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Phoenix Dactylifera Hydrochar as a Green Modification Material Based on Glassy Carbon Electrodes for the Detection of Methylene Blue

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Abstract: A novel electrochemically sensitive sensor has been developed based on Hydrochar derived from Phoenix dactylifera was prepared for the detection of Methylene Blue (MB). These hydrochar (HC) have been used for the modification of the glassy carbon electrode (GCE). This electrode was characterized by scanning electron microscopy (SEM). The electrochemical properties of MB in the modified electrode (HC/GCE) were studied by square-wave voltammetry (SWV) and cyclic voltammetry (CV) under optimized conditions. Owing to a synergistic effect, the HC/GCE exhibited an obvious electrocatalytic effect on positively charged MB. The influence of experimental variables (accumulation time, supporting electrolyte, pH) was studied. Under optimized conditions, the constructed sensor illustrated a linear voltammetric curve for the MB in the concentration interval from 10^{-4}M to 10^{-10}M, with a detection limit of 0.2nM. A study of the effect of interference on sensor functionality was carried out, as well as an analysis of MB recovery in real wastewater samples. The modified electrode offers numerous advantages, including easy preparation, low detection limit, high sensitivity, good repeatability, short response time and an effective detection platform for MB in wastewater.

Keywords: Biomass, Methylene Blue, Glassy Carbon electrode, Electrochemical detection.

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1. INTRODUCTION

Methylene blue (MB) dye is an indicator used in various diagnostic tests and has several important aspects. MB is classified as a thiazine dye, characterized by its dark blue or bluish-green color. When it presents in alcoholic or aqueous media, it turns dark blue. It is odorless and has an air stability (1-3). In medicine, MB is used as a dye and indicator to visualize blood vessels (4,5). MB was initially proposed for sentinel node detection in various malignancies, including breast cancer (6). In the human body, it activates reductase enzymes that reduce MB to leukomethylene blue, which in turn converts methemoglobin to hemoglobin (7). Methemoglobinemia (MetHb) can develop when there is an excess of methylene blue (MB) in the body through the oxidation of hemoglobin (8). Although its applications are numerous across multiple disciplines, MB has been identified like an extremely toxic dye for newborns, causing different problems such as hyperbilirubinemia, renal failure, hemolytic anemia, hypertension, nausea, headaches, mental confusion, deep sweating and precordial pain (9-13). In addition, MB has a strong inhibitory effect on sperm motility in healthy individuals (14).

MB is commonly used in the textile, leather, cosmetics and other additional fields for various applications. Typically, residues of MB are released into various water sources, resulting in undesirable colored water that causes environmental pollution (15,16). The presence of dyes modifies the

characteristics of water such as color, taste, odor, pH, and density. Dyes cause water to become highly opaque, limiting the penetration of light and consequently reducing the levels of dissolved oxygen, thereby negatively impacting aquatic ecosystems (17). Therefore, it is essential to develop an effective technique for the detection and elimination of MB to ensure the safety of treated liquid effluent discharges. Some of the frequently employed analytical methods for MB detection include capillary electrophoresis (18), UV-Vis spectroscopy (19,20), electrochemical and surface enhanced raman spectroscopy (21) and liquid chromatography coupled to tandem mass spectrometry (8).

Despite their high sensitivity and selectivity, these methods are often difficult to implement due to their higher cost, the difficulty of sample pretreatment and the time required to perform the analysis.
Such problems can be solved by using electrochemical techniques which are relatively simple, cost-effective, accessible methods with high selectivity and sensitivity (22-25).

MB detection was performed using a gold electrode (26), a carbon paste electrode modified with thiol-functionalized clay (27), a gold nanoparticle-based glassy carbon electrode (28) and a MWCNTs-modified glassy carbon electrode (29).

Biomass is a renewable form of organic substance derived from plant and animal waste, which is used as a raw material (30). A multitude of biomasses with a porous structure and a variety of components can be carbonized to form porous biomass-derived carbon products (31,32).

