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معامل التأثير العربي 1.63
العدد 23

مجلة التربوي

مجلة علمية محكمة تصدر عن كلية التربية

جامعة المرقب

العدد الثالث والعشرون
يوليو 2023م

- المجلة ترحب بما يرد عليها من أبحاث وعلى استعداد لنشرها بعد التحكيم .
- المجلة تحترم كل الاحترام آراء المحكمين وتعمل بمقتضاها .
- كافة الآراء والأفكار المنشورة تعبر عن آراء أصحابها ولا تتحمل المجلة تبعاتها .
- يتحمل الباحث مسؤولية الأمانة العلمية وهو المسؤول عما ينشر له .
- البحوث المقدمة للنشر لا ترد لأصحابها نشرت أو لم تنشر .

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ضوابط النشر:

يشترط في البحوث العلمية المقدمة للنشر أن يراعى فيها ما يأتي :

- أصول البحث العلمي وقواعده .
- ألا تكون المادة العلمية قد سبق نشرها أو كانت جزءا من رسالة علمية .
- يرفق بالبحث تزكية لغوية وفق أنموذج معد .
- تعدل البحوث المقبولة وتصحح وفق ما يراه المحكمون .
- التزام الباحث بالضوابط التي وضعتها المجلة من عدد الصفحات ، ونوع الخط ورقمه ، والفترات الزمنية الممنوحة للتعديل ، وما يستجد من ضوابط تضعها المجلة مستقبلا .

تنبيهات :

- للمجلة الحق في تعديل البحث أو طلب تعديله أو رفضه .
- يخضع البحث في النشر لأولويات المجلة وسياستها .
- البحوث المنشورة تعبر عن وجهة نظر أصحابها ، ولا تعبر عن وجهة نظر المجلة .

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Molecularly imprinted polymer (poly-pyrrole) modified glassy carbon electrode on based electrochemical sensor for the Sensitive Detection of Pharmaceutical Drug Naproxen

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Abstract: In this study, A simple and efficient new electrochemical sensor based on molecularly imprinted polymer(MIP) has been developed for selective detection of the Naproxen(NAP). The sensor was prepared by electropolymerization via cyclic voltammetry (CV) of pyrrole onto a glassy carbon electrode (GCE) in the presence of (NAP) molecules. The extraction of (NAP) molecules embedded in the polymeric matrix was carried out by overoxidation in sodium hydroxide medium using CV. Various important parameters affecting the performance of the imprinted film (MIP) coated sensor were studied and optimized using differential pulse voltammetry (DPV). The highest anodic signal of NAP was obtained in a phosphate buffer solution of pH 7.0. The linear response range for NAP was 9.2×10^{-7} M to 3.0×10^{-5} M, and the limit of detection was as low as 3.0×10^{-9} M. The results of our investigation indicate that the MIP sensor was useful for the determination of NAP with excellent selectivity, high sensitivity, repeatability, and reproducibility.

Introduction

Naproxen is a proprionic acid derivative related to the arylacetic acid group of nonsteroidal anti-inflammatory drugs. The chemical name for naproxen (NAP) is 2-(6-methoxynaphthalen-2-yl) propanoic acid [1]. It works by inhibits some enzymes, which results in the inhibition of the synthesis of certain prostaglandins [2]. However, there are two major concerns associated with the use of naproxen. First, overuse can cause adverse side efects such as stomach pain, ulcers, and stomach bleeding[3] . the recommended daily dosage of naproxen for temporary pain management using an oral immediate release tablet is 550 mg, followed by 275 mg orally every 6 to 8 hours, or 550 mg every 12 hours as needed, which should not exceed 1375 mg/day[4, 5]. the naproxen overdose include serious toxicity with seizures, altered cognitive status, and metabolic acidosis. Secondly, naproxen has recently been classified as an emerging pollutant in wastewater, in that significant concentrations have been found in the plasma and bile of fish exposed to treated euent discharged by wastewater treatment plants[6]. Methods such as high-performance liquid chromatography (HPLC), UV spectrophoto metry, spectrofluorimetry and mass spectrometry have been commonly employed to analyze pharmaceutical drugs,however, these techniques are generally time-consuming and costly.The electrochemical techniques provides an accurate, fast, and cost-efective alternative to those detection methods. For instance Afkhami et al. reported an enantioselective naproxen biosensor based on a chiral modified gold electrode decorated with gold nanoparticles[7]. Hendawy et al. reported nanomaterial-based carbon paste electrodes for the detection of naproxen and its degradation produc[8] Over the last decades, the exploration of graphene and graphene based nanomaterials has garnered tremendous attention due to their unique electronic,

structural, and physical attributes[9]. The structure of graphene includes a single layer of carbon sp^2 hybridized hexagonal lattices that form honeycomb structures with a high surface area, which are both electronically and thermally conductive.

