

Fast and Simple Method for Determination of Sumatriptan Succinate Based on a Mesoporous Material

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Abstract: A type of mesoporous carbon is synthesized in this work and its structural properties were characterized by nitrogen physisorption isotherms and Raman spectroscopy. Because of the large surface area and high crystallinity of the prepared material, we used it to modify the glassy carbon (GC) electrode. The obtained modified electrode (CMK-3/GCE) was successfully applied for simple and rapid determination of Sumatriptan succinate (Sum) in standard solutions and pharmaceutical tablets by using differential pulse voltammetry (DPV) method. The modified electrode displayed a decrease in the over potential and an obvious increase in the peak current compared with the bare glassy carbon electrode. The study of experimental parameters showed that the oxidation reaction is totally irreversible and maximum current response was obtained at pH=5 in 0.05 phosphate buffer. Under the optimum experimental conditions, Sum could be linearly detected in the wide concentration range of 1.50 μ M-120 μ M. The detection limit was down to around 0.8 μ M (S/N=3). Since the prepared modified electrode exhibits a very good resolution between the DPV peaks of Sumatriptan, Paracetamol and Ascorbic acid, it can be applied for simultaneous detection of Sumatriptan in the presence of these compounds in pharmaceutical preparations.

Key words: Mesoporous material • CMK-3 • Sumatriptan succinate • Voltammetry • Electrochemical sensor

INTRODUCTION

In recent years, well-ordered mesoporous materials with high specific surface area, large pore volume, optimal pore size, good mechanical stability and chemical inertness are highly attractive for a wide range of applications including energy conversion and storage devices [1,2], supporting matrix for catalysis [3,4], electrodes for electrochemical double layer capacitors [5,6], electrode materials in lithium batteries [7,8], electrochemical biosensor [9-11] and as advanced adsorbent for water and air purification [12,13]. Due to the unique properties of ordered mesoporous carbons (OMCs) such as high specific surface area and electrical conductivity they have been also used for the fabrication of sensing electrode for the measurements of biomolecules and chemical species [14-16]. For instances, Yang *et al.* reported OMC modified glassy carbon electrode acting as an interference free detection sensor

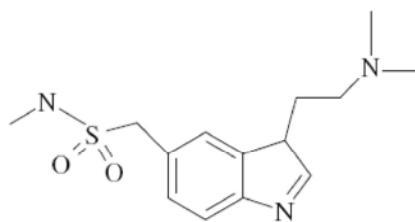


Fig. 1: Structure of Sumatriptan.

for Sudan I [14]. In another work, Zheng *et al.* constructed OMC/Nafion composite film electrode as a sensor for simultaneous determination of dopamine (DA), ascorbic acid (AA) and uric acid (UA) [15]. In addition, Bai *et al.* showed that OMC based sensors have electro catalytic capabilities towards the oxidation of the thiol containing compounds [16].

Sumatriptan succinate (Sum), a triptan drug including a sulfonamide group (Fig. 1), is used in human medicine for the treatment of migraine and cluster headache attacks

[17]. Oral administration of the drug is an effective and well-tolerated treatment for acute migraine, with a dose of 100 mg appearing optimal in terms of efficacy: side effect ratio. Various techniques have been applied for the analytical determination of Sum in pharmaceutical formulations and clinical preparations in the literature including: capillary electrophoresis [18], high performance liquid chromatography (HPLC) [19], spectrophotometry [20], mass spectrometry [21]. However, these methods suffer from some disadvantages such as expensive instrumentation, long analysis times, tedious sample preparation and in some cases, low sensitivity and selectivity that makes them unsuitable for a routine analysis. In contrast, electrochemical determination methods using electrochemical sensors and biosensors have shown significant advantages such as, high sensitivity, short analysis time, simplicity and inexpensive equipment. Sum is an electro active compound that can be oxidized electrochemically; however, few studies have been conducted for determination of this compound by electrochemical sensors [22, 23].