In the last few years, biomass-derived products (PCs) have received considerable attention because of their special characteristics. These include excellent chemical stability, high surface area, economical precursors and a simple, environmentally-friendly preparation process (33). Biomass has been used in a number of studies for electrochemical applications. For example, Chen and his team (34) developed an activated carbon from banana stalks as a precursor material, to be used in an electrochemical application as a nitrite (NO_2^-) sensor. The three-dimensional porous structure elaborated from the kenaf stem is proving to be an excellent support for a biosensing platform (35). In addition, a hierarchical meso-macropore pore carbon derived from seaweed has been effectively applied to quantify H_2O_2 concentrations in human urine samples (36). This research shows that functional porous carbons obtained from biomass sources have great potential as innovative electrode materials.

Hydrothermal carbonization is a thermochemical conversion method that transforms biomass into hydrocarbon (37). This process, carried out in the presence of water under autogenous pressure at relatively low temperatures (generally between 150 and 300°C), has great potential as a treatment solution for biodegradable waste (38). The resulting end product, known as hydrochar, manifests itself as a solid material rich in oxygenated functional groups, consisting mainly of carbon. The particularly attractive characteristics of hydrochar are generating considerable interest in its potential applications as a substitute for carbon materials (35,39).

This article presents the modification of a glassy carbon electrode by hydrochar (HC/GCE) for MB detection. The hydrochar was created by hydrothermal carbonization of Phoenix dactylifera biomass. The chemical properties of this hydrochar give it remarkable electrocatalytic activity for MB detection. The electrode exhibited a great performance with many advantages like, easy preparation, rapid response time, high sensitivity and selectivity with LOD of 0.2 nM. In conclusion, this approach has been used effectively to identify MB concentration in wastewater samples, with promising results.

2. EXPERIMENTAL

2.1. Instrumentation
The voltammetric tests were all done with a BIOLOGIC Sciences VMP3 potentiostat/galvanostat, model (SP: 50). The ECLAB data acquisition software was utilized to oversee and track the experiments. The surface morphology of the modifier was examined using the FEI-Quanta 650 scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX).

2.2. Chemicals and Reagents
The GCE was procured from Lorraine ltd (Shanghai, Chine). The counter-electrode and reference electrode were obtained from Metrohm AG (Herisau, Switzerland). Potassium dihydrogen Phosphate, Potassium Chloride, Sodium Acetate, Sodium Hydroxide, dipotassium Hydrogen Phosphate, Alumina oxide, N,N-Dimethylformamide (DMF), Methylene blue, Methanol and Hydrochloric Acid were supplied by Fluka Chemika (Sébastien Brant, France). All solutions were produced with distilled water. All materials utilized were of analytical grade and employed without undergoing additional purification procedures. A 0.1 M phosphate buffered solution (PBS) was obtained by combining 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4. To adjust the pH of PBS solutions (pH 4-8), (0.1M) HCl and (0.1M) NaOH solutions were employed during the preparation process.

2.3. Hydrochar Preparation
Hydrochar has been prepared by the hydrothermal carbonization (HTC) process. Phoenix dactylifera kernels were washed using distilled water, then dried at 80°C for a week. It was then ground and sieved to obtain a 50 µm powder. 5g of the biomass obtained was mixed with 25 ml of distilled water. This mixture was ultrasonicated for one hour, then placed in an oven at 200°C for 24 hours. Finally, the black powder obtained was filtered. The resulting solid product, called hydrochar (HC).

2.4. Modified Electrode Preparation

Firstly, the GCE surface was refined using alumina powder with sizes of 0.05µm and 0.3µm. Then, it was carefully washed many times using distilled water and methanol using an ultrasonic bath. After this, the GCE was air-dried at room temperature. Next, 1 mg of biomass was dissolved in 1mL DMF. This solution was placed in an ultrasonic bath for 24 hours, to form a stable suspension. The purpose of this step was also to release protons from the hydroxyl groups to facilitate interaction between the modifier and methylene blue. Finally, 5µl of suspension was dropped on the surface of the electrode and the electrode (HC/GCE) was dried under an infrared lamp to evaporate any residual solvent and firmly fix the modifier to the electrode surface.

2.5. Electrochemical Measurements

The setup for the experiment consisted of a three-electrode device. It includes HC/GCE electrode as working electrode, a platinum wire as a counter-electrode and a saturated calomel electrode as the reference electrode. The unmodified and modified electrodes were analyzed by the CV method for electrochemical characterization. Furthermore, the detection tests for MB were conducted using the SWV technique. A 10^{-4} M solution of MB in different buffer solutions (0.1M) was prepared.

