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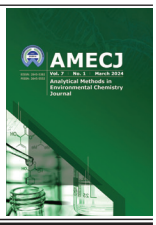

Determine methylene blue based on carbon paste electrode modified with nanoparticles of nickel oxide-nitrogen carbon quantum dots and carbon structures by cyclic voltammetry

Khalil Ibrahim Alabid [a,*] **and Hajar Naser Nasser** [b]

[a]*Ph.D. candidate of Analytical Chemistry Department, Faculty of Science, Tishreen University, Syria*
[b]*Analytical Chemistry Department, Faculty of Science, Tishreen University, Syria*

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ABSTRACT

This paper deals with an electrochemical method for the determination of methylene blue (MB) by fabrication of an electrode based on a carbon paste modified with nano-nickel oxide and nitrogen carbon quantum dots (NiO-NCQD), graphene-carbon nitride (G-C_3N_4), reduced graphene oxide (rGO), and graphite powder and paraffin oil are as a plasticizer. This electrode is used as a working electrode. The analytical method used is cyclic voltammetry (CV), The oxidation-reduction curve of methylene blue was shown using this electrode. It is a quasi-reversible curve, and it works at (pH =1) and the best acid used is HCl a concentration of (0.1M). It was also found that the linear range is within the range of (7.99-31.98 mg L^{-1}), where the oxidation equation for it can be described by the equation $I_{OX}=1.508C_{MB}+229.5$ and while the redaction equation is $I_{Red}=-2.236C_{MB}-232.5$ where is the correlation coefficient (R^2=0.9823) and (R^2=0.9722) for both oxidation and reduction respectively. The standard deviation (SD) and relative standard deviation (RSD%) were obtained at (0.361 mg L^{-1} and 0.294 mg L^{-1}) and (4.52% and 3.68%) for both oxidation and reduction respectively. Retrospective, the limit of quantitative (LOQ) and limit of detection (LOD) were achieved at (99.65%; 99.70%), (0.24 mg L^{-1}; 0.13 mg L^{-1}), and (0.071 mg L^{-1}; 0.039 mg L^{-1}) for both oxidation and reduction respectively. Methylene blue was analyzed by UV-Vis spectrophotometry at (663 nm).

1. Introduction

Dyes are colored aromatic organic compounds (VOCs) that absorb light in the visible [1]. Many organic dyes leak into water due to industrial facilities, thus causing harm to the environment [2]. One of these organic dyes is methylene blue (MB) with the chemical formula shown in Figure 1 [3]. The Methylene blue (MB) with a formula of $C_{16}H_{18}ClN_3S$ [4] is also called Methylthioninium chloride [5]. MB is from the phenothiazine family, and it is called 3,7 -Bis(dimethylamino) phenothiazine [6], heterocyclic dye [7], cationic dye [8], and it is a basic dye [9]. Methylene blue is used in many applications, for example: in the dyeing of cotton, wool, paper [9], and tattoo [11]. It seeps from industrial facilities into the aquatic environment [12] and has a toxic effect [13]. MB has harmful effects on humans/ environment, and exposure to it causes encephalopathy in humans [14]. Moreover, MB has beneficial usage, such as the treatment of high hemoglobin in the case of high levels of more than 20%, which causes a problem for patients [15], the detection of Alzheimer's [16], the treatment of COVID-19 [17], useful in surgery [18], can be biologically utilized as a drug [19], and

*Corresponding Author: Khalil Ibrahim Alabid
Email: khalilibrahimalabid@gmail.com
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other uses. The toxicity of methylene blue can be removed from aquatic media using many catalysts and adsorbents such as biomass [20], bacteria [21], activated charcoal [22], treated or mixed nano-metal oxides [23], reduced graphene oxide, metal oxides [24], nano carbon structure [25], and other nanomaterials such as functionalized Nano graphene with aminopropyl trimethoxysilane-phenanthrene-4-carbaldehyde (NGO@APTMS-PNTCA)[26]. MB is affected by pH (acidic or alkaline) and methylene blue has several forms in acidic and alkaline mediums (Fig. 1 and 2) [27].

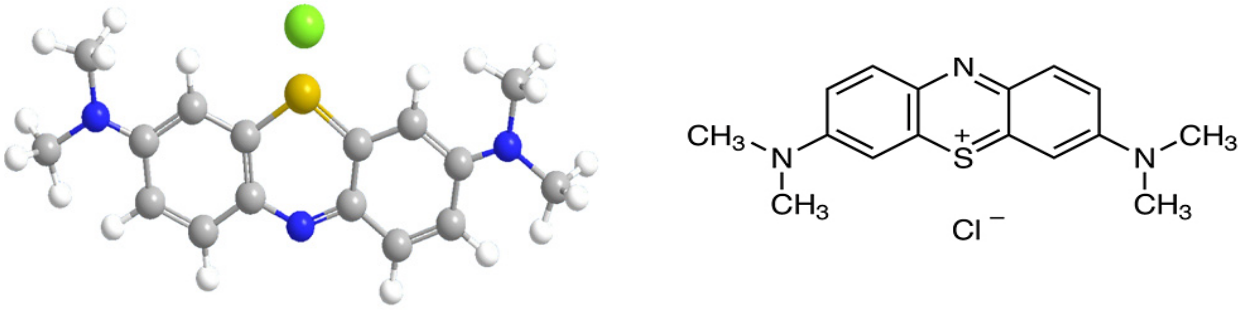
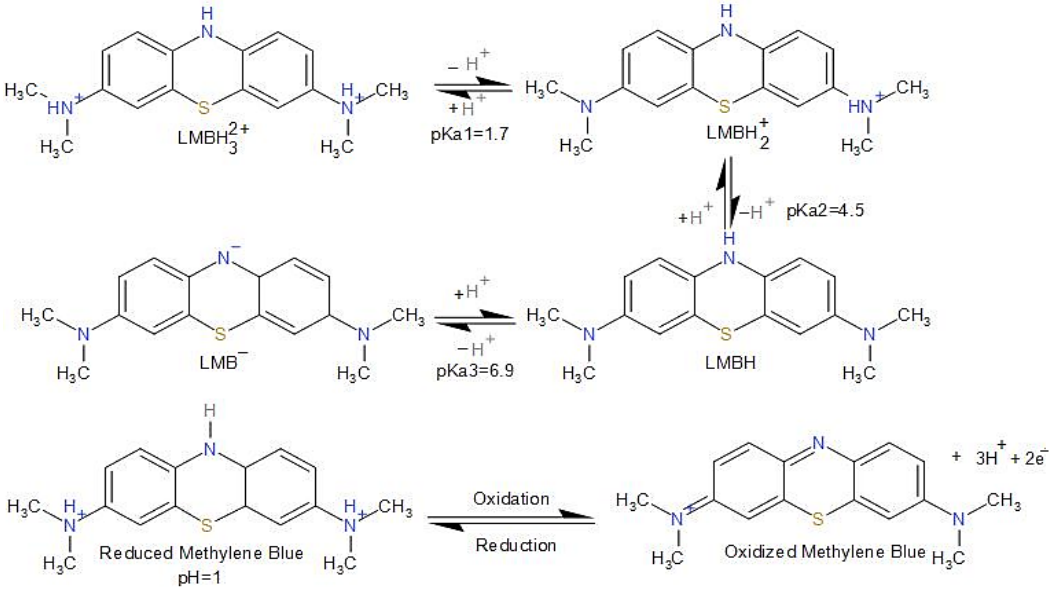


