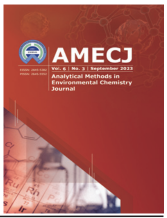
Anal. Methods Environ. Chem. J. 6 (3) (2023) 19-35

AMECJ

Research Article, Issue 3
Analytical Methods in Environmental Chemistry Journal
Journal home page: www.amecj.com/ir



Determination of 2,4-dinitrophenylhydrazine using carbon paste modified with nanoparticles by cyclic voltammetry, high-performance liquid chromatography and spectrophotometry methods

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ARTICLE INFO:
Received 12 May 2023
Revised form 25 Jul 2023
Accepted 17 Aug 2023
Available online 28 Sep 2023

Keywords:
2,4-Dinitrophenylhydrazine,
Graphene-carbon nitride nanoparticles,
Nitrogen carbon quantum dots,
Electrochemical,
High-performance liquid chromatography

ABSTRACT

The research deals with the manufacture of an electrode using modified carbon paste to determine 2,4-dinitrophenylhydrazine (2,4-DNPHZ), The modified carbon paste electrode (NiO-NCQD/g-C_3N_4/MCPE). The results show the presence of oxidation and reduction peaks, and it is subject to a quasi-reversible system; the best value of pH is (1) using sulfuric acid with a concentration of (0.1M), and scan rate is 100 mv sec^{-1}, it was linearity range of (1-1000) µM for oxidation, and (100-1000) µM for reduction, with correlation coefficient ($R^2=0.9717$) and ($R^2=0.9914$) for each of them, respectively. The proposed electrochemical method was compared with two methods they are spectrophotometry at a wavelength 360 (nm) and high-performance liquid chromatography (HPLC) at wavelengths (340 and 250) nm. It turned out that the electrochemical method (NiO-NCQD/g-C_3N_4/MCPE) was superior to the spectrophotometry method in terms of the detection limit. It turns out that there is no significant difference between (HPLC) and (NiO-NCQD/g-C_3N_4/MCPE) in terms of accuracy. The proposed electrochemical method is a new analytical method characterized by accuracy, repeatability, and reliability.

1. Introduction

The material of 2,4-Dinitrophenylhydrazine (2,4-DNPHZ) is a water pollutaFnt compound active in explosives. It belongs to the nitro-aromatic (NAC) and is a hydrazine derivative [1-3]. 2,4-Dinitrophenylhydrazine has weak decomposition in water [4] but is soluble in organic solvents such as (Methanol, Acetonitrile, Tetrahydrofuran THF… etc.) [4]. It forms a yellow color solution, and long-term exposure to 2,4-DNPHZ has many adverse health effects as a highly toxic compound [5]. It is used in industry as a detection reaction of ketones and aldehydes. It seeps through wastewater from industrial effluents and causes water pollution. Due to Figure 1, 2,4-Dinitrophenyl hydrazine is oxidized to 2,4-Dinitrophenyldizine material.

It is used in many applications, such as Alzheimer’s detection [6]. It is also used as a surface enhancer for an adsorbent material such as magnetite or aluminum oxide to remove many heavy metal ions that are harmful to the environment, including Arsenic (As) and vanadium (V) [7-10]. It is used to determine the protein carbonyl [11] and in synthesizing Thiazolidin-4 as one of the biologically active drugs in treating malaria [12].

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https://doi.org/10.24200/amecj.v6.i03.245

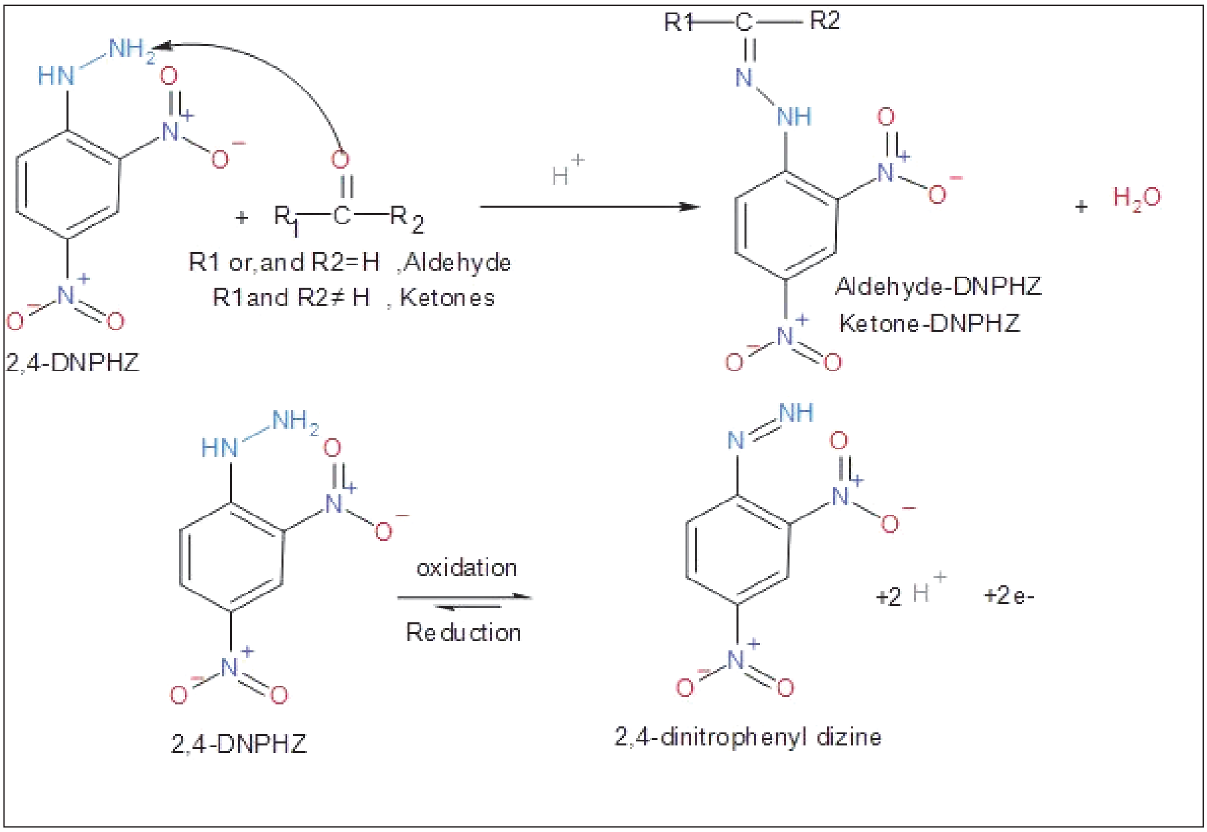


Fig. 1. Chemical equation for the reaction of 2,4-DNPHZ with aldehydes and ketones, and oxidation 2,4-Dinitrophenyl hydrazine to 2,4-Dinitrophenyldizine.

Through the reference study, it was found that there is a scarcity of direct methods for analyzing 2,4-dinitrophenylhydrazine; most of the reference studies used this compound as a reagent, where it was used as a selective reagent or as a derivatization reagent for the determination of aldehydes and ketones in spectroscopic, chromatographic, and electrochemical analytical methods. In high-performance liquid chromatography, it is also used in the measurement of free and bound malondialdehyde in plasma [13], determination of linear aliphatic aldehydes in heavy metal-containing waters [14], determination of malondialdehyde in normal human urine [15]. It is also used in analyzing carbonyl (aldehyde and ketones) in food, drug, and blood serum as a reagent of pre-column derivative in the HPLC technique [16]. It is used in the analysis of amino acids [17], aldehydes in air [18], total carbonyl in meat [19], and aldehydes in food samples [20]. In spectrophotometry, it is also used as a reagent in the analysis of many drugs using spectrophotometry [21-24], such as tetracycline hydrochloride [25], catechol, resorcinol [26], and nateglinide as a drug for the treatment of diabetes [27]. Interaction of haloperidol and 2,4-Dinitrophenylhydrazine used for the quantification in drug formulations [28], spectroscopic, cytotoxicity and molecular docking studies on the interaction between 2,4-dinitrophenylhydrazine derived Schiff bases with bovine serum albumin [29] at a wavelength near 360 nm [30]. In the electrochemical method, 2,4-dinitrophenylhydrazine was used in electrochemical methods such as Indirect determination of dopamine and paracetamol [31]. 2,4-dinitrophenylhydrazine and its derivatives can be removed from aqueous media using multi-walled carbon nanotubes (MWCNTs) [32]. Carbon nitride graphene (G-C_3N_4) is used in many applications, including removing and dissolving many organic pollutants [33-36]. Carbon paste electrodes (CPE) are important for chemically inert electrode surface renewability, low ohmic resistance, easy fabricating, environmentally friendly, and low cost. However, its stability, kinetics, and selectivity are weak. To solve this problem, surface modification (MCPE) is resorted to by modifiers [37]. Cyclic voltammetry analysis is one of the important analytical methods through which the quantitative and qualitative analysis of the studied material can be done. In addition to the possibility of studying the behavior of the studied material, such as diffusion coefficient (*D*), charge transfer coefficient (α.nα), the mass transport (m_{trans}), constant (K^0), Gibbs free energy (ΔG), also, the highest occupied molecular orbital (*HOMO*), lowest unoccupied molecular orbital (*LUMO*), and others were used [37-38]. In previous studies, 2,4-Dinitrophenylhydrazine was used as a reagent in spectroscopic methods and as a derivation material for aldehydes and ketones in chromatographic analysis; this compound is one of the organic compounds harmful to the environment and has toxicity to many organisms. So, this research is also one of the important electrochemical analytical methods. It is an easy and simple method that can be applied in environmental monitoring and fields concerned with this compound. This research is one of the rare studies concerned with determining a 2,4-dinitrophenylhydrazine pollutant by an electrochemical method.