3. RESULTS AND DISCUSSION

3.1. Biomass and Hydrochar Characterization

Figure 1 shows that the surface morphology changed significantly as a result of the HTC process. SEM analysis of the hydrochar revealed the formation of a porous surface, coarser and rougher than that of the initial biomass prior to HTC treatment. In addition, an increase in particle size and pore volume was observed. The presence of cavities, pores and rough surfaces on the hydrochar testifies to the creation of an interconnected porous structure.

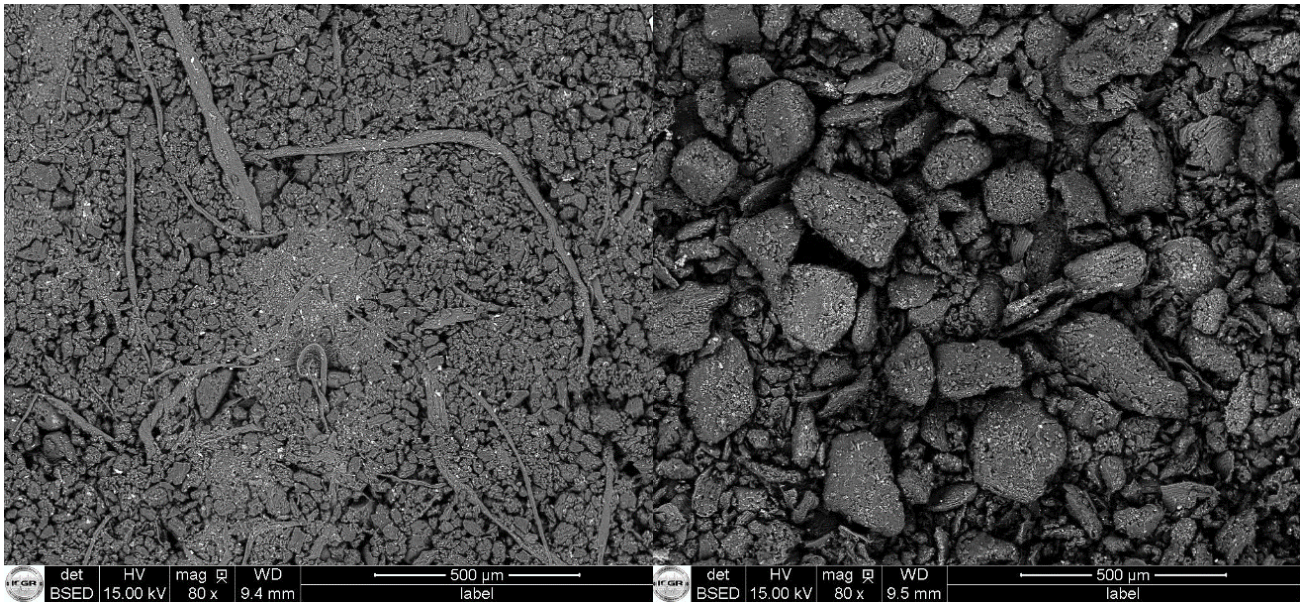

Figure 1: SEM images of Biomass (left) and Hydrochar (right).

3.2. Voltammetric Analysis

SWV is an electroanalytical technique known for its sensitivity and quick response, offering excellent resolution for analyzing the signal of the analyte. In this study, the voltammetric behavior of the MB dye was investigated using both unmodified and modified electrodes in a 0.1 M, PBS (pH=6) solution. The potential range for the analysis was set from -0.5 V to 0.2 V. At the unmodified electrode, the oxidation of the MB dye occurred at -0.21 V, accompanied by a peak current reaching a maximum of 50 µA. The electrode modified with HA/GCE showed an increase in MB response current to 325 µA, as shown in Figure 2.

