Study of the behavior and determination of phenol Based on modified carbon paste electrode with nickel oxide-nitrogen carbon quantum dots using cyclic voltammetry

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**ABSTRACT**
The behavior of phenol was studied and determined using the modified carbon paste electrode (MCPE) with nickel oxide nanoparticles doped by nitrogen carbon quantum dots as nanoadsorbent (NiO-NCQD) and cyclic voltammetry (CV). The MCP electrode was manufactured in a laboratory. The modified carbon paste consisted of 12% (NiO-NCQD), 44% of graphite powder and 44% of paraffin oil to get a modified carbonate paste. Cyclic voltammetry can provide behavior information; as such: diffusion coefficient (D), charge transfer coefficient (α.nα), the mass transport (m_{trans}) found that diffusion coefficient, the reducing of mass transport (m_{trans}) by increasing the phenol concentration in the solution, and increasing of constant K when the concentration of phenol increased in the solution. Also, the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and Gibbs free energy (ΔG) are studied and calculated. In this study, E_{HOMO}=-4.92eV, E_{LUMO}=-0.32eV, and ΔG=-4.17 were considered. The drinking water samples from Latakia city were analyzed based on NiO-NCQD adsorbent using the MCPE method (NiO-NCQD/MCPE). The phenol concentration in the drinking water sample in Latakia was achieved less than the quantitative detection limit (LOQ), and the proposed procedure was validated by spiking samples.

**Keywords:** Phenol, Cyclic voltammetry, Modified carbon paste electrode, Nickel oxide nanoparticles, Nitrogen carbon quantum dots, Kinetic

**1. Introduction**
Phenol is described as an aromatic organic compound C₆H₅OH. Phenol and its derivatives are the main pollutants in water sources [1]. It is highly toxic [2-4] and enters the human body through ingestion, inhalation, or contact with the skin; exposure to phenol for long periods causes severe damage. Among these damages: Damage to the lungs, liver, kidneys, urinary and reproductive tracts, cardiovascular disease, shortness of breath, neurological problems, as well as severe abdominal pain, gastrointestinal irritation, nausea, vomiting, diarrhea, sweating, coma, and death. Ingestion of 1g of phenol is a lethal dose [5-9]; phenol increases oxidative stress in biological materials, disrupting endocrine metabolism and promoting cancer [10]; the maximum permissible level of phenol according to the world health organization (WHO) that its concentration does not exceed one µg L⁻¹ in drinking water [11]. Phenol and total phenol can be estimated spectrophotometrically in the visible (VIS) [12-19], in the ultraviolet (UV) [20], and High-Performance Liquid Chromatography (HPLC) [21-22]. Schema 1 showed the phenol oxidation (one-electron oxidation) and reaction process [23,24].
Cyclic voltammetry is one of the most important electrochemical techniques that help provide information about the kinetics, mechanics, and behavior of the studied material [25]; it is also possible from cyclic voltammetry to know if the reaction is subject to oxidation, reduction, or both. It has three cases: reversible, quasi-reversible, or irreversible [26]. Cyclic voltammetry can provide kinetic and mechanistic information; as such:

- Diffusion coefficient (D) [27-30]
- Mass transport ($m_{trans}$) [31-33]
- Charge Transfer Coefficient ($\alpha$, $n_\alpha$) [34]
- Constant $K_0$ [35]
- The highest occupied molecular orbital (HOMO)
- The lowest unoccupied molecular orbital (LUMO) [36, 37]
- Gibbs free energy ($\Delta G$) [38]
- Interface trap density (Dit) [39]

**Schema 1.** The oxidation and reaction of phenol

The diffusion coefficient is calculated from Randles-Sevcik irreversible Equation 1 [27-30]. The mass transport is given by Equation 2 [31-33]. Also, the charge transfer coefficient (CTC) is given by Equation 3 [34]. Constant ($k^0$) is defined by the standard rate constant ($k^0$) ratio to mass transfer. It is given by Equation 4 [35]. The HOMO-LUMO values are given by Equations 5 and 6 [36-37]. Gibbs free energy $\Delta G$ is given by Equation 7 [38].