Fig.1. Chemical structure of methylene blue



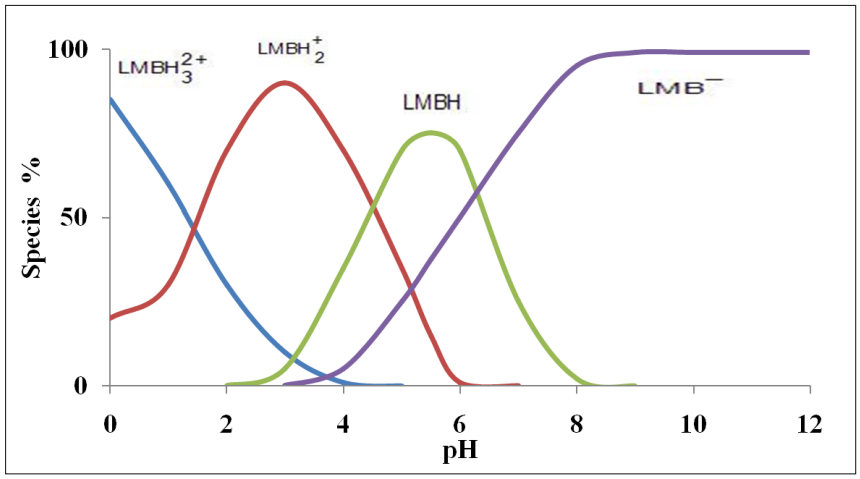


Fig. 2. Distribution diagrams of the protonated species of methylene blue LMB a with pH LMB Leuco-Methylene Blue, LMBH Mono-Protonated form of LMB

Methylene blue is affected by oxidation and reduction and gives two electrons in a highly acidic medium [28], and it can also be analyzed by chromatographic methods using high-performance liquid chromatography (HPLC) [29]. Cyclic voltammetry(CV) can provide kinetic and mechanistic information, the behavior of methylene blue in the electrochemical cell was studied using CV, where several parameters were determined, namely: such as diffusion coefficient (D) Equation 1 [30-32], mass transport, Equation 2 electrochemical reversibility (Λ) Equation 3, Gibbs free energy (ΔG) Equation 4, interface trap density (Dit) Equation 5, constant (K^0) Equation 6, highest Occupied Molecular Orbital (HOMO) Equation 7, Lowest Unoccupied Molecular Orbital (LUMO) Equation 8 [33], thermodynamic equilibrium constants (K_{th}) expresses the extent to which the studied substance is affected by temperature and Gibbs free energy (ΔG) Equation 9 [34], Electronegativity (χ) Equation 10, Electronic Chemical (μ) Equation 11, Chemical hardness () Equation 12, the electrophilicity index (ω) Equation 13 [35], the maximum transferred charge capacity (ΔNmax), Equation 14 [34], Softness (σ) Equation 15 [36] electron affinity (A), Equation 16 and The ionization energy (I) Equation 17 [37].
All Equations are shown in below Table 1.

Table1. The equations and parameters of kinetic and mechanistic information of Cyclic voltammetry(CV)

Equations	Equations	Parameters	Parameters
$I_{p,f}^{quasi} = 0.436\ n.F.A.C.(\frac{nFDv}{RT})^{\frac{1}{2}}$ (Eq.1)	$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2}$ (Eq.10)	i_p: Peak current (A)	A: the gate area,
$m_{trans} = (\frac{\pi nFDv}{RT})^{\frac{1}{2}}$ (Eq.2)	$\mu = \frac{(E_{HOMO} + E_{LUMO})}{2}$ (Eq.11)	F: Faraday's constant ($C.mol^{-1}$)	Cox: accumulation capacitance
$\Lambda = \frac{k^0}{(\frac{\pi nDFv}{RT})^{\frac{1}{2}}}$ (Eq.3)	$\eta = \frac{(E_{LUMO} - E_{HOMO})}{2}$ (Eq.12)	C: Concentration ($mol.cm^{-3}$)	n: Number of electrons in the redox reaction
ΔG = Eox - Ered - Eg + C (Eq.4)	$\omega = \frac{\mu^2}{2\eta}$ (Eq.13)	T: Temperature (K)	A: Electrode area (cm^2)
$Dit = \frac{C_{OX} * \Delta V}{q\ A * Eg}$ (Eq.5)	$\Delta Nmax = -\frac{\mu}{\eta}$ (Eq.14)	v: Scan rate ($V\ s^{-1}$)	R: Gas constant ($J\ mol^{-1}K^{-1}$)
$K^0 = \Lambda\ .\ m_{trans}$ (Eq. 6)	$\sigma = \frac{1}{\eta}$ (Eq.15)	K^0: constant	D: Diffusion coefficient ($cm^2.s^{-1}$)
E_{HOMO} eV= [E_{ox} - $E_{1/2}$ + 4.8] (Eq.7)	A=-ELUMO (Eq.16)	E_{ox}: Oxidation potential	Λ: Electrochemical reversibility
$E_{LUMO} = (E_{HOMO} - Eg)$ (Eq. 8)	$I = -E_{HOMO}$ (Eq.17)	Eg: Optical Bandgap E_{red}: Redaction potential	i_0: exchange current density ($A\ m^{-2}$)
$K_{th} = \exp\left(-\frac{\Delta Gad}{RT}\right)$ (Eq.9)	----------	$E_{1/2}$: Half-oxidation potential for peak	q: electron charge ΔV: flat-band voltage shift

