than in acidic or basic medium (Fig. 4a and 4b). Thus, the pH 7.0 was chosen as the optimum pH for electrooxidation of MO at the surface of MCSNP/SPCE. The Fig. 4c shows potential–pH diagram constructed by plotting the peak potential values as function of pH. As can be

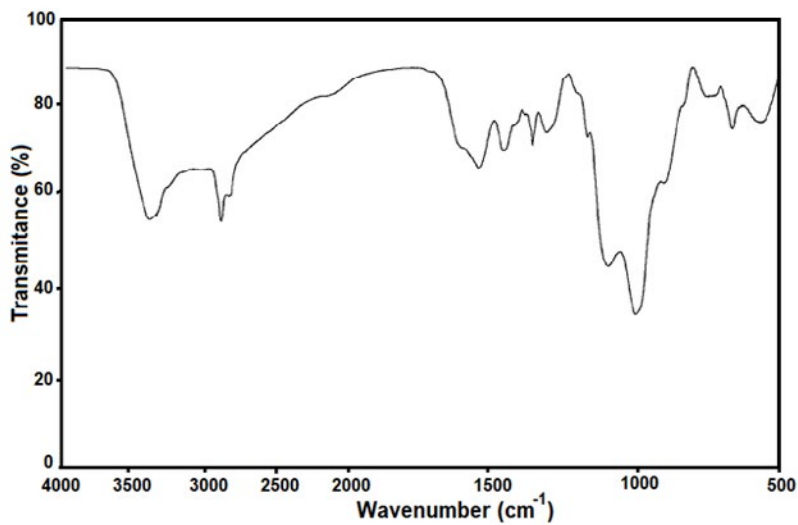


Fig. 3. FT-IR of MCSNP.

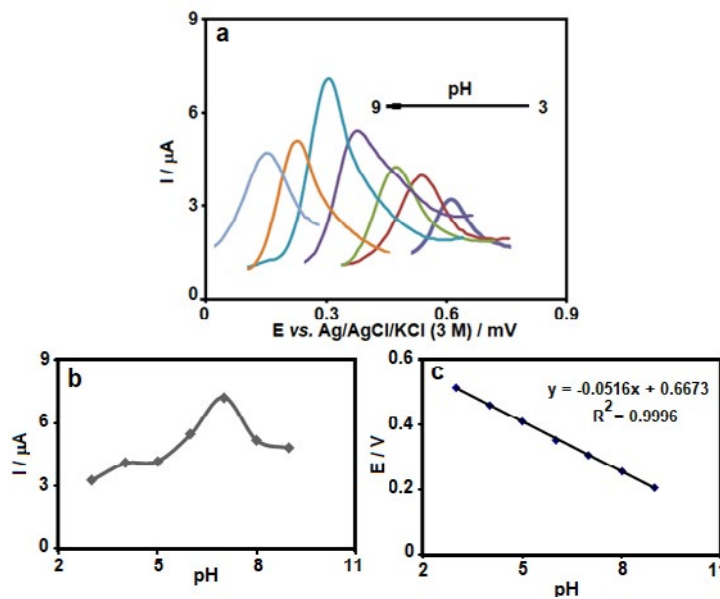


Fig. 4. (a) SWVs (at 50 mV s⁻¹) of the MCSNP/SPCE in the presence of 200.0 μM MO at various buffered pHs, (b) plot of I_p vs. pH and (c) plot of E_p vs. pH.



seen, the slope is 51.6 mV/pH indicating that the system obeys the Nernst equation, for an equal electron and proton transfer reaction [42].

The CV responses for the electro-oxidation of 90.0 μM MO at an unmodified SPCE (curve a) and MCSNP/SPCE (curve b) was showed in Fig. 5. As it can be easily noticed, in comparison with unmodified SPE, the peak potential for the oxidation of MO at the MCSNP/SPCE is shifted by about 80 mV toward negative values. Also, in comparison with unmodified SPE, the peak current for the oxidation of MO at surface of MCSNP/SPCE was about 100 % greater than it at surface of unmodified SPE.

