Immobilized copper ions on MWCNTS-Chitosan thin film: Enhanced amperometric sensor for electrochemical determination of diclofenac sodium in aqueous solution

Md Shalauddin a, Shamima Akhter b, Samira Bagheri a,*, Mohd Sayuti Abd Karim c, Nahrizul Adib Kadri d, Wan Jefrey Basirun a,b

a Institute of Nanotechnology and Catalysis (NANOCAT), University of Malaya, 50603, Kuala Lumpur, Malaysia
b Department of Chemistry, Faculty of Science, University of Malaya, 50603, Kuala Lumpur, Malaysia
c Department of Mechanical Engineering, Faculty of Engineering, University Malaya, Kuala Lumpur, Malaysia
d Department of Biomedical Engineering, Faculty of Engineering, University Malaya, Kuala Lumpur, Malaysia

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A B S T R A C T
A simple and effective electrochemical sensor was designed by the drop cast method for the detection of Diclofenac Sodium (DS), a widely used painkiller, by combining the significant catalytic property of multi-walled carbon nanotubes (MWCNTs), excellent adsorption capacity and film forming ability of Chitosan and synergistic catalytic effect of Chitosan-copper complex. The characteristics of newly proposed composite (MWCNTs/CTS-Cu/GCE) were investigated by different techniques like Fourier Transform Infrared Spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM) and Energy dispersive X-ray analysis (EDX). The electrochemical performance of the newly modified composite was studied by using Cyclic voltammetry (CV), Electrochemical impedance spectroscopy (EIS), Square wave voltammetry (SWV). Under the optimum conditions, the anodic peak current for Diclofenac sodium (DS) was linear and the range is between 0.3 and 200 μmol L⁻¹ with the detection limit of 0.021 μmol L⁻¹ at pH 4.0. Finally, this modified composite exhibit good selectivity, sensitivity and stability for the detection of Diclofenac sodium (DS) from the pharmaceutical dosage form and real samples.

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Introduction

Diclofenac sodium (DS) (sodium [o-(2,6-dichloroanilino) phenyl] acetate) shown in Scheme 1, is a safe and well known non-steroidal anti-inflammatory drug (NSAIDs) which is popular and widely used all over the world. It is applied as the analgesic, anti-rheumatic, anti-inflammatory and anti-thermal and for the treatment of arthritis and degenerative joint disease [1]. After administration orally, DS is absorbed very well and undergoes a huge hepatic metabolism. Its half-life (t½) is 1–2 h, protein binding affinity approximately 99% and volume of distribution (Vd) is 0.171/kg. This drug enters through synovial fluid. As this drug is frequently used for...
several diseases, it is essential to determine the low concentration of DS from pharmaceuticals preparations and also from the environment [2]. Prolong administration of DS can be responsible for life-threatening cardiac problems like heart attack and stroke with the patients having diabetes and also Shy-Drager syndrome [3]. When the concentrations of DS is up to 1 mg/L then it is considered as a harmful agent for various environmental species [4]. Therefore, we need a technique for the measurement of DS in trace amounts which are simple, accurate, fast, cost-effective and selective. Voltammetric techniques have these benefits although electrooxidation for DS generally shows low response when using normal electrode [5].

For the diclofenac quantitative determination, several methods have been reported, for example spectrophotometric [6,7], fluorometry [8], and chromatography [9,10]. However, there are some limitations for these techniques. They are very time-consuming and chemical reagents are required to perform these techniques, therefore interest have been attracted towards the methods of electrochemical due to their fast response, large sensitivities, simple operation, and the possibilities of miniaturization [11,12]. Among the electrochemical methods, various voltammetric/amperometric [13,14] and potentiometric techniques [15,16] have been reported for the determination of diclofenac [17].