It is defined by the ratio of standard rate constant (k^0) to mass transfer. (K0=i0/F , C: It is the electrostatic interaction energy for the initially formed ion pair, generally, this symbol refers to the energy gap law).
This research aims to determine the concentration of methylene blue (MB) in aqueous media and its electrochemical behavior in a volt-ampere cell by CV by manufacturing an electrode from carbon paste modified with nanomaterials (NiO-NCQD, rGO, G-C_3N_4). Many parameters related to the behavior of this pollutant were calculated using cyclic voltammetry, such as diffusion coefficient (D), mass transport (m_{Trans}), electrochemical reversibility (Λ), Gibbs free energy (ΔG), interface trap density (Dit), constant (K^0), highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), thermodynamic equilibrium constants (K_{th}), Gibbs free energy (ΔG), Electronegativity (χ), Electronic Chemical (μ), Chemical hardness (), the electrophilicity index (ω), the maximum transferred charge capacity (ΔNmax), Softness (σ), electron affinity (A), and the ionization energy (I). In addition, a comparison was made between the two methods using carbon paste modified by CV and UV-Vis spectrometer. The results showed that there is no difference between the two methods in terms of accuracy.

2. Experimental

2.1. Instrumental

The voltammetry system is used for trace analysis and education. The accessories with VA computer software and all electrodes for a complete measurement system: Multi-Mode Electrode pro (MME pro), Ag/AgCl reference electrode, and Pt as auxiliary electrode were used. In this study, a modern voltammetric was connected to a PC based on a USB port (Metrohm797; volt-amperometry analyzer with analyzer cell, USA). A spectrophotometric device D-Lab model SP-UV1000 was used. Sartorius pH meter type PB-11 was used from Data Weighing System Company (pH meter and mV meter; DWS Inc.,).

2.2. Reagents and Materials

Methylene Blue (MB) was purchased from Merk (CAS N.: CAS 61-73-4, Germany). The concentrated hydrochloric acid purity 37% (CAS N.: 7647-01-0, Sigma, Germany), monosodium phosphate (CAS N.: 7558-80-7, Sigma), sodium hydroxide (CAS N.: 1310-73-2), sulfuric acid with purity is 98% (CAS N.: 7664-93-9), acetic acid CH_3COOH its purity is 99.5% (CAS N.: 64-19-7, Merck, Germany), the pure and solid H_3BO_3 (CAS N.: 10043-35-3), phosphorous acid with purity is 85% (CAS N.: 13598-36-2, Sigma) and potassium fur cyanide $K_3[Fe(CN)_6]$. 3H2o as solid and high purity (CAS N.: 13746-66-2, Sigma) were prepared from Sigma. The quartz cells 1cm inner diameter, copper wire, small glass tubes with an inner diameter of 8 mm and a length of about 70 mm, a scale, and a micropipette were prepared.

2.3. Synthesis and Characterization

Several materials were manufactured and described in previous research such as reduced graphene oxide (rGO) [38], graphene-carbon nitride (G-C_3N_4) [39], and nickel oxide nitrogen carbon quantum dots (NiO-NCQD) [40].

2.4. Sample Preparation and Procedure

The preparation of electrode and standard solutions is as follows:

2.4.1.Manufacture of the electrode body

The electrode body was made of a glass tube cut to a length of 50∓0.5 mm so that it is open from both ends. Inside it is a copper wire whose lower end is connected with the modified carbon paste, and its upper end is connected to the device, the modified carbon paste consists of nickel oxide nitrogen carbon quantum dots (NiO-NCQD) of (10%) graphene-carbon nitride G-C_3N_4 powder (10%), reduced graphene oxide (10%), graphite powder (30%), paraffin oil (40%) as a plasticizer. This electrode is used as a working electrode, it is symbolized by the symbol (NiO-NCQD/g-C_3N_4/rGO/CPME) the measuring cell is a platinum auxiliary electrode and the comparison electrode is silver chloride silver with a constant potential of 0.222V.

2.4.2.Preparation of standard solutions

First, the standard solution of MB was prepared based on 0.032 g of MB powder which was transferred completely into a volumetric flask of 100 mL distilled water to the capacity mark solution with a concentration of 10 mM. A solution of monosodium phosphate modified with phosphorous acid based on a buffer solution of (0.1M) monosodium phosphate NaH_2PO_4 was prepared and a solution of phosphorous acid (H_3PO_4; 1.08 M) was added to it until the PH changed to pH=1. For the preparation of the sulphur acid solution, a solution of (0.1M) sulphur acid is prepared by taking 0.2776 mL of concentrated sulfuric acid with a purity of 98% and a density of 1.84 g cm^{-3} for a volume of 50 mL distilled water (DW) up to the capacity mark, and we get the pH of

1. For modified Britton-Robinson Buffer solution (BRB), a buffer solution is prepared from BRB, which consists of H_3PO_4 (0.2076M) with acetic acid (CH_3COOH; 0.04M) and boron acid (H_3BO_3; 0.04M) concentrations on the pH value of 1. For the preparation of phosphorous acid solution, a solution of 1.08M of phosphorous acid was prepared by taking 3.64 mL of concentrated phosphorous acid with a purity is 85% and density of 1.71 g cm^{-3} for a volume of 50 mL and it was supplemented with distilled water (DW) until the capacity mark reached to the pH value 1. Finally, a solution of hydrochloric acid 0.1M was prepared by taking 0.414 mL of concentrated hydrochloric acid based on a purity of 37% and density of 1.19 g cm^{-3} in 50 mL of distilled water (DW) up to the capacity mark to get a pH value 1.