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

Effect of Scan Rate

The effect of potential scan rates on the oxidation current of MO (Fig. 6), have 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

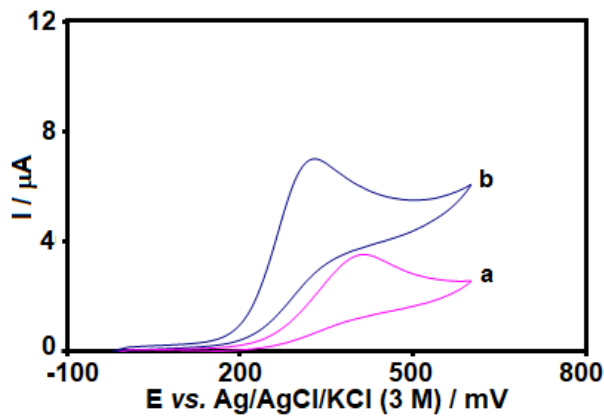


Fig. 5. CVs for SPCE (a) and MCSNP/SPCE (b) in 0.1 mol L⁻¹ PBS (pH= 7.0) with the scan rate of 10 mV s⁻¹ and in the presence of 90.0 μM MO.

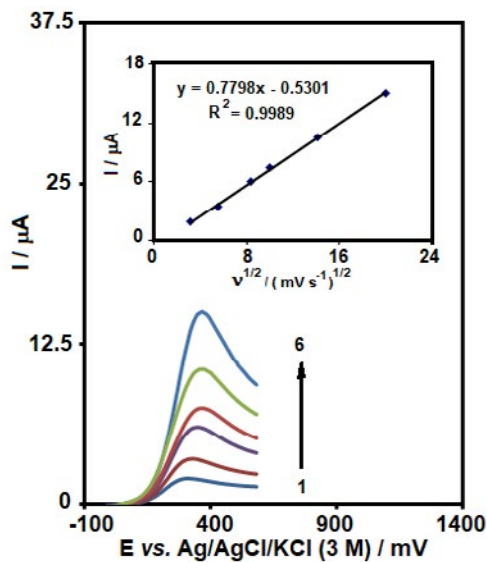


Fig. 6. LSVs of MCSNP/SPCE in 0.1 M PBS (pH 7.0) containing 30.0 μM MO at various scan rates; numbers 1-6 correspond to 10, 30, 70, 100, 200 and 400 mV s⁻¹, respectively. Inset: Variation of anodic peak current vs. square root of scan rate.

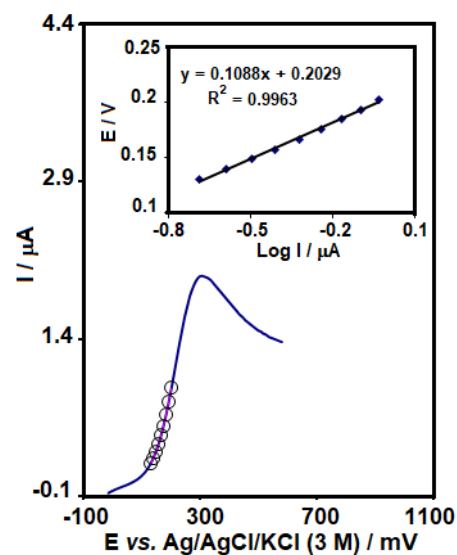


Fig. 7. LSV of MCSNP/SPCE (at 10 mV s⁻¹) in 0.1 mol L⁻¹ PBS (pH 7.0) containing 30.0 μM MO. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV.

dependence of the anodic peak current (I_p) on the square root of the potential scan rate ($v^{1/2}$).

Tafel plot was drawn from data of the rising part of the current voltage curve recorded at a scan rate of 10 mVs^{-1} for MO (Fig. 7). This part of voltammogram, known as Tafel region, is affected by electron transfer kinetics between substrate (MO) and MCSNP/SPCE. Tafel slope of 0.1088 V was obtained which agree well with the involvement of one electron in the rate determining step of the electrode process [42] assuming charge transfer coefficients, $\alpha=0.46$ for MO.

