



Anal. Bioanal. Chem. Res., Vol. 7, No. 3, 365-373, July 2020.

Development of an Electrochemical Sensor for a Sensitive Determination of Metanil Yellow

Mahmoud Roushani^{a,*}, Zeinab Rahmati^a and Behruz Zare Dizajdizi^a

Department of Chemistry, Ilam University, Ilam, Iran

(Received 21 October 2019 Accepted 13 February 2020)

In this work, we introduced a sensitive electrochemical sensor in order to accurately detect metanil yellow (MY). Multi-walled carbon nanotube-chitosan (MWCNTs-Chit) nanocomposite was applied to fabricate the sensor on the glassy carbon electrode. The scanning electron microscopy (SEM) was used to investigate the physical morphology of the modified electrode surface. The rate of the electron transfers between MY and electrode can be quickened by the attendance of MWCNTs-Chit nanocomposite due the high surface area, good conductivity as well as excellent catalytic property. The sensitively quantitative detection of MY was carried out by the monitoring increase of differential pulse voltammetric (DPV) responses of the sensor. The prepared MWCNTs-Chit/GC electrode illustrated a linear response to MY concentration in the range of 1.0-300.0 μM with a sensitivity and a limit of detection ($S/N = 3$) of 20.0 $\text{nA } \mu\text{M}^{-1}$ and 0.3 μM , respectively. Accordingly, to determine MY in real samples with satisfactory results, we applied the proposed sensor.

Keywords: Electrochemical sensor, Metanil yellow, Nanocomposite

INTRODUCTION

Metanil yellow (3-(4-Anilinophenylazo) benzene sulfonic acid) (Fig. 1A) can be regarded as an azo dye. In Azo dyes one can find the presence of one or more azo bonds (-N=N-). It is worth mentioning that they can be applied for industrial uses such as textiles printing, dyeing, food, cosmetics, and textile industry [1,6]. The extensive discharge of such dyes through wastewater effluents has had considerable environmental concerns, both due to their color and also many azo dyes and their breakdown products (aromatic amines) which are toxic, carcinogenic, and not readily biodegradable [7-10]. Thus, for both environmental and health reasons, the accurate, sensitive and fast detection of these dyes in industry or domestic effluents has gained considerable attention. Some physicochemical methods, such as high-performance liquid chromatography [11], thin layer chromatography (TLC) [12,13] and solid phase spectrophotometry [14,15] were applied for determination

of MY. These methods are not only time consuming, but also are economically unsuitable. So, in this work, a method, having some specific advantages over other methods regarding its time requirement, labor need, material consumption, and simplicity, is proposed for the determination of MY.

Recently, carbon nanotubes because of some specific features such as electrocatalytic activity, wide potential window, high electrical conductivity, and large surface-to-volume ratio have received considerable attention in research activities for MWCNT-based sensors development in the field of electroanalytical chemistry [16,18]. As a polysaccharide, Chitosan (Chit) can be derived from deacetylation of chitin. It is worth noting that Chit, due to its significant features such as excellent film-forming ability, high permeability towards water, good adhesion and biocompatibility, has gained excessive attention in constructing electrochemical sensors [19,20].

In this study, the analytical performance and the fabrication of an electrochemical sensor-based MWCNT-Chit nanocomposite modified GCE have been reported. The

