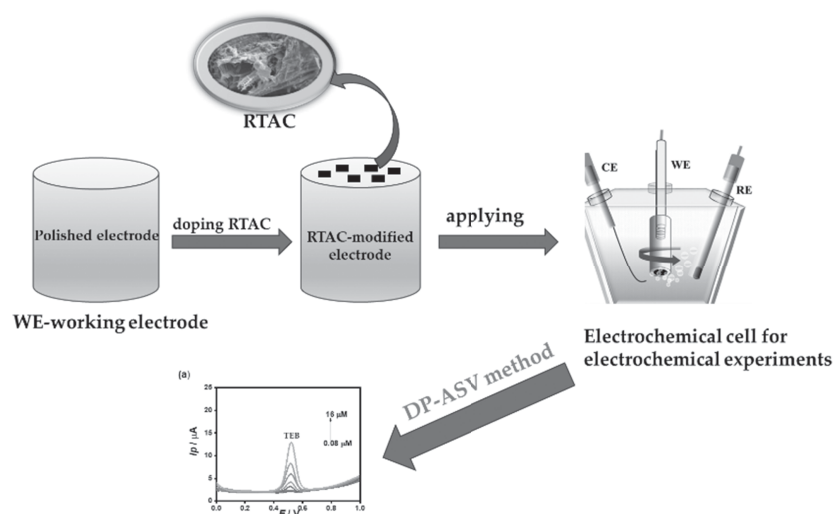# The Emerging Issue of Using Rice Straw-Derived Carbon Material in Detecting Abused Weight Medication

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Abstract:

In this work, the experimental test is concentrated on developing a modified electrode - RTAC-modified GCE. RTAC or activated carbon extracted from rice straw would be applied to modify the bare GCE. This modified electrode would detect an abused pharmaceutical in feedstock - Terbutaline (TEB). The electrochemistry method employed in the test is a differential pulse anodic stripping voltammetry (DP-ASV). The DP-ASV analysis outcomes described that TEB would be determined with good selectivity and high sensitivity on RTAC/GCE, expressing a defined peak at 515 mV. The LOD - limit of detection and LOQ - limit of quantitation of TEB in this paper were calculated to be 0.237 µM and 0.782 µM, leading to the RTAC/GCE application in detecting TEB being ensured. It could be understood that the employed sensor is optimal to apply to find the analyte due to its fabulous selective and sensitive properties.

Keywords: *DP-ASV, terbutaline, RTAC/GCE, modified electrode, abused weight medication*

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Introduction

Terbutaline sulfate (TEB) is a synthetic compound that activates β2-adrenoceptors. It is employed in the treatment of chronic bronchitis, bronchial asthma, and the management of preterm labor (Han et al., 2012; Hashem et al., 2012; Zhou et al., 2017). However, due to its ability to increase lean meat and decrease fat in various animals, it has been improperly used as a significant feed additive in livestock. TBS is highly stable and difficult to metabolize, making it prone to accumulate in animal tissues, posing a potential risk of food poisoning in humans. As a result, China and the European Union (denoted EU) have prohibited the use of TEB as a feed additive. Many countries worldwide have similar restrictions, mandating that TBS residues must not be present in animal-derived food products. Additionally, TEB is considered a prohibited substance by the World Anti-Doping Agency because it can enhance the performance of athletes (World Anti-Doping Agency, 2014).