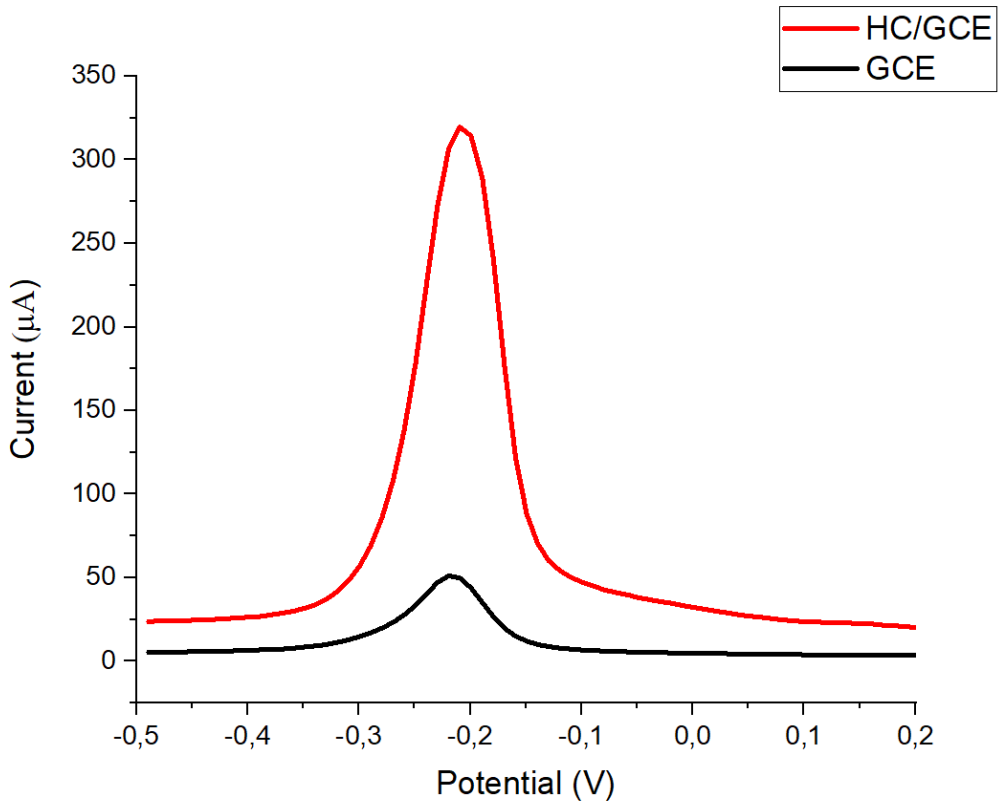

Figure 2: Comparative SWVs of (10^{-4}M) MB at the unmodified and modified electrodes in a potential range of -0.5 to 0.2 with an accumulation time of 60s in PBS (pH=6).

This increase is due to the presence of hydrochar, characterized by its porous structure offering a large surface area. This characteristic increases the active surface of the electrode, enhancing the adsorption and electrochemical reactions of the species concerned (40). This increase in specific surface area improves MB detection sensitivity. This increase is also due to the presence of negatively charged deprotonated hydroxyl groups on the surface of the modified electrode, facilitating interaction with the positively charged MB.

Figure 3 illustrates the suggested mechanism for the oxidation of MB, which involves the transfer of two protons and two electrons (29,41,42).

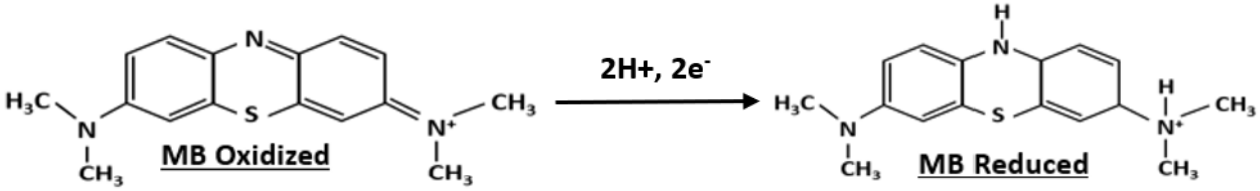

Figure 3: Suggested oxidation mechanism for MB at HC/GCE.