*Corresponding author. E-mail: m.roushani@ilam.ac.ir

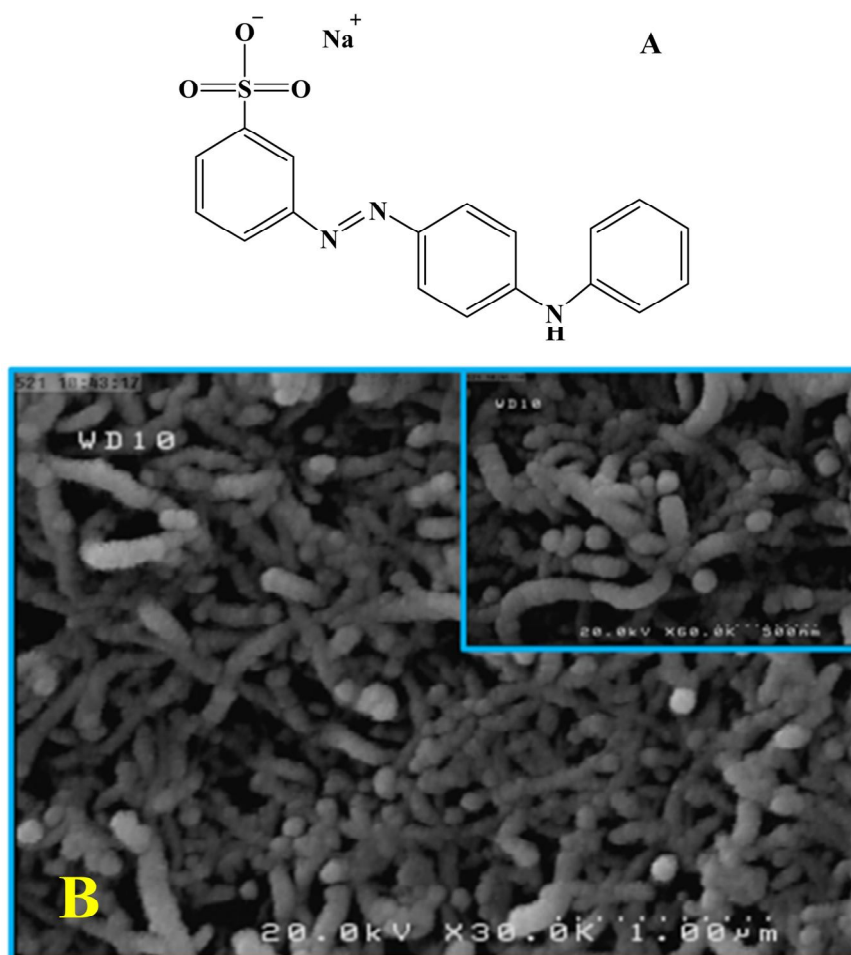


Fig. 1. (A) Chemical structure of MY and (B) SEM image of MWCNT-Chit/GCE.

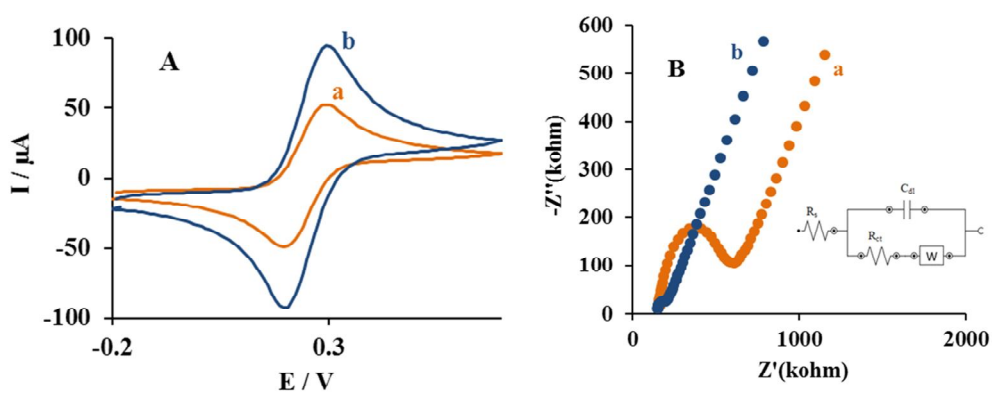


Fig. 2. Cyclic voltammograms (A) and Nyquist plots (B) for GCE (a) and MWCNTs-Chit/GCE (b) in the presence of 5.0 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ solution containing 0.1 M KCl. Scan rate for the cyclic voltammetry studies was 100 mV s^{-1} .

sensor was fabricated by drop-coating of nanocomposite on the surface of GCE and it was successfully used to determine MY. Based on our knowledge, the determination of MY concentration in wastewater using electrochemical method has not yet been reported.

MATERIALS AND METHODS

Reagents

MY, Chitosan and MWCNTs were purchased from Merck (Darmstadt, Germany), and were used without further purification. All other reagents were purchased from Sigma-Aldrich, Merck or Fluka chemical companies. The chemicals were in analytical grades and used as received without further purification. Double distilled water was used for the preparation of the solutions. The buffer solution (0.1 M) was prepared from Na_3PO_4 , NaH_2PO_4 and Na_2HPO_4 while the pH was adjusted with 0.1 M H_3PO_4 or 1.0 M NaOH.