Several different analytical techniques have been applied to identify TEB, such as liquid chromatography-tandem mass spectrometry (LC-MS/MS) (R. Li et al., 2022), ultra-performance liquid chromatography (UPLC) (Qu et al., 2011), microemulsion high-performance liquid chromatography (MELC) (Althanyan et al., 2011), high-performance thin-layer chromatography (HPTLC) (Faiyazuddin et al., 2010), and chemiluminescence (Han et al., 2012; Hao et al., 2013). While these methods are effective for detecting TEB, many of them involve complex sample preparation steps like liquid-liquid extraction and solid-phase extraction. Unfortunately, these processes are time-consuming, demand a significant amount of solvent, and often involve intricate procedures. In contrast, electrochemical sensors (Baytak et al., 2016; Felix et al., 2016; Gopal & Reddy, 2018; Y. Li et al., 2012; Wang et al., 2015) have garnered increased attention due to their rapid response, compact instruments, and user-friendly operation, offering advantages over larger instrument-based approaches. However, the literature contains limited reports on electrochemical methods for detecting TEB (Baytak et al., 2016; Felix et al., 2016; Gopal & Reddy, 2018). To overcome the challenge of the weak electrochemical signal produced by TEB on a bare electrode, it is essential to modify the electrode with appropriate catalytic materials to amplify signals and improve selectivity and sensitivity.

It is commonly recognized that carbon dots (CDs) have attracted enormous attention in sensor applications because of their outstanding performance. CDs stand out because of their ready availability, affordability, and abundant sources (Fan et al., 2020; Sharma et al., 2017), motivating numerous researchers to push for the advancement of their real-world utilization.

Electrochemical sensors have found extensive application in various analytical fields such as food analysis, the analysis of biological macromolecules, environmental analysis,

and more, primarily due to their notable attributes of high sensitivity and uncomplicated instrumentation (Brown & Schoenfisch, 2019; Hein et al., 2020; Huang et al., 2020; Lin et al., 2020). Among the materials considered ideal for use in electrochemical sensors, CDs-based materials stand out due to their excellent conductivity and substantial specific surface area (Huang et al., 2015, 2017; Zhang et al., 2015). Nevertheless, CDs have not yet seen widespread adoption in electrochemical sensors. It is maintained that a strong belief that the advantageous factors, including their broad range of synthetic sources, the presence of numerous functional groups (Zhang et al., 2015), and the capability to form composites with other materials (Huang et al., 2017; H. Li et al., 2020), provide CDs with an ever-increasing potential for the advancement of electrochemical sensors.

Therefore, in this study, RTAC extracted from rice straw has been doped onto the surface zone of the bare GCE to generate RTAC/GCE. It would be applied to detect TEB through the DP-ASV method in suitable conditions.

Material and apparatus

Chemical reagents

TEB ($C_{12}H_{19}NO_3.2H_2SO_4$), sodium hydrogen phosphate (Na_2HPO_4), citric acid ($C_6H_8O_7$), boric acid (H_3BO_3) were transported from the German-based Merck company to our laboratory in Vietnam. Britton–Robinson buffer solutions, abbreviated as B–R buffer, at a pH of 3 were created through a combination of 0.5 M solutions of H_3BO_3, H_3PO_4, and CH_3COOH. To attain the target pH of 3.2, adjustments were made using 1.0 M solutions of H_3PO_4 or 1.0 M solutions of KOH.

Apparatus

The electrochemical transfer kinetics were studied using DP-ASV with the assistance of a CPA-HH5 Computerized Polarography Analyzer from Vietnam, which featured a three-electrode system. The WE - a glassy carbon electrode (denoted as GCE) with a diameter value of 2.80 ± 0.10 mm, was modified for this purpose. Additionally, an Ag/AgCl/3.0 M KCl reference electrode and a Pt wire auxiliary electrode were employed in the analysis.

The preparation and formation of RTAC/GCE

To prepare and modify the electrons, we employed a 0.062 cm^2 electrode with a diameter value of 2.80 ± 0.12 mm. In the initial stage of the modification process, we

