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# Molecularly Imprinted Electrochemical Sensor for Detection of Prednisolone in Human Plasma as a Doping Agent in Sports

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This work was carried out on the synthesis of poly(4-vinylpyridine)- molecularly imprinted polymer on graphene oxide (4-VP/MIP/GO) as an electrochemical sensor for detection of prednisolone as a doping agent in sports. The GO was prepared using the modified Hummers method and electrodeposited on a glassy carbon electrode (GCE). The GO/GCE was modified by MIP which was prepared from tetrabutylammonium perchlorate and acetonitrile, and then 4-VP was electrodeposited on MIP/GO/GCE. Results of morphological analysis of modified electrodes using FESEM revealed GO was overlapping of flake nanosheets on the surface with cracks and fractures. The surface morphology of 4-VP/MIP/GO/GCE also showed a highly porous structure due to created cavities from the agglomeration of 4-VP and MIP molecules on corrugated edges of GO nanosheets. Results of electrochemical studies using DPV technique showed good stability, high selectivity, acceptable linear range (1μM to 120μM), highest selectivity (0.7397μA/μM) and lowest detection limit (0.004μM) in comparison with the other synergetic effect of GO nanosheets and 4-VP and MIP molecules. The validity and precision of 4-VP/MIP/GO/GCE to the determination of prednisolone were evaluated in pharmaceutical samples and human biological fluids and results exhibited acceptable recovery values (96 to 99.38 %) and RSD values (2.53 to 3.89 %). Therefore, 4-VP/MIP/GO/GCE can be used as an accurate and reliable sensor for determination of prednisolone as a doping agent in sports.

**Keywords:** Graphene oxide; Molecularly imprinted polymers; Prednisolone; Steroidabuse; Clinical Samples; Differential pulse voltammetry

## 1. INTRODUCTION

Nowadays, gain an advantage in competitive sports leads to doping and use of banned substances as athletic performance-enhancing drugs such as anabolic-androgenic steroids which are considered unethical and prohibited, by most international sports organizations, including the International Olympic Committee [1, 2]. Therefore, using steroids can lead to athletes being penalized or banned from participating in sports [3, 4]. More importantly, using performance-enhancing steroids can have serious, long-term health consequences [5, 6].

Steroids are the medical term for the drugs such as testosterone, methyltestosterone, androstenedione, danazol, and prednisolone that can aid in the treatment of blood disorders, connective tissue disease, some cancers, intractable arthritis, some sexual dysfunctions and other serious illnesses [7, 8]. But, because of their potentially serious side effects such as liver problems heart problems, stroke, blood clots, cancer, they must be prescribed and used only under close medical supervision [9, 10]. Therefore, many researchers have been conducted on gas chromatography, liquid chromatography, mass spectrometry, fluorimetry, spectrophotometry, enzyme-linked immunosorbent assay, radio immune assay, nuclear magnetic resonance spectrometry, yeast estrogen screen assay, photodiode-array and electrochemical detection methods to identify the rapid and simple way of steroid abuse and doping detection [11-16]. Among them, electrochemical techniques as great interest analyses have been shown a wide range of applications in food and environmental analyses and clinical diagnostics due to their ease of use, low cost and their capability to refinement and optimization in the past decade [17, 18]. Modification and miniaturization of the electrochemical sensor by nanomaterials and various composites improve the selectivity and sensitivity [19-23]. Prednisolone (11,17-Dihydroxy-17-(2- hydroxyethyl)-10,13-dimethyl-1,2,6,7,8,9,11,12,14,15,16,17-dodecahydrocyclopenta[a]phenanthren-3-one) is as a corticosteroid is a medication used to treat certain types of allergies, inflammatory conditions, tuberculous meningitis, rheumatic, autoimmune disorders, respiratory, gastrointestinal diseases and cancers, and abused for doping in sports. Limited and few electrochemical studies have been performed for prednisolone sensors [24-31] which indicated the limit of detection, sensitivity and accuracy of these sensors need to improvement for application in pharmaceutical samples and physiological samples of athletes. Therefore, this work was carried out on synthesis of 4-VP/MIP/GO/GCE as low cost electrochemical sensor for detection of prednisolone as a doping agent in sports to promote the sensing properties of a nanostructured electrochemical sensor in pharmaceutical samples and human biological fluids.