Apparatus

The electrochemical measurements such as cyclic voltammetry (CV), differential pulse voltammetry (DPV), electrochemical impedance spectroscopy (EIS) and amperometry were carried out using a μ -AUTOLAB electrochemical system Potentiostat/Galvanostat (Eco-Chemie, Switzerland) equipped with NOVA 2.1 software. A 10 ml glass cell containing three electrodes was used to do the measurements: a modified or unmodified GCE as a working electrode, a platinum wire as an auxiliary electrode and an Ag/AgCl (3 M KCl) as a reference electrode. During the measurements, the PB in the cell was not stirred. The scanning electron microscopy (SEM) images were obtained with a Vega3-Tescan electron microscope, Czech Republic. A Metrohm pH meter of 780 model from Switzerland was used for adjustment of the pH.

Preparation of the Modified Electrode

Before modification, alumina slurry was used in order to polish the glassy carbon electrode. Afterward, the electrode was sonicated thoroughly with ethanol in order to separate the impurities. Then, we aimed at drying it in air. Afterwards, it was in 2.0 ml of DMF and acetic acid that we dispersed 2.0 mg of MWCNTs and 1.0 mg of chitosan,

respectively, and ultrasonicated for 20 min until a homogenous suspension of MWCNTs and chitosan was obtained. Then, we aimed at mixing the two suspensions and ultrasonicated them for 20 min. Next, 5.0 μl of the suspension was coated onto GCE and air-dried freely at ambient temperature. The obtained electrode was denoted as MWCNTs-Chit/GCE.

RESULTS AND DISCUSSION

Characterization of the MWCNTs-Chit/GC Modified Electrode

The SEM analysis was used in order to obtain further information on the MWCNTs-Chit/GCE morphology. Consequently, the results revealed that the GCE surface was covered by numerous nanotubes which increased the area of electrode and supplied active sites for the MY adsorption (Fig. 1B).

The electrochemical characteristic of bare GCE and MWCNTs-Chit/GCE were studied by CV, in 0.1 M KCl solution which contained 5.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$ redox probe at scan rate of 0.1 V s^{-1} . Figure 2A illustrates oxidation and reduction peaks. In comparison to the bare GCE, the high intensity of peak current and low peak potential separation ΔE_p ($E_{pa} - E_{pc}$) can be explained by the fast electron-transfer kinetic and large electroactive surface area features of the MWCNTs-Chit nanocomposite.

The below Randles Sevcik equation and execution CV were used to compute the electroactive surface area of the sensing platform [21]:

$$I_p (2.69 \times 10^5) n^{3/2} A D^{1/2} C^* \nu^{1/2}$$

where I_p , n , D ($\text{cm}^2 \text{s}^{-1}$), A (cm^2), C^* (mol cm^{-3}) and ν (Vs^{-1}) denote the peak current of probe, electron-transfer number, diffusion coefficient, electroactive surface area, concentration of $\text{K}_3\text{Fe}(\text{CN})_6$ and scan rate of potential sweep, respectively. From the slope of I_p vs. $\nu^{1/2}$ plot, and the D value for $\text{K}_3\text{Fe}(\text{CN})_6 = 7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [22], and $n = 1$, the electroactive surface area value of the MWCNTs-Chit/GCE and GCE was computed to be 0.064 and 0.0314 cm^2 , respectively. The results illustrated a fundamental improvement in surface area, especially after being modified by the MWCNTs-Chit nanocomposite.

Moreover, as it is evident from Fig. 2B, the EIS was used to characterize the interfacial properties of the modified electrode. In this sense, the classical semicircular part in the high frequency region and the linear part in the low frequency region are being consistent to the interfacial electron-transfer resistance (R_{ct}) and the diffusion process, respectively. Figure 2B inset illustrates an equivalent circuit achieved by the fitting EIS data. The standard Randles equivalent-circuit model includes charge transfer resistance (R_{ct}), electrolyte resistance (R_s), Warburg impedance (W) and the double layer capacitance (C_{dl}). On the modified electrode (blue curve a) the R_{ct} value was obviously decreased, implying the relatively fast charge transfer compared to the GCE. This result is in accordance with the above CV observation.