In this study, electrochemical sensors can offer the straight forward advantage of being able to distinguish one specific species in complex mixtures. Also, they are considered to have technical simplicity, good sensitivity and easy adaptability for in situ analysis with relatively cheap instrumental set-ups [10, 11]. The use of voltammetric methods with solid electrodes was recommended for the determination of trace amounts of important species in real samples[12].In recent years carbon paste electrode (CPE), which is made up of carbon particles and an organic liquid, is widely applied in the electroanalytical community due to its low cost, ease of fabrication, high sensitivity and selectivity for detection and renewable surface [13-15].

2. Experimental

2.1. Materials

Naproxen supplied from Egyptian Company for Chemicals and Pharmaceuticals, Standard solutions were prepared daily by diluting of the stock solution with the selected supporting electrolyte. Orthopho- sphoric acid 85%, potassium dihydrogen phosphate KH_2PO_4, disodium hydrogen phosphate Na_2HPO_4, and sodium phosphate Na_3PO_4 were mixed with different amounts and diluted with distilled water to obtain the phosphate buffer solutions (0.02 M) with the required pH .

2.2. Methods and Instrumentation :

2.2.1 electrochemical behavior of naproxen on bare GCE :

The voltammetric oxidation of NAP at the glassy carbon electrode (GCE) was investigated in phosphate buffer solutions in the pH range 2.0 - 9, using DPV techniques. Fig.1 shows representative DPV obtained at GCE . NAP is oxidized, yielding one oxidation peak,The largest peak was at pH 7 . and the peak potential of anodic peak of NAP is shifted linearly towards more negative values and peak current also increased up with increasing pH values.

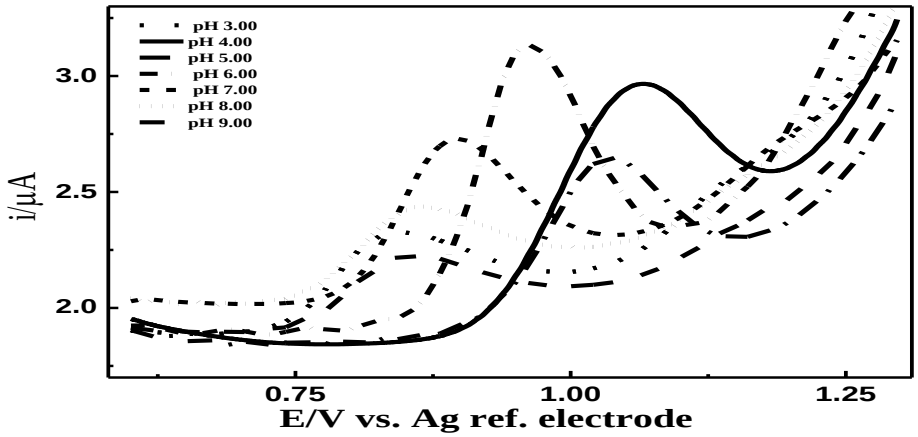

Fig 1: Effect of pH on determination of 1.0×10^{-4} M NAP using Differential pulse voltammograms at glassy carbon electrode in 0.2 M phosphate buffer solution.

Naproxen was subjected to CV studies with the aim of a detailed characterization of its electrochemical oxidation behavior on the GCE . CV for 1.0×10^{-4} M NAP in PBS pH 7 is shown in Fig. 2, the scanning was started at 0.8V in the positive direction. By reversing at +1.40 V, no reduction signal corresponding to the anodic response was observed in the cathodic branch. Scan rate studies over a range of 10-100 mV s^{-1} were carried out to assess whether the processes were under diffusion or adsorption control. A linear response was observed with the square root of the scan rate with a slope of 0.52, very close to the theoretical value of 0.50, which is expected for an ideal reaction condition for diffusion-controlled electrode process [16] .