## 2. MATERIALS AND METHOD

### *2.1. Synthesize the polymeric MIP/modified electrode*

The modified Hummers method was used for preparing the GO from graphite powder [32]. 2 g graphite powder (99.99%, Huixian City Wanda Graphite Mold Factory, China) was added to a mixture of 80mL $H_2SO_4$ (96%, Merck, Germany) and 20mL $HNO_3$(65%, Merck, Germany) an ice water bath. Then, 12 g $KMnO_4$ (≥99.0%, Sigma-Aldrich) was gradually added to the resulted suspension. After then, the mixture was stirred at 35°C for 80 minutes. Next, 100ml deionized water was gradually added into the mixture under the stirring condition at 45°C for 60 minutes, followed by the addition of 10 ml $H_2O_2$ (35%, Shijiazhuang Chemical Tech Co., Ltd., China) under the stirring condition at 30°C for 40 minutes to obtain bright yellow suspension. The suspension was centrifuged at 2000 rpm/minutes for 20 minutes. The supernatant was removed and obtained graphite oxide was ultrasonically dispersed in 2mL of 0.1 M phosphate buffer solution (PBS) pH 7 for 100 minutes to separate/exfoliate stacked graphene oxide sheets. The 0.1M PBS was prepared from 0.1 M $NaH_2PO_4$ (99%, Merck, Germany) and 0.1 M $Na_2HPO_4$ (≥99.0%, Sigma-Aldrich) in volume ratio of 1:1.

Prior to the modification, the GCE surface was cleaned through the polishing with alumina powder (0.3μm, ATM GMBH, Germany) on a polishing cloth and then ultrasonically washed with triple distilled water and ethanol for 5 minutes, respectively, and dried at room temperature. For modification the GCE by GO [33], the electrodeposition was conducted on an Autolab PGSTAT 30 potentiostat-galvanostat (Eco ChemieAutolab B.V., Utrecht, the Netherlands) in conventional three electrode-electrochemical cell which contained GCE as working electrode, and Pt plate as counter electrode and Ag/AgCl (3M KCl) as reference electrode. The cyclic voltammetry (CV) technique was applied in dispersed GO nanosheets in 0.1 M PBS pH 7 as electrolyte under magnetic stirring condition and the potential range between -0.1 and 0.9 V at a scan rate of 10mV/s for fifty cycles.

For modification of the GCE and GO/GCE surface with MIP [34], the homogeneous mixture of 0.1 g tetrabutylammonium perchlorate (TBAP, ≥98%, Sigma-Aldrich) and 200 ml acetonitrile (ACN, 99%, Merck, Germany) were dropped on the electrode surface. Next, the electrode was dried under a gentle flow of dry nitrogen at room temperature. In order to the preparation of 4-VP/MIP/GO/GCE, 4-VP/MIP/GCE and 4-VP/GCE, the deposition of poly(4-vinylpyridine) (4-VP, ≥94.5%, Sigma-Aldrich,) was performed using the Auto lab system in the electrochemical cell which contained modified or bare GCE as the working electrode and Pt plate as counter electrodes. A mixture of 0.15 M 4-VP, 0.1 M TBAP and 0.1 M ACN were prepared in equal volume ratios as electrolytes. The deposition was performed at 1.0 V for 15 minutes. Subsequently, the 4-VP modified electrode was rinsed with CAN. Then, the modified electrode was over oxidized through CV technique from −0.45 to 1.65 V at a scan rate of 20 mV/s scan rate for 10 scans in prepared Britton–Robinson buffer (BRB) pH 9.0which prepared from a mixture of 0.4 M acetic acid (≥99%, Shanghai Wandefa Trade Co., Ltd., China), 0.4 M phosphoric acid (99%, Merck, Germany) and 0.4 M boric acid (99.5%, Sigma-Aldrich) solutions in equal volume ratio, and 0.1 M NaOH (99%, Xinjiang Zhongtai Import And Export Co., Ltd., China) solution was used to adjust the pH. The over-oxidation process was carried out in a conventional three-electrode cell which contained the modified or bare GCE as a working electrode, a Pt plate as counter electrode and Ag/AgCl (3M KCl) as reference electrodes.