Electrochemical Behavior of MY at the MWCNTs-Chit/GC Modified Electrode

The CV evaluated the electrochemical behavior of MY on both the modified and bare GC electrodes at the scan rate of 0.1 V s^{-1} in the PBS (0.1 M, pH = 7.0) (Fig. 3). Evidently, redox peak currents of MY (I_{pa} and I_{pc}) on MWCNTs-Chit/GCE (curve b) represented much higher peak currents than those on the bare GCE (curve a) as well as peak potential shift to negative values (shift value $\sim 0.1 \text{ V}$) with peak separation value more less than on the bare GCE. This excellent increases in intensity of the MY peak currents and shifts of peak potential can be expressed as an excellent catalytic effect of nanocomposite, indicating that the MWCNTs-Chit nanocomposite was a favorable electrochemical sensing-material for accurate and rapid determination of MY.

Optimization of Experimental Variables

Optimization of the MWCNTs-Chit-modified GCE fabrication. We investigated the effect of the MWCNTs amount and Chit on the modified electrode response. $5.0 \mu\text{l}$ MWCNTs-Chit suspension of different MWCNTs and Chit amounts were dropped onto the GC electrode and dried at room temperature to obtain different MWCNTs-Chit/GC electrodes. The results clarified that the current response of the sensor reached maximum value when the ratio of MWCNTs to Chit is 2.0. Therefore, 2.0 mg ml^{-1} of MWCNTs and 1.0 mg ml^{-1} of Chit suspension were used in

order to construct the sensor.

Influence of supporting electrolyte pH. The pH of a solution is an impressive factor in electrochemical sensing. In order to investigate the pH effect on efficiency, the oxidation peak potential (E_{pa}) of MY signal was studied in 0.1 M PBS with a pH range of -0.7 to 0.7 at scan rate of 100.0 mV s^{-1} . Figure 4A illustrates that the current response of the modified electrodes is reversible and by increasing the pH value, the formal potential (E°) is shifted to the more negative potential demonstrating that the protons were participated in the oxidation process. The linear relationship between the formal potential and the pH value was expressed as follows: $E_{pa} = 0.6409 - 0.0563 \text{ pH}$ ($R^2 = 0.9852$) (Fig. 4B). The slope of the plot of E° vs. pH value (56.3 mV) is near to the Nernst slope (59 mV) demonstrating that an equal number of electrons and protons have participated in the oxidation reaction. Unlike E_{pa} , the oxidation peak current (I_{pa}) of MY increased with the pH from 2.0 to 7.0 and reached to the maximum value at pH = 7.0 and, then, declined. Thus, the pH = 7.0 was chosen for the following electrochemical experiments (Fig. 4C).

Effect of the Potential Scan Rate

Figure 5A illustrates our aim at recording CVs in PBS (pH 7.0) at different scan rates. Accordingly, the reaction kinetics for MY electrooxidation on MWCNTs-Chit/GCE surface were obtained. The oxidation and reduction peak currents (I_{pa} and I_{pc}) of 0.3 mM MY were linearly increased (Fig. 5B) which clarified the point that electrochemical reaction of MY can be regarded as a diffusion controlled process.

We reached a linear relationship between the redox potentials (E_{pa} and E_{pc}) and $\log v$ with the regression equation as $E_{pa} = 0.0634 \log v + 0.1322$ ($R^2 = 0.9957$) and $E_{pc} = -0.0609 \log v + 0.2409$ ($R^2 = 0.9924$), respectively (Fig. 5C). Based on the Laviron's equation [23] (Eq. (1) and Eq. (2)) and measured values for S_a ($S_a = 2.3RT/(1 - \alpha)nF$) and S_c ($S_c = -2.3RT/\alpha nF$), the α value calculated from the ratio, $S_a/|S_c| = (\alpha/(1 - \alpha))$ was found to be 0.51 and n was calculated to be 1.93 ($\Sigma 2$).