In the present study, a mesoporous material (CMK-3) was synthesized and used for fabrication of a modified glassy carbon electrode. Owing to the large surface area and relatively good crystallinity of the CMK-3, the prepared electrode was successfully employed for sensitive, rapid and selective determination of Sumatriptan succinate in standard solutions and pharmaceutical tablets by differential pulse voltammetry (DPV) method.

Experimental

Chemicals and Reagents: Sumatriptan succinate (>99.0% purity, Natco India) was used without further purification. Stock solutions of Sum were freshly prepared as required in appropriate buffer solution. Tablets of Sum were purchased from Hakim Pharmaceutical Co. (Tehran, Iran). Triblock copolymer P123 (EO20PO70EO20, EO = ethylene oxide, PO = propylene oxide, 5800) was supplied from Aldrich Co. and tetraethyl orthosilicate (TEOS, Si (OCH₂CH₃)₄), sucrose, NaCl, NaOH, HCl, acetone and ethanol were purchased from Merck Co. (Germany). Phosphate buffers solution (PBS) was prepared by mixing of Na₂HPO₄ and NaH₂PO₄ (0.1M) and adjusted the desired pH with 0.1M H₃PO₄ or NaOH solutions.

Apparatus: All the electrochemical experiences were performed on a Palmsens Instrument (Netherlands) with a conventional three electrode cell. The glassy carbon

(2mm diameter, Azar electrode: Iran), an Ag/AgCl electrode (in saturated KCl solution) and a piece of Pt wire were served as working, reference and counter electrode, respectively. The sample solutions were purged with high-purity nitrogen gas for at least 15 min at the beginning of the experiments to remove oxygen. The nitrogen adsorption-desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2000 analyzer. Prior to the characterization of textural properties by nitrogen sorption technique, sample was degassed for 5 h at 70 °C. The specific surface area was calculated according to the BET (Brunauer-Emmet and Teller) model [24], while the pore size and pore volume were calculated using the Barrett-Joyner-Halenda (BJH) formula [25] based on the desorption branch of the isotherm. Raman experiments were carried out at room temperature with a Dilor micro-Raman spectrometer.

Synthesis of the Materials

Synthesis of SBA-15: SBA-15 was synthesized as reported by Zhao *et al.* [26]. In a typical synthesis, 2 g P123 was dissolved in 75 mL of 2 M HCl solutions at 40 °C and 4.16 g of tetraethyl ortho silicate was then added. After magnetically stirring the solution at 40 °C for 24 h, the mixture was transferred to an autoclave, which was kept at 100 °C for 48 h under static condition. The resulting material was recovered by filtration and washing with distilled water. Subsequently, the sample was calcined at 550 °C in air for 6 h to remove the organic template P123 and to obtain SBA-15.

Synthesis of CMK-3: The mesoporous carbon (CMK-3) was prepared by using mesoporous silica material SBA-15 as hard template and sucrose as carbon source according to the process described by Liu *et al.* [27]. Briefly, one gram of SBA-15 was added to 5 mL aqueous solution containing 1.25 g sucrose and 0.14 g H₂SO₄. The resulting sludge was heated in an oven at 100 °C for 6 h and then 160 °C for another 6 h. In order to obtain fully polymerized and carbonized sucrose inside the pores of the silica template, 5 mL aqueous solution containing 0.8 g sucrose and 0.09 g H₂SO₄ was added again and the mixture was subjected to the thermal treatment described above. Then, it was carbonized in an argon flow at 900 °C for 6 h with a heating rate of 5 °C min⁻¹. Finally, the mesoporous carbon (CMK-3) was obtained by removing the silica matrix using a 4 M NaOH solution (50 vol.% ethanol-50 vol.% H₂O) at room temperature followed by filtration, washing and drying at 120 °C for 4 h.