2.4.3. Test solution for electrode

Weigh approximately 0.0329 g of $K_3[Fe(CN)_6]$ and 0.186 g of KCl. Then, transfer completely to a 25mL of DW to a concentration solution of $K_3[Fe(CN)_6]$ (5Mm) and 0.1 M of KCl.

2.4.4. Preparation of solution for spectrophotometric measuring

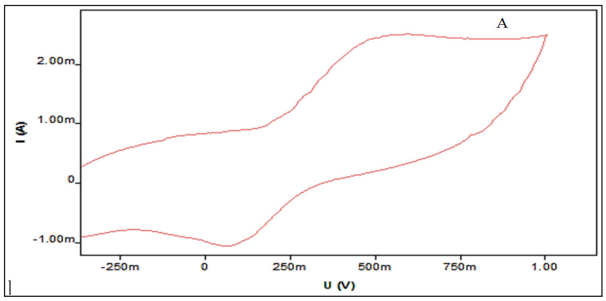
First, 0.025 g of MB powder was transferred completely to a volumetric flask of 25 mL capacity and the volume was completed with distilled water (DW), so the concentration is 1000 mg L^{-1} (1.0 g L^{-1}) was made then, the different standard solution samples of 1, 2, 4, 6, 8, 10 mgL^{-1} was prepared from it by dilution with DW.

3. Results and Discussion

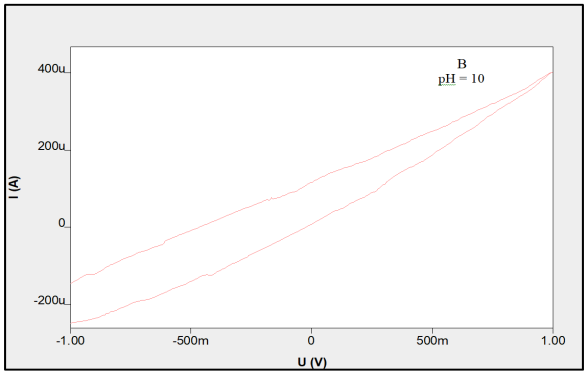
The prepared electrode was tested by test solution, to ensure the work of the prepared electrode before starting the measurement procedure, as shown in Figure 3A. It was found that the electrode worked and was reliable, identified the contaminant methylene blue, and determined the optimal conditions for work, including pH, scanning speed, and scanning rate.

3.1. The effect of pH

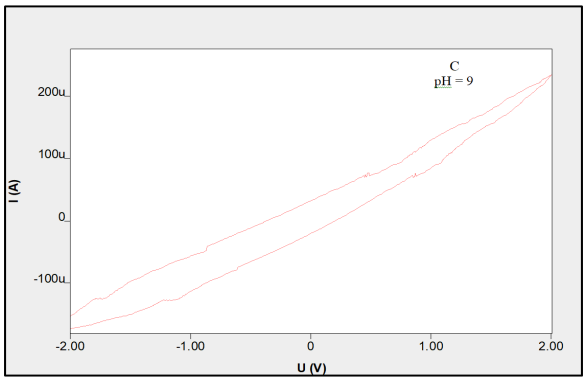
The effect of the pH value was studied within the pH range from 1 to 10, where the scanning was done within a potential scanning range (-1 to +1) V. At a range of pH (5-10) has no peak, while a redaction peak appeared within the pH range of 1 to 4. Also, an oxidation peak has appeared within the range of pH (1-2). The results of pH based on NiO-NCQD/g-C_3N_4/rGO/CPME electrode are shown in Figures 3A-3M.



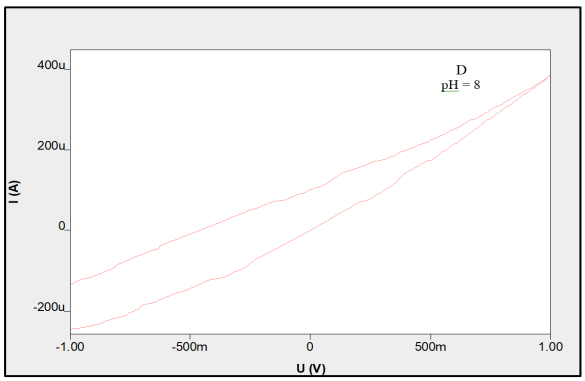
A) Curve Graph 5mM of and 0.1M of KCl



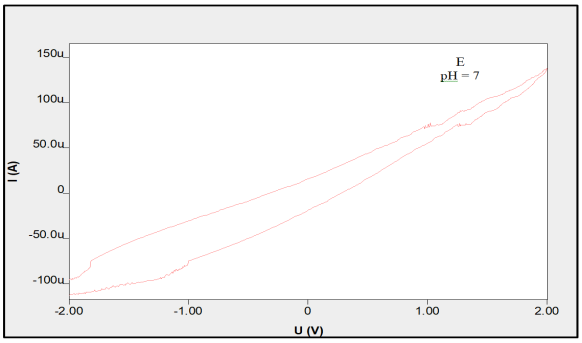
B) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH =10



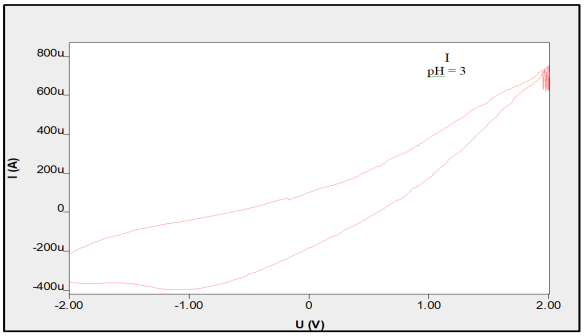
C) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH = 9



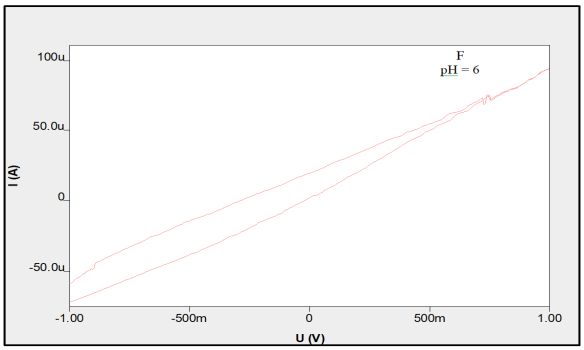
D) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH = 8