$$E_{pa} = E^{0'} + 2 \frac{3RT}{(1 - \alpha)nF} \log v \quad (1)$$

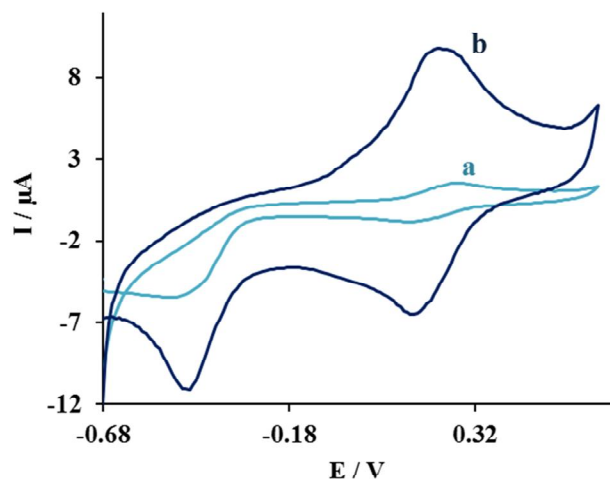


Fig. 3. CVs of GCE (a) and MWCNT-Chit/GCE (b) recorded in 0.1 M PBS (pH = 7.0) containing 0.3 mM MY at scan rate of 100 mV s^{-1} .

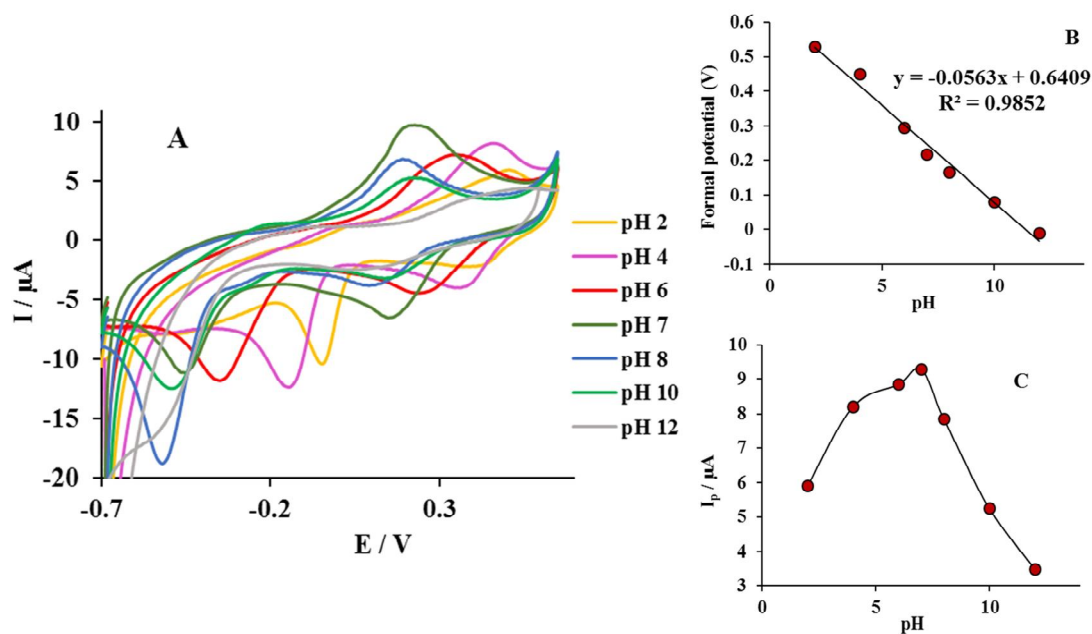


Fig. 4. (A) CVs of GC/MWCNTs electrode in 0.3 mM MY at various pHs of PBS (pH = 2.0, 4.0, 6.0, 7.0, 8.0, 9.0 and 10) for left to right, respectively, scan rate of 100 mV s^{-1} . (B) The relationship between the formal potential and pH. (C) The relationship between the peak current and pH.

$$E_{pa} = E^{0'} - 2 \frac{3RT}{\alpha nF} \log v \quad (2)$$

Accordingly, in Eqs. (1) and (2), α is the electron-

transfer coefficient, n is the number of electrons transferred in electrode reaction, v is the scan rate of applied potential range, R , T and F represent their usual meaning. In this