3.3. Influence of the Scan Rate

Cyclic voltammetry experiments were conducted to evaluate the impact of scan rate on MB dye peak current, varying scan rates from 10 to 250 mV/s as seen in (Fig.4a). The objective was to identify if the electrochemical reactions were controlled by adsorption or diffusion processes by examining the correlation between signal strength and scan speed, The objective was to identify if the electrochemical reactions were controlled by adsorption or diffusion processes by examining the correlation between signal strength and scan speed. The curve of I= f (V) with a linear plot in (Fig.4b) indicates that adsorption controls the reaction process and the curve of I= f ($V^{1/2}$) with a linear plot in (Fig.4c) suggests that the reaction is controlled by diffusion. Log (I_p) = f (log (V)) with a slope of 0.58, as shown in (Fig.4d), indicates the presence of adsorption and diffusion processes in the reaction. The dominance of the diffusion process is evident as the R^2 of the curve I= f (V) in (Fig.4b) is lower than the R^2 of the curve I= f ($V^{1/2}$) in (Fig.4c).

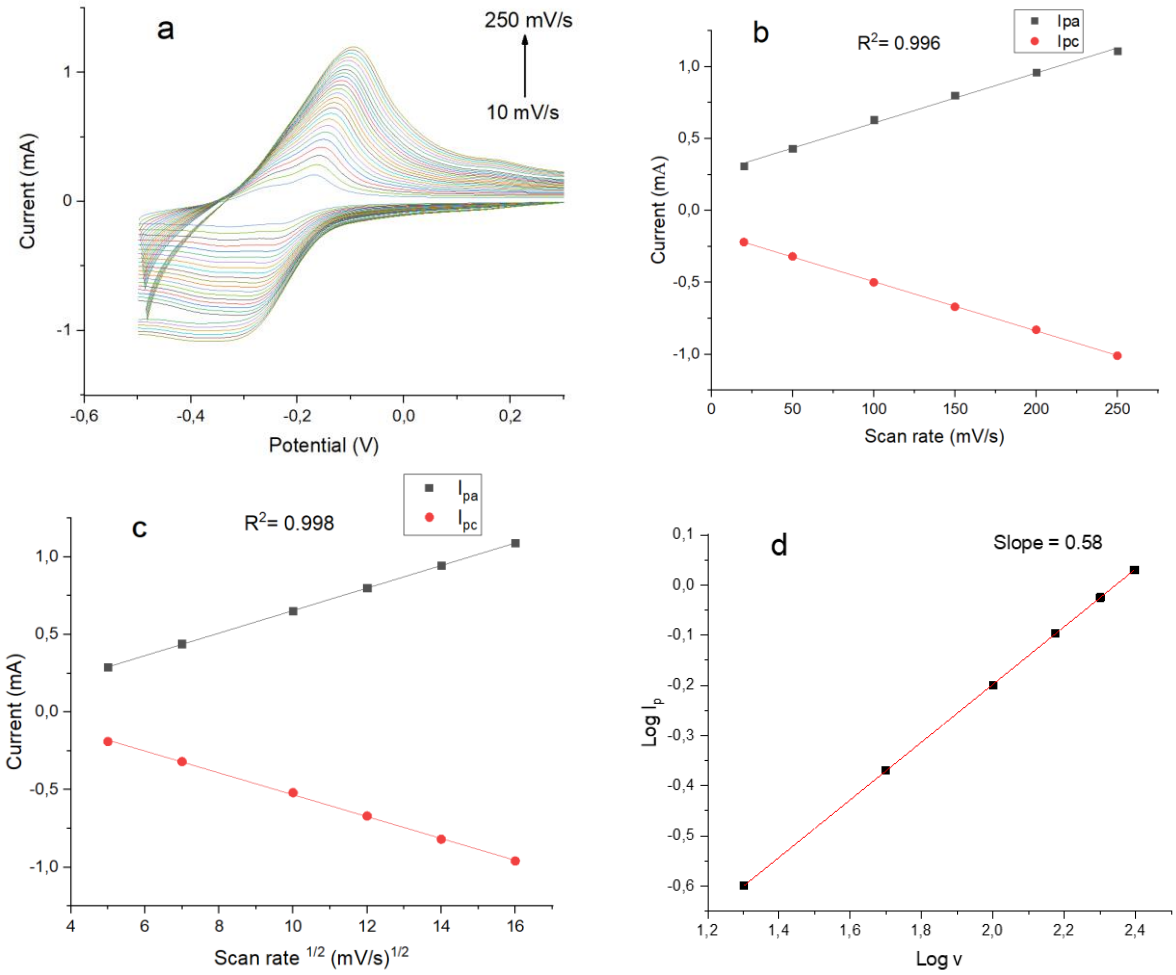

Figure 4: (a) CV of (10^{-4}M) MB at different scan rates, (b) influence of the evolution of v on the intensity of the redox current, (c) influence of the evolution of $v^{1/2}$ on the intensity of the redox current and (d) Plot of the log of the oxidative peak current vs log of scan rate in PBS (pH=6).