2. Experimental

2.1. Instrument and Reagents

SHIMADZU SPP-M20A high-performance liquid chromatography HPLC device connected to a Diode Array Detector, Chromatographic column C18, with dimensions of of 25cm×0.46cm×5µm, pH metric device, a device voltammetry by Metrohm made in Switzerland, model 797VA. The materials used are characterized by high purity, namely 2,4-Dinitrophenylhydrazine ($(O_2N)2C_6H_3NHNH_2$; CAS N.: 119-26-6) produced by Sigma, Germany. The monosodium phosphate (α-Naphthyl Acid Phosphate, Monosodium Salt; CAS N.: 81012-89-7), methanol (99.8%; CAS N.: Number: 67-56-1), concentrated sulfuric acid (95.0-98.0%; CAS N.: 7664-93-9; E.C. N.: 231-639-5), boric acid (CAS Number: 10043-35-3), phosphorous acid (CAS N.: 13598-36-2; M.W.: 82.00), sodium hydroxide (CAS N.: 1310-73-2; M.W.: 40.00), glassware of various sizes, boiled and cooled double distilled water (DW, Sigma, Germany) were used..

2.2. Preparation of Reagents and solutions

The 2,4-Dinitrophenylhydrazine standard solution was prepared. A group of solutions was prepared for the analytical methods.

2.2.1. Standard solution for Cyclic voltammetry (CV):

0.0792g of 2,4-DNPHZ powder is taken and transferred to a volumetric flask of 100 mL capacity to which is added an to get a water: ethanol solution 25:75 V/V solution of concentration 4mM.

2.2.2. Standard solution for the spectrophotometry method:

0.0396 g of 2,4DNPHZ powder is taken and transferred to a 100 mL of volumetric flask containing 24.823 mL double-distilled water, then 0.277 mL concentrated sulfuric acid and 75 mL ethanol are added, so its concentration is 396.0 mg L^{-1}, then the standard series (5,10,15, 20) mg L^{-1} is prepared from it which is stretching the chain with 0.1M sulfur acid.

2.2.3.Standard solution for HPLC:

0.0301g of 2,4DNPHZ powder is taken and transferred to a 100 mL volumetric flask and dissolved using a solution of 20% sulfuric acid; its concentration is 301 mg L^{-1}. The solution is left to cool down, and then the standard series (0.5-0.1; 1-5) mg L^{-1} is prepared in 20% sulfuric acid, filtered by a micro-membrane filter (0.45 µm) and then measured using high-performance liquid chromatography (HPLC). A temperature of 30°C with a flow rate of 1.0 mL per 1 min was used.

2.3. Procedure and preparation of NiO-NCQD/g-C_3N_4 adsorbent

An electrode was made (in the laboratory) from a glass tube open at both ends, then connected

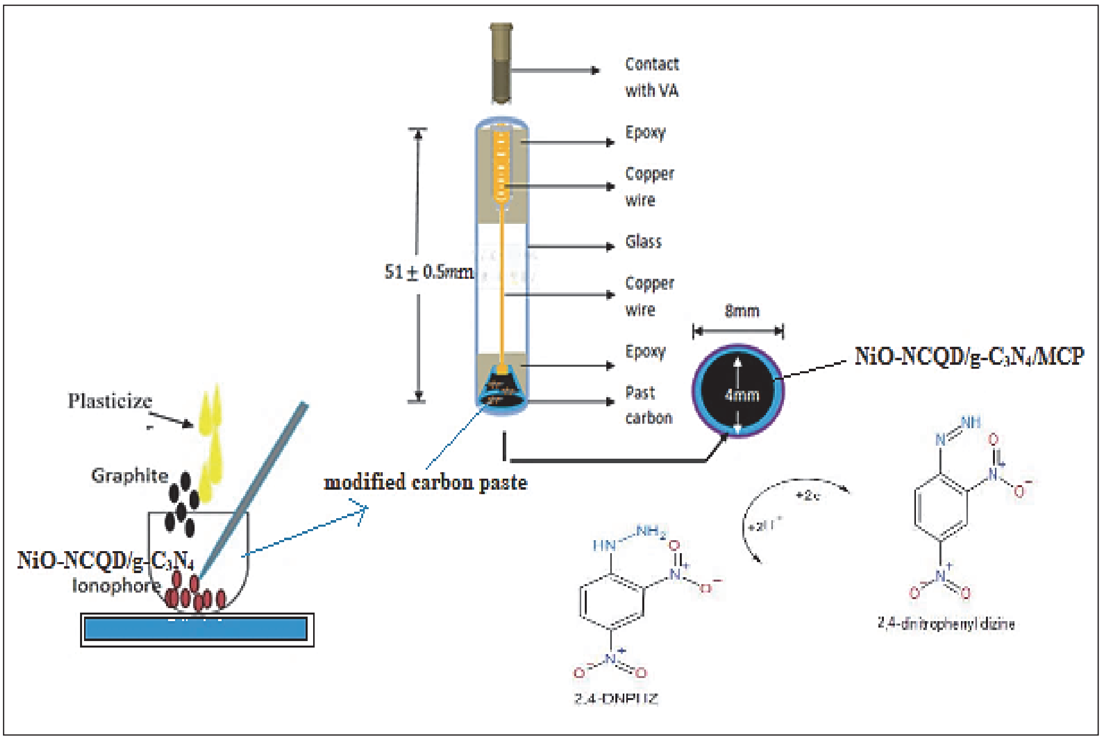


Fig. 2. Procedure based on components of the fabrication of a NiO-NCQD/g-C3N4/MCPE

by a copper wire and a support material. Then, a modified carbon paste was prepared and placed at the lower end of the electrode. Modified carbon paste using NiO-NCQD nano-composite (mix of NiO Nanoparticles (20nm) are added nitrogen quantum carbon dot as nanoadsorbent to get NiO-NCQD nanocomposite), graphene–nitride carbon g-C_3N_4, graphite and paraffin oil, for a total weight from modified carbon paste 0.5g, Symbolizes the factory electrode (NiO-NCQD/g-C_3N_4/MCPE), as in Figure 2. Nickel oxide nanoparticles studded with nitrogen quantum carbon dots were synthesized and characterized in previous work .[39] The 2,4-dinitrophenylhydrazine was determined using NiO-NCQD/g-C_3N_4/MCPE by cyclic voltammetry. Also, after sample preparation, 2,4-dinitrophenylhydrazine was measured by high performance liquid chromatography and spectrophotometry methods.

2.4. Preparation of acid and buffer solutions

2.4.1. Preparation of sulfuric acid solution:

The sulfuric acid solution is prepared at a concentration of 0.1M to get pH 1.

2.4.2.Preparation of monosodium phosphate buffer with H_2SO_4 solution:

A phosphate buffer was prepared from NaH_2PO_4 at a concentration of 0.1M, modified by a solution of H_2SO_4 (0.2 M) to get pH 1.

2.4.3.Preparation Britton–Robinson Buffer solution with H_2SO_4 solution:

Britton–Robinson Buffer solution (BRB) containing H_3PO_4 with a concentration of 0.04M, acetic acid CH_3COOH at a concentration of 0.04M and boron acid H_3BO_3 with a concentration of 0.04 M then modified with a solution H_2SO_4 with a concentration of 0.1M to get pH (1).

2.4.4.Preparation of monosodium phosphate buffer with H_3PO_4 solution:

A phosphate buffer was prepared from NaH_2PO_4 at a concentration of 0.1M and modified by a solution of H_3PO_4 (0.48M) to get pH 1.

2.4.5. Preparation of phosphorous acid solution:

Phosphorous acid solution is prepared at a concentration of 0.48M to get pH 1.