Electrode Preparation and Electrochemical Measurements:

In this study, 2 mg of the prepared mesoporous carbon was dispersed in 10mL of N,N-dimethyl formamide (DMF) and the mixture was sonicated for 30 min to obtain a homogeneous black suspension. Prior to the surface modification, the glassy carbon electrode (GCE) was polished successively with 1 μ m, 0.3 μ m and 0.05 μ m alumina slurries and then thoroughly rinsed with double-distilled water. After rinsed with nitric acid/acetone (1:1, v/v) and double-distilled water, the electrode was dried in air. Then 10 μ L of obtained suspension was casted on the GCE surface and allowed to dry at room temperature. The resulting modified electrode was denoted by CMK-3/ GCE.

RESULTS AND DISCUSSION

Characterization of the Mesoporous Carbon: Fig. 2 displays the N₂ adsorption/desorption isotherms of CMK-3. The isotherm shows a distinct hysteresis loop at 0.4-0.45, which indicates the mesoporous nature of the prepared material [28]. According to BET method, the specific surface area (S_{BET}) of CMK-3 is estimated to be 940 m²/g. As can be seen from Fig. 2b, the average pore diameter of CMK-3 calculated with BJH method found to be about 3.6.

The Raman spectroscopy was carried out to examine the crystallinity nature of the prepared carbon materials. As can be seen in the Fig. 3, the prepared materials show two characteristic peaks of the D band at around 1340 cm⁻¹ and the G band at around 1595 cm⁻¹. The G band is related to the optically active E_{2g}, which is due to the stretching vibration modes of C=C bonds of typical graphite layers. On the other hand, the D band is associated with the presence of defects in the graphite layer. It can be noted that the relative intensity ratio of the D and G bands (I_D/I_G ratio) is proportional to disorder in graphite material and increases with higher defect sites in the graphite carbon [29,30]. The I_D/I_G ratio of CMK-3 is 1.10 indicating its crystalline structure.

Electrochemical Behavior of CMK-3-GCE: In order to investigate the electrochemical properties of the synthesized mesoporous material, the cyclic voltammetry (CV) response of CMK-3/GCE was compared with bare glassy carbon electrode. The cyclic voltammetry experiments were performed in 1mM K₃[Fe(CN)₆] / 0.1 M KCl solution with a scan rate of 50 mV/s and the obtained results are shown in Fig.4. As shown in this figure,

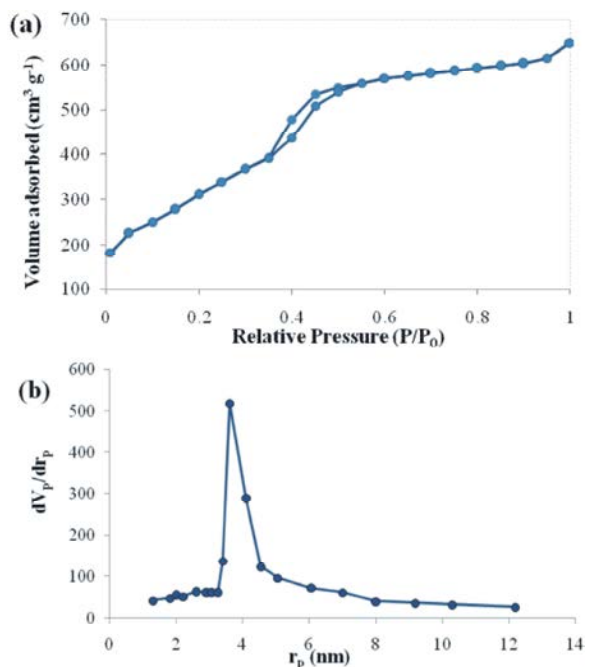


Fig. 2: (a) Nitrogen adsorption-desorption isotherm and (b) Pore size distribution of CMK-3