Chronoamperometric Measurements

Chronoamperometric measurement of MO at MCSNP/SPCE was carried out by setting the working electrode potential at 500 mV vs. $\text{Ag}/\text{AgCl}/\text{KCl}$ (3.0 M) for the various concentrations of morphine (Fig. 8). For electroactive materials (MO) 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, Eq. 1 [42]:

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

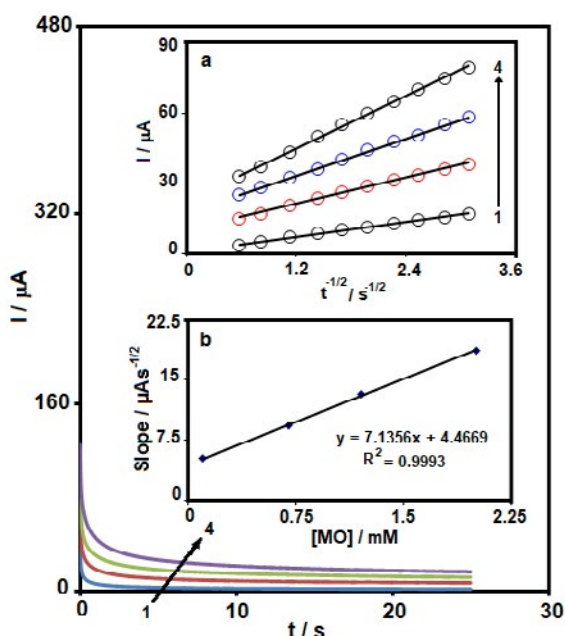


Fig. 8. Chronoamperograms obtained at surface of MCSNP/SPCE in 0.1 M PBS ($\text{pH} 7.0$) for different concentration of MO. The numbers 1–4 correspond to $0.1, 0.7, 1.2$ and 2.0 mM of MO. Insets: I vs. $t^{-1/2}$ (a) and slope of straight lines vs. MO concentration (b).

In this equation, I is current (A), n is number of electrons (to reduce/oxidize one molecule of analyte), F is faraday constant (96485 C/mol), A is area of the (planar) electrode (cm^2), t is time (s), D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$) and C_b is the bulk concentration (mol cm^{-3}). Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of MO (Fig. 8a). The slope of the resulting straight lines were then plotted vs. MO (Fig. 8b) concentrations. From the resulting slope and Cottrell equation the mean value of the D was found to be $4.34 \times 10^{-6} \text{ cm}^2/\text{s}$ for MO.

Calibration plot and limit of detection

The electro-oxidation peak current of MO at the surface of the MCSNP/SPCE can be used for determination of MO in solution. Since, DPV has the advantage of an increase in sensitivity and better characteristics for analytical applications, therefore, DPV experiments were performed using single MCSNP/SPCE in 0.1 M PBS containing various concentrations of MO (Fig. 9). The results showed that the electrocatalytic peak currents of MO oxidation at the surface of MCSNP/SPCE was linearly dependent on the MO concentrations,

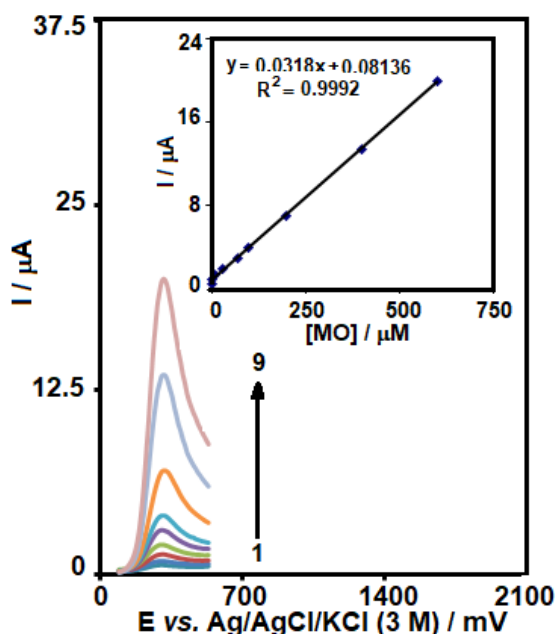


Fig. 9. DPVs of MCSNP/SPCE in 0.1 M PBS ($\text{pH} 7.0$) with various MO concentrations. Numbers 1-9 correspond to: $0.1, 2.5, 10.0, 30.0, 70.0, 100.0, 200, 400.0$ and 600.0 µM of MO. Inset: I_p vs. MO concentration.