### *2.2. Preparation of real samples*

Real samples were prepared from pharmaceutical and human plasma sample. Prednisolone 5mg tablets were purchased from local pharmacy that each tablet contains 5mg prednisolone. 10 tablets were powdered and ultrasonically dissolved in 50 ml of 0.1 M PBS that it is used as real pharmaceutical sample (5mg/ml prednisolone solution). For preparation the real sample from human plasma, the prednisolone-free plasma sample was provided from Capital Medical University Beijing Hospital of Traditional Chinese Medicine (Beijing, China). 10mL of plasma specimens were diluted to 100mL with the 0.1 M PBS. The standard addition method was applied to analytical studies of real samples.

*2.3. Characterizations*

Differential pulse voltammetry (DPV) analyses were conducted on Autolab system in conventional three electrode-electrochemical cell containing modified or unmodified GCE as working electrode, and Pt plate as a counter electrode and Ag/AgCl (3M KCl) as reference electrode, and 0.1 M PBS as electrochemical electrolyte. The morphology of surface of electrodes was studied usingfield emission scanning electron microscopy (FESEM, Carl Zeiss Sigma NTS Gmbh, Öberkochen, Germany).

## 3. RESULTS AND DISCUSSION

*3.1. Morphological study*

Figure 1 shows FESEM images of GO, and 4-VP/MIP/GO/GCE. FESEM image of GO from Figure 1a shows the overlapping of flake layers on the surface. The rough and holey morphology of GO with cracks and fractures is observed which can form due to the carbon atoms rearrangement of carbon atoms during the graphitization treatment [35]. Figure 1b shows the highly porous structure of 4-VP/MIP/GO/GCE due to created cavities from the agglomeration of 4-VP and MIP molecules on corrugated edges of GO nanosheets. The combination of MIP and 4-VP as co-functional monomers could enhance the functionality of adsorption and conductivity [36].

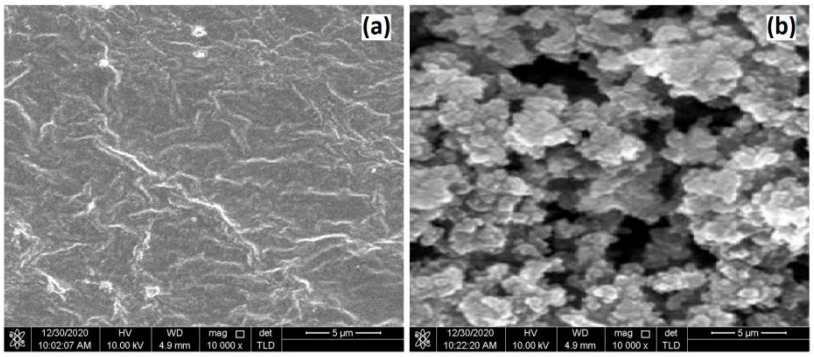



**Figure 1.** FESEM images of (a) GO, and (b) 4-VP/MIP/GO.

*3.2. Electrochemical study*

Electrochemical measurements in absence and presence of 6 µM prednisolone solutions were carried out using the DPV technique in 0.1 M PBS pH 7 at 10 mV/s scan rate. Figure 2 displays DPV curves of electrodes which reveal the oxidation peak at -0.27, -0.25, -0.24 and -0.22 V for GCE, 4-VP/GCE, 4-VP/MIP/GCE and 4-VP/MIP/GO/GCE, respectively, indicating to the oxidation of cyclopentanone part of the molecule [37]. Comparison between the DPV curves of GCE, 4-VP/GCE and 4-VP/MIP/GCE reveals the 4-VP and MIP role in enhancing the electrocatalytic current. Studies have been shown that MIP possess some excellent performance parameters such as chemical stability,

reusability and low cost, and also created an imprinted cavity with ligands attached to the polymer matrix can act as specific receptors (binding sites) which are directly attached to the analyte [38, 39].In addition, the application of poly(4-vinylpyridine) for modification of the electrode surface showed further and very substantial increase of the void volume of the membranes [40, 41]. The higher electrochemical response and lower potential are observed for 4-VP/MIP/GO/GCE (Figure 2d) that can be related to the synergetic effect of GO nanosheets and 4-VP and MIP molecules. The GO nanosheets provide high specific surface area, high porosity, and high electrical conductivity which promote sensitivity [42]. Moreover, the functional groups and defects on the edges of nanosheets enhance electroactivity and electron transfer rate [43, 44].