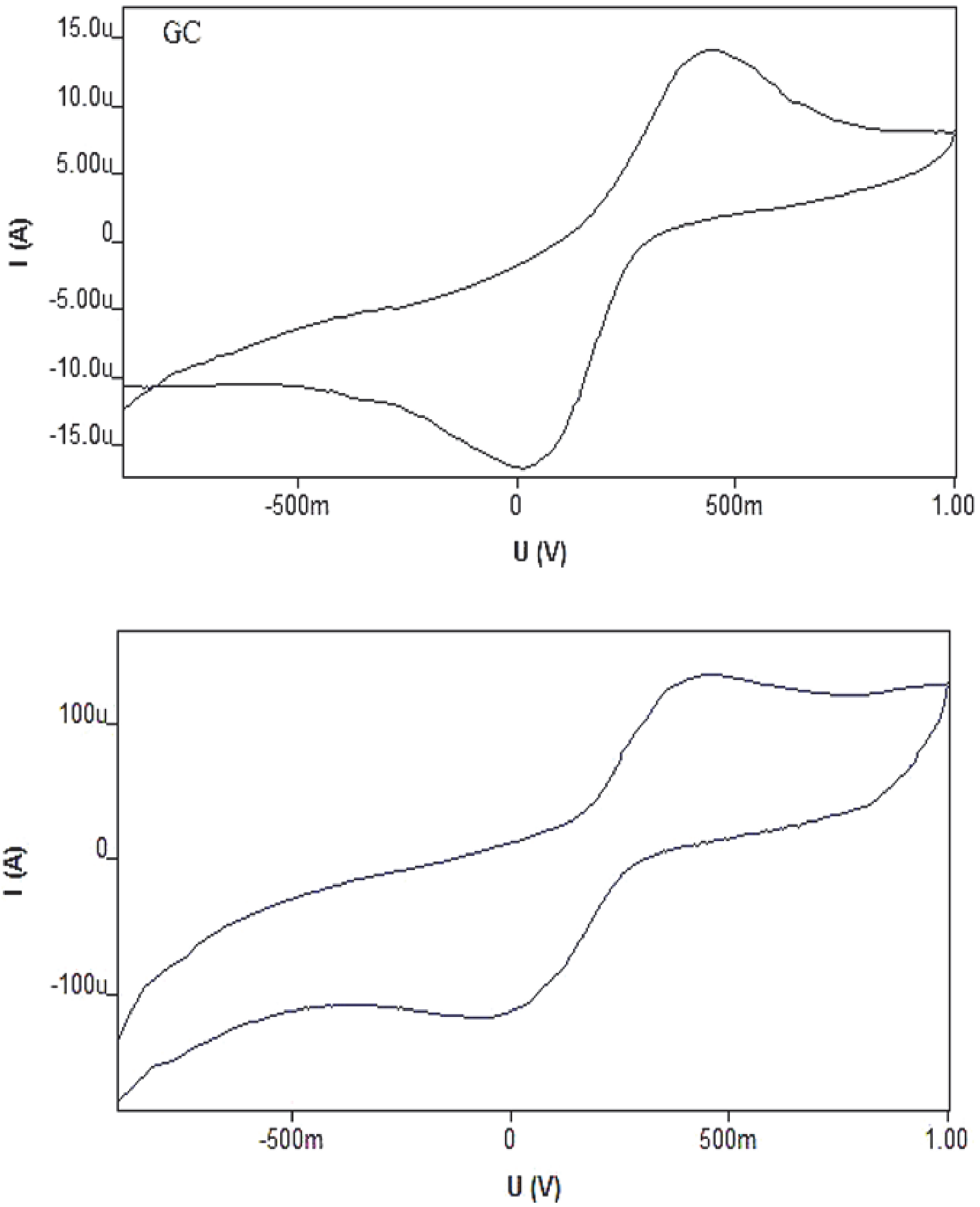


Fig. 3. Oxidation and reduction of ferrous ions using a 5mM electrode test solution of K4 [Fe $(CN)_6$].$3H_2O$ in the presence of a 0.1M KCl on GC and (NiO-NCQD/g-C_3N_4/MCPE)

3. Results and Discussion

3.1. Ensure electrode manufacturing

The ferrous ions were oxidized using the prepared electrode (MCPE) and the glassy carbon electrode (GC), as shown in Figure 3. This electrode can be used in oxidation and reduction by comparing the curves. Also, electrochemistry based on carbon glassy electrodes was used for studying hydrazine and aldehydes [40].

3.2. Effect of the electrochemical percentage of the active material

The effect of the percentage of the active material on the peak current was studied in determining 2,4-DNPHZ, as in Figure 4. It was found that the best of them is 12% nickel oxide doped with quantum dots (NiO-NCQD) with 12% of carbon nitride sheets (C_3N_4), 38% of graphite powder (GP), and 38% of paraffin oil, as in Figure 4.

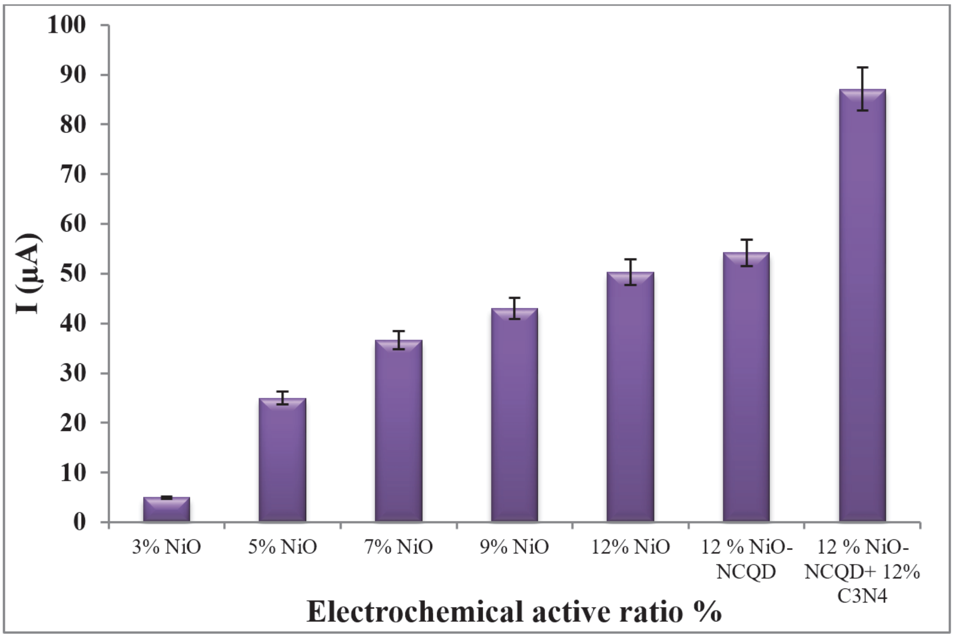
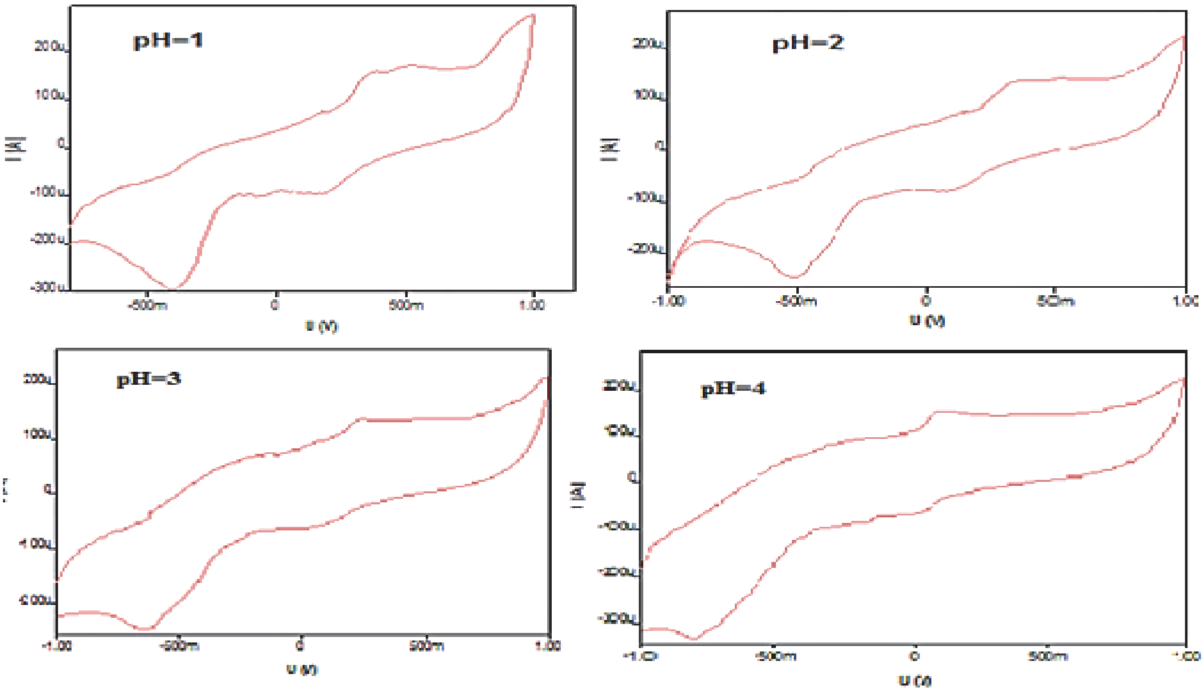


Fig. 4. Effect of the percentage of electrochemical active on the peak current for 2,4-DNPHZ

3.3. The Effect of pH

The Effect of pH was studied from pH 1 to 8 on peak current for 2,4-DNPHZ, shown in Figures 5a and 5b. Due to the Figure, the best recovery was obtained at pH 1.0 (Because of the appearance of an oxidation peak next to OX≈0.5V and the appearance of a return peak next to R≈-0.48V). The peak is clearer at pH =1, as for the rest of the pH (8-2), the height of the peak is not clear despite the increase in I $_{(P)}$ (µA) of the current. It was also observed in the range pH (8-2), where there is only an oxidation peak (ox), but there is no reduction peak (Red). Notice the appearance of an oxidation peak next to Eox≈0.5V and a reduction peak next to Ered≈-0.48V. The oxidation and reduction system is quasi-reversible because ΔE=0.98V is greater than 0.059.2, and $I_{ox}/I_{red} < 1$. Moreover, it is also noticed that the oxidation and reduction peak potential increases with decreasing the pH value, as in Figures 5a and 5b.