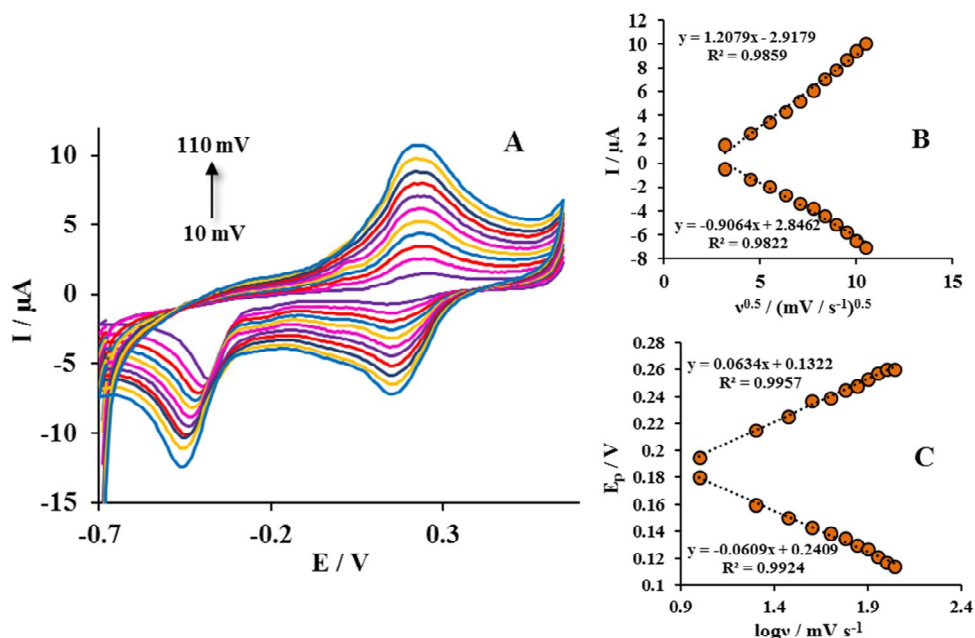


Fig. 5. (A) Cyclic voltammetric responses of a MWCNT-Chit/GC electrode in PBS (pH 7) at scan rates (inner to outer) of 5.0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 and 110 mV s^{-1} . (B) Plot of peak currents vs. the square root of scan rate and (C) Variation of peak potential vs. $\log v$.

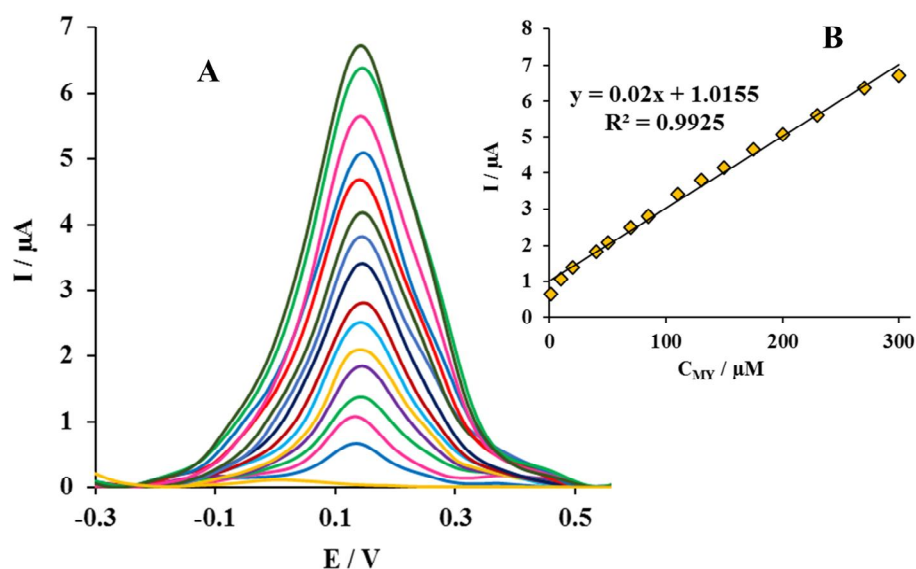


Fig. 6. (A) DPV response of different concentrations of MY (10 to 300 μM) in pH 7.0 PBS. (B) Linear curves of oxidation peak current vs. different concentrations of MY.