In recent years, chemically altered electrodes have drawn huge attention because of their versatile approaches in several analyses [18–20]. Carbonaceous nanostructured materials that include carbon nanofibers [21], mesoporous carbons [22], carbon nanotubes (CNTs) [23,24]. These materials have been used substantially for the purpose of fabrication of the modified electrodes which have several applications not only in analytical measurements but also in industrial electrochemistry [25]. They are widely recognized due to having some advantages like cost-effectiveness, width potential range, represent suitable electrocatalytic response for several redox reactions, relatively compatible and inert [26,27]. CNTs a type of carbonaceous materials and is composed by the folding of graphene layers within carbon cylinders [28], CNTs can be comprised of single-walled nanotubes (SWCNTs) [29] or multi-walled nanotubes (MWCNTs) [30]. CNTs have been drawn the attention due to possessing some unique characteristics such as good mechanical strength, higher electrical conductivity, and better chemical stability [31]. One of the crucial approaches of this kind of materials is an early electrochemical determination of cancer by applying advantageous and suitable biosensors in the clinical diagnostic purposes and protection of public health [32,33]. Since their breakthrough CNTs have been drawn significant attention for the several investigations [34,35]. CNTs possess some exceptional properties such as striking structural, chemical, electrical, mechanical characteristics [36]. They also can exhibit superconductor, metallic and semiconducting transport of electrons and it contains a hollow core which is suitable for the storage of guest molecules. Moreover, CNTs includes the elastic modulus configuration which is largest among all of the known materials [37]. These extraordinary properties of CNTs represent them as incredibly appealing for the determination of specific electrochemical detection and chemical sensors in the mainstream [38,39].

Chitosan (CTS) a linear copolymer is composed by d-glucosamine and N-acetyl-d-glucosamine. CTS contain active amino and hydroxyl groups which are responsible for the excellent capacity of adsorption for organic substances and heavy metal cations [40]. Furthermore, CTS display many outstanding characteristics including biocompatibility, the ability of film formation, biodegradation, low toxicity and so on [41]. Based on these benefits, chitosan matrix incorporated sensors have been unfolded for the detection of NSAIDs paracetamol [42–44]. The chitosan and metal complexes contain an annulus chelating configuration and possess the features of natural enzymes. That is why they expose advantageous catalytic activity for many chemical reactions [45,46].

Multiple attempts have been established to determine DS that include thin layer chromatography (TLC) [47], spectrophotometry [48,49], high performance liquid chromatography (HPLC) [50,51], gas chromatography [52,53], spectrofluorimetry [54], liquid chromatography (LC) [55], capillary zone electrophoresis [56], voltammetry [57,58] from the biological fluids. Spectrophotometry requires extensive preparations of samples by extraction process or chemical reaction. Gas chromatography requires extraction step and also derivatization before separation and detection [59]. These techniques have some drawbacks including expensiveness, time-consuming and often requires pretreatment steps, sometimes sensitivity and selectivity in the specific detections [60].

Electrochemical methods are applied substantially to overcome these limitations because this method ensures some sensitive and outstanding characteristics like selectivity, simplicity, reproducibility, cost-effectiveness [23,61–63].

For the determination of drug from the pharmaceutical preparations and human body fluids, electrochemical techniques have been proved to be highly sensitive. However, electrochemical methods are simple and dynamic because of having some benefits such as rapid response, high sensitivity

Scheme 1 – Chemical structure of Diclofenac sodium.

CCH₂COONa

NH₂

Cl

Cl

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and selectivity, cheap instrumentation and a wide range of linearity [59,64]. Mao and co-workers established a chitosan–copper modified electrode for the measurement of paracetamol [65]. Ya and Co-workers reported a chitosan–copper complex modified with MWCNTs ionic liquid electrode to detect hydrogen peroxide [66]. To the best of our knowledge, an electrochemical sensor for the detection of diclofenac sodium based on chitosan-copper complex modified with multi-walled carbon nanotubes has not been reported.