The interface trap density (Dit) can be obtained by Equation 8 [39].

$$i_p = \mp 0.4961\sqrt{\alpha \cdot n_\alpha \cdot nF \cdot A \cdot C \left(\frac{nF}{RT}\right)^{\frac{1}{2}}}$$

(Eq.1)

Where, $i_p$: Peak current (A), $n$: Number of electrons, $F$: faraday’s constant (C. mol $^{-1}$), $A$: electrode area (cm$^2$), $\alpha$: transfer coefficient of the redox reaction, $C$: concentration (mol. cm$^{-3}$), $R$: gas constant (J. mol$^{-1}$ K$^{-1}$), $T$: Temperature (K), $D$: diffusion coefficient (cm$^2$s$^{-1}$), $v$: Scan rate (V s$^{-1}$).

$$m_{trans} = \left(\frac{nF}{RT}\right)^{\frac{1}{2}}$$

(Eq.2)

$$\alpha \cdot n_\alpha = \frac{15.1RT}{\Delta E_p F}$$

(Eq.3)

Where $\alpha$: is the charge transfer coefficient and represents a measure of the symmetry barrier in a non-reversible electrode process, $n_\alpha$: is the number of electrons involved in the rate-determining step.
Where: \( i_o \): exchange current density (A m\(^{-2}\)), in the case where the oxidation is irreversible it must be: \( k_0 \ll m_{\text{trans}} \), as for according to Nicholson, must be \( k_0 < 3.5 \times 10^{-4} \times \sqrt{v} \).

\[
E_{\text{HOMO}} eV = [E_{\text{ox}} - E_{1/2} + 4.8]
\]

\[
E_{\text{LUMO}} = (E_{\text{HOMO}} - E_g)
\]

Where: \( E_{\text{ox}} \): oxidation potential (From CV), \( E_{1/2} \): half-oxidation potential for peak, \( E_g \): Optical Bandgap (from absorption studies).

\[
\Delta G = E_{\text{ox}} - E_{\text{red}} - E_g + C
\]

Where: \( E_{\text{ox}} \): Oxidation potential, \( E_{\text{red}} \): Reduction potential, \( E_g \): the excited singlet state energies, \( C \): is the electrostatic interaction energy for the initially formed ion pair, generally considered negligible in polar solvents.

\[
\text{Dit} = \frac{E_{\text{ox}} - \Delta V}{q A \times E_g}
\]

2.2. Reagents and Materials

All chemicals with high purity were purchased from Sigma or Merck Company (Germany). Phenol \( \text{C}_6\text{H}_6\text{O} \) purchased from Acros Organics Company (AC221755000, molecular weight 94.11g mol\(^{-1}\), specific density \( d=1.070 \text{ g cm}^{-3} \), high purity 99%). The monopotassium dihydrogen phosphate (\( \text{KH}_2\text{PO}_4 \)) was prepared from Sigma, Germany (CAS No.: 7778-77-0). The boiled and cooled double distilled water (DDW, 18.2 M\( \Omega \)cm, 1.5 L, Sigma).

2.3. Synthesis of NiO-NCQD nanocomposite

Take 0.6 g of NiO Nanoparticles (20nm) are added with 30 mL of nitrogen quantum carbon dot after filtering it with a micro-filter (syringe with filter 0.45\( \mu m \)) and subjected to ultrasonic for 1.5h, then washed three times with distilled water and dried in an oven at 60 for 12h to get NiO-NCQD nanocomposite.

2.4. General procedure

2.4.1. Fabrication of selective electrode

The selective electrode is made (in the laboratory). It consists of a glass tube that is open at both ends and contains at its lower end modified carbon paste at the upper back; it is connected to the device. A copper wire conducting electric current is connected between the modified carbon paste and the device. The modified carbon paste using NiO-NCQD nanocomposite (12\%).
graphite (44%), and paraffin oil (44%) for a total weight of the modified carbon paste of 0.5 g; the components are mixed in specific proportions and then packed in the electrode body is made of glass. Symbolizes the factory electrode (NiO-NCQD/MCPE) shown in Figure 1. Then the electrode is connected to the voltamperometric cell (VA), which consists of a working electrode (WE) and a comparison electrode, and it is usually an Ag/AgCl electrode where its potential is 0.222v at 25°C and an Auxiliary Electrode (AE).

2.4.2. Preparation of stock solution and monopotassium phosphate buffer
To prepare a 0.1036 M phenol solution, take 0.974 g of phenol, then dissolve it into 100 ml distilled water using a volumetric flask. The buffer was prepared from KH$_2$PO$_4$ at a concentration of 0.1 M and a solution of KOH potassium hydroxide at 0.1 M by mixing different volumes of both of them to obtain a pH of 4 and 7.

3. Results and discussion
3.1. Effect of pH
The effect of pH is studied within the range of (3-8) on the current intensity I(µA) of a standard phenol solution shown in Figure 2.
From the previous drawing curve, Through the values of I and U(V), it is noted that it two peaks

![Fig. 1. Schematic of factory electrode components (NiO-NCQD/MCPE)](image1)

![Fig. 2. Effect pH on ip and U(V) for 1 mM phenol on the electrode (NiO-NCQD/MCPE)](image2)
and achieves the highest value of peak current = 49.5µA, 72µA at pH =7 respectively, so these two values are adopted. In the case of phenol, when used CV method, it undergoes an oxidation process only without reduction, so the system is irreversible, phenol concentration is studied with ranges of phenol (10 - 250 - 500 – 750 – 1000) µM by (CV) method using a buffer solution of at pH (4,7), scan rate = 100mv.s⁻¹ = 0.1v. s⁻¹ both of pH (4,7), step voltage is 0.04166V and 0.05991V for both (pH =4,7), respectively, using the electrode (NiO-NCQD/MCPE).