cleansed the electrode surface with ethanol, followed by a polishing step using alumina oxide particles measuring 0.050 μm in size. A suspension solution of RTAC was created by dispersing RTAC in ethanol solvent at a concentration of 1 mg mL^{-1} and subjecting it to ultrasonication for 60 min. Subsequently, we obtained the modified electrode by depositing 5.20 μL of the RTAC solution onto the glassy carbon electrode's (GCE) surface, which was allowed to dry at room temperature (Scheme 1). Therefore, the modified electrode RTAC/GCE has been generated for the next tests.
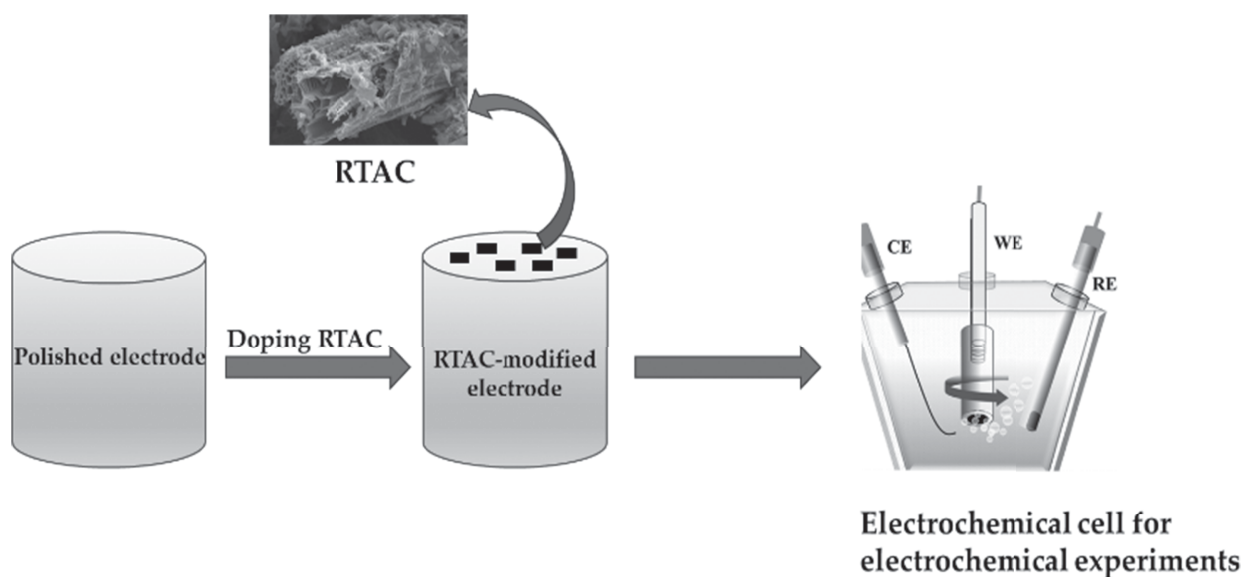
Scheme 1. The illustration of modifying GCE by RTAC for the electrochemical tests.

The differential pulse anodic stripping voltammetry

This study employed the differential pulse anodic stripping voltammetry (DP-ASV) with several machine parameters: the scan potential from 0 V to +0.9 V, rest time: 10 s, pulse amplitude +0.06 V, scan rate 20 mV/s, each potential step time 0.3 s, accumulation time 0.3 s.