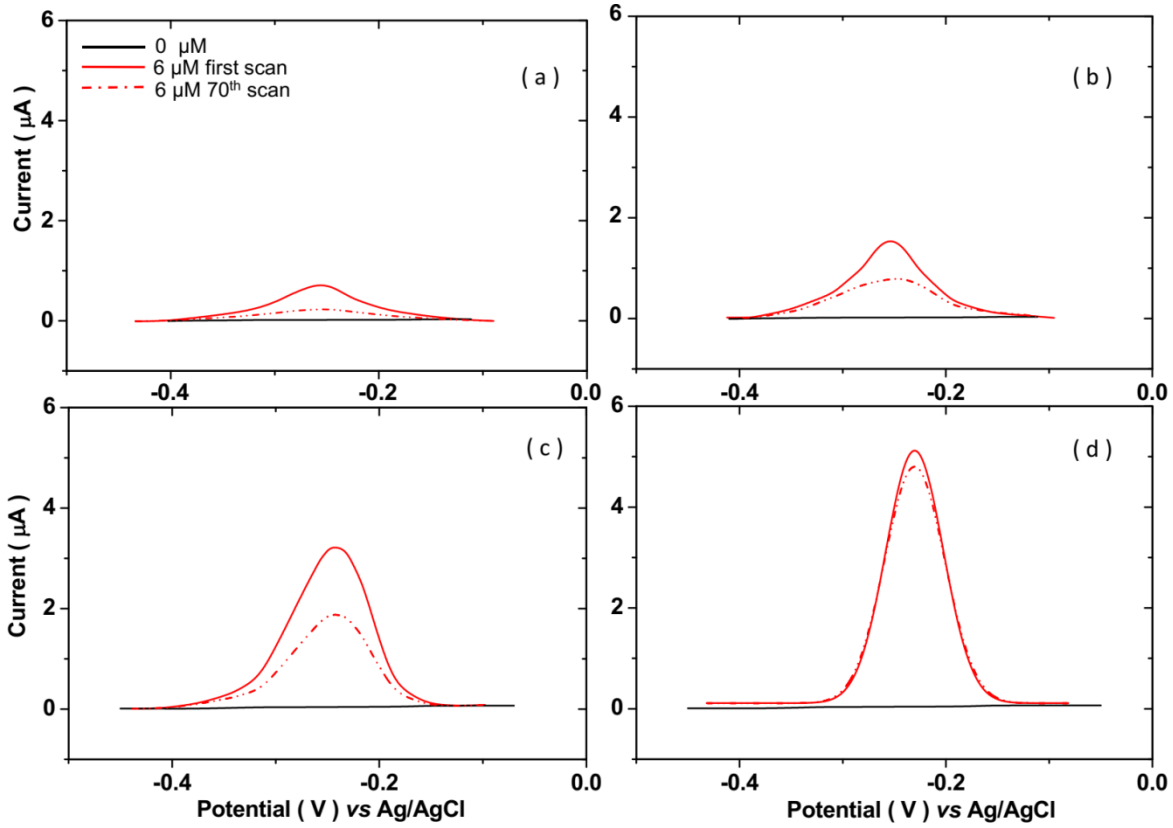
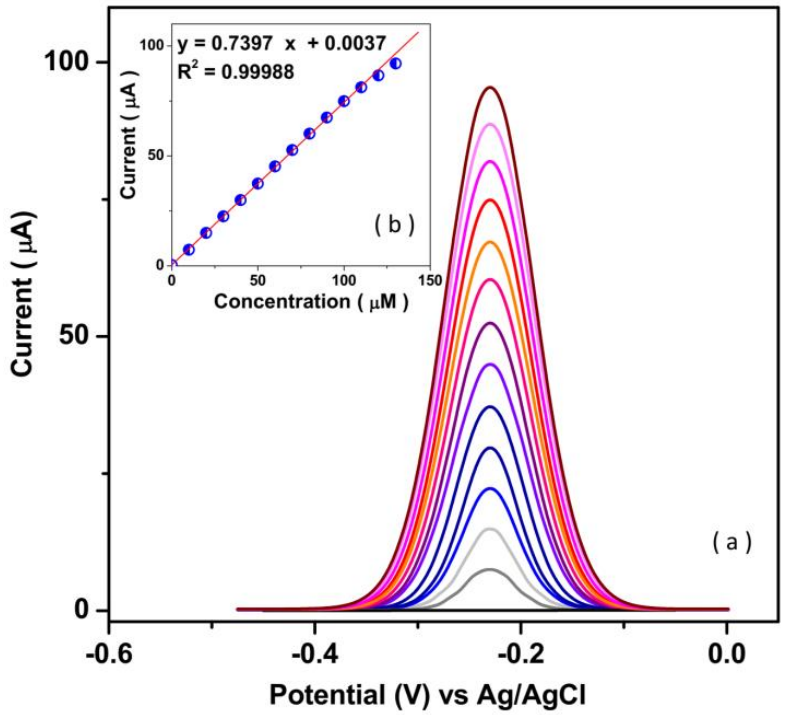