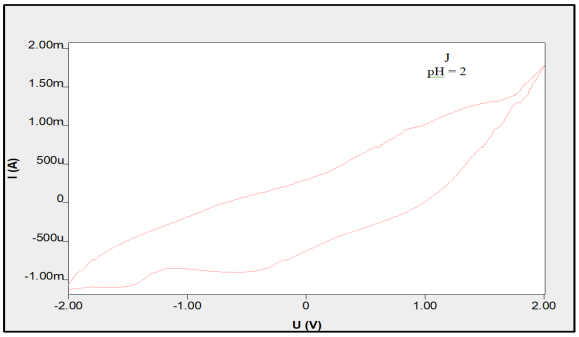
E) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH = 7



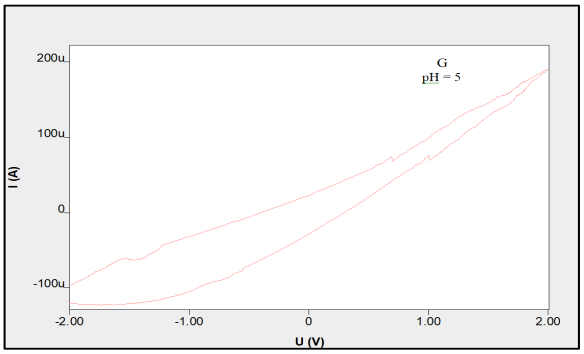
I) Oxidation curve of methylene blue oxidation and reduction of 0.5m M methylene blue at pH = 3



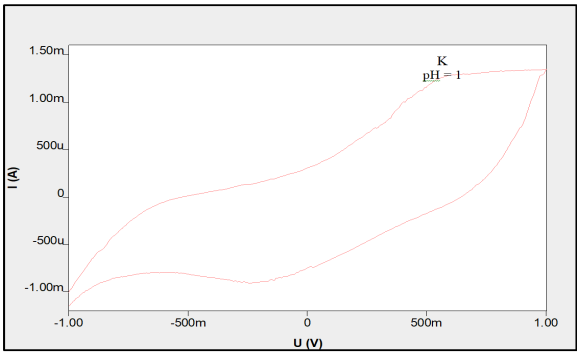
F) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH = 6



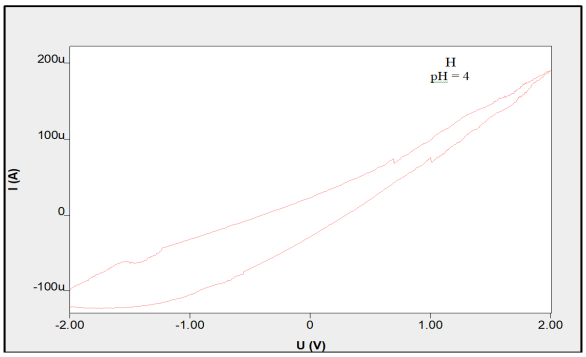
J) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH = 2



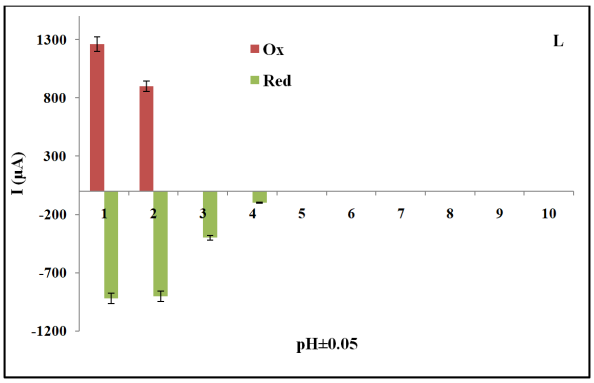
G) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH = 5



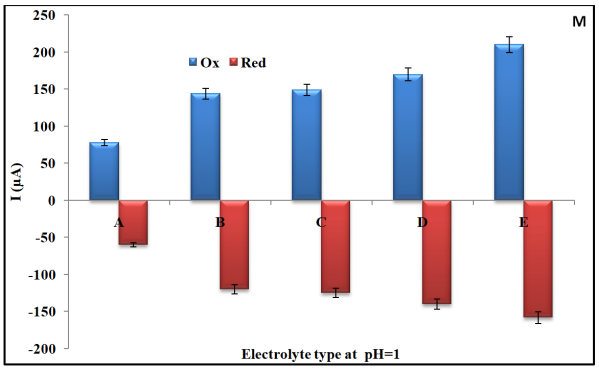
K) Effect of pH on the value of the oxidation current strength and the return of a 0.5 mM MB



H) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH = 4



L) Oxidation curve of methylene blue oxidation and reduction of 0.5mM methylene blue at pH = 1



M) Effect of the type and nature of the medium used at pH = 1 on the oxidation and redaction current of a 0.25 mM methylene blue solution where, A: mono-sodium phosphate with phosphorous acid, B: 0.1M sulfur acid, C: modified (BRB), D: Phosphorous acid, E: Hydrochloric acid 0.1M.

Fig. 3. Curves by electrode (NiO-NCQD/g-C3N4/rGO/CPME) from A to M.

The previous curve shows the oxidation peak at a potential value of 0.585V and a redaction peak at a potential value of -0.21V, so the practical potential difference is ΔE=0.795V, which is a value greater than $\Delta E=0.059/2=0.0295V$ using the manufactured electrode (NiO-NCQD/g-C_3N_4/rGO/CPME), it is a semi-reversible curve subjected to oxidation equation in the middle (pH=1), according to the following oxidation and redaction Equation. The effect of the type of medium was evaluated. Several media were used at pH 1, which are hydrochloric acid, sulfuric acid, phosphorous acid, modified peritoneal, and monosodium phosphate modified with phosphorous acid which is shown in Figures 3L and 3M. It was found from the previous curve that the best acid used was 0.1M hydrochloric acid.