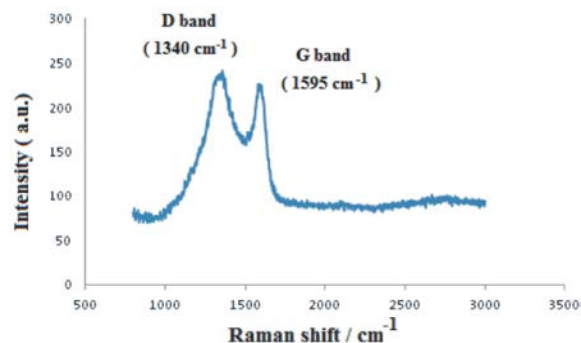


Fig. 3: Raman spectrum of CMK-3 in the 800-3000 cm⁻¹ region.

the electrochemical response current at the CMK-3/GCE is much larger in comparison with bare glassy carbon electrode. Furthermore, the difference in potential between the anodic and cathodic peaks (ΔE_p) is 95 and 118 mV (versus Ag|AgCl) for CMK-3/GCE and bare GCE, respectively. The order in terms of electron transfer efficiency, is therefore CMK-3/GCE > bare GCE, confirming the better electron transfer kinetics and catalytic activity in the case of mesoporous carbon modified electrode. The greatly enhanced electro catalytic behavior of the mesoporous carbon used in this study is attributed to its high surface area and good crystallinity observed through Nitrogen adsorption-desorption and Raman spectroscopy.

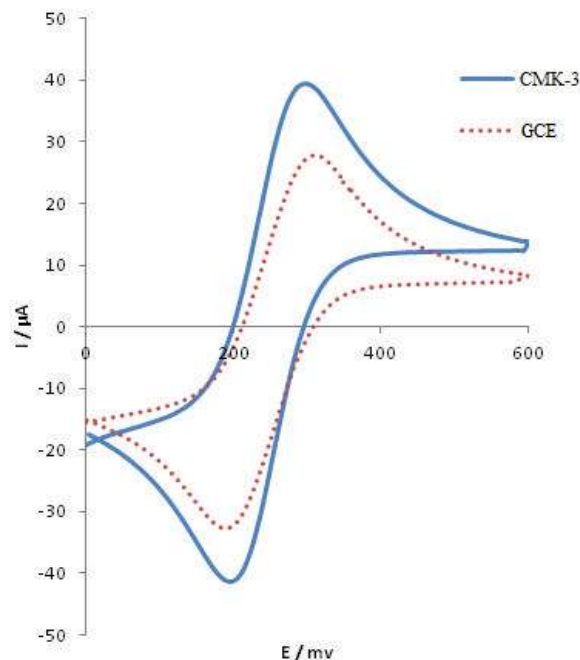


Fig. 4: CVs obtained at bare GCE and CMK-3 electrodes in 1mM $K_3Fe(CN)_6$ /0.1 M KCl solution at a scan rate of 50 mV s^{-1} .

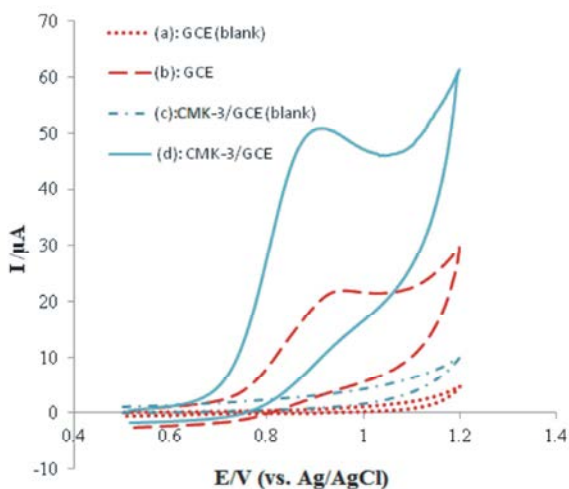


Fig. 5: CVs of the GCE (a, b), CMK-3/GCE (c, d) electrodes in 0.05M phosphate buffer (pH 5) without (a, c) and with (b, d) 0.5mM Sum. Scan rate: 50mV s^{-1} .

