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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 .n α), 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 K⁰ 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.

1. Introduction

Phenol is described as an aromatic organic compound C_6H_5OH . 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 μ g 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].

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Schema 1. The oxidation and reaction of phenol

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 (α . n_a), [34], and constant K^0 [35], the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) [36, 37], Gibbs free energy (ΔG) [38] and interface trap density (Dit) [39].

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 ΔG is given by Equation 7 [38]. The interface trap density (Dit) can be obtained by Equation 8[39].

$$i_{p} = \mp 0.4961 \sqrt{\alpha} . n_{\alpha} nFA_{real} C \left(\frac{nFvD}{RT}\right)^{\frac{1}{2}}$$
(Eq.1)

Where, i_p : Peak current (A), n: Number of electrons, F: faraday's constant (C. mol⁻¹), A: electrode area (cm²), α : 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 (cm²s⁻¹), v: Scan rate (V s⁻¹).

$$m_{trans} = \left(\frac{\pi n F D \nu}{RT}\right)^{\frac{1}{2}} \qquad (Eq.2)$$

$$\alpha. n_{\alpha} = \frac{15.1 \text{RT}}{\Delta E_{\text{p}} F}$$
(Eq.3)

Where α : 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.

$$k^0 = \frac{i_0}{F}$$
 (Eq.4)

Where: i_o : exchange current density (A m⁻²), in the case where the oxidation is irreversible it must be: $k^0 \ll m_{trans}$, as for according to Nicholson, must be $k^0 < 3.5 \times 10^{-4} \times v^{1/2}$.

$$E_{HOMO} eV = [E_{ox} - E_{1/2} + 4.8]$$
 (Eq.5)

$$E_{LUMO} = (E_{HOMO} - E_g)$$
 (Eq.6)

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

$$\Delta G = E_{ox} - E_{red} - E_{g} + C \qquad (Eq.7)$$

Where: E_{ox} : Oxidation potential, E_{red} : Redaction 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.

$$Dit = \frac{C_{OX} * \Delta V}{q_{A*E_g}}$$
(Eq.8)

A, q, Cox, V, and Eg are the gate area, electron charge, accumulation capacitance, flat-band voltage shift, and bandgap.

Carbon/graphite paste electrodes (CPE) are important for being chemically inert, easy to fabricate, electrode surface renewability, low ohmic resistance, low cost, and environmentally friendly. However, its kinetics, stability, and selectivity are weak. To solve this problem, surface modification (CPE) is resorted to by modifiers [40]; therefore, in this study, modified carbon paste electrodes were relied upon, as they are more selective and sensitive to organic compounds. This research is one of the critical research studies on the behavior of phenol in the electrochemical cell and determines the concentration of phenol in a drinking water sample using a selective electrode for carbon paste with nanoparticles by cyclic voltammetry.

2. Experimental

2.1. Instruments

Voltammetry system for trace analysis and education. Complete accessories with VA Computrace software and all electrodes for a complete measurement system: Multi-Mode Electrode pro (MME pro), Ag/AgCl reference electrode, and Pt auxiliary electrode. In this study, a modern voltammetric was connected to a PC based on a USB port (Metrohm 797; volt-amperometric analyzer with analyzer cell). Sartorius pH meter type PB-11 was used from Data Weighing System Company (pH meter and mV meter; DWS Inc., USA)

2.2. Reagents and Materials

All chemicals with high purity were purchased from Sigma or Merck Company (Germany). Phenol C_6H_6O purchased from Acros Organics Company (AC221755000, molecular weight 94.11g mol⁻¹, specific density d=1.070 g cm⁻³, high purity 99%). The monopotassium dihydrogen phosphate (KH₂PO₄) was prepared from Sigma, Germany (CAS No.: 7778-77-0). The boiled and cooled double distilled water (DDW, 18.2 M Ω .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 μ 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_2PO_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(μ A) of a standard phenol solution shown in Figure 2.

From the previous drawing curve, Through the values of and U(V), it is noted that it two peaks



Fig. 1. Schematic of factory electrode components (NiO-NCQD/MCPE)



Fig. 2. Effect pH on ip and U(V) for 1 mM phenol on the electrode (NiO-NCQD/MCPE)

and achieves the highest value of peak current = 49.5μ A, =72 μ A 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) μ M 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 . n_{α}), 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° , 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 probably due to concentration, increasing phenol concentration, cause the blockage of the electrode surface. In the case where the oxidation is irreversible, it must be: K°<m $_{\rm trans}$, according to Nicholson, must be $k^0 < 3.5 \times 10^{-4} \times v^{(1/2)}$, from previous curves, In this research, K⁰ <m trans and $K^0 < 3.5 \times 10^{-4} \times 0.1 = 3.5 \times 10^{-5}$, the HOMO-LUMO values are studied from cyclic voltammetry using modified carbon paste using NiO-NCQD nanocomposite, where $E_{0x} = 0.43$ 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

рН	СµМ	Ι (μΑ)	D×10 ⁹ (m ² ·s ⁻¹)	n _α α.	m _{trans}	K°×107	(Dit) eV ⁻¹ cm ⁻²
4	1000	90	0.036278	1.615581	2.20006E-05	1.485325000	2.95483E+13
	750	72	0.033772	1.974600	2.1227E-05	1.18826000	2.85093E+13
	500	64	0.060039	1.974600	2.83026E-05	1.056231000	3.80124E+13
	250	56	0.194084	1.870673	5.08868E-05	0.924202000	6.83445E+13
	10	45	88.63469	1.653153	0.001087458	0.742663000	1.46053E+15
7	1000	104	0.048443	1.615581	2.54229E-05	1.716375904	3.41447E+13
	750	99	0.067397	1.870673	2.99869E-05	1.633857832	4.02745E+13
	500	92	0.151635	1.615581	4.4979E-05	1.518332531	6.04099E+13
	250	83	0.594651	1.341237	8.90721E-05	1.369800001	1.1963E+14
	١0	69	220.0211	1.565762	0.001713337	1.138749398	2.30113E+15

 Table 1. Values of charge transfer coefficient, diffusion coefficient, and mass transport of phenol at pH=4 and pH=7 using (NiO-NCQD/MCPE)







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

 $E_{IUMO=}$ 0.32 ev, As for the value of Gibbs free energy ΔG was -4.17. In this case, ΔG , the reaction is spontaneous in the direction with electric current. The interface trap density (Dit) of the electrode has a value within (2.95483×10+13-1.46053×10+15) eV-1 cm⁻² at pH=4 and (3.41447×10⁺¹³- 2.30113×10⁺¹⁵) eV⁻¹ 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 $25\pm2^{\circ}$ 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 $10\mu M$ (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 KH_2PO_4 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



Fig. 5. Determination of phenol concentration in drinking water using the proposed electrode (NiO-NCQD/MCPE) at pH = 7

Table 2. Phenol analysis in water samples $(n=5)$ at $pH = 4$ at $pH = 7*$												
Sample	Added Phenol (µM)	Expected Phenol (µM)	Found phenol (µM)	RSD (%)	Recovery (%)							
Drinking			LOQ		-							
Water	250	250.0002	[240.2-259.8]	3.15672	100.0001							
Drinking	*	*	LOQ *	*	*							
Water	250*	232.8361*	[220.27-245.41] *	4.3488*	93.1344*							

the drinking water sample in Latakia is less than the quantitative detection limit (LOQ) of the method, that is, less than 10μ M (0.9411 mg L⁻¹).

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