

# Individual and simultaneous electrochemical determination of metanil yellow and curcumin on carbon quantum dots based glassy carbon electrode

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## ABSTRACT

Adulteration of medicinally valuable curcumin (CU) with harmful chemicals as metanil yellow (MY) in recent years have demanded for quick detection techniques of the adulterants. The voltammetric behavior of CU and MY on bare glassy carbon electrode (BGCE) and carbon quantum dots modified glassy carbon electrode (CQDs/GCE) was studied by both cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in phosphate buffer solution of pH 5.4. The MY responded to the CQDs/GCE with two anodic peaks at  $-0.004$  V and  $0.136$  V and two cathodic peaks at  $-0.112$  and  $-0.048$  V. Under similar conditions CU exhibited two anodic peaks at  $0.28$  V and  $0.55$  V and one cathodic peak at  $0.25$  V. The overlapped voltammogram obtained for CU and MY on BGCE was well separated on the CQDs/GCE. The interference studies revealed that the compounds, demethoxycurcumin and bisdemethoxycurcumin, which are commonly associated with CU, did not interfere with the detection of MY. Real sample was analyzed with fabricated electrode and the recovery values  $> 98\%$  were obtained.

## 1. Introduction

The polyphenol curcumin (1,7-bis (1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadione-3,5-dione) is an important natural phytochemical found in the rhizomes of *Curcuma longa* or turmeric, which is known for its medicinal properties. Due to its high medicinal potential with virtually no side effects, this compound has attracted considerable interest in recent years [1–3]. Curcumin has been shown to possess antioxidant, antitumor activities, antiviral, antibacterial, antifungal, immunomodulatory and anti-inflammatory [4–6]. It has also been reported that curcumin regulates classic and alternative pathways in the nervous system, and is being used in the treatment of Alzheimer's disease, multiple sclerosis, and dementia [7–9]. It is yellow colored common food additive used as both coloring agent and spice. Currently, adulteration of curcumin with various non-permitted dyes including, sudan and metanil yellow is common in countries of Asia for economic gain. Metanil yellow (sodium salt of *m*-[(*p*-anilinophenyl) azo] benzene sulphonic acid) is a highly toxic and mutagenic monoazo dye. Their excess utilization, beyond the safe limits, in colored food can cause allergies, hyperactivity, liver damage, infertility, anemia, cancer and birth defects [10]. So it is beneficial if we could develop a method to

screen the presence of MY in such compound.

Due to high sensitivity, accuracy, and precision of the electrochemical techniques are widely used for the determination of biological and environmental analysis [11, 12]. With the development of more sensitive pulse methods, the electroanalytical studies are more frequently used for the industrial and environmental applications. Most of the electroanalytical techniques are based on the concept of continuously changing the applied potentials to the electrode/solution interface and the resulting measured current [13], therefore the modification of electrode surface by physical or chemical means will play crucial role in such measurement by enhancing the sensitivity, selectivity and reproducibility [11–14]. Several approaches have been made to fabricate the modified electrode for the electrochemical detection/analysis of biological and environmental samples [15–17]. In most of the cases carbon based electrodes such as carbon paste, glassy carbon, carbon nano fibers, carbon nanotubes etc. modified with modifiers like chemical compounds, nano materials, ionic liquids or surfactants were used as a working electrode [16–21].

Both MY and CU are electrochemically active, therefore they can be detected electrochemically. Li et al., fabricated graphene modified glassy carbon electrode for the electrochemical detection of curcumin

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[22]. Electrochemical behavior of curcumin at a platinum electrode was explored by Masek et al. [23]. Later in 2015 Semiha Çakır et al. developed PdNp-graphite electrode by aqueous solution process with  $\text{Al}^{3+}$  for electrocatalytic oxidation of curcumin [24]. Recently Zhang et al. reported the electrochemical determination of curcumin by using electrochemically reduced graphene oxide modified glassy carbon electrode [25]. Electro activity of MY on Pt electrode has also been studied and an irreversible cathodic peak due to the reduction of  $\text{N}=\text{N}$  was reported by Jain et al. [26]. Different methods like high performance liquid chromatography - electrospray ionization tandem mass spectrometry [27], high performance capillary electrophoresis [28], micellar chromatographic method [29] were also been used for detection of metanil yellow.

Carbon quantum dots (CQDs) are emergent star in the nanocarbon family, due to their benign, abundant and inexpensive nature [30]. CQDs are a new class of carbon nanomaterials with sizes < 10 nm, first obtained during purification of single-walled carbon nanotubes through preparative electrophoresis in 2004 [31]. CQDs show high aqueous solubility, robust chemical inertness, easy functionalization, and high resistance to photo bleaching, low toxicity and good biocompatibility [30, 32–35].

Till now, there hasn't been any report on the electrochemical detection of MY in the presence of CU, therefore we made an attempt to address this issue. In our previous report we explained about the synthesis and characterization of hydroxyl passivated CQDs, which was applied for the fabrication of modified glassy carbon electrode (CQDs/GCE) and used for the electrochemical detection of dopamine [36]. In this work, we extended the application of the same CQDs for the fabrication of CQDs/GCE for the electrochemical detection of MY and CU simultaneously.

## 2. Materials and methods

### 2.1. Reagents and chemicals

Metanil yellow and curcumin were purchased from Merck, Mumbai, India. Demethoxycurcumin and bisdemethoxycurcumin were purchased from sigma-aldrich, Milwaukee, WI, USA. A fresh solution of CU and MY was prepared by dissolving them in ethanol. 0.1 M Phosphate buffer (5.4 pH) as the supporting electrolyte. All the reagents were extra pure and were used without further purification. The garden fresh turmeric was used for real sample analysis and a MY added turmeric powder as the adulterated sample.