Results and discussion

The electrochemical behavior of RTAC/GCE and GCE

The electrochemical technique called the DP-ASV method has been employed to investigate the electrochemical behaviors of two electrodes: a modified electrode, RTAC/GCE and a bare one, GCE (Figure 1). Figure 1 shows the signal peaks of TEB made by the two mentioned above electrodes.
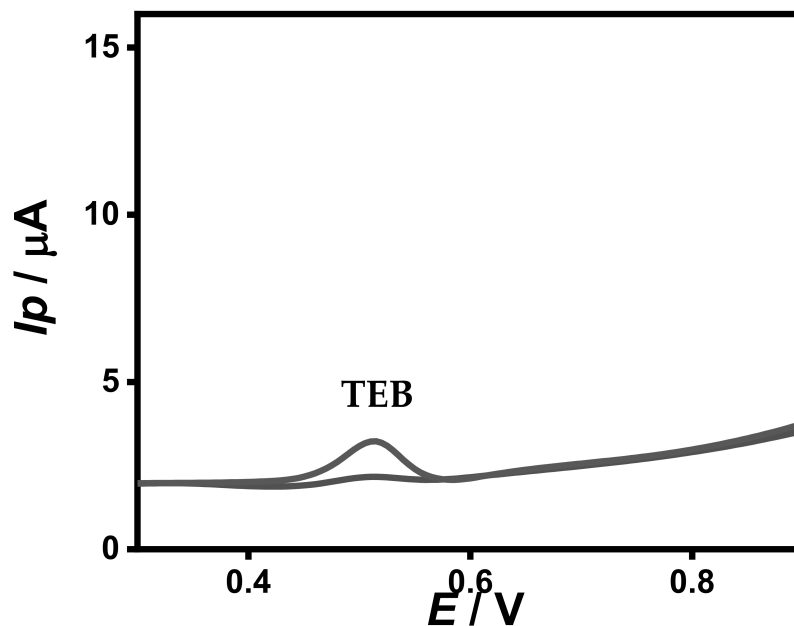
Figure 1. The DP-ASV lines of TEB with two employed electrodes: RTAC/GCE and bare GCE. Experimental conditions: the scan potential from 0 V to +0.9 V, rest time: 10 s, pulse amplitude +0.06 V, scan rate 20 mV/s, each potential step time 0.3 s, accumulation time 0.3 s.

In this figure, it is seen that the TEB signal peaks formed by RTAC/GCE and bare GCE are completely different. Through the DP-ASV technique, the TEB peak made by the bare GCE is an abroad peak, whereas a defined peak could be observed for RTAC/GCE, at 0.51 V. In addition, the RTAC/GCE's peak current is higher than bare GCE, approximately 1.5 fold. Therefore, RTAC/GCE would be selected for the next experimental tests.

The electrochemical determination of TEB through the rice straw-derived modified GCE with the detection limitation (LOD)

In Figure 2a, the DP-ASVs of TEB, featuring various concentrations in a 0.1 M BRBS buffer solution (pH = 6.2), are depicted. Figure 2b, meanwhile, showcases the description of the linear concentration, spanning from 0.09 µM to 10 µM, along with the inclusion of the linear regression equation as follows:

$$I_p \ (\mu A) = (0.118 \pm 0.044) + (0.6178 \pm 0.0089)C_{TB} \ (\mu M) \qquad R = 0.999$$

According to the *3σ* rule with some obtained results of several solution of TEB with concentration from 0.09 µM to 10 µM, the LOD of TEB is found to be 0.237 µM. The LOQ – limit of quantitation of TEB in this study is 0.782 µM. The sensitivity value of the

measurement I_p is the acquired slope value in the regression equation I_p-C_{TEB}. The calcultaed sensitivity was 0.6178 μA/μM.
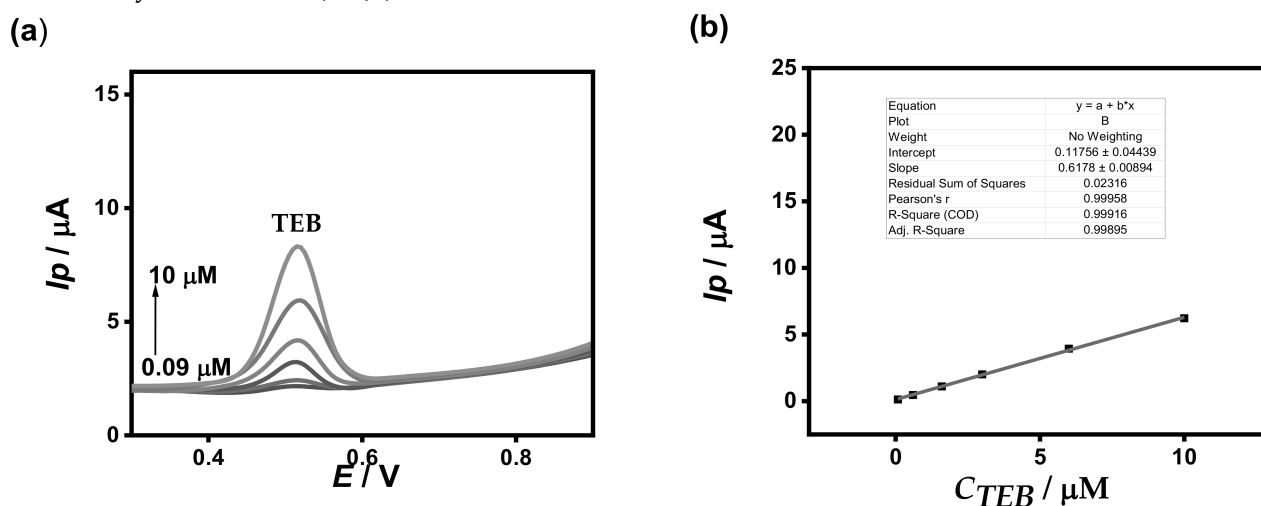