**Figure 2.** DPV curves of (a) GCE, (b) 4-VP/GCE, (c) 4-VP/MIP/GCE and (d) 4-VP/MIP/GO/GCE in 0.1 M PBS pH 7 at scan rate of 10 mV/s in absent and presence of 6µM prednisolone solution (first and 70$^{th}$ scan).

Figure 2 also shows the stability of electrocatalytic currents of GCE, 4-VP/GCE, 4-VP/MIP/GCE and 4-VP/MIP/GO/GCE through the successive DPV scans in PBS pH 7 containing 6 µM prednisolone solutions at scan rate 10mV/s. As observed from Figure 2a, the weak peak current of GCE is approximately disappeared after successive 70 sweeps. For 4-VP/GCE, 4-VP/MIP/GCE and 4-VP/MIP/GO/GCE is observed that the decrease in oxidation current peaks after successive 70 sweeps is 49%, 35% and 6%, respectively, which indicated the higher stability responses of 4-VP/MIP/GO/GCE due to a combination of 4-VP and MIP molecules with GO modified electrode through the non-covalence and covalence binding interactions between monomers and functionalized

group on GO which yield remarkable binding sites [36, 45]. Moreover, poly(4-vinylpyridine) as a pyridine containing functional monomer is the most stable polymer ligand for surface modification [46].GO nanosheets as ultrahigh strength and flexibility nanostructure can also improve the mechanical strength of 4-VP/MIP/GO/GCE by serving as structural-reinforcing agents [47, 48]. Thus, the 4-VP/MIP/GO/GCE was selected for the following electrochemical studies of prednisolone because of higher stability and sensitivity.

Figure 3 shows the DPV curves and obtained of calibration plot of 4-VP/MIP/GO/GCE for successive additions of 10µM prednisolone solution in 0.1 M PBS pH 7.0 at scan rate of 10 mV/s. it is observed that the electrocatalytic current is linearly increased with increasing the prednisolone content from 1 µM to 120 µM, and there is a departure from linearity for higher concentration due to saturation of the active sites on the modified electrode. The sensitivity and limit of detection of 4-VP/MIP/GO/GCE as prednisolone sensors are obtained 0.7397µA/µM and 0.004 µM, respectively.




**Figures 3.** (a) The DPV curves and (b) calibration plot of 4-VP/MIP/GO/GCE in 0.1 M PBS pH 7 at scan rate of 10mV/s under successive additions of prednisolone solution.

The obtained sensing results of the 4-VP/MIP/GO/GCE are compared with other reported prednisolone electrochemical sensors in Table 1. The comparison reveals that the resulted sensing properties in this study are comparable that other prednisolone electrochemical sensors. The obtained sensitivity and limit of detection for 4-VP/MIP/GO/GCE is better than the other reported electrodes that it attributed to cavities of the polymeric matrix which can increase the porosity and improve the diffusion of ions and the electrochemical reaction on the electrode surface [49, 50]. GO nanosheets not

only increase specific surface area but also provide the specific places for chemical recognition in the polymer matrix [49, 51]. Furthermore, the lower detection limit value is a good characteristic for the proposed prednisolone sensor for clinical application.