Cyclic voltammetry can provide behavior information; as such: the diffusion coefficient (D), charge transfer coefficient (α, a), the mass transport (m_trans), and the values of each are calculated (Table 1).

3.2. Effect of phenol concentration

The curve of each diffusion coefficient, charge transfer coefficient, constant K_o, and mass transport and interface trap density (Dit) are studied for the phenol concentrations, as in Figures 3(A-D).

From previous curves, the mass transport and diffusion coefficients with the increase of phenol concentration, probably due to increasing phenol concentration, cause the blockage of the electrode surface. In the case where the oxidation is irreversible, it must be: K_o <m_trans, according to Nicholson, must be k_o <3.5 ×10^4× ν^1/2, from previous curves, In this research, K_o<m_trans and K_o <3.5 ×10^-4×0.1= 3.5×10^-5, the HOMO-LUMO values are studied from cyclic voltammetry using modified carbon paste using NiO-NCQD nanocomposite, where E_{ox} = 0.43 V, and E_{1/2} = 0.31 V, the gap from absorption studies at 270 nm=4.6 from (UV) so, E_{HOMO} = 4.92 ev, optical band, so

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<th>pH</th>
<th>CµM</th>
<th>I (µA)</th>
<th>D×10⁹ (m²·s⁻¹)</th>
<th>n α a</th>
<th>m_trans</th>
<th>K_o×10⁷</th>
<th>Dit (eV⁻¹ cm²)</th>
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Fig. 3. Effect of phenol concentration on
A) charge transfer coefficient,
B) constant K0,
C) diffusion coefficient,
D) mass transport,
F) and interface trap density on the surface of the proposed electrode NiO-NCQD/MCPE.
$E_{\text{LUMO}} = 0.32 \text{ ev}$, As for the value of Gibbs free energy $\Delta G$ was -4.17. In this case, $\Delta G$, the reaction is spontaneous in the direction with electric current. The interface trap density (Dit) of the electrode has a value within $(2.95483 \times 10^{13} - 1.46053 \times 10^{15}) \text{ eV}^{-1} \text{ cm}^{-2}$ at pH=4 and $(3.41447 \times 10^{13} - 2.30113 \times 10^{15}) \text{ eV}^{-1} \text{ cm}^{-2}$ at pH=7. The large values indicate good corresponding and, as noted, interface trap density (Dit) decrease in value with increasing concentration. Stirring the solution has a significant effect on the response, so the solution is stirred initially in the pre-measurement stage at a rate of 2000 rpm, where the motion of a chemical compound in solution inside the electrochemical cell are, principally three: (convection, migration, and diffusion), stirring the solution helps in homogenizing the solution in addition, stirring and adding the buffer solution both help to get rid of unwanted motion (migration and convection), it remains the diffusion. It is the most important that expresses the behavior of phenol within the electrochemical cell; during the stirring stage, nitrogen gas gurgles inside the electrochemical cell solution for 50 sec. The effect of temperature on behavior where the temperature of the solution was fixed during all stages of the study at 25±2°C.

### 3.3. Application on drinking water samples by the proposed electrode (NiO-NCQD/MCPE)

A drinking water sample from Latakia city was analyzed using the proposed method, and it was found that the sample was less than the detection limit (<LOD) of the method. The standard addition method found that the sample does not contain phenol, according to Table 2 and Figures 4-5. Due to previous curves, the results can be placed in Table 2.

It is noted from the above that the phenol concentration in the drinking water sample in Latakia is less than the quantitative detection limit (LOQ) of the method, less than 10µM (0.9411 mg L⁻¹).

### 4. Conclusion

This paper deals with fabricating a phenol-selective electrode using carbon paste modified with Nickel Oxide nanoparticles (NiO) doped with Nitrogen Carbon Quantum Dots (NCQD) using Cyclic voltammetry. The electrode was manufactured in a laboratory. Results best conditions are obtained at pH= 7.0 and 4.0 using KH₂PO₄ buffer, buffer, and the behavior of a phenol solution is studied in an electrochemical cell (Cyclic voltammetry) using NiO-NCQD/MCPE. The phenol concentration in

![Fig. 4. Determination of phenol concentration in drinking water using the proposed electrode (NiO-NCQD/MCPE) at pH = 4](image-url)
the drinking water sample in Latakia is less than the quantitative detection limit (LOQ) of the method, that is, less than 10µM (0.9411 mg L⁻¹).

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6. References


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