Table 1. Comparison of the efficiency of electrochemical methods used in detection of MO.

Electrode	Method	Modifier	LOD (μM)	LDR (μM)	Ref.
CPE	SWV	Carbon nanotubes	0.09	0.2-250.0	[43]
CPE	CV	ZnO/ Carbon nanotubes	0.06	0.1-700	[44]
CPE	SWV	NiO/ Carbon nanotubes	0.01	0.05-520	[45]
CPE	DPV	Multiwall carbon nanotubes/n-hexyl-3-methylimidazolium hexafluoro phosphate	0.02	0.6-600	[46]
SPE	DPV	Magnetic core shell manganese ferrite nanoparticles	0.02	0.1-600	This work

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

Sample	Spiked, μM	Found, μM	Recovery, %	RSD, %
MO Ampoule	0.0	10.0	---	2.5
	10.0	19.8	98.0	2.8
	20.0	30.3	101.5	3.0
	30.0	40.8	102.7	2.7
Urine	0	Not detect	---	---
	10.0	9.8	98.0	2.9
	20.0	19.5	97.5	2.4
	30.0	31.0	103.3	2.7

over the range of 1.0×10^{-7} – 6.0×10^{-4} M (with a correlation coefficient of 0.9992) and the detection limit (3σ) was obtained 2.0×10^{-8} M. These values are comparable with values reported by other research groups for electro-oxidation of morphine at the surface of chemically modified electrodes (see Table 1).

The repeatability and stability of MCSNP/SPCE

The electrode capability for the generation of a reproducible surface was examined by CVs data obtained in optimum solution pH from MO that prepared MCSNP/SPCE. The calculated RSD for various parameters was accepted as the criteria for a satisfactory surface reproducibility (2-4 %). This degree of reproducibility is virtually the same as that expected for the renewal or ordinary screen printed electrode surface. In addition, the long-term stability of the MCSNP/SPCE was tested over a 3-week period. When CVs were recorded after the modified electrode was stored in an atmosphere at room temperature, the peak potential for MO oxidation was unchanged and the current signals showed only less than 2.1 % decrease of the initial response. The antifouling properties of modified electrode towards MO oxidation and its oxidation products were investigated by recording the cyclic voltammograms of modified electrode before and after using in the presence of MO. Cyclic voltammograms were recorded in the presence of MO after having cycled the potential for 20 cycles

at a scan rate 50 mV s^{-1} . The peak potentials were unchanged to positive values and the currents decreased by less than 3.6 %. Therefore, at the surface of MCSNP/SPCE, not only the sensitivity increase, but the fouling effect of the analyte and its oxidation product also decreases. However, we regenerated the surface of MCSNP/SPCE before each experiment.

Real Sample Analysis

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

The amount of MO in ampule was found to be 10.01 mg/mL. It was found that there is no significant difference between the result obtained by the MCSNP/SPCE and the nominal value on the ampule label (10.0 mg/mL). The t-test was applied to both sets of results and showed that

there was no significant difference at the 95% confidence level.

CONCLUSION

In this work, by using magnetic core shell manganese ferrite nanoparticles as modifier in modification of SPCEs, a novel sensor has been developed that provides a sensitive method for the determination of MO. The proposed protocol demonstrated herein is novel, simple, portable, inexpensive and easy-to-use fabrication method for the measurement of MO concentration in ampoule 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 MO. Under optimized conditions, DPV exhibited linear dynamic ranges from 0.1–600 μM with detection limit of 20.0 nM.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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