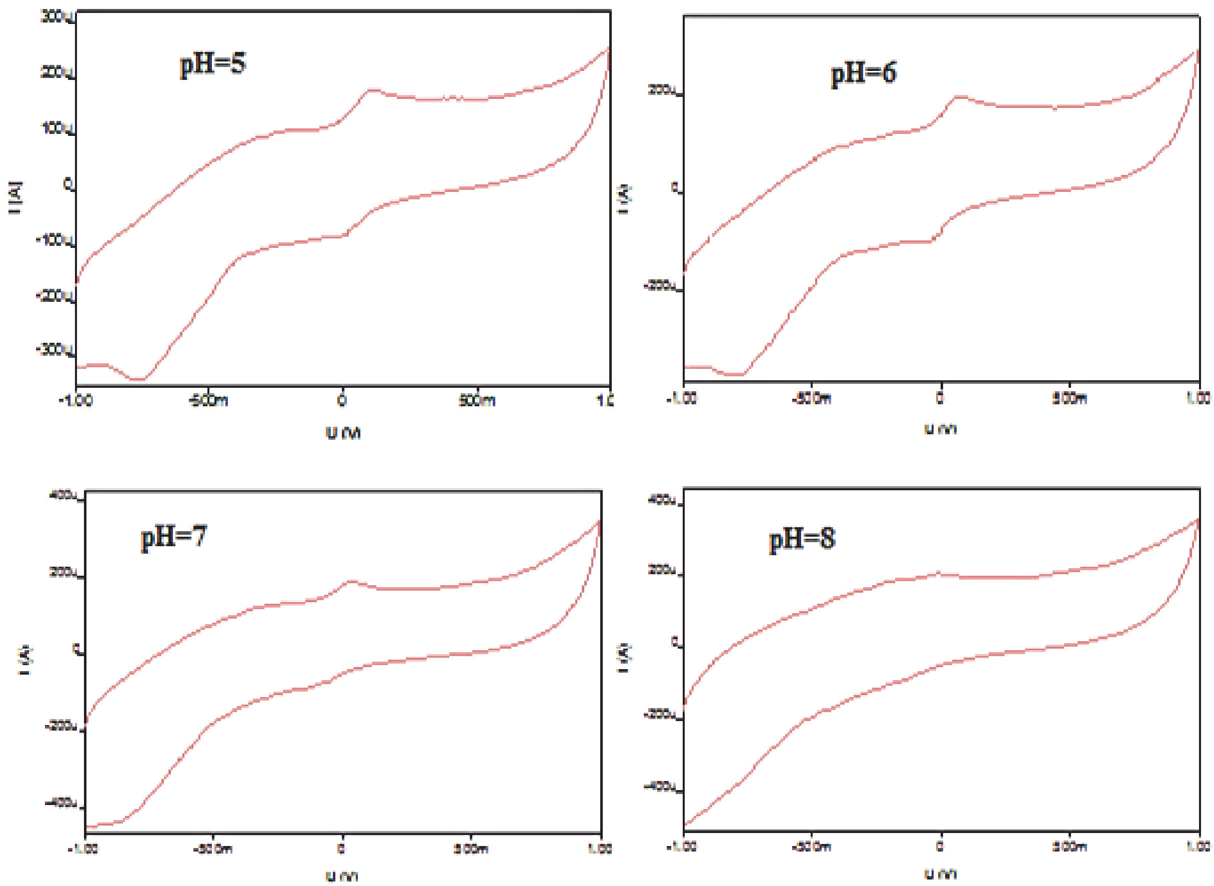


Fig. 5a. Effect of the pH from (1-8) on the peak of oxidation and reduction by (NiO-NCQD/g-C_3N_4/MCPE) for 2,4-DNPHZ

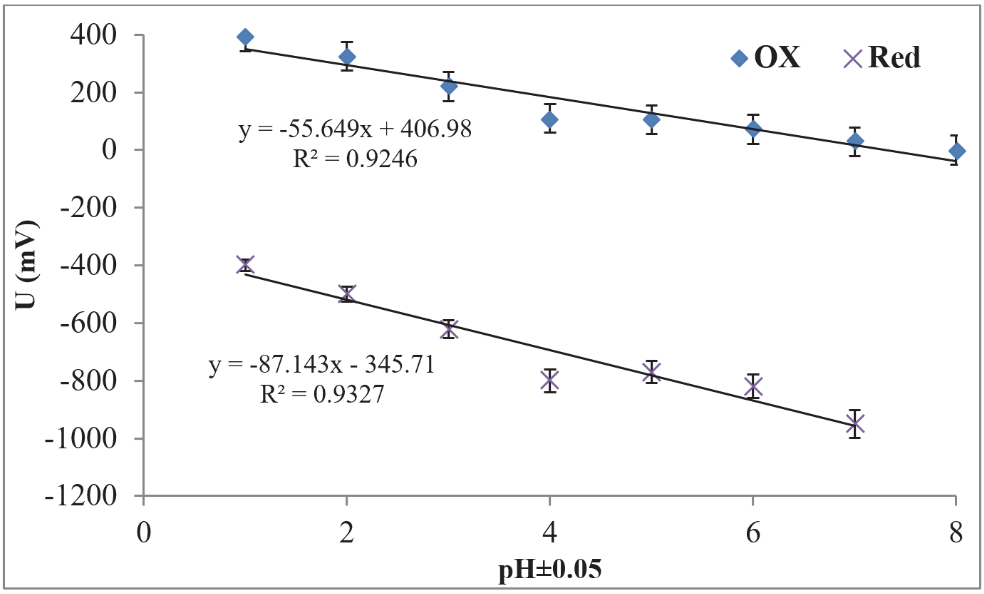


Fig. 5b. Effect of the pH from (1-8) on the peak of oxidation and reduction and effect of pH value on the peak potential U (mV) by (NiO-NCQD/g-C_3N_4/MCPE) for 2,4-DNPHZ

3.4. Effect of the type of acid

Several buffer and acid solutions were prepared at pH 1: sulfuric acid solution, monosodium phosphate with sulfuric acid, Britton–Robinson Buffer with sulfuric acid, monosodium phosphate with phosphorous acid, and phosphorous acid solution as in Figure 6. Due to Figure 6, sulfuric acid with a concentration of 0.1M was the best acid for determining 2,4-dinitrophenylhydrazine (2,4-DNPHZ) by (NiO-NCQD/g-C_3N_4/MCPE) at pH=1.