In the current study, MWCNTs/CTS-Cu modified GCE was applied for the detection of DS. The electrochemical response of DS for the hybrid composite MWCNTs/CTS-Cu/GCE was analyzed by using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. The outcomes of experiments demonstrated that MWCNTs/CTS-Cu/GCE hybrid shows the incredible capability to extend the active surface area and also increases the transfer of electrons between electrode and analytes. Ultimately, to investigate the efficacy of the proposed electrode for the analytical applications, it was applied for the voltammetric detection of DS from real samples including pharmaceutical tablet preparations and human urine samples. The method we proposed and developed is simple, sensitive, rapid and selective for the detection of DS from real samples.

**Experimental**

**Chemical reagents**

We obtained MWCNTs from Baytubes, Germany, diclofenac sodium (DS), chitosan (CTS), CuCl2·2H2O and phosphate buffer solution (PBS) were collected from Sigma-Aldrich, Malaysia. The rest of the chemicals used in the experiment were of analytical grade and used without any kind of further purification. De-mineralized water was used to prepare the standard and buffer solution. The stock standard solution was prepared by using 0.001 mol L⁻¹ concentrations of Diclofenac sodium. The DS solution was preserved in the refrigerator at 4 °C. For more dilution, De-mineralized water was used. 0.2 mol L⁻¹ PBS solution was prepared by dissolving the specific amounts of di-potassium hydrogen phosphate (K2HPO4) and potassium dihydrogen phosphate (KH2PO4) in 250 ml volumetric flask. Finally, to proceed the electrochemical experiments for detection of DS, 0.2 mol L⁻¹ PBS (pH 4.0) was used.

**Apparatus**

An Autolab Potentiostat containing a three electrode system (EcoChemie, The Netherlands) was used for determining all measurements of voltammetric technique like Cyclic voltammetry (CV), square wave voltammetry, and electrochemical impedance spectroscopy (EIS). A modified GCE of 3 mm diameter containing (MWCNTs/CTS-Cu/GCE) composite was used as a working electrode (Metrohm Switzerland), at the same time a platinum wire performed as a counter electrode (Metrohm Switzerland), and Ag/AgCl/KCl (3.0 mol L⁻¹) was employed as a reference electrode.

**Purification methods of MWCNTs**

According to the literature, MWCNT has been purified [67]. At 600 °C MWCNT was heated for 2 h and immersed in 6 mol L⁻¹ HCl solution for 24 h and then centrifuged. Then the precipitate was then collected carefully and washed with double distilled water and air dried. Then, MWCNT was functionalized chemically through a sulfuric acid and nitric acid mixture (3:1) by using ultrasonication for 8 h. After that, MWCNT was filtered and rinsed with doubly distilled water until its pH reaches to 7.0. Then it was dried for 5 h at 120 °C. Finally, functionalized MWCNTs enriched with carboxyl group was obtained.

**Preparation of electrode**

By using a polishing kit, bare GCE was polished with 0.32 μm Al2O3 water slurry and the GCE was washed with double distilled water, then sonicated for 10 min with subsequently in a ratio 1:1 aqueous HNO3, acetone, and doubly distilled water. The suspension of MWCNTs was formulated by dispersing of 1.0 mg MWCNTs in the 5.0 mL (v/v) mixture of double distilled water, ethanol and sodium dodecyl sulphate (3:1:1) and then sonicated for 30 min. 10.0 μL of a black suspension was drop cast on the surface of the GCE and dried in air to form a film of MWCNT on the surface of GCE and to prepare MWCNT modified GCE.

Chitosan solution was prepared by dissolving 0.25 mg of chitosan powder in 50 ml 0.10 mol L⁻¹ acetic acid and sonicated for 30 min and then the electrode was dipped into the chitosan solution for 30 min 0.1 gm of CuCl2·6H2O was mixed in 100 ml doubly distilled water to prepare a copper solution and subsequently sonicated for 30 min and then again dip the electrode in the copper solution for 30 min. The modified GCE electrode (GCE/MWCNTs/CTS-Cu) was prepared by the following steps. At first, 5 μL of MWCNTs suspension was taken through a micropipette and drop cast to make a coat on the surface of the GCE to form MWCNTs/GCE and then completely dried in air. Then the dried electrode was immersed into the chitosan solution for 30 min and positively charged chitosan was self-assembled with the negatively charged MWCNTs. After 30 min the electrode removed from the solution and slightly rinsed with doubly distilled water to prepare for the next step. Finally, MWCNTs/CTS/GCE was immersed in the copper solution for 30 min. This time Cu²⁺ was adsorbed on chitosan through self-assembly method. The modified electrode was withdrawn from copper solution and washed with double distilled water and air dried.