3.4. Experimental Parameters Optimization

Various parameters have been optimized to maximize the current response of the MB by the use of the co-doped electrode. The choice of electrolyte is crucial to achieve a robust and strong signal of the target analyte. Therefore, various supporting electrolytes were investigated: PBS, KCl, HCl, and acetate at pH 7.0 with a concentration of 0.1 M.

PBS proved to be the most suitable supporting electrolyte, where the analyte showed oxidation with a maximum current response and a definite peak relative to other electrolytes. The bar graph in (Fig.5a) illustrates that PBS is the optimal supporting electrolyte for MB detection.

The impact of pH was studied using PBS solutions with pH ranging from 4 to 8. As shown in (Fig.5b), the strongest signal was obtained at pH 6.0. In an acidic electrolyte medium, the presence of a high concentration of H^+ ions result in a reduction of the oxidation peak of MB. This phenomenon can be attributed by the fact that the hydroxyl groups of the hydrochar, being already negatively charged, tend to attract protons from the solution instead of the MB molecule, which reduces the response of the oxidation peak.

As the pH of the solution increases, the competition between cationic MB and H^+ ions decrease due to a decrease in the concentration of H^+ ions in the medium. This leads to a greater interaction between the modifier and MB molecules, promoting their preconcentration at the electrode surface. When the pH of the solution exceeds 6, the presence of a high concentration of OH^- ions can prevent the access of cationic MB molecules to the electrode surface. Consequently, a decrease in the intensity of the MB current peak is observed. Hence, the pH value of 6 was identified as the optimal pH for PBS.

The effect of the accumulation time of MB on the surface of the modified electrode was examined in the range of 5 seconds to 120 seconds (Fig.5c). A rise in the current intensity is observed with an increase in the accumulation time from 5 seconds to 60 seconds. After a duration of 60 seconds, a decline in intensity values is observed, suggesting saturation of the binding sites required for MB attachment to the electrode surface. Therefore, 60s is the optimal accumulation time. Examining the accumulation potential, we found no significant change.