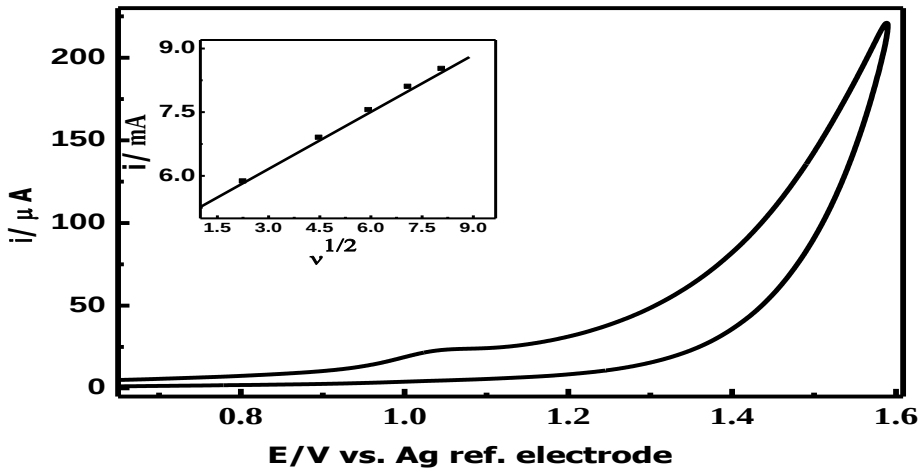

Fig. 2: CV of 5.0×10^{-4} M NAP at GCE in 0.2 M PBS (pH 7.0). Scan rate100 mV s^{-1}. Inset: Plot of anodic peak current for the oxidation of NAP against the square root of potential sweep rate .

2.2.2. Electrochemical imprinting of NAP into PPy

The NAP imprinted PPy / GCE (MIP) was obtained by electrodeposition on the surface of GCE using CV in potential range between 0.8 V and +1.5 V during 3 cycles (scan rate 100 mVS^{-1}) (Fig. 3A) in 0.1 M NaClO4 supporting electrolyte including 10 mM Py and 10 mM NAP. During the electropolymerization process, the NAP molecules diffuse towards the surface of GCE and trapped in the polymer matrix as a result of ability of these molecules to interact with Py. An oxidation peak at about 1.12 V was clearly observed on the first scan . Then, this peak decreased slightly on the next scan. After 2nd scan, the peak current started to be stable. These results indicate that the Py was successfully electropolymerized onto surface of GCE.In addition, the decrease of the peak current by increasing scan cycle seems to be related with the continual formation of PPy films that hinders Py monomer further access to the surface of modified electrode [17].

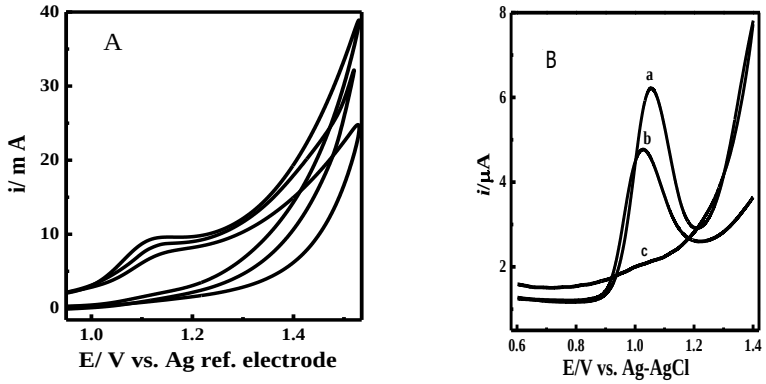

Fig. 3(A): Cyclic voltammograms taken during the electropolymerization of .01M pyrrole in 0.1M $NaClO_4$ supporting electrolyte in the presence of 1.0 mM NAP . and (B) DPV on GCE of 5.0×10^{-5} M NAP in 0.2 M phosphate buffer solution of pH 7.0 at (a) MIP electrode , (b) bare electrode, and (c) non-imprinted electrode.

The imprinting of the template molecule (NAP) on the PPy film can be explained by non-covalent interactions between the template and polymer matrix.This interaction may be attributed to the formation of a hydrogen bond between the -OH group in NAP and N-H group of Py[18]. In order to break the interactions, we used 0.2 M phosphate buffer solution as a desorption agent. To extract the NAP molecules from polymer, ausing by CV between - 0.6 and 1.3 V in 0.02 M phosphate buffer pH 7.0, until all NAP molecules were stripped from the imprinted PPy film and the oxidation peak corresponding to NAP was no longer observed . The obtained differential pulse voltammograms for 10^{-5} M NIP at the PPy-GCE-MIP, PPy-GCE-NIP and bare GCE electrodes are presented in Fig. 3B. It was noteworthy that the PPy GCE-MIP (curve a) electrode produced a noticeably higher oxidation peak current at 1.1V than the bare GCE (curve b) and PPy-GCE-NIP (curve c). The current response of PPy-GCE-MIP was nearly 4 times that of the bare GCE. It was evident that the PPy-GCE-MIP electrodes adsorbed a signifcant amount of NIP from the sample solution,