**Preparation of pharmaceutical sample**

5 tablets of diclofenac sodium (DS) were taken and crushed in a mortar-pestle to get the fine powder. The required amount of DS was transferred into a 50 ml volumetric flask and then dissolved in PBS (pH 4.0). Then the mixture was sonicated for 5 min to get the solution. After sonication, the solution was filtered to get the suitable aliquot and then stored in the refrigerator for the next use.
Preparation of urine specimen

The healthy volunteer was chosen to collect urine specimen, after taking an adequate sample kept it in cool temperate for the next experiment. The sample (35.0 mL) was centrifuged at 2500 rpm for 15 min. By using a filter paper the supernatant was filtered two times and diluted with PBS in a volumetric flask (100 ml). Then the solution was moved into an electrochemical cell for the analysis.

Results and discussion

Morphologies of different electrodes

The morphological studies for different electrodes have been denoted in Fig. 1A (FESEM) and Fig. 1B (EDX). Fig. 1c exhibits a clear morphology of MWCNTS/CTS-Cu modified electrode which was characterized by FESEM. It shows that CuCl₂ was distributed successfully on the surface of MWCNTs and it did not interrupt the regular morphology of MWCNTS and CTS. For better understanding, we pointed out some portion indicating the distribution of copper. In Fig. 1b explains that CTS polymer was distributed homogeneously on the surface of MWCNTs. The morphology of CTS polymer is different than the morphology of MWCNTs (Fig. 1a). This result reveals that a successful composite (MWCNTs/CTS-Cu) was prepared by the incorporation on the GCE surface, as a consequence, the surface area was increased and promoted the analyte (DS) adsorption.

The EDX result (Fig. 1B) indicates that the composite contains carbon, oxygen and copper elements with 98.94 wt%, 3.41 wt%, and 1.70 wt% respectively. This result confirms that, the presence of copper on the surface of modified electrode.

FTIR studies

FTIR spectra of pristine (a), MWCNTs (b), MWCNTs and Chitosan (c), MWCNTs, Chitosan and Copper (d) are shown in Fig. 2. In the pristine spectroscopy (curve a) and MWCNTs (curve b) carried the same characteristics of their functional group like methylene stretching bands for asymmetric/symmetric at 2923 cm⁻¹ and 2852 cm⁻¹ was obtained [39] and the stretching vibrations of COOH- group at 1740 cm⁻¹ was also observed [68]. It is clear
that the peaks for MWCNTs are sharper than the pristine peaks.

Curves 3 illustrates the combination of MWCNTs and chitosan. For MWCNTs, the peaks were observed at 2920 cm\(^{-1}\) and 1746 cm\(^{-1}\) which ensure the presence of \(=\text{CH}_2\) and \(-\text{COOH}\) group. Absorption band for chitosan was found at 3370 cm\(^{-1}\) (O=H and N–H stretching vibrations), 1558 cm\(^{-1}\) (N–H bending vibrations), and 1082 cm\(^{-1}\) (C–O–C stretching vibrations) \([69]\). The presence of these functional groups proved that the sample contained MWCNTs and Chitosan. Simultaneously, curve 4 showed the same bands for MWCNTs and chitosan that already presented in curve 3 but in curve 4, some extra band has been observed for copper around at 456 cm\(^{-1}\) \([70]\).