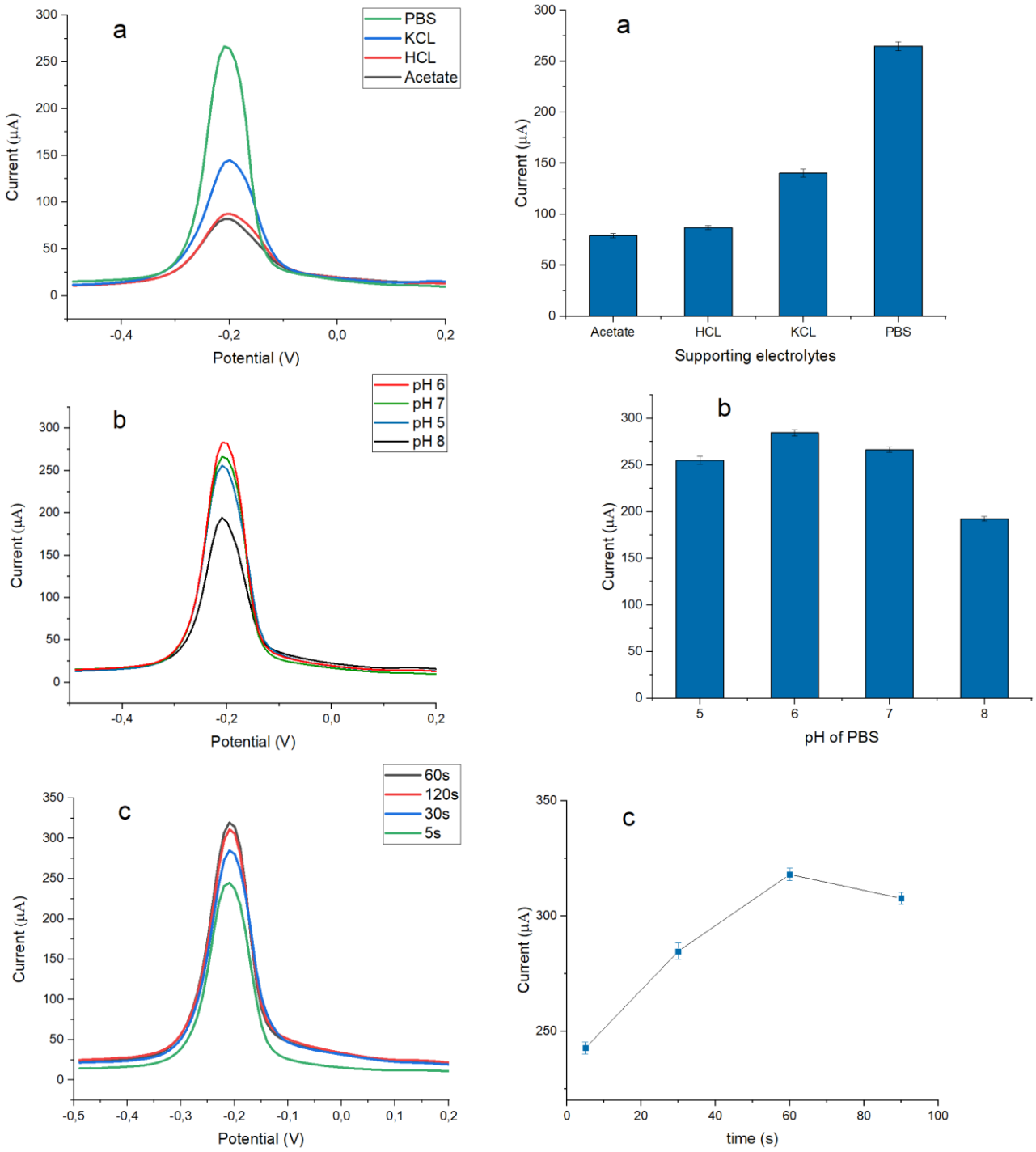

Figure 5: Variation of experimental parameters (a) electrolyte, (b) Electrolyte pH, (c) Accumulation time on the response of the HC/GCE in presence of 10^{-4}M (MB).

3.5. Calibration Study

The SWV was employed to evaluate the detection capability of the co-doped electrode that was prepared with the previously mentioned optimal physicochemical parameters. Different concentrations of MB were examined and the results are illustrated in (Fig.6a).

(Fig.6b) displays a linear correlation between peak current and MB concentration, ranging from 10^{-4} M to 10^{-10} M. A calibration curve demonstrating the linearity between peak current and concentration (10^{-4} M to 10^{-10} M) is represented in (Fig.6b).

The limit of quantification (*LOQ = 10 σ/m*) and detection (*LOD = 3 σ/m*) for the target analyte were determined based on the calibration curve, following the guidelines set by *IUPAC* (43). The calculated LOD and LOQ of MB are $2x10^{-10}$M and $4x10^{-10}$M respectively. Table 1 compares different modified electrodes for MB determination.