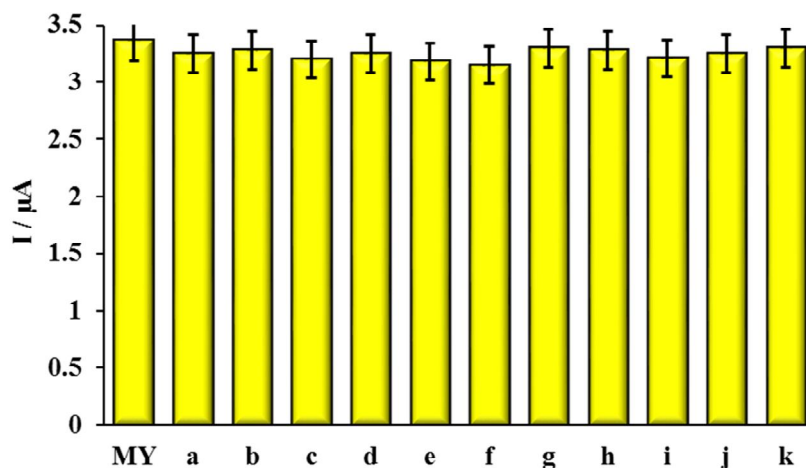


Fig. 7. Influence of the coexisting substances on the electrochemical response of MY on MWCNTs-Chit/GCE; solution composition: (1) 0.15 mM MY in 0.1 M PBS (pH = 7.0); (a to k) with 1.0 mM (a) sunset yellow (oxidation potential in PBS pH = 7: ~ 7.5 V), (b) tartrazine (~ 9.5 V), (c) brilliant blue (~ -0.3), (d) vitamin C (~ -0.15 V), (e) sodium salicylate, (f) sodium acetate, (g) glucose, (h) citric acid, (i) crocin (~ 0.6 V), (j) benzoic acid and (k) safranal (~ 1.1 V).

Table 1. Determination of MY in Wastewater Samples (n = 5)

| Sample | Added (μM) | Founded (μM) | RSD (%) | Recovery (%) |
|------------|----------------------------|------------------------------|------------|-----------------|
| Wastewater | 0 | 0 | - | - |
| | 10 | 10.12 | 2.5 | 101.2 |
| | 25 | 24.6 | 2.6 | 98.4 |
| | 50 | 51.7 | 3.0 | 103.4 |

sense, the number of H^+ in the reaction is 2 due to the fact that we have the same number of electrons and protons in the electrode reaction.

DPV Determination of MY

DPV was used in order to study the sensing performance and the applied possibility of MWCNTs-Chit/GC modified electrode toward MY detections. As Fig. 6A illustrates, under the optimal experiment conditions, the typical DPV curves were recorded for MY oxidation. The anodic peak currents (I_{pa}) of MY were

found to be proportional to its concentration in the range of 1.0-300.0 μM with linear regression equations of $I_{\text{p}} (\mu\text{A}) = 0.02 C (\mu\text{M}) + 1.0155$ ($R^2 = 0.9925$) (Fig. 6B). By applying the equation of $\text{LOD} = 3.3\sigma/m$, σ is the standard deviation of the response for blank solution, m is the slope of the calibration curve and the limit of MY detection (LOD) was calculated as 0.3 μM .

Reproducibility and Long Term Stability

It was in MY solution that the electrode-to-electrode reproducibility was also tested between five different

modified electrodes. The resulting relative standard deviation (RSD) anodic peak currents was calculated to be 2.3%, indicating an acceptable reproducibility of the sensor in the MY detection.

The stability of the MWCNTs-Chit/GCE toward MY determination was inspected by repetitive cycling of the electrode potential over the range of -0.7 and 0.7 V in PBS (pH 7.0) containing 50 μ M MY. The results indicated that after 50 repetitive cycles at a scan rate of 100 mV s^{-1} , a noticeable change was not observed at the peak current intensity and potential separation during 50 cycles. One of the important advantages of this study is high stability of the modified electrode response which can be contributed to the efficiency of the MWCNTs-Chit/GCE nanocomposite in oxidation of MY.

Interference Studies

Under the optimized experimental condition, the effect of some foreign interferences on the determination of MY were evaluated. The interferences structurally comprised similar molecules and possible coexisting additives with higher concentrations than that of MY. As shown in Fig. 7, the peak current strength after addition MY solution had no obvious difference compared with those recorded after addition MY mixture with other analogs. Therefore, this method can potentially be used for the MY detection. Figure 7 shows responses of the sensor in the absence and presence of analogs are obtainable. Based on the obtained results, these tested interferences had no significant interference on the DPV response of MY.