3.2. The effect of scan rate

The scan rate was studied within the range of 10, 30, 50, 70, and 100 *mv sec*$^{-1}$ on the peak current $I_{(p)}$ as shown in Figures 4A and 4B, and it was observed that it is the best scan rate is100 *mv sec*$^{-1}$.

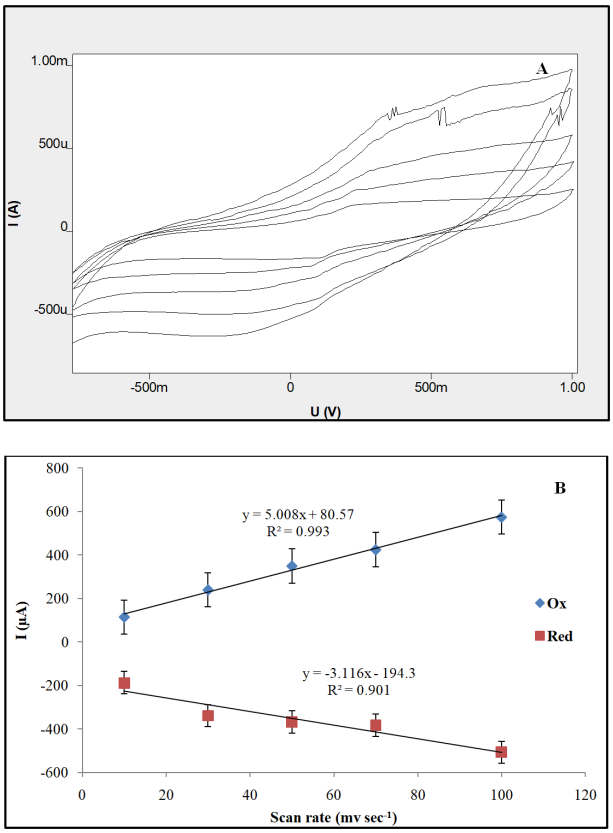


Fig. 4. Effect of scan rate (10-30-50-70-100) mv/sec on a 0.25Mm methylene blue solution at pH=1 at 0.1M hydrochloric acid by electrode (NiO-NCQD/g-C_3N_4/rGO/CPME)

From the scanning rate in Figures 3 and 4, it is concluded that the relationship between the potential scanning rate (*mv sec*$^{-1}$) and the peak current intensity I (µA) for both oxidation and reduction is linear. Also, it showed a directly proportional to the value of the oxidation peak current intensity, and inversely proportional to the value of the reduction peak current intensity. Whereas the value of the correlation coefficient was obtained at R^2=0.9938 and R^2=0.9019 for both oxidation and reduction, respectively. Also, the equation of the line for each of them is *y=5.0082x+80.574* and *y=-3.116x-194.37* for both oxidation and reduction, respectively**.**

3.3. Analytical application

A standard solution was prepared from Methylene blue within the range (25-100) µM or (7.99-31.98) mg L^{-1} (Fig. 5A), which was studied at (pH=1) of (0.1M) hydrochloric acid in water samples. All samples were measured using an electrochemical method by Cyclic voltammetry (CV) method based on the electrode (NiO-NCQD/g-C_3N_4/rGO/CPME). The standard curve for the oxidation and reduction of methylene blue in terms of concentration and the current strength of the oxidation and reduction peaks is shown in Figure 5B.

Due to Figure 5B, it was found that the concentration of methylene blue can be determined within the linear range (25-100) µM or (7.99-31.98) mg L^{-1}, where the oxidation equation was $I_{Ox}=1.508C_{MB}+229.5$ and the correlation coefficient (R^2=0.9823), while the redaction equation is $I_{Red}=-2.236C_{MB}-232.5$ and the correlation coefficient (R^2=0.9722).

3.4. Studying the behavior of methylene blue in aqueous solutions

The behavior of methylene blue has been studied in aqueous solutions for a range of concentrations of methylene blue (25-50-75-100) µM using the proposed electrode and at (pH=1) using (0.1M) hydrochloric acid. In this study, diffusion coefficient (D), mass transport (m_{trans}), constant (K^0), electrochemical reversibility (), and interface trap density (D_{it}) were shown in Table 2. The values in Table 2 are plotted and shown in graphical curves in Figure 6. Effect of the concentration of methylene blue using electrode (NiO-NCQD/g-C_3N_4/rGO/CPME) on Diffusion coefficient (D), Mass transport (m_{trans}), Constant (K^0), Electrochemical reversibility (Λ), and interface trap density (D_{it}) were shown in Figure 6.

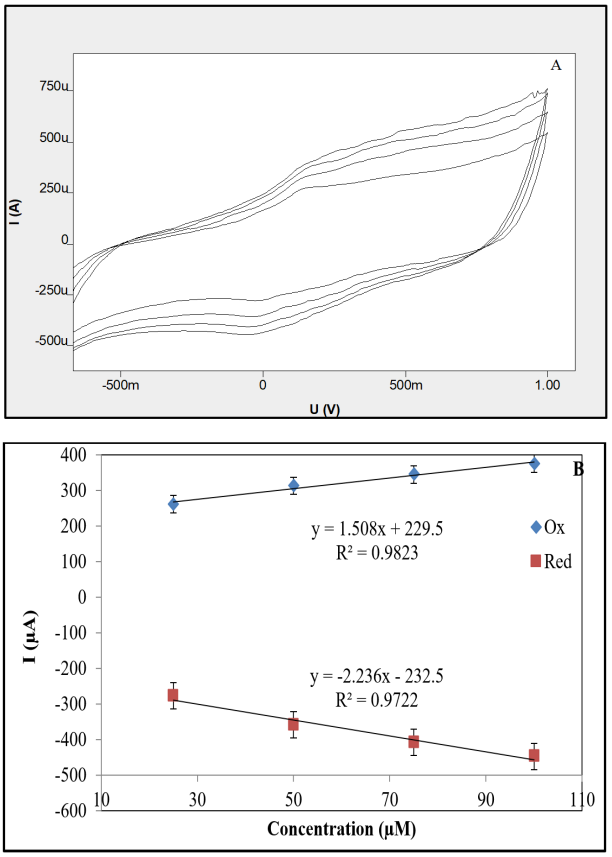


Fig. 5. A standard series of methylene blue (25-50-75-100)µM at PH=1 using 0.1M hydrochloric acid by electrode (NiO-NCQD/g-C_3N_4/rGO/CPME)