Figure 2. (a) The DP-ASV lines of TEB in various concentrations: 0.09, 0.6, 1.6, 3, 6, 10 μM; (b) The relation of *Ip vs.* C_{TEB} (μM). Experimental conditions: the scan potential from 0 V to +0.9 V, rest time: 10 s, pulse amplitude +0.06 V, scan rate 20 mV/s, each potential step time 0.3 s, accumulation time 0.3 s, pH = 6.2.

The comparison of the results acquired and prior findings

Table 1 provides a comparison between the linear range and LOD of the RTAC/GCE electrode and previously reported modified electrodes. The data in Table 1 reveals that the RTAC/GCE electrode exhibits a notably extensive linear range and a low LOD, which positions it in a comparable range to other electrodes. Consequently, this indicates that the RTAC/GCE electrode is an efficient choice for determining of TEB in water samples in the next studies.

Table 1. In comparison to modified electrodes previously published for TEB detection

No.	Electrode	Method	Linear range (μM)	LOD (μM)	LOQ (μM)	Ref.
1	MWCNTs/graphene/GCE	DPV	2.2 – 40.3	0.63	1.89	(Gopal & Reddy, 2018)
2	Poly-ACBK (acid chrome blue K)/graphene oxide-Nafion/GCE	LSV	0.0041 – 0.162	0.0062	0.0186	(Lin et al., 2013)

No.	Electrode	Method	Linear range (µM)	LOD (µM)	LOQ (µM)	Ref.
3	GNS-MWCNT-PANI/ GCE	DPV	0.024 – 80.3	0.0055	0.0165	(Kalambate et al., 2017)
4	$Eu_2O_3NPs/CNTs/GCE$	SWV	0.029 – 9.52	0.0034	0.0102	(Teker & Aslanoglu, 2019)
5	RTAC/GCE	DP-ASV	0.090 – 10.0	0.237	0.782	This work

Note: MWCNTs: multiwalled carbon nanotubes, ACBK: acid chrome blue K, GNS: graphene nanosheet, CNTs: carbon nanotubes, LSV: linear sweep voltammetry, SWV: square wave voltammetry, DPV: differential pulse voltammetry.

Conclusion

The work study expresses that the used electrode would be applied to detect TEB – an abused weight medication. Following the surface modification of the GCE with RTAC, the resultant product was employed for the quantification of TEB using voltammetric techniques, DP-ASV. The application of the DP-ASV method to detect TEB, with an LOD value of 0.237 µM, underscores the exceptional performance of the RTAC/GCE material. The results further demonstrate that the used modified electrode exhibits favorable electrocatalytic activity in improving the peak currents for the electrooxidation of TEB. The application of the DP-ASV technique enables the efficient collection of substantial TEB peaks, facilitating their exclusive examination of the RTAC-modified glassy carbon electrode (GCE). The promising analytical results and the straightforward preparation of the RTAC-modified GCE render it a compelling material for developing strongly sensitive and selective electrochemical sensors.

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