Volta Metric Behavior of Sum at the CMK-3/ GCE:

Fig. 5 shows the cyclic voltammograms for the oxidation of 0.5 mM Sum in 0.05M phosphate buffer of pH=5.0 at the surface of GCE (dotted line) and CMK-3/GCE (solid line). As seen, a broad electro-oxidation wave with a peak potential of about 0.97V is observed at the bare GCE.

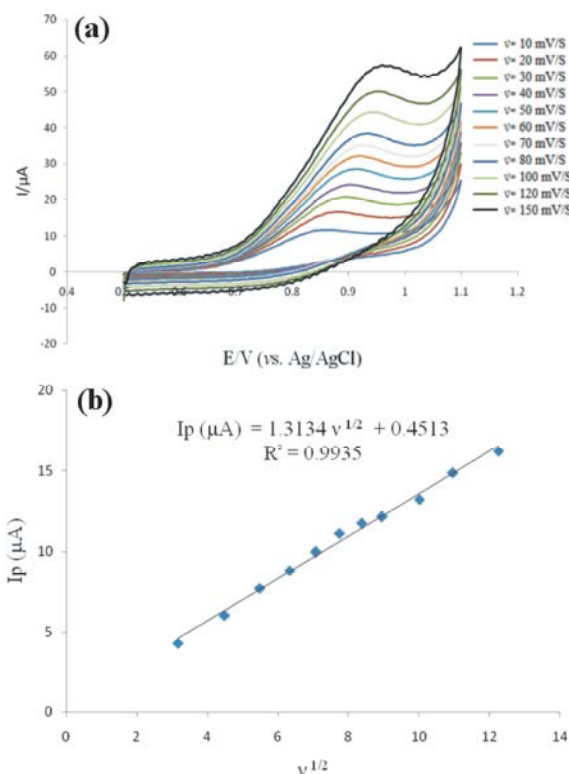


Fig. 6: (a) Cvs of 0.1 mM Sum at CMK-3/GCE in various potential scan rates ($10\text{-}150\text{ mV s}^{-1}$) bottom to up (b) plot of peak current vs. square root of scan rate

On the other hand, CMK-3/GCE with a well-defined anodic peak at 0.91 V shows electro-catalytic activity toward Sum. In addition to reducing the anodic over potential, a considerable enhancement in the peak current (about 3 folds) was also obtained. This is most likely to be attributed to the large surface area, specific electronic structure and high electrical conductivity of the used mesoporous carbon, which probably provide many favorable sites for electron transfer to biomolecules.

The effects of scan rate over the range of $10\text{-}150\text{mVs}^{-1}$ on the peak current and potential has also been investigated at the surface of the CMK-3/GCE in a phosphate buffer of pH 5.0 in the presence of 0.1mM Sum. As shown in the Fig.6, no cathodic peak is observed on the reverse scan even at low scan rates. The results showed the anodic peak current increased linearly with the square root of the scan rate (Fig. 6b). The peak potential shifted to a more positive value on the increase of the scan rate, confirming the irreversible nature of the oxidation process. The mentioned results indicate that the oxidation reaction of Sum at the surface of CMK-3/GCE is an irreversible diffusion-controlled process.