Table 2. The values of the diffusion constant, the transmitted mass, the velocity constant, and the reflection coefficient of the oxidation and reflux peaks, Methylene blue in aqueous by electrode (NiO-NCQD/g-C_3N_4/rGO/CPME)

CμM	Form	$D * 10^9$ $(m^2 \cdot s^{-1})$	m_{trans}	K^0	$\Lambda * 1000$	Dit $eV^{-1}cm^{-2}$
25	Oxidation	177.4497	0.0021	2.1537E-06	0.9895	3.1609E+15
50		63.8003	0.0013	2.5828E-06	1.9791	1.8953E+15
75		34.4500	0.0009	2.8468E-06	2.9687	1.3927E+15
100		23.0170	0.0007	3.1026E-06	3.9583	1.1384E+15
25	Reduction	199.8728	0.0023	-2.2857E-06	-0.9895	3.3547E+15
50		83.46421	0.0014	-2.9541E-06	-1.9792	2.1678E+15
75		47.94469	0.0011	-3.3584E-06	-2.9688	1.6431E+15
100		32.53039	0.0009	-3.6885E-06	-3.9584	1.3534E+15

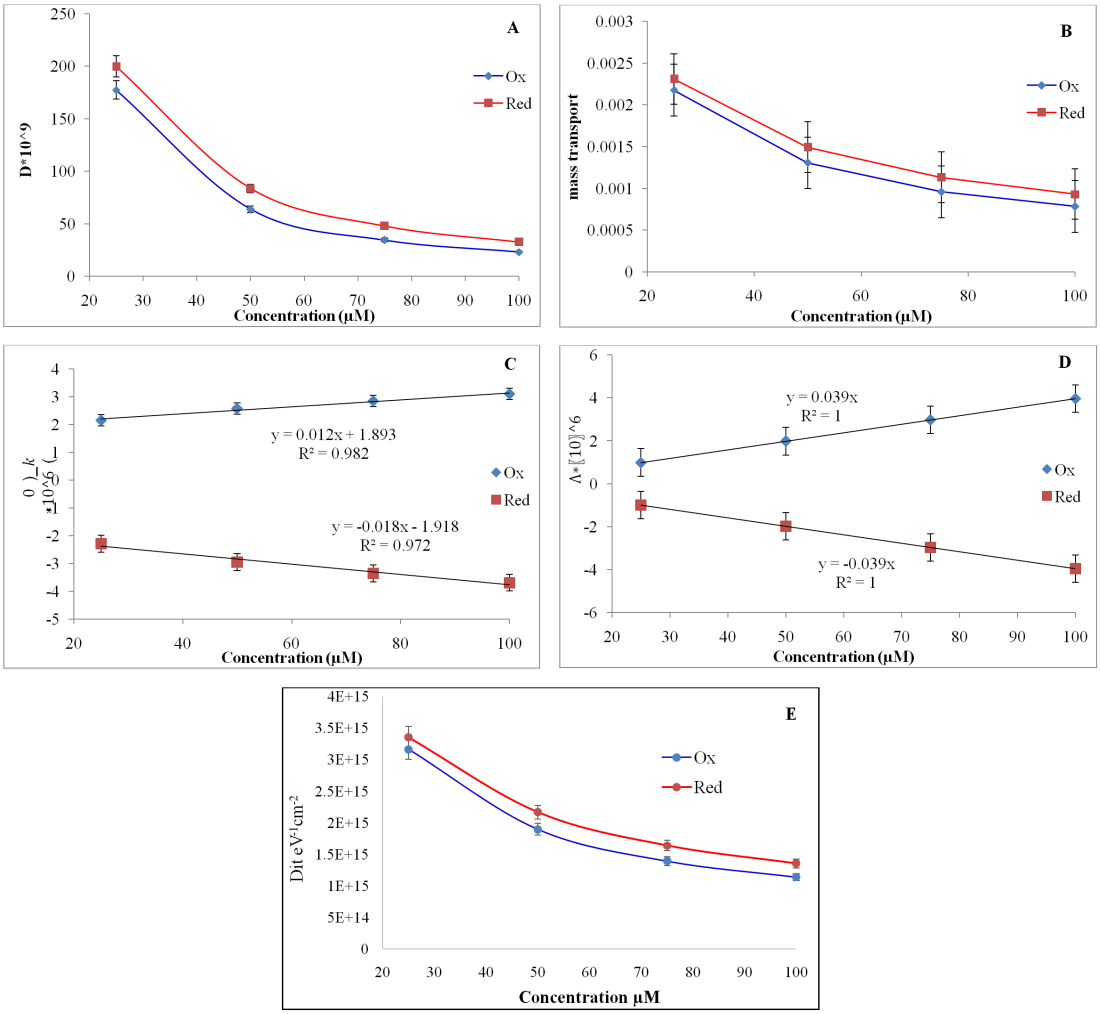


Fig.6. Effect of the concentration of methylene blue using the electrode (NiO-NCQD/g-C_3N_4/rGO/CPME) on different parameters. A)Diffusion coefficient (D), B) Mass transport (m_{trans}), C) Constant (K^0), D) Electrochemical reversibility, E) Interface trap density (D_{it})

The diffusion coefficient and the mass transport to the electrode surface decreased with the increase in the concentration of methylene blue in aqueous media. Also, some physical and chemical properties were calculated in Table 3.

It is concluded from the value of the chemical voltage that the electrons in the molecule (MB) need an energy of (3.8842 eV) in order to exit the equilibrium system, and the molecule receives an additional electronic charge from its surroundings within its studied system of (-12.905 eV) from the value of the electrophilicity index, the molecule has a resistance to charge transfer of (-1.7107 eV) from the value of chemical hardness, and the compound is an electron acceptor since the value of the maximum charge capacity is positive, and the compound has an energy difference between the vacuum energy level and the minimum level of the conduction band, its value is (-2.17351 eV) of electronic affinity, and the reaction is spontaneous from the free energy of gypsum, this indicates that the oxidation of (MB) Spontaneous oxidation in the studied solution in the presence of an electric current (generated by the auxiliary stream), and the solution of this pollutant is thermodynamically balanced at Laboratory temperature and normal pressure, knowing that the energy gap value is equal to (3.42149 eV) .