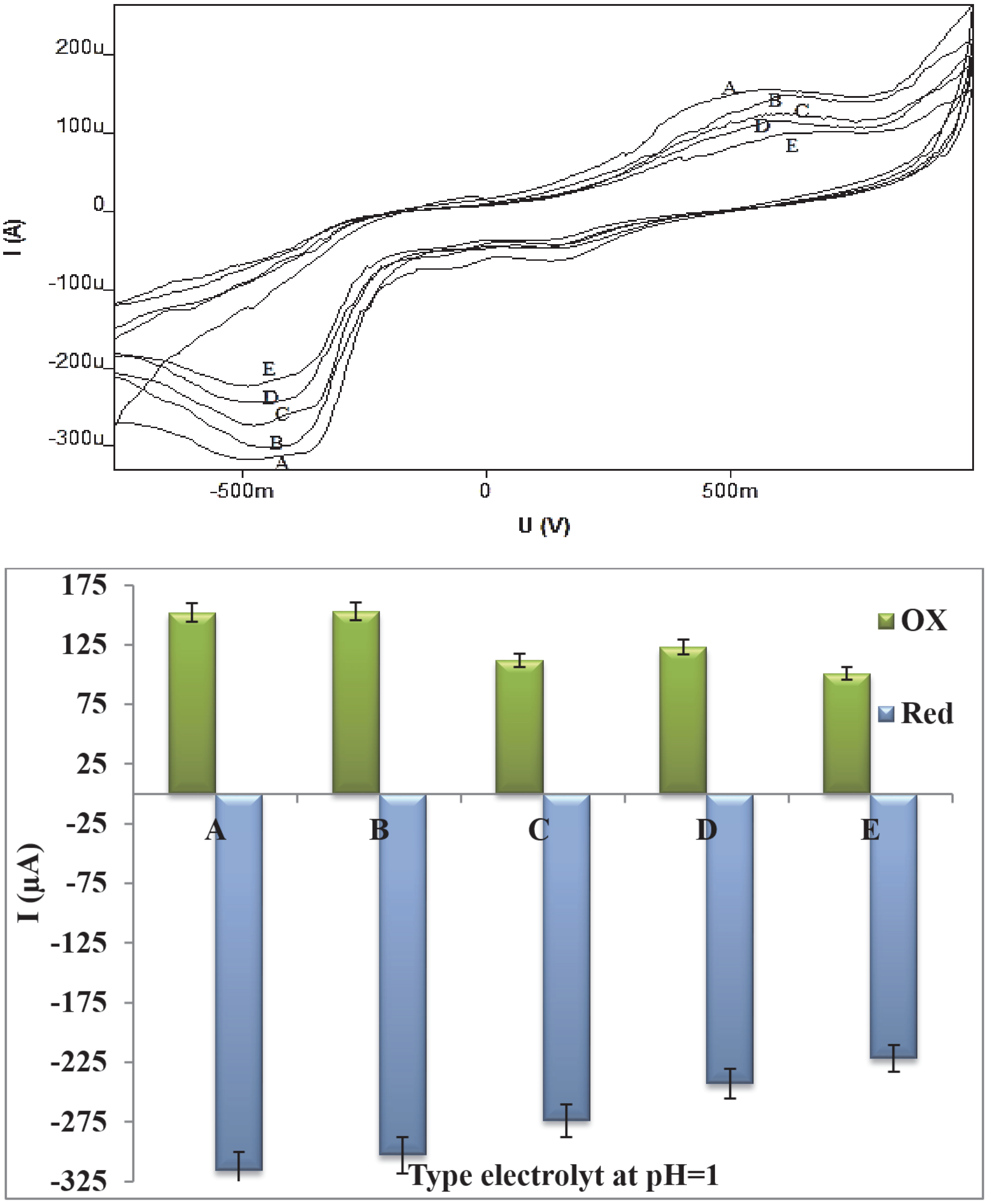


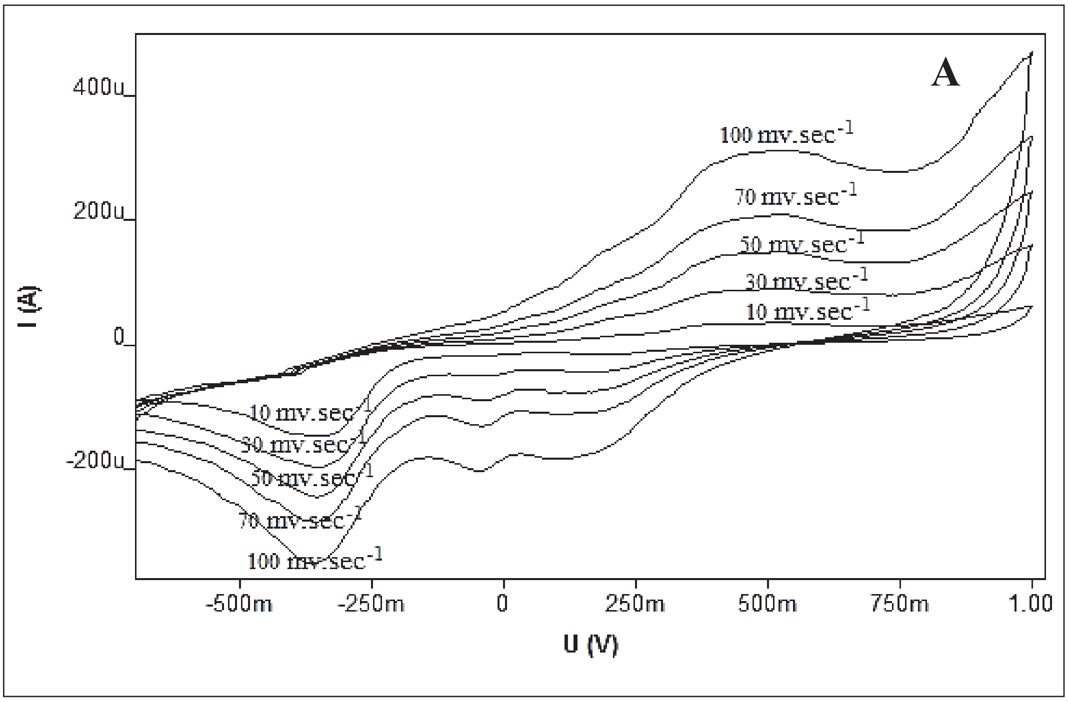
Fig. 6. Effect of the type of acid Effect on the I (µA) and Potential U(V) for both oxidation and redaction of 2,4DNPHZ effect of the kind of acid effect of on the I (µA) for both oxidation and redaction of 2,4DNPHZ A) H_2SO_4 (0.1M) pH=1 B) $NaH_2 PO_4$ (0.1M) modified by $H_2 SO_4$ (0.1M) until pH=1 C) BRB (0.04M for each) modified by $H_2 SO_4$ (0.1M) until pH=1 D) NaH_2PO_4 (0.1M) modified by $H_3 PO_4$ (0.48M) to get pH=1 E) $H_3 PO_4$ (0.48M) pH=1

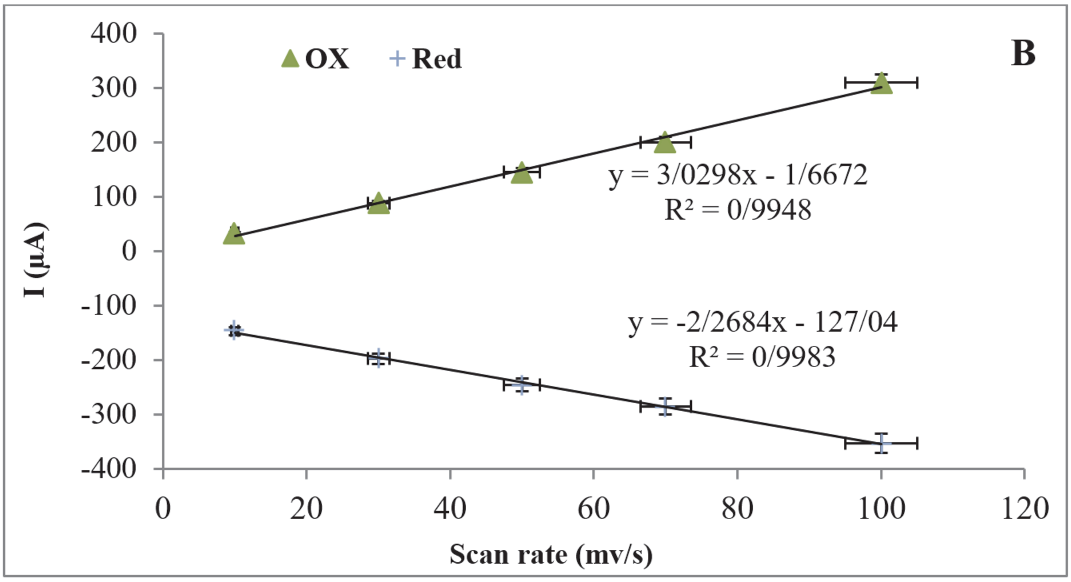
3.5. The effect of scan rate

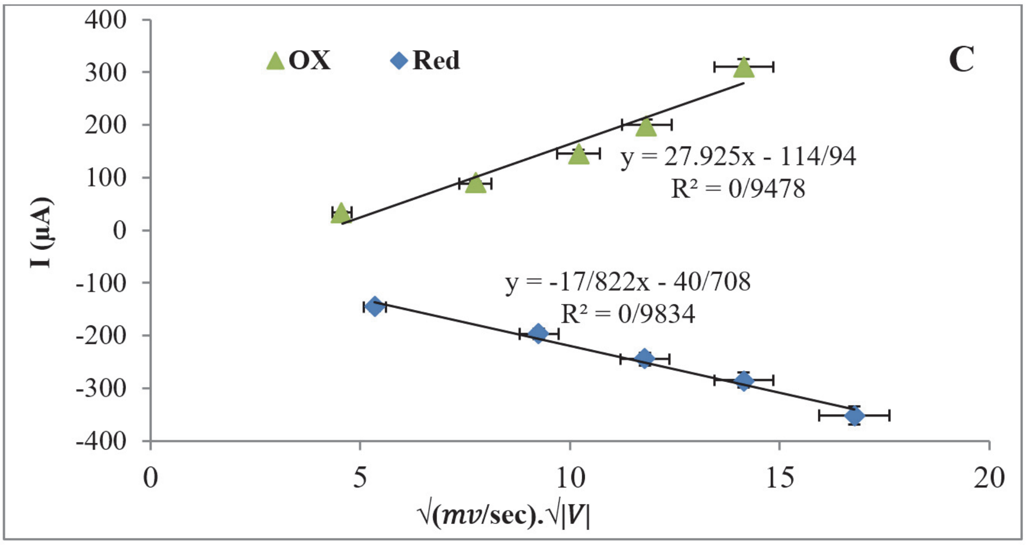
The scan rate was studied within the range (10, 30, 50, 70, 100) mv sec $^{-1}$ on the peak current $I_{(P)}$ shown in Figure 7A. It also studied the relationship of the scan rate multiplied by the peak potential in terms of the peak current, as in Figures 7B and 7C. Due to the results, the best scan rate is 100 mv.sec^{-1}. It was found that the relationship is linear between each of the oxidation and reduction peaks with the peak current $I_{(P)}$.

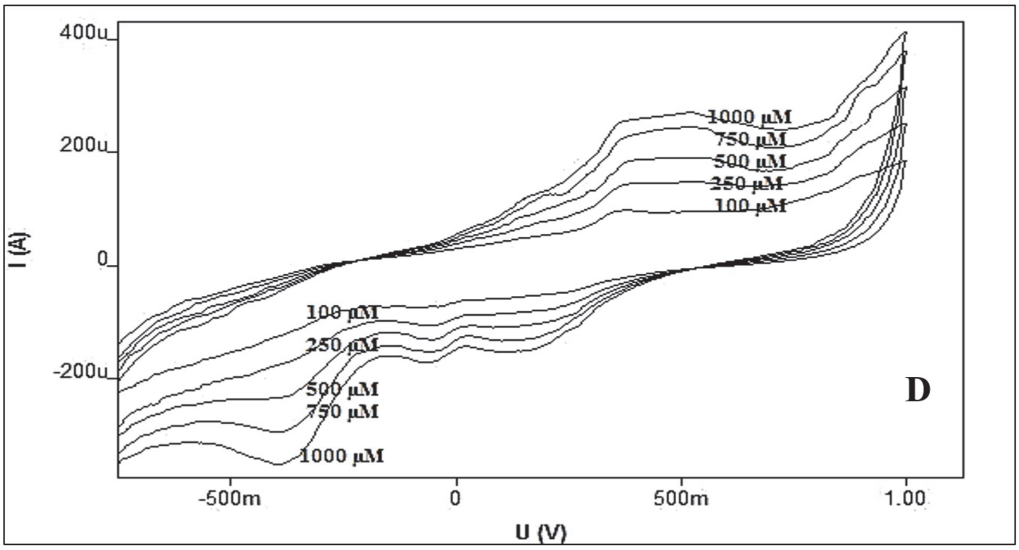
3.6. Analytical Detection Limit

A standard series of 2.4-DNPHZ was prepared within the range (1, 25, 50, 75, 100, 250, 500, 750, 1000) µM as in Figures 7D-7F; the previous curves were drawn in terms of the concentration of 2,4-DNPHZ and the peak current strength for both oxidation and reduction as in Figure 7.






C
▲OX
◆Red
y = 27.925x - 114/94
R² = 0/9478
y = -17/822x - 40/708
R² = 0/9834
I (μA)
400
300
200
100
0
-100
-200
-300
-400
0
5
10
15
20
√(mv/sec).√|V|


D
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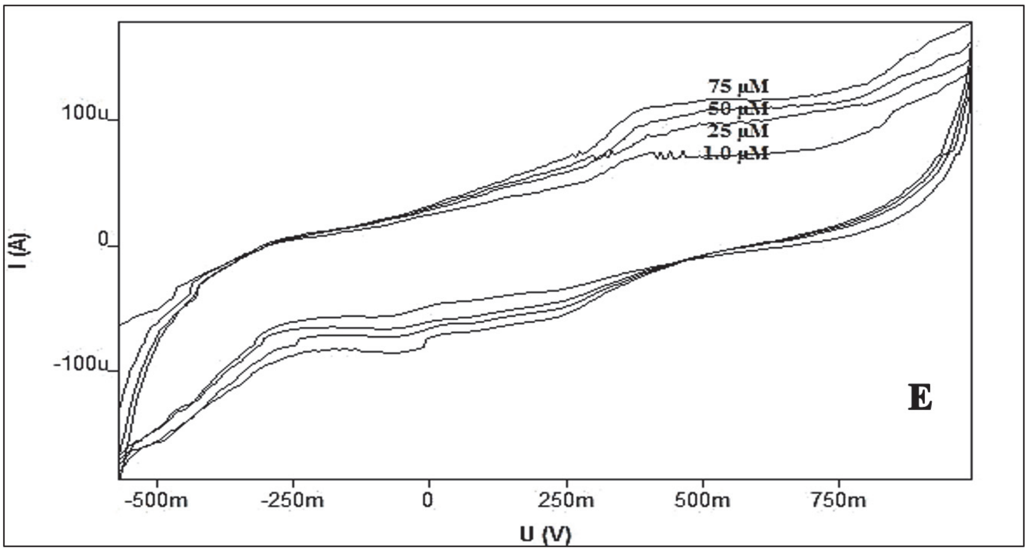
E
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75 μM
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25 μM
1.0 μM