Optimization of electrochemical measurement conditions

The pH of the medium has important influence on the polymeric film. Differential pulse (DPV) peak currents are dependent on the pH, in the range of 2.0-9.0. The best response was observed at pH 7.0 according to the lowest non-imprinting response with an oxidation peak at 0.95 V. According to the results, NAP molecules which specifically adsorbed to the imprinted binding sites show different electrochemical oxidation behavior from the non-specific NAP molecules bonded to the polymeric film in different pHs .

The effect of monomer concentration on the analytical response of imprinting and non-imprinting GCE to NAP was studied. The films were grown in solutions of constant concentration of NAP with a series of monomer concentrations in the range of 0.001- 0.05 mM Py by cycling potential between - 0.6 V and +1.3 V. Increasing the monomer concentration may cause a rapid polymerization and increase the sensor sensitivity. However, a high concentration of the monomer might cause a nonselective electrochemical response to the template[18]. The best response of MIP

electrode to NAP (the higher the better) according to the NIP response (the lower the better) was 10 mM. According the results, the optimal monomer concentration was chosen 10 mM for the next experiments.

The numbers of cycles was evaluated by comparison of MIP electrode responses to the NIP using constant concentration of NAP. The applied cycling potential was between -0.55 V and +1.4 V. The response of MIP electrodes to NAP molecule increased with increasing the number of cycles up to 5. Hence, the optimal number of cycle was chosen 3 for the next experiments. The higher cycles cause more extensive electro- polymerization, and the formation of thicker film with less accessible imprinted sites occurred. So the sensitivity of the method decreased.

Practical application on samples for Naproxen

In order to evaluate the feasibility of the developed method for the determination of NAP in some its samples, was carried out using the MIP based electrochemical sensor. and the results were listed in Table 1 with the recoveries between 90.30 % and 98.75 %. These results indicated that the SPCE- MIP sensor could be successfully applied for the determination of NAP in the standard solutions .

Table 1: Analytical results of recovery and reproducibility (n=5) in the standard solutions. By the voltammetric methods.

(µM)	Found (µM)	Recovery (%)
10.00	9.03	90.30
20.00	19.14	95.70
30.00	28.72	95.73
40.00	39.50	98.75

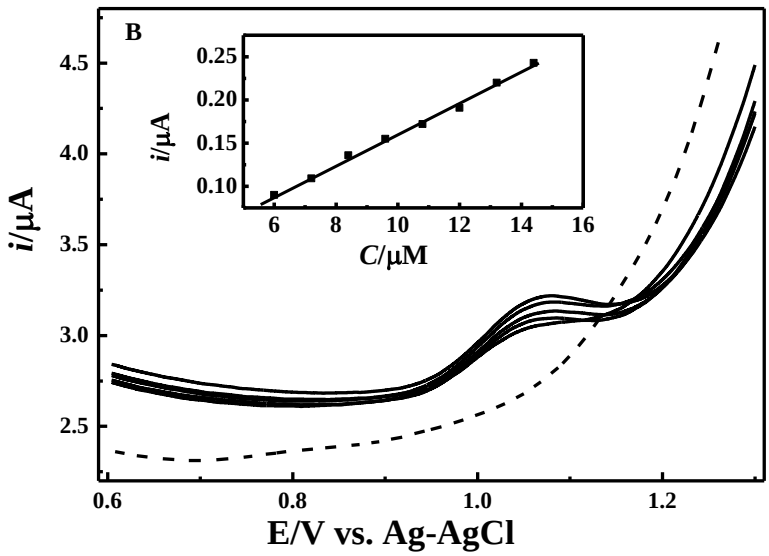

Fig 4: DPVs for the determination of NAP µg in different standard solutions with 0.2 M phosphate buffer solution of pH 7.0 at MIP; the dotted lines (...) represent the blank; inset: calibration curve of NAP in different standard solutions at MIP. Step potential 6 mV, modulation amplitude 50 mV and scan rate 50 mV/s

Conclusion

Finally, a sensor for NAP detection was developed by configuring MIP. the PPy with plenty of cavities could bind NAP through hydrogen bonds between nitrogen and oxygen-containing groups of the polymer and NAP. Such an electrochemical sensor exhibits a high current response, low detection limit and good selectivity.

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