**Electrochemical behaviour of DS at MWCNTs/CTS-Cu/GCE thin film**

The electrochemical behaviour of 5.0 \times 10^{-5} mol L\(^{-1}\)Diclofenac sodium was investigated by applying cyclic voltammograms on bare GCE (Fig. 3a), MWCNTs/GCE (Fig. 3b) and MWCNTs/CTS-Cu/GCE modified electrode (Fig. 3c) respectively, in PBS (pH 4.0) where the applied potential range was 0.3–0.8 V vs. Ag/AgCl at 100 mVs\(^{-1}\) scan rate. It was clearly shown in Fig. 3a, only oxidation peak is present, but there is no reduction peak due to the low conductivity of GCE. After modification of GCE electrode (Fig. 3b and c), a rapid increase in the current density was observed because of the extended surface area with the excellent catalytic effect of Cu\(^{2+}\) ions. This remarkable change of current occurred due to the decline of peak potential and it demonstrates that this modification influenced the electrochemical reactions and also promoted the electron transfer rate.

**Influence of scan rate**

The effect of potential scan rate of the modified electrode on the oxidation reaction of diclofenac sodium (DS) was investigated by cyclic voltammetry. CVs for 50 \mu mol L\(^{-1}\) concentrations of diclofenac sodium in phosphate buffer solution of pH 4.0 at the MWCNTs/CTS-Cu/GCE composite with scan rate ranging from 10 to 400 mVs\(^{-1}\) was investigated (Fig. 4A). From Fig. 4A, it is clear that the anodic peak current is rising with the increasing of potential scan rate. Furthermore, the anodic peak currents are proportional to the scan rate which is shown in Fig. 4B, and the linear regression equations are \(I_p (\mu A) = 0.283 v (mV s^{-1}) + 2.494 (R^2 = 0.958)\), which demonstrates that the electrochemical oxidation of DS at MWCNTs/CTS-Cu/GCE electrode is a surface controlled process.

**Influence of pH**

The electrochemical behaviour of DS is directly influenced by the pH of the electrolyte. To study the effect of pH on the electro-oxidation of DS at the MWCNTs/CTS-Cu/GCE modified electrode, CV of 5.0 \times 10^{-5} mol L\(^{-1}\) DS were recorded at different pH values ranging from 4.0 to 9.0 (Fig. 5A). It was marked that, when the pH of the supporting electrolyte was raised slowly, the peak potential started shifting towards the negative values due to the participation of proton in the oxidation reaction which is shown in Fig. 5A. The plots of \(E_{pa} vs\) pH values exhibit the linear relationship (Fig. 5B) and the subsequent equation: \(E_{pa} (V) = -0.032 pH + 0.853 (R^2 = 0.998)\).

Besides, when the pH value increases from 4.0 to 9.0, the current of the anodic peak of DS increased gradually. At pH 4.0, we observed the highest peak, but further increase up to the pH 9.0 caused the decline of the peak height gradually. So, pH 4.0 was considered as the optimum supporting electrolyte and further used for all experiments.

**Analytical characterization and method validation**

Under optimum conditions, the calibration curve was constructed and described using MWCNTs/CTS-Cu/GCE. Fig. 6A exhibits the square wave voltammograms (SWV) for several concentrations of DS by following optimum conditions. In Fig. 6, linear range 0.3–200 \mu mol L\(^{-1}\) was observed with line equation of \(I_p (\mu A) = 1.139 \cos (\mu mol L^{-1}) + 0.128 (r^2 = 0.997)\) (Fig. 6B). The limit of detection (LOD) \(= 3S_b/m\), where LOD denotes the limit of detection, \(S_b\) for standard deviation for the blank sample and \(m\) for the slope of the calibration graph, LOD for the modified electrode was obtained to be 0.021 mol L\(^{-1}\). \(S_b\) was evaluated by six blank samples.