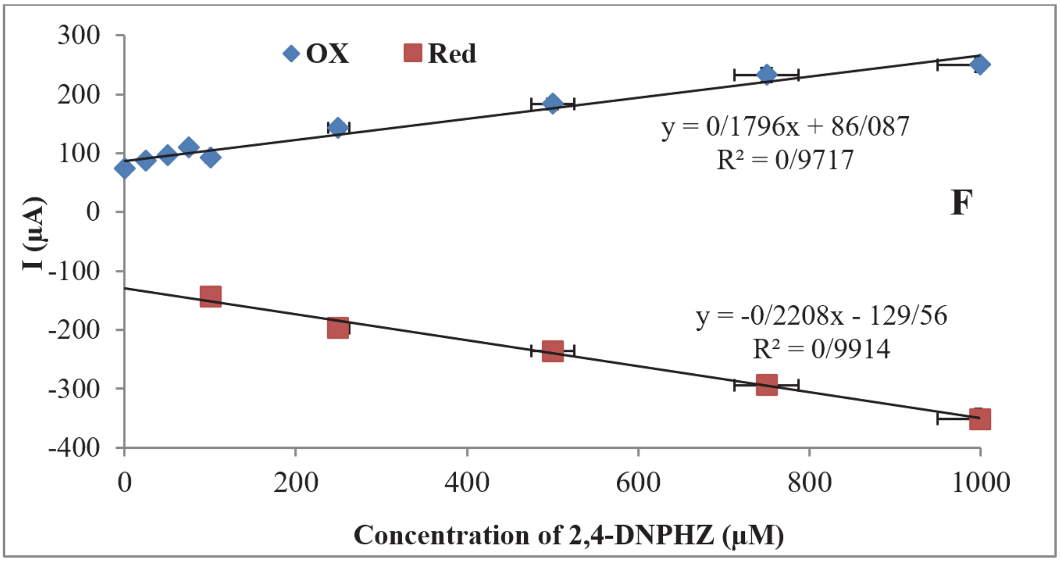


Fig. 7. Curve the oxidation-reduction peak of 2,4-DNPHZ

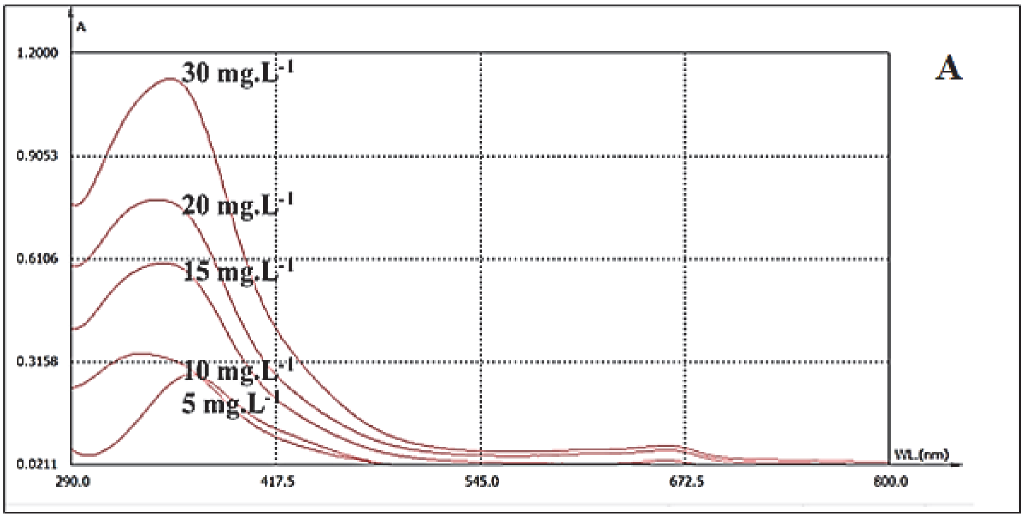
A) Effect of Scan rate on the peak current
B) Scan rate (mv/s) vs I(µA)
C) root effect of vs I(µA)
D) effect of concentration on peak current (100 -250 - 500 –750- 1000)µM
E) effect of concentration on peak current (1-25-50-75) µM
F) Curve concentration vs I (µA)

It was shown from the previous Figures that the field of linearity upon 2.4-DNPHZ lies within the range of (1-1000) µM for oxidation and (100-1000) µM for reduction with an equation of $I_{OX}=0.1796C_{2,4\text{-DNPHZ}}+86.087$ for oxidation and $I_{Red}=-0.2208C_{2,4\text{-DNPHZ}}-129.56$ for Redaction, with correlation coefficient $R^2=0.9717$ and $R^2=0.9914$ for each of them, respectively. Statistical treatments were calculated as Tabe 1. Concentrations are calculated from a mathematical relationship (Randles-Sevcik) of Equation 1.

3.7. Determine for 2,4-DNPHZ using spectrophotometry and HPLC

The 2,4-DNPHZ is analyzed based on spectrophotometry in Figures 8A and 8B. It was shown by spectral scanning that λmax= 360nm, a standard series of 2,4-DNPHZ was prepared. The absorbance was studied by concentration dependency, as in Figures (8A and 8B), that its equation is $C_{ppm}=26.1491*A+0.2686$, the minimum concentration that can be analyzed by UV-Vis spectrometry is 5 mg L^{-1}, so it was examined by chromatographic (HPLC) methods as well, in proportion to the detection limit of the proposed method. When determining this compound using high-performance liquid chromatography (HPLC), it was found that the retention time Rt≈1.9 min. Through the largest possible area in terms of wavelength, it was found that the best two wavelengths are 340nm and 250nm as in Figure 8C-8E. A standard series of 2,4DNDH is analyzed by HPLC within the range (5, 1, 0.5, 0.1) mg L^{-1}, as shown in Figure 8F. Statistical treatments were calculated for HPLC, where the number of measurements is three (n=3), the average taken Concentration $\bar{x}$ = 1.262626 µM (0.25g L^{-1}). The electrochemical method (NiO-NCQD/g-C3N4/

$$i_p = \mp 0.436 nFA_{real} C \left(\frac{nFvD}{RT}\right)^{\frac{1}{2}} \ldots\ldots\ldots\ldots\ldots\ldots \text{quasi} - \text{reversible} \qquad (Eq.1)$$


A
A
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0.9053
0.6106
0.3158
0.0211
30 mg.L-1
20 mg.L-1
15 mg.L-1
10 mg.L-1
5 mg.L-1
WL.(nm)
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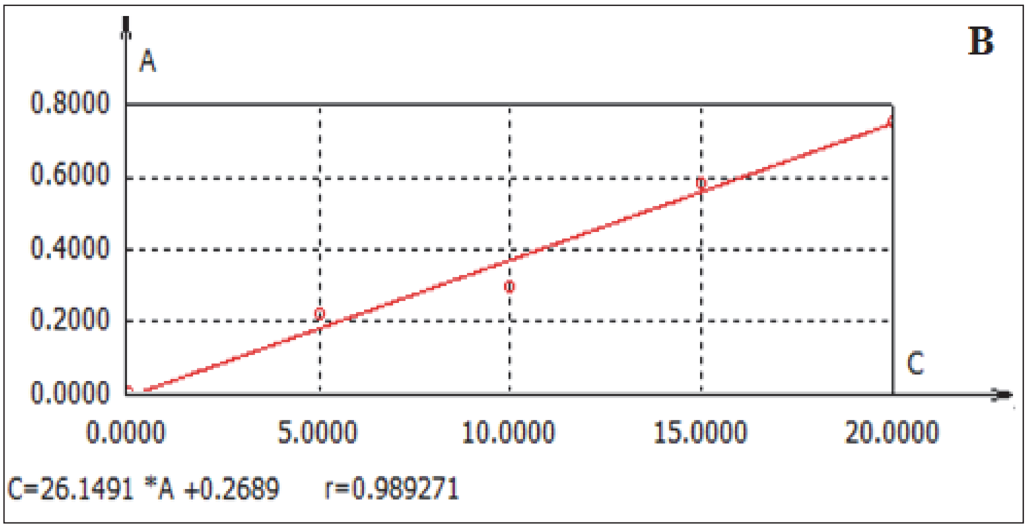
417.5
545.0
672.5
800.0


B
A
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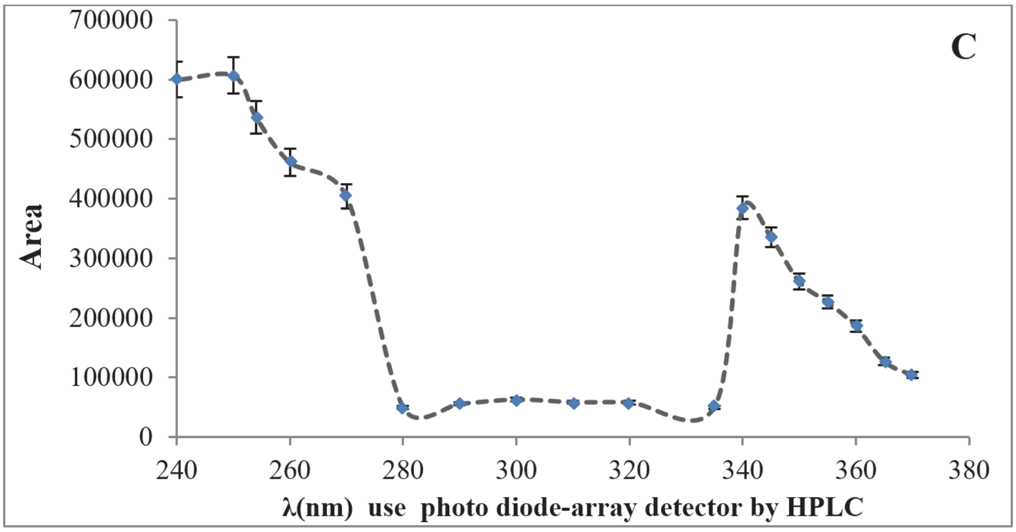
C=26.1491 *A +0.2689
r=0.989271