**Table 1.** Comparison between the obtained sensing results of the 4-VP/MIP/GO/GCE with other reported prednisolone electrochemical sensors.

| **Electrodes** | **Technique** | **Detection limit (μM)** | **Linear range (μM)** | **Sensitivity (μA/μM)** | **Ref.** |
|---|---|---|---|---|---|
| 4-VP/MIP/GO/GCE | DPV | 0.004 | 1–120 | 0.7397 | This work |
| Whatman SG81 silica-coated paper /Screen-printed electrode | DPV | 33.277 | 27.77–1388.88 | - | [24] |
| β-cyclodextrin/carbon paste electrode | DPV | 1 | 0.56–20 | 0.3055 | [25] |
| Ordered mesoporous carbon /GCE | SWV [a] | 0.057 | 0.06–40 | 0.644 | [26] |
| SWNTs/edge plane pyrolytic graphite electrode | OSWV [b] | 0.009 | 0.01–100 | 0.1897 | [27] |
| GCE | OSWV | 0.34 | 1–20 | 0.20091 | [28] |
| Mercury film silver based electrode | DPAdSV[c] | 0.010 | 0.052–25 | - | [29] |
| Hanging mercury drop electrode | DPAdSV | 0.011 | 0.02–0.4 | 0.21672 | [30] |

[a]Square wave voltammetry, [b]Osteryoung square wave voltammetry, [d]Differential pulse adsorptive stripping voltammetry

Table 2 presents the results of the interference study of 4-VP/MIP/GO/GCE to the determination of prednisolone in presence of main metabolites in body fluids through the DPV measurements in 0.1 M PBS pH 7.0 at a scan rate of 10 mV/s for successive injections of 1μM prednisolone and 10 μM of ascorbic acid, uric acid, xanthine, albumin, hypoxanthine, glucose, nitrite and dopamine as interferents.

**Table 2.** The electrocatalytic peak current of DPV measurements of 4-VP/MIP/GO/GCE in 0.1M PBS pH 7 at scan rate of 10mV/s for successive injections of 1 μM prednisolone and 10μM of interferents

| **substance** | **Added (μM)** | **Electrocatalytic peak current response (μA) at** -0.22 V | **RSD* (%)** |
|---|---|---|---|
| Prednisolone | 1 | 0.7402 | ±0.0121 |
| Ascorbic acid | 10 | 0.0217 | ±0.0038 |
| Uric acid | 10 | 0.0289 | ±0.0027 |
| Xanthine | 10 | 0.0306 | ±0.0032 |
| Albumin | 10 | 0.0121 | ±0.0021 |
| Hypoxanthine | 10 | 0.0092 | ±0.0027 |
| Glucose | 10 | 0.0373 | ±0.0078 |
| Nitrite | 10 | 0.0210 | ±0.0111 |
| Dopamine | 10 | 0.0221 | ±0.0072 |

*Relative standard deviation

It is found that the modified electrode demonstrates the remarkable peak current to additions of prednisolone solution, and injections of other interference substrates do not exhibit any significant electrocatalytic peak current. Therefore, the interference substrates in Table 2 do not interfere with the determination of prednisolone and the 4-VP/MIP/GO/GCE can be used as a selective prednisolone sensor in an analysis of biological fluid samples such as human urine and blood plasma.

The validity, precision, and applicability of 4-VP/MIP/GO/GCE to the determination of prednisolone were evaluated in pharmaceutical samples and human biological fluids. In order to study the prepared real pharmaceutical sample of prednisolone tablets, the DPV measurements were carried out using 4-VP/MIP/GO/GCE in the prepared real sample with 0.1 M PBS pH 7 at a scan rate of 10mV/s in successive additions of prednisolone solution. Figures 4a and 4b depict the obtained DPV responses and calibration plots, respectively, illustrating the prednisolone concentration in the prepared sample is 0.98 mg/ml that it is in agreement with the prepared real sample prednisolone concentration solution of tablets (1mg/ml). Moreover, it is observed from Table 3 that it is obtained the acceptable recovery values (96.50 to 99 %) and RSD values (2.77 to 3.89 %) for prepared real samples of prednisolone tablets. For the study the applicability of sensor in human biological fluids, it was not found the real samples of urine and blood plasma for patients which undergoing treatment with prednisolone in local health centers and hospitals. Thus, the prednisolone-free plasma sample was studied using the standard addition method. DPV measurements were also conducted on 4-VP/MIP/GO/GCE in 0.1 M PBS pH 7 at a scan rate of 10mV/s for prepared real samples of human plasma. Table 3 also presents the prednisolone concentration in real plasma samples and analytical results. It is indicated to acceptable values of recovery (96 to 99.38%) and RSD (2.53 to 3.51%). Therefore, 4-VP/MIP/GO/GCE can be used as an accurate and reliable sensor for determination of prednisolone in clinical samples.