### 2.2. Apparatus and procedure

Electrochemical experiments were performed with a VSP-potentiostat/galvanostat (Biologic Science Instruments) consisting a conventional three-electrode system with a bare or CQDs modified glassy carbon electrode (3 mm in diameter) as the working electrode, a platinum wire electrode as the counter electrode and a saturated calomel electrode as the reference electrode. The glassy carbon electrode was cleaned thoroughly by polishing with successive slurries of 1.0, 0.3 and 0.05  $\mu\text{m}$  alumina in distilled/deionized water on a polishing micro cloth prior to the modification. The electrode was sonicated in distilled/deionized water for 10 min between slurries. Subsequently, 0.5  $\mu\text{L}$  nafion oil (0.5 wt%) was added on to its surface followed by the addition of 7  $\mu\text{L}$  CQDs (0.1 mg/mL) and then air dried for 15 min.

### 2.3. Electrochemical determinations

CV in the potential range from  $-0.6$  to  $1.3$  V was used to study the electrochemical behavior of both MY and CU on BGCE and CQDs/GCE in PBS of pH 5.4. The detection limit and selectivity of the electrode was established by DPV in the potential window of  $-0.6$  to  $1.0$  V.

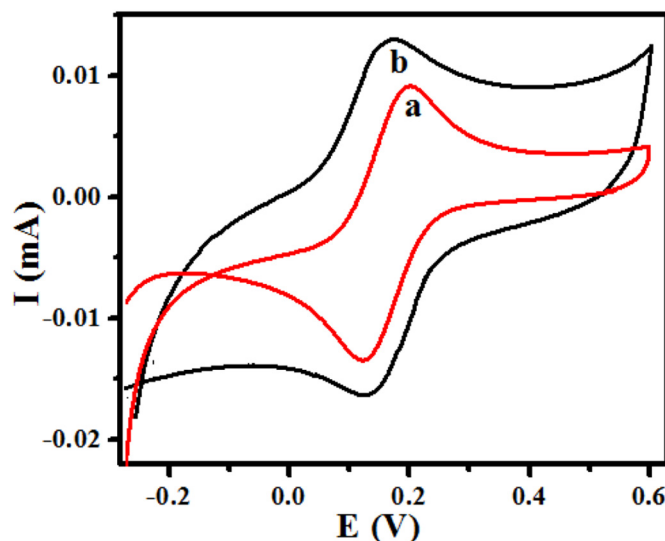


Fig. 1. Cyclic voltammograms of BGCE (curve a), CQDs/GCE (curve b) in 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  in 0.1 M KCl with a scan rate of 50 mV/s.

## 3. Results and discussion

### 3.1. Preparation of CQDs/GCE

The CQDs was prepared from maltose by the procedure reported in our earlier work [36]. Briefly, the charring product obtained by the microwave digestion of maltose was stirred for half an hour at 800 rpm with a much diluted solution of NaOH (100 mL of  $8 \times 10^{-5}$  M) of pH 7.4). For the fabrication of CQDs/GCE, 0.5  $\mu\text{L}$  nafion oil was added on to the cleaned surface of glassy carbon electrode followed by the addition of 7  $\mu\text{L}$  CQDs and then air dried for 15 min.

### 3.2. Electrochemical characterizations

Electrochemical property of the fabricated electrode was explored by treating potassium ferricyanide/ferrocyanide probe in KCl supporting electrolyte. Fig. 1 showed the cyclic voltammogram of  $\text{K}_3\text{Fe}(\text{CN})_6$  in 0.1 M KCl at 50 mV/s on bare and modified electrodes. In case of BGCE (curve a), the oxidation peak was observed at a potential 181 mV with a peak current of 9.1  $\mu\text{A}$  and the reduction potential was obtained at 113 mV with peak current  $-13.5 \mu\text{A}$ . The peak to peak separation on BGCE was 68 mV. In comparison with BGCE, the modified electrode illustrated higher oxidation (13  $\mu\text{A}$ ) and reduction current ( $-17.5 \mu\text{A}$ ) with a shift in potential (curve b). The observed peak separation potential of 62 mV, was nearer the value of 59/n mV expected for a reversible system, suggesting the reversible behavior of the redox couple of  $\text{K}_3\text{Fe}(\text{CN})_6$  on CQDs/GCE in KCl medium. The increase in peak current and shift in peak potential confirmed the electro catalytic performance of the fabricated electrode. The concentration of CQDs and the time taken for the electrode preparation was optimized. It was observed that 7  $\mu\text{L}$  concentrations of CQDs for 15 min were sufficient to produce maximum sensitivity (Fig. S1a & S1b).

### 3.3. Electrochemical behavior of MY on CQDs/GCE

The electrochemical behavior of CQDs/GCE and BGCE in the presence of 2  $\mu\text{M}$  MY in 0.1 M PBS of pH 5.4 was investigated by CV at a scan rate of 50 mV/s. As showed in Fig. 2, at BGCE, two anodic peaks ( $\text{Epa}_1$  and  $\text{Epa}_2$ ) and two cathodic peaks ( $\text{Epc}_1$  and  $\text{Epc}_2$ ) were obtained. The  $\text{Epa}_1$  and  $\text{Epa}_2$  were located at a potential of 0.325 V and 0.451 V with a peak current of 4.3  $\mu\text{A}$  and 5.2  $\mu\text{A}$  respectively. Similarly the  $\text{Epc}_1$  and  $\text{Epc}_2$  were obtained at a potential of 0.403 V and 0.242 V with a peak current of  $-5 \mu\text{A}$  and  $-5.7 \mu\text{A}$  respectively. For the CQDs/GCE,

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