3.5. Comparison of methylene blue analysis using the proposed electrode with the Cyclic voltammetry method and the spectrophotometric method

It is studied spectroscopically in the visible field (VIS), where standard solutions of methylene blue solutions including 1, 2, 4, 6, 8, and 10 mg L^{-1} were prepared and then scanned spectroscopically as in Figure 7A. It appears from the previous curve that the maximum absorption value of Methylene blue was observed at 663nm, which has a high colour intensity, and the absorption curve in terms of concentration was shown in Figure 7B.

Table 3. Some properties and constants of physical chemistry of the electrochemical behavior of methylene blue organic pollutant (MB) within the electrochemical cell based on cyclic amperometric voltage using a probe (NiO-NCQD/g-C_3N_4 / rGO/ MCPE)

(HOMO)	5.595eV	**(K_{th})**	1.001
(LUMO)	2.1732ev	**(ΔN_{max})**	2.271eV
(Eg)	3.421eV	**(σ)**	-0.585eV
(ΔG)	-2.626 KJ mol^{-1}	**(I)**	-5.595eV
(χ)	-3.884eV	**(A)**	-2.173eV
(ω)	-12.905eV	**(μ)**	3.884eV
(η)	-1.7107eV		

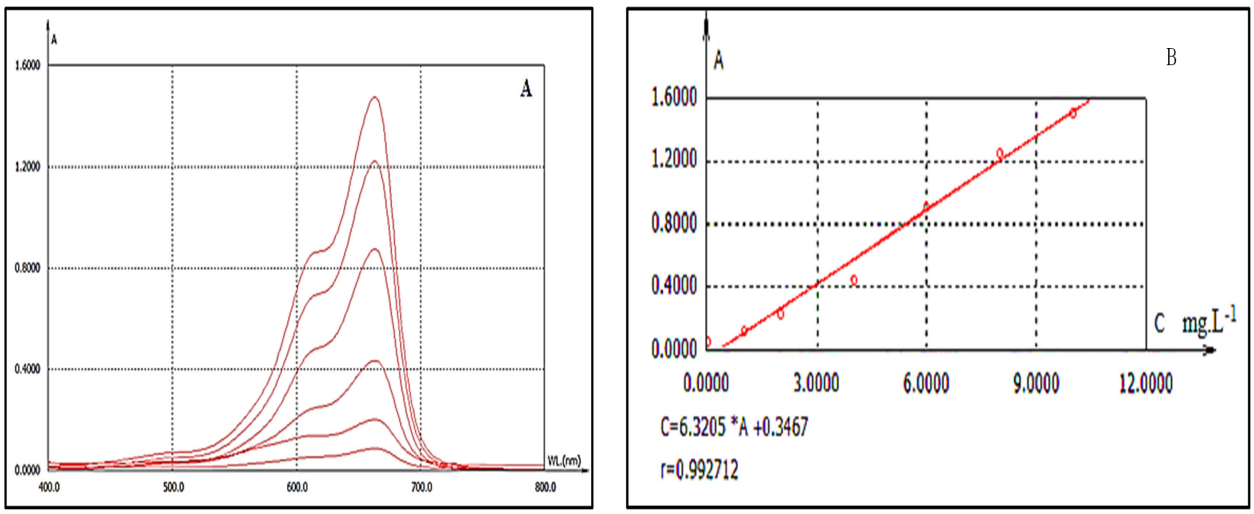


Fig. 7. Curve for methylene blue (1,2,4,6,8,10) mg L^{-1}

A) Scanning spectroscopy of wavelength and absorbance **B**) concentration vs absorbance

Table 4. Comparison of the determination of Methylene blue using the electrode (NiO-NCQD/g-C_3N_4/rGO/CPME) with the spectrophotometric method in the visual field at 663nm

Methods		Standard concentration	Xn = 3 (mgL^{-1})	SD (mgL^{-1})	RSD (%)	R (%)	LOQ (mgL^{-1})	LOD (mgL^{-1})
CV	Ox	7.99 (mgL^{-1})	7.97	0.36	4.52	99.64	0.24	0.07
	Red		7.97	0.29	3.69	99.70	0.13	0.04
UV-Vis	VIS		8.22	0.25	3.07	102.87	---	---

Proposed Method: (NiO-NCQD/g-C_3N_4/rGO/CPME) with CV
Spectrophotometry: UV-Vis

From the previous curve, it appears that Methylene Blue has an Equation of C_{MB}=6.305×A+0.3467 and a correlation coefficient of R^2=99.2712.

The proposed method was applied to a standard sample of 7.99 mg L^{-1} concentration in two ways, comparing of spectroscopic method with the CV method based on NiO-NCQD/G-C_3N_4/ rGO/ MCPE, to ensure the validity and accuracy of the proposed method by calculating the statistical parameters which was shown in Table 4. It was also calculated by the value of F_{ex}. So, the value of F_{ex} was 2.04 for oxidation and 1.35 for reduction which is smaller than the value of F_{tab}=19.0 as a confidence level of 95% with α = 0.05 and n = 3. Therefore, there is no significant difference between the two methods.

4. Conclusions

This paper deals with an electrochemical method for the determination of methylene blue (MB) by fabrication of an electrode (NiO-NCQD/G-C_3N_4/ rGO/CPME), This electrode is used as a working electrode. The oxidation-reduction curve of methylene blue was shown using this electrode. It is a quick-reversible curve, and it works at (pH=1) and the best acid used is HCl a concentration of (0.1M). It is found that the linear range is within the range of 25-100 µM. Several constants were studied to determine the behavior of methylene blue within the electrochemical cell. The CV method was compared to spectrophotometry at 663nm and there is no difference between the determination of MB by the CV and spectrophotometry methods.

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