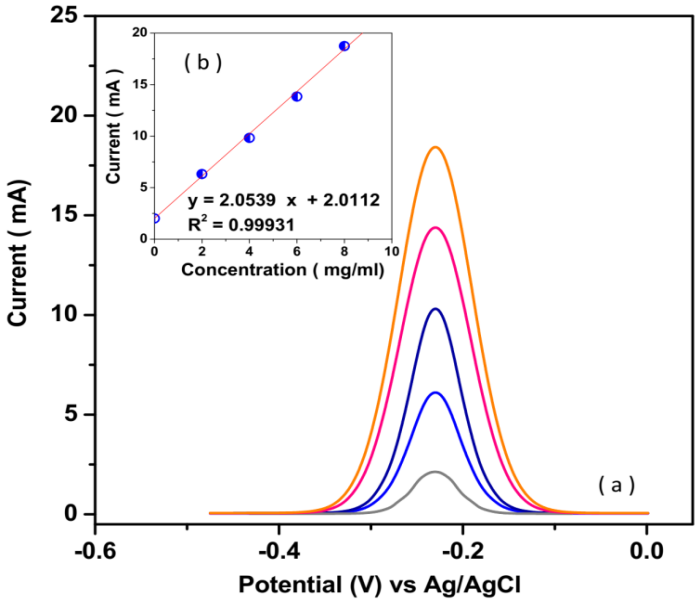



**Figure 4.** (a) The DPV response and (b) calibration plot of 4-VP/MIP/GO/GCE in prepared real sample of prednisolone tablets with 0.1 M PBS pH 7 at scan rate of 10mV/s in successive additions of prednisolone solution.

**Table 3.** Analytical results of 4-VP/MIP/GO/GCE to determination prednisolone in prepared real samples of prednisolone tablets and human plasma.

| **Sample** | **Added (**mg/ml**)** | **Found (**mg/ml**)** | **Recovery (%)** | **RSD (%)** |
|---|---|---|---|---|
| prednisolone tablets | 0.00 | 0.98 | - | - |
| | 2.00 | 1.95 | 97.50 | 2.97 |
| | 4.00 | 3.87 | 96.75 | 3.15 |
| | 6.00 | 5.90 | 98.33 | 2.77 |
| | 8.00 | 7.92 | 99.00 | 3.89 |
| Human plasma | 0.00 | 0.00 | - | - |
| | 2.00 | 1.92 | 96.00 | 2.53 |
| | 4.00 | 3.93 | 98.25 | 2.99 |
| | 6.00 | 5.91 | 98.50 | 3.31 |
| | 8.00 | 7.95 | 99.38 | 3.51 |

## 4. CONCULUSION

This study presented the synthesis of 4-VP/MIP/GO/GCE as an electrochemical sensor for the determination of prednisolone as a doping agent in sports. The modified Hummers method was applied to the preparation of GO nanosheets which were electrodeposited on GCE. The MIP was modified on GO/GCE, and then 4-VP was electrodeposited on MIP/GO/GCE. Results showed GO nanosheets surface with cracks and fractures, and morphology of 4-VP/MIP/GO/GCE indicated high porous structure due to created cavities from the agglomeration of 4-VP and MIP molecules on corrugated edges of GO nanosheets. Results of electrochemical studies showed good stability, high selectivity, acceptable linear range, highest selectivity and lowest detection limit in comparison with the other synergetic effect of GO nanosheets and 4-VP and MIP molecules. The validity and precision of 4-VP/MIP/GO/GCE to the determination of prednisolone were evaluated in pharmaceutical samples and human biological fluids and results exhibited the acceptable recovery values and RSD values. Therefore, 4-VP/MIP/GO/GCE can be used as an accurate and reliable sensor for the determination of prednisolone in clinical samples.

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