C
700000
600000
500000
400000
300000
200000
100000
0
Area
240
260
280
300
320
340
360
380
λ(nm) use photo diode-array detector by HPLC

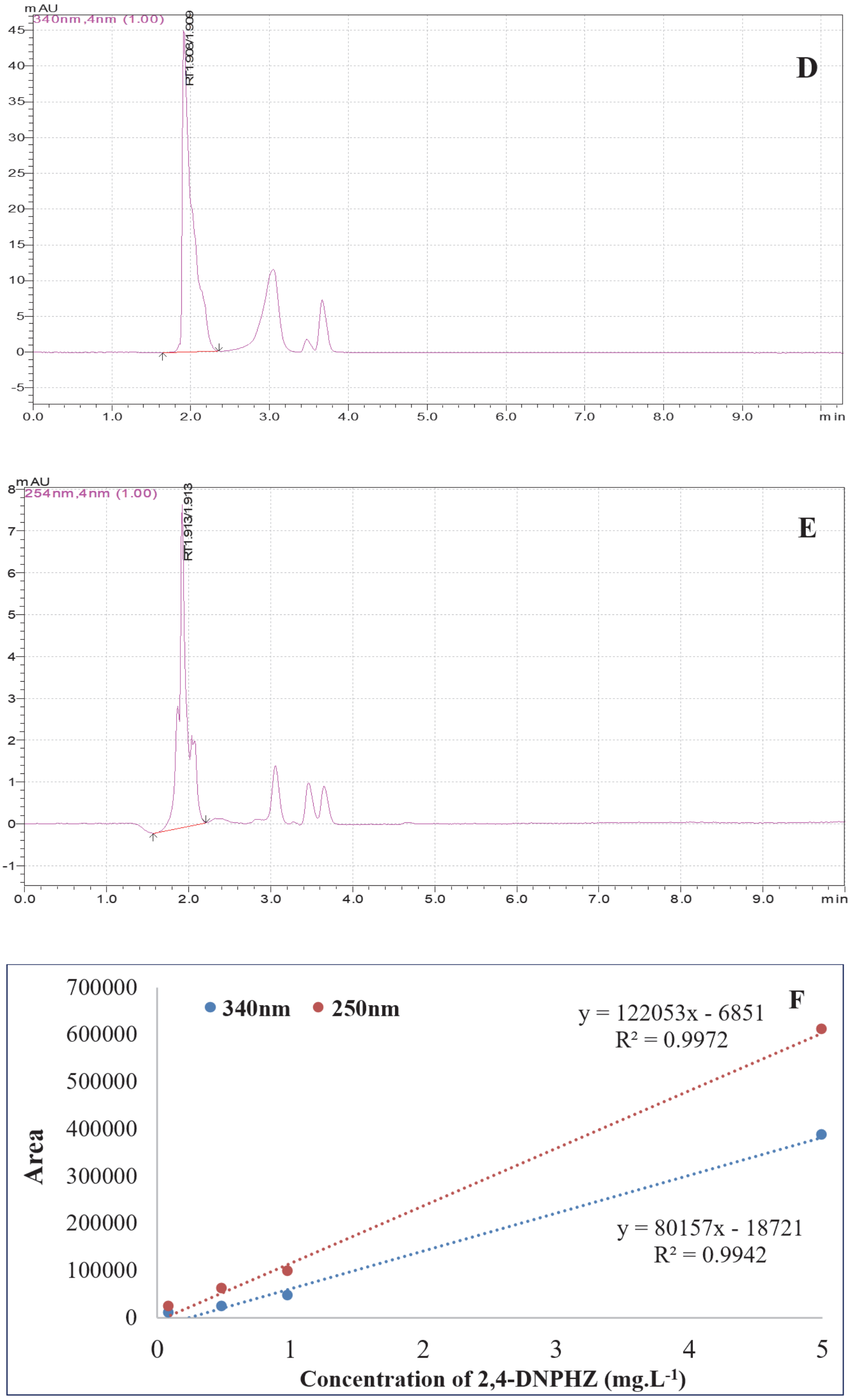


Fig. 8. Curve for 2,4-DNPHZ by High-performance liquid chromatography

A) absorbance vs wavelength,

B) absorbance vs concentration (5, 10, 15, 20) mg L^{-1}

C) wavelength (nm) vs. area by HPLC using a photodiode-array detector.

D) Using a photodiode-array detector, a chromatogram at a concentration of 5 mg L^{-1} at 340 nm.

E) chromatogram at a concentration of 5 mg L^{-1} at 254 nm

F) A standard series within the range (5-1-0.5-0.1) mg L^{-1} vs area.

MCPE) by (CV) of determining this pollutant is the best of the Spectrophotometry method. So, the electrochemical and chromatographic method is compared in Table 1.

The method proposed in this research (NiO-NCQD/g-C_3N_4/MCPE) is characterized by accuracy, reliability and good repeatability in Table 1. The results showed that the technique has a deviation of (0.02624747 µM), a relative standard deviation of a percent (2.08278875%), a quantitative detection limit (0.564097738 µM) and a detection limit (0.43843 µM). The value of the t-student was calculated (0.67361). So, the proposed method is characterized by reliability.

It turned out that the analysis using (HPLC) for analyzing the pollutant (2,4-DNDH) is characterized by analytical accuracy and validity. The results of the HPLC method were compared with (NiO-NCQD/g-C_3N_4/ MCPE) for the organic pollutant (2,4-DNDH). The value F-Test (3.819345) compared with the reference value F-Tab (19.000) at a confidence level of 95%. Comparing proposed methods based on the NiO-NCQD/g-C3N4/ MCPE with HPLC technique showed no significant difference between the two methods for determining (2,4-DNDH) in terms of accuracy.

4. Conclusions

In this study, the manufacture of an electrode using modified carbon paste (NiO-NCQD/g-C_3N_4/MCPE) was used to determine 2,4-dinitrophenylhydrazine (2,4-DNPHZ) by the cyclic voltammetry (CV). The modified carbon paste method was compared with high-performance liquid spectrophotometry (HPLC) and chromatography (UV-Vis). It turned out that the electrochemical method (NiO-NCQD/g-C_3N_4/MCPE) is superior to the spectrophotometry method in terms of detection limit (LOD). Also, there is no significant difference in accuracy between the HPLC method and NiO-NCQD/g-C3N4/ MCPE method. The electrochemical method is a new analytical method characterized by accuracy, repeatability, and reliability with low cost.

5. References

[1] W. A. Adeosun, A. M. Asiri, H. M. Marwani, Real time detection and monitoring of 2, 4-dinitrophenylhydrazine in industrial effluents and water bodies by electrochemical approach based on novel conductive polymeric composite, Ecotoxicol. Environ. Safe., 206 (2020) 111171. https://doi.org/10.1016/j.ecoenv.2020.111171

[2] E. Zhang, P.Ju, Z. Zhang, H. Yang, L.Tang, X.Hou, J. J. Wang, A novel multi-purpose Zn-MOF fluorescent sensor for 2, 4-dinitrophenylhydrazine, picric acid, La^{3+} and Ca^{2+}: Synthesis, structure, selectivity, sensitivity and recyclability, Spectrochim. Acta Part A: Mol. Biomol. Spect., 222 (2019) 117207. https://doi.org/10.1016/j.saa.2019.117207

[3] K. Ahmad, A. Mohammad, P. Mathur, S. M. Mobin, Preparation of SrTiO3 perovskite decorated rGO and electrochemical detection of nitroaromatics, Electrochim. Acta, 215 (2016) 435-446. https://doi.org/10.1016/j.electacta.2016.08.123

[4] G. Zgherea, C. Stoian, S. Peretz, synthesis and physico-chemical characterization of 2.4-dinitrophenyl hidrazones derived from carbonyl compounds with some importance

Table 1. Analytical, statistical processors for Determination of (2,4-DNPHZ) by two methods (NiO-NCQD/g-C_3N_4/ MCPE) and (HPLC)

Method	concentration µ. mol L^{-1}	(n=3)	R (%)	SD (µ. mol.L^{-1})	RSD (%)
Adsorbent	1.25000	1.2602079	100.8166295	0.02624747	2.08278875
HPLC	1.262626	1.209843	95.81958	0.010157	4.239873

Adsorbent: NiO-NCQD/g-C_3N_4/ MCPE

in the study of food quality, Annals of the University Dunarea de Jos of Galati Fascicle VI-Food Technol., 33 (2009) 83-89. https://ores.su/en/journals/annals-of-the-university-dunarea-de-jos-of-galati-fascicle-vi-food-technology

[5] Y. Q. Lu, J. K. Jiang, W. D. Huang, Clinical features and treatment in patients with acute 2, 4-dinitrophenol poisoning, J. Zhejiang Uni. Sci. B, 12 (2011) 189-192. https://doi.org/10.1631/jzus.B1000265

[6] M. A. Smith, L. M.Sayre, V. E. Anderson, P. L. Harris, M. F. Beal, N. Kowall, G. Perry, Cytochemical demonstration of oxidative damage in Alzheimer disease by immunochemical enhancement of the carbonyl reaction with 2, 4-dinitrophenylhydrazine, J. Histochem. Cytochem., 46 (1998) 731-735. http://www.jhc.org