The primary requirement for a successful sensor depends on its repeatability, reproducibility, and stability. The repeatability of the newly modified electrode for the measurement of DS was studied by accomplishing six measurements with the same DS standard solutions by utilizing the same electrode. The relative standard deviation (RSD) for the modified electrode response toward the DS solution (50.0 \mu mol L\(^{-1}\)) was 2.55%. The reproducibility of the modified electrode was also investigated. Six different electrodes were prepared with the same composite and were studied by performing the DS solution (50.0 \mu mol L\(^{-1}\)). For the responses between electrodes, the relative standard deviation was 2.88%. The results demonstrated that both of the repeatability and reproducibility of the proposed sensor for the measurement of DS are satisfactory. The electrode remained stable till 9 weeks. But after 9 weeks, the response of the electrode reduced and the noise increased. The reproducibility and stability of the
Electrode are high. It demonstrated that the proposed electrode was acceptable for the evaluation of real samples.

**Electrochemical impedance spectroscopy (EIS)**

Electrochemical impedance spectroscopy (EIS) is commonly applied to the measurement of the impedance change of the modified electrode surface. The electrode transfer resistance ($R_{\text{ct}}$) value depends on the dielectric and insulating features at the electrode/electrolyte interface which can be achieved from the semicircle diameters of the Nyquist plot. The results of impedance spectra for bare GCE (a), MWCNTs/GCE (b), and MWCNTs/CTS-Cu/GCE (c), were obtained in 0.1 mol L$^{-1}$ of KCl, which contained 5 mmol L$^{-1}$ K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ with the frequency ranges from 0.1 kHz to 100 kHz shown in Fig. 7. By the fitting of the data, charge transfer resistance ($R_{\text{ct}}$) value obtained from bare GCE was 1134 K$\Omega$. After addition of MWCNTs, the $R_{\text{ct}}$ value decreased to 98.2 K$\Omega$, which can be described by the remarkably improved electrical conductivity of MWCNTs. For the final composite MWCNTs/CTS-Cu/GCE, the $R_{\text{ct}}$ value further decreased to 24.84 K$\Omega$, due to the less electron transfer resistance of the MWCNTs/CTS-Cu/GCE compared to that of the MWCNT/GCE. This result indicates that the electrode was modified effectively with the proposed composite and it directly improved the conductivity.

**Interference study**

Generally, DS suffers interference in the presence of some biological molecules. The effect of various substances which can interrupt the measurement of DS potentially experimented under the optimum conditions. The interference

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**Fig. 4** — (A) CV of 50 μmol L$^{-1}$ diclofenac sodium on the MWCNTs/CTS-Cu/GCE at different scan rate (10 mVs$^{-1}$ to 400 mVs$^{-1}$) in PBS (pH4.0). (B) A variation of the peak current with the scan rate.

**Fig. 5** — (A) Effect of the pH in the range 2–9 using PBS on the cyclic voltammetric response for 50 μmol L$^{-1}$ DS at MWCNTs/CTS-Cu/GCE. (B) Anodic peak potential as a function of pH.
study was done by adding various biological compounds and ions to PBS (pH 4.0) with the presence of 20.00 \( \mu \text{mol L}^{-1} \) DS. The study showed the common ions like sodium, potassium, and chloride ion could not interrupt the measurement of DS. To study the regular interference in the presence of biological compounds for the detection of DS, various concentrations of fructose, glucose, citric acid, sucrose, and urea did not interfere with the current response of DS. The results ensure that the proposed method is highly selective for the detection of DS from biological samples and also pharmaceutical dosage forms.

Real sample analysis

To evaluate the acceptability of the suggested electrode (MWCNTs/CTS-Cu/GCE) for real sample analysis, we used the different strength of diclofenac sodium tablets and human urine specimen. After preparing the sample, it was diluted adequately according to the previous description. For the investigation of DS from tablets and human urine, a square wave voltammetric technique was used. After adding the human urine, DS was detected and calculated the recovery values which are presented in Tables 2 and 3. From Table 2, we can see that the recovery results were between 98.4 and 99.7 which can be considered as acceptable. Table 1 represents the comparison of different modified electrodes and also analytical parameters for the evaluation of DS which is shown in the literature [3,57,71–74]. The comparative study reveals the acceptability of the present technique with the previous techniques, in terms of the limit of detection. This remarkable response is responsible for the immobilization of MWCNTs/CTS-Cu composite at the surface of GCE that ensure the