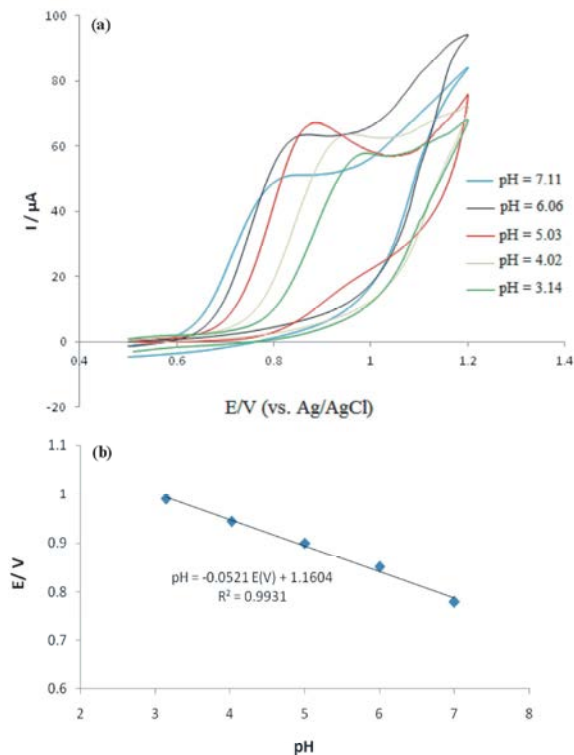


Fig. 7: (a) CVs of 1 mM Sum at CMK-3/ GCE in various pHs, (b) variation of anodic peak potential vs. various pHs at scan rate of 50 mV s⁻¹.

Effect of pH: To optimize the experimental conditions for the determination of Sum, the electrochemical response of Sum was investigated at different pH values in the range of 3.0-7.0 using 0.05M phosphate buffers as supporting electrolyte. Fig.7.a shows that the anodic peak potential shifts negatively with increasing pH, which indicates participation of H⁺ in the oxidation process. As seen in Fig.7.b, the linear relationship between the peaks potential (E_p) and pH can be expressed with the following equation:

$$\text{pH} = -0.0521 E(\text{V}) + 1.1604 \quad (R^2 = 0.9931)$$

The slope of 52.1mV per pH unit indicates that equal numbers of electrons and protons are involved in the electro oxidation of Sum at the surface of the modified electrode. The results also indicate that the anodic peak current of Sum increased from pH=3.0 and reached top value at about pH=5.0 and the further increase in the pH decreased the electrochemical response. Therefore, phosphate buffer with pH=5 was used as optimum supporting electrolyte in all voltammetric determinations.

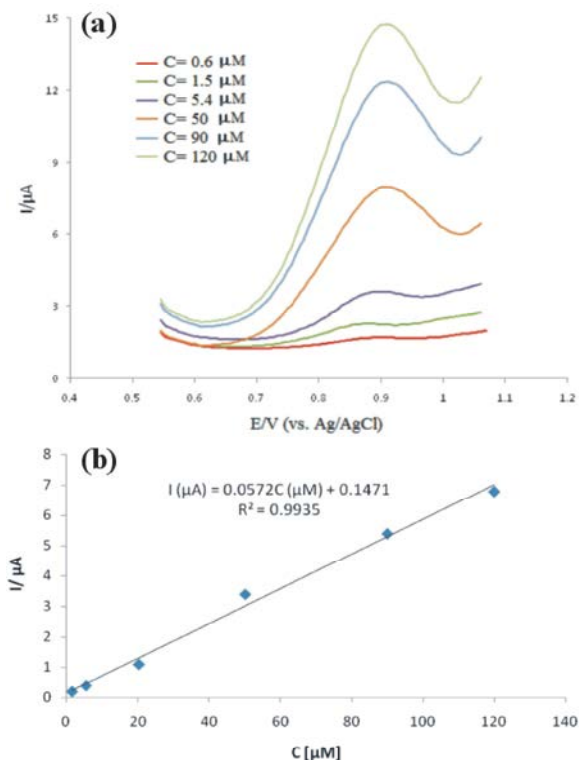


Fig. 8: (a) DPVs (50 mV pulse amplitude, 5mV step potential) for the oxidation of 1.5, 5.4, 20.2, 50.1, 90 and 120 μM Sum at CMK-3/GCE, (b) plot of the peak current versus the Sum concentration.