Analytical Application of the MWCNTs-Chit/GCE

The applicability of the sensor for the MY detection was investigated by determination of MY in a wastewater sample. The wastewater sample was provided from a factory in Ilam city. The sample (10 ml) at 5000 rpm for 15 min was centrifuged and it was filtered out (0.45 μm), and was diluted five times with the pH 7.0 (PBS). The different concentration of MY was measured in an artificially prepared specimen by adding known amounts of MY to wastewater samples and were used as real samples. As listed in Table 1, the recoveries were in the range of 99.1-102.5% and calculated RSDs values were in a good range of 0.025-0.03. The acceptable obtained precision and

accuracy reveals the applicability of the proposed sensor for analysis of MY in real samples.

CONCLUSIONS

This work presents an electrochemical method based on modified GC electrode using MWCNT-Chit nanocomposite for determination of MY by DPV technique. The modified electrode displayed excellent catalytic activity to MY oxidation. Under optimized conditions, the fabricated sensor showed acceptable reproducibility, low detection limit, high selectivity and long term stability toward the MY monitoring. The sensor was applied to determine MY in real a sample with satisfactory results.

REFERENCES

- [1] Z. Cheng, X. Quan, Y. Xiong, L. Huang, *Ultrason. Sonochem.* 19 (2012) 1027.
- [2] A. Stolz, *Appl. Microbiol. Biotechnol.* 56 (2001) 69.
- [3] Z. Cheng, X. Quan, Y. Xiong, L. Huang, *Ultrason. Sonochem.* 19 (2012) 1027.
- [4] A. Stolz, *Appl. Microbiol. Biotechnol.* 56 (2001) 69.
- [5] M. Arulkumar, P. Sathishkumar, T. Palavannan, *J. Hazard. Mater.* 186 (2011) 827.
- [6] T.D. Pham, M. Kobayashi, Y. Adachi, *Colloid Polym. Sci.* 293 (2015) 1877.
- [7] K.T. Chung, C.E. Cerniglia, *Mutat. Res.* 277 (1992) 201.
- [8] M.A. Brown, S.C. De Vito, *Environ. Sci. Technol.* 23 (1993) 249.
- [9] B. Prevot, C. Baiocchi, M.C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marci, L. Palmisano, *Environ. Sci. Technol.* 35 (2001) 971.
- [10] P. Neppolian, H.C. Choi, S. Sackthivel, B. Arabindoo, V. Murugesan, *Chemosphere* 46 (2002) 1173.
- [11] S. Bonan, G. Fedrizzi, S. Menotta, C. Elisabett, *Dyes and Pigments* 99 (2013) 36.
- [12] S.M. Dugar, J.N. Leibowitz, R.H. Dyer, *J. Assoc. off Anal. Chem.* 77 (1994) 1335.
- [13] H. Oka, Y. Ikaia, T. Ohno, N. Kawamura, J. Hayakawa, K. Harada, *et al. J. Chromatogr. A* 674 (1994) 301.
- [14] F. Capitan, L.F. Capitan-Vallvey, M.D. Fernandez, I.

- de Orbe, R. Avidad, *Anal. Chim. Acta* 331 (1996) 141.
- [15] L.F. Capitan-Vallvey, M.D. Fernandez, I. de Orbe, R. Avidad, *Talanta* 47 (1998) 861.
- [16] P.M. Ajayan, *Chem. Rev.* 99 (1999) 1787.
- [17] F. Valentini, A. Amine, S. Orlanducci, M.L. Terranova, G. Palleschi, *Anal. Chem.* 75 (2003) 5413.
- [18] M. Roushani, M. Karami, B. Zare Dizajdizi, *Microchim. Acta* 184 (2017) 473.
- [19] Y. Liu, M.K. Wang, F. Zhao, Z.A. Xu, S.J. Dong, *Biosens. Bioelectron.* 21 (2005) 984.
- [20] M. Roushani, K. Bakyas, B. Zare Dizajdizi, *Mater. Sci. Engin. C* 64 (2016) 54.
- [21] J. Bai, J.C. Ndamanisha, L. Liu, L. Yang, L. Guo, *J. Solid State Electrochem.* 14 (2010) 2251.
- [22] M.P. Siswana, K.I. Ozoemena, T. Nyokong, *Electrochim. Acta* 52 (2006) 114.
- [23] E. Lavion, *J. Electroanal. Chem.* 101 (1979) 19.