Table 1 — The comparison of various electrodes for the determination of DS.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Linear Range ((\mu\text{M}))</th>
<th>Detection limit ((\mu\text{M}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs/Cu(OH)\textsubscript{2}/Nanoparticles/IL-GCE</td>
<td>0.18–119</td>
<td>0.04</td>
<td>[71]</td>
</tr>
<tr>
<td>MWCNT/PEG</td>
<td>0.047–12.95</td>
<td>0.017</td>
<td>[57]</td>
</tr>
<tr>
<td>IL/MWCNTs paste electrode</td>
<td>0.3–750</td>
<td>0.09</td>
<td>[3]</td>
</tr>
<tr>
<td>Vinylferrocene/MWCNTs paste electrode</td>
<td>5–600</td>
<td>2</td>
<td>[72]</td>
</tr>
<tr>
<td>MWCNTs and IL-modified carbon ceramic electrode</td>
<td>0.05–50</td>
<td>0.018</td>
<td>[73]</td>
</tr>
<tr>
<td>IL-modified CNT paste electrode</td>
<td>0.5–300</td>
<td>0.2</td>
<td>[74]</td>
</tr>
<tr>
<td>Cu/CTS/MWCNTs/GCE</td>
<td>0.3–200</td>
<td>0.021</td>
<td>This work</td>
</tr>
</tbody>
</table>

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Diclofenac sodium detection in tablet samples

<table>
<thead>
<tr>
<th>Sample (mg/tablet)</th>
<th>Labeled (mg/tablet)</th>
<th>Found (mg/tablet)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
<th>HPLC (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mg</td>
<td>50 mg</td>
<td>49.4 mg</td>
<td>98.80</td>
<td>2.8</td>
<td>50.2</td>
</tr>
<tr>
<td>100 mg</td>
<td>100 mg</td>
<td>97.6 mg</td>
<td>97.6</td>
<td>2.2</td>
<td>100.8</td>
</tr>
</tbody>
</table>

Recovery test results for Diclofenac sodium by using human urine samples (n = 3).

<table>
<thead>
<tr>
<th>Added (mM)</th>
<th>Found (mM)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
<th>HPLC (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>ND</td>
<td>—</td>
<td>—</td>
<td>ND</td>
</tr>
<tr>
<td>10</td>
<td>9.97</td>
<td>99.7</td>
<td>1.8</td>
<td>10.13</td>
</tr>
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<td>50</td>
<td>49.20</td>
<td>98.4</td>
<td>2.6</td>
<td>50.34</td>
</tr>
<tr>
<td>100</td>
<td>98.88</td>
<td>98.88</td>
<td>2.4</td>
<td>98.44</td>
</tr>
</tbody>
</table>

* ND Not detected.

extended surface area, synergistic electrocatalytic effect, and excellent conductivity. Moreover, the results from voltammetric methods have an excellent similarity with HPLC technique results for determination of DS.

Conclusions

In this work, MWCNTs-CTS-Cu has been introduced by a simple sonication and drop cast method and applied as a novel sensing platform for the electrochemical determination of diclofenac sodium (DS). MWCNTs show superior electrocatalytic activity and chitosan has excellent adsorption and film forming capacity. Chitosan and metal composite contain the annulus chelating configuration and also contain the properties of natural enzymes. Due to these reasons, chitosan and copper composite has a synergistic effect on the electrocatalytic activity. That is why GCE modified with MWCNTs-CTS-Cu composite exhibits high electrocatalytic activity toward the electrooxidation of diclofenac sodium and also shows a good linear range and selectivity to DS concentration change. These results demonstrate that the proposed composite has significant potential for the measurement of diclofenac sodium from the pharmaceutical dosage form and real sample.

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