Electrochemical Determination of Sum: In order to quantitate the current resulting from the electro-oxidation of Sum at CMK-3/GCE, the sensitive differential pulse voltammetric (DPV) technique was applied. Fig. 8 displays the DPV plot and calibration graph for the oxidation of different concentrations of Sum at the surface of CMK-3/GCE. The peak current was found to behave a linear relationship with the concentration of Sum over the range of 1.5μM-120μM with the slope of 0.0572μAμM⁻¹ (Fig. 8.b). Finally, the limit of detection is obtained to be 0.80μM at the signal to noise ratio of 3 (S/N = 3).

The modified electrode with a relative standard deviation (R.S.D.) of 3.31% for 50μM Sum (n=6) exhibited good reproducibility. The stability of the prepared electrode was also examined. The loss of only 4.4% of oxidation peak current relative to the initial response was observed when the electrode was kept in ambient conditions for 1 month. These results proved the excellent stability of CMK-3/ GCE electrode. In comparison with two other reported references [29, 30], the presented work illustrate a very simple and fast assay for the electro analytical determination of Sumatriptan succinate.

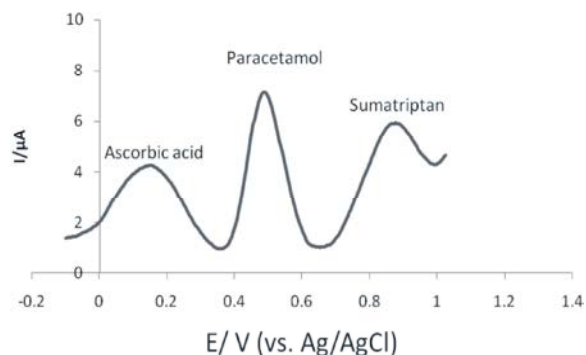


Fig. 9: DPVs of solution containing of 50 μ M ascorbic acid, paracetamol and sumatriptan in 0.05M phosphate buffer of pH=5.0, (50 mV pulse amplitude and 5 mV step potential).

Table 1: Results of the recovery analysis of Sum spiked in tablet samples

Spiked (μ M)	Expected (μ M)	Found* (μ M)	Recovery (%)
0	10	9.89	-
5	16	15.32	95.75
25	35	34.84	99.54
50	60	62.53	104.22

* Average of four replicate measurements

Interference Studies: The effect of some common interfering species on the oxidation peak current of Sum was investigated. Fig 9 shows the DPV for a solution containing 50 μ M of Ascorbic acid, Paracetamol and Sumatriptan succinate at pH=5.0 by using CMK-3/GCE. As obviously shown, three well-defined waves with a very good resolution are resulted for these compounds at the surface of applied electrode. The E_p of 381mV and 338mV were calculated for Sum-Paracetamol and Ascorbic acid-Paracetamol oxidation peaks, respectively. This result indicates the applicability of Sum detection at the surface of graphitic carbon mesoporous modified electrode in the presence of ascorbic acid and paracetamol.

Pharmaceutical Studies: In order to verify the applicability of the proposed sensor in pharmaceutical samples, the tablets containing 100 mg of Sumatriptan were analyzed. The real sample solutions containing 10 μ M Sum in phosphate buffer of pH=5 were prepared and the spiked recoveries determined using standard addition method. It can be seen from table 1, that the value of recovery lies in the range of 95.75-104.22%, revealing that the proposed sensor could be efficiently applied to determination of Sumatriptan succinate in commercial pharmaceutical samples.

CONCLUSION

In this work, a kind of carbon mesoporous material (CMK-3) was synthesized and its electro catalytic activity was compared with a Glassy carbon electrode. The results showed that CMK-3/GCE remarkably enhanced the oxidation and reduction peaks of the $K_3[Fe(CN)_6]$ probe. The CMK-3/GC modified electrode successfully was used for determination of Sumatriptan succinate in the presence of Ascorbic acid and Paracetamol. The fabricated electrode with a detection limit of 0.8 μ M (S/N=3) was used to the determination of Sum in real pharmaceutical samples with satisfying recoveries.

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