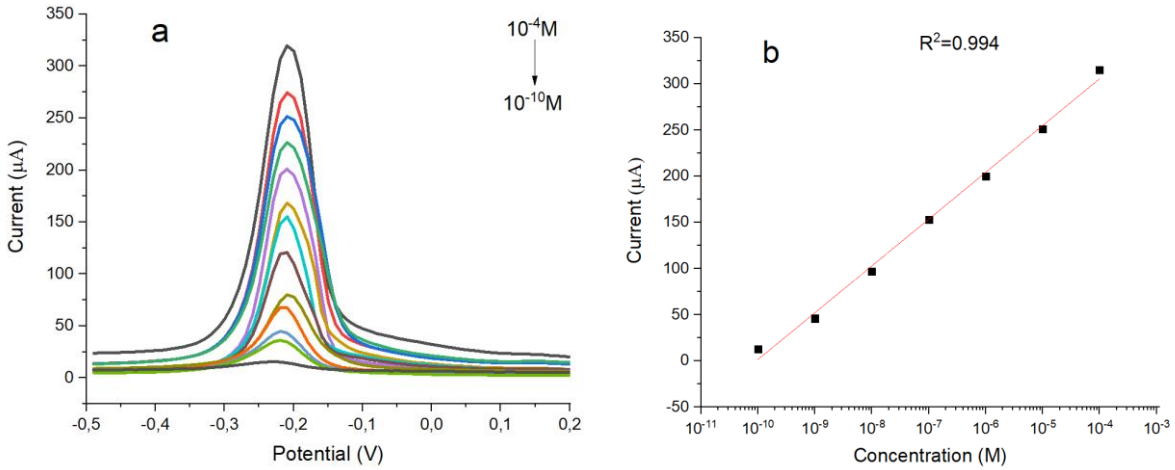

Figure 6: (a) SWV of MB detection on the HC/GCE for various concentrations under optimal conditions, (b) calibration curves of MB in PBS (pH=6).

Table 1: Comparison of the HC/GCE detection limits with other modified electrodes.

Methylene Blue	Electrode Modifier	LOD (nM)	Reference
Oxidation	Self-doped TiO_2 nanotubes	475	(44)
Oxidation	Thiol functionalized Clay	400	(27)
Oxidation	Ibu-AuNps	3.9	(28)
Oxidation	NH_2-fMWCNTs	0.21	(29)
Oxidation	HC/GCE	0.2	This Work

3.6. Interference Study

The interference generated by other substances present in the actual sample plays a central role in determining a sensor's selectivity. Table 2 shows various substances and dyes for their interference on the MB dye current signal using the modified sensor. Each interferant was combined in a 1:1 ratio with the MB dye solution. Positive values indicate an increase in the actual response of (10^{-4}M) MB.

According to the data in the table, ions such as Mg^{2+}, Mn^{2+}, Remazol Red, Remazol Yellow and Methyl Orange produced no interference effect, while the other components showed a positive interference effect. According to the data obtained, the influence of interference remains well within the tolerable limit of ±5%. This means that the sensor developed is selective for the detection of MB in real samples containing other substances.

Table 2: Effect of interference (%) in MB determination by other compounds.

Compound	Interference (%)	Compound	Interference (%)
Mg^{2+}	0.0	**Pb^{2+}**	+3.0
Mn^{2+}	0.0	**Remazol Yellow**	0.0
Zn^{2+}	+1.5	**Blue Patent**	+1.0
Cu^{2+}	+2.0	**Remazol Red**	0.0
-	**-**	**Methyl Orange**	0.0

4. RECOVERY OF MB IN WASTEWATER SAMPLES

The applicability of HC/GCE was tested for the determination of MB in wastewater samples recovered from Rabat area. The wastewater was first filtered and different concentration of MB were added. Recovery rates ranged from 92% to 96% (table 3). In addition, the relative standard deviation of five parallel determinations using electrodes from different batches proved to be less than 5%. This indicates that HC/GCE exhibits remarkable reproducibility, making it suitable for analytical determinations in real sample matrices.

Table 3: Determination of MB in wastewater.

Conc. added (M)	Conc. Found (M)	Recovery (%)	RSD% (n=5)
5.5×10^{-5}	5.2×10^{-5}	94.5%	3.5
1.35×10^{-5}	1.25×10^{-5}	92.6%	2.3
5.5×10^{-6}	5.3×10^{-6}	96%	4.1

5. CONCLUSION

In this work, we successfully developed a novel electrochemical sensor by modifying a glassy carbon electrode with hydrochar derived from Phoenix dactylifera. This modified electrode (HC/GCE) demonstrated exceptional electrocatalytic activity for the detection of Methylene Blue (MB). The hydrochar was prepared through hydrothermal carbonization of the biomass, resulting in a porous structure with excellent electrochemical properties. The sensor's performance was extensively evaluated through various experiments. Cyclic voltammetry and square wave voltammetry analyses indicated a significant increase in the response current of positively charged MB at the HC/GCE compared to an unmodified electrode.

In conclusion, the hydrochar-modified glassy carbon electrode (HC/GCE) presented a highly sensitive, selective, and efficient platform for the electrochemical detection of Methylene Blue. This sensor holds great promise for practical applications in wastewater analysis, environmental monitoring, and related fields.

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