[7] F. Talebzadeh, S. Sobhanardakani, R. Zandipak, Effective adsorption of As (V) and V (V) ions from water samples using 2, 4-dinitrophenylhydrazine functionalized sodium dodecyl sulfate-coated magnetite nanoparticles, Sep. Sci. Technol., 52 (2017) 622-633. https://doi.org/10.1080/01496395.2016.1262873

[8] S. Sobhanardakani, M. Ahmadi, R. Zandipak, Efficient removal of Cu(II) and Pb(II) heavy metal ions from water samples using 2,4-dinitrophenylhydrazine loaded sodium dodecyl sulfate-coated magnetite nanoparticles, J. Water Sup. Res. Technol. AQUA, 65 (2016) 361-372. https://doi.org/10.2166/aqua.2016.100

[9] A. Afkhami, M. Saber-Tehrani, H. Bagheri, Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2, 4-dinitrophenylhydrazine, J. Hazard. Mater., 181 (2010) 836-844. https://doi.org/10.1016/j.jhazmat.2010.05.089

[10] S. Sobhanardakani, R. Zandipak, 2, 4-Dinitrophenylhydrazine functionalized sodium dodecyl sulfate-coated magnetite nanoparticles for effective removal of Cd(II) and Ni(II) ions from water samples, Environ. Monit. Assess., 187 (2015) 1-14. https://doi.org/10.1007/s10661-015-4635-y

[11] I.Dalle-Donne, M.Carini, M.Orioli,, G.Vistoli, L. Regazzoni, G. Colombo, G. Aldini, Protein carbonylation: 2, 4-dinitrophenylhydrazine reacts with both aldehydes/ketones and sulfenic acids, Free Radical Biol. Med., 46 (2009) 1411-1419. https://doi.org/10.1016/j.freeradbiomed.2009.02.024

[12] P.D.Neuenfeldt, B.B.Drawanz, G.M.Siqueira, C. R.Gomes, S. M. Wardell, A. F. Flores, W. Cunico, Efficient solvent-free synthesis of thiazolidin-4-ones from phenylhydrazine and 2, 4-dinitrophenylhydrazine, Tetrahedron Lett., 51 (2010) 3106-3108. https://doi.org/10.1016/j.tetlet.2010.04.026

[13] J. Pilz, I. Meineke, C.H. Gleiter, Measurement of free and bound malondialdehyde in plasma by high-performance liquid chromatography as the 2, 4-dinitrophenylhydrazine derivative, J. Chromatogr. B Biomed. Sci. Appl., 742 (2000) 315-325. https://doi.org/10.1016/S0378-4347(00)00174-2 .

[14] Y.L. Lin, P.Y. Wang, L.L. Hsieh, K.H. Ku, Y.T. Yeh, C.H. Wu, Determination of linear aliphatic aldehydes in heavy metal containing waters by high-performance liquid chromatography using 2, 4-dinitrophenylhydrazine derivatization, J. Chromatogr. A, 1216 (2009) 6377-6381. https://doi.org/10.1016/j.chroma.2009.07.018.

[15] O. Korchazhkina, C. Exley, S.A. Spencer, Measurement by reversed-phase high-performance liquid chromatography of malondialdehyde in normal human urine following derivatisation with 2, 4-dinitrophenylhydrazine, J. Chromatogr. B, 794 (2003) 353-362. https://doi.org/10.1016/S1570-0232(03)00495-1.

[16] S. Uchiyama, Y. Inaba, N. Kunugita, Derivatization of carbonyl compounds with 2, 4-dinitrophenylhydrazine and their subsequent determination by high-performance liquid chromatography, J. Chromatogr. B, 879 (2011) 1282-1289. https://doi.org/10.1016/j.jchromb.2010.09.028

[17] R. Nawaz, T. Rasheed, T. Iqbal, M. Bilal, S. Majeed, Development of 2,4-dinitrophenylhydrazine-modified carbon paste electrode for highly sensitive electrochemical sensing of amino acids, Monatshefte für Chemie-Chemical Monthly, 151 (2020) 505-510. https://doi.org/10.1007/s00706-020-02580-y

[18] F. Lipari, S. J. Swarin, 2, 4-Dinitrophenylhydrazine-coated Florisil sampling cartridges for the determination of formaldehyde in air, Environ. Sci. Technol., 19 (1985) 70-74. https://doi.org/10.1021/es00131a007

[19] F. Soglia, M. Petracci, P. Ertbjerg, Novel DNPH-based method for determination of protein carbonylation in muscle and meat, Food Chem., 197 (2016) 670-675. https://doi.org/10.1016/j.foodchem.2015.11.038

[20] T.Wang, X.Gao, J.Tong, L.Chen, Determination of formaldehyde in beer based on cloud point extraction using 2, 4-dinitrophenylhydrazine as derivative reagent, Food Chem., 131 (2012), 1577-1582. https://doi.org/10.1016/j.foodchem.2011.10.021

[21] M. Al-Ani, L. U. Opara, D. Al-Bahri, N. Al-Rahbi, Spectrophotometric quantification of ascorbic acid contents of fruit and vegetables using the 2, 4-dinitrophenylhydrazine method, J. Food Agri. Environ., 5 (2007) 165. www.world-food.net

[22] P.S. Praveen, B. Anupama, V. Jagathi, G.D. Rao, Spectrophotometric determination of Tolperisone using 2, 4-dinitrophenylhydrazine reagent, Int. J. Res. Pharm. Sci., 3 (2010) 317-320. www.ijrps.pharmascope.org

[23] P. Nagaraja, A. K. Shrestha, Spectrophotometric method for the determination of drugs containing phenol group by using 2, 4-dinitrophenylhydrazine, E-J. Chem., 7 (2010) 395-402. https://doi.org/10.1155/2010/328061

[24] H. Li, W. Goldberg, L. Verheyen, M. Foston, A method for the quantification of surface aldehyde content in cellulose nanocrystals using 2, 4-dinitrophenylhydrazine, SSRN J., (2022) 1-15. https://papers.ssrn.com/sol3/papers.cfm?abstract_id=4148789

[25] R. M. Khaleel, D. H. Mohammed, Spectrophotometric determination of tetracycline hydrochloride using 2, 4–dinitrophenyl hydrazine as coupling reagent, J. Phys. Conf. Ser., 1664 (2020) 012084. https://doi.org/10.1088/1742-6596/1664/1/012084.

[26] D. H. Mohammed, F. K. Omar, Spectrophotometric determination of catechol and resorcinol by oxidative coupling with 2, 4-dinitrophenyl hydrazine, Egypt. J. Chem., 64 (2021) 5061-5065. https://doi.org/10.21608/ejchem.2021.57506.3253

[27] M. Sireesha, R.S. Chandan, B.M. Gurupadayya, A. Shravya, Spectrophotometric determination of Nateglinide using 2, 4-dinitrophenyl hydrazine and potassium ferricyanide in pharmaceutical dosage form, Der Pharma Chem., 3 (2011), 497-506. https://www.derpharmachemica.com

[28] N. Rahman, S. Sameen, M. Kashif, Spectroscopic study on the interaction of haloperidol and 2, 4-dinitrophenylhydrazine and its application for the quantification in drug formulations, Anal. Chem. Lett., 6 (2016) 874-885. https://doi.org/10.1080/22297928.2016.1265898.

[29] S. Behera, R. Behura, M. Mohanty, R. Dinda, P. Mohanty, A.K. Verma, B.R. Jali. Spectroscopic, cytotoxicity and molecular docking studies on the interaction between 2, 4-dinitrophenylhydrazine derived Schiff bases with bovine serum albumin, Sens. Int., 1 (2020) 100048. https://doi.org/10.1016/j.sintl.2020.100048

[30] M. Kiamehr, B. Alipour, M. Nasrollahzadeh, S. M. Sajadi, Catalytic reduction of 2, 4-dinitrophenylhydrazine by cuttlebone supported Pd NPs prepared using Conium maculatum leaf extract, IET Nanobiotechnol., 12 (2018) 217-222. https://doi.org/10.1049/iet-nbt.2017.0005

[31] W. Boumya, M. Achak, M. Bakasse, M. A. El Mhammedi, Indirect determination of dopamine and paracetamol by electrochemical impedance spectroscopy

using azo coupling reaction with oxidized 2, 4-dinitrophenylhydrazine (DNPH): Application in commercial tablets, J. Sci. Adv. Mater. Dev., 5 (2020) 218-223. https://doi.org/10.1016/j.jsamd.2020.04.003

[32] M. P. Georgopoulou, C. V. Chrysikopoulos, Evaluation of carbon nanotubes and quartz sand for the removal of formaldehyde–(2, 4-dinitrophenylhydrazine) from aqueous solutions, Ind. Eng. Chem. Res., 57 (2018) 17003-17012. https://doi.org/10.1021/acs.iecr.8b03996

[33] A. Mohammad, M. Ehtisham Khan, M. Hwan Cho, Sulfur-doped-graphitic-carbon nitride (S-*g*-C_3N_4) for low cost electrochemical sensing of hydrazine, J. Alloys Compd., 816 (2020) 152522. https://doi.org/10.1016/j.jallcom.2019.152522

[34] I. Kolesnyk, J. Kujawa, H. Bubela, V. Konovalova, A. Burban, A. Cyganiuk, W. Kujawski, Photocatalytic properties of PVDF membranes modified with g-C3N4 in the process of Rhodamines decomposition, Sep. Purif. Technol., 250 (2020) 117231. https://doi.org/10.1016/j.seppur.2020.117231

[35] H. Mirzaei, M. H. Ehsani, A. Shakeri, M. R.Ganjali, A. Badiei, Preparation and photocatalytic application of ternary Fe_3O_4/GQD/g-C_3N_4 heterostructure photocatalyst for RhB degradation, J. Pollut., 8 (2022) 779-791. https://doi.org/10.22059/POLL.2022.331685.1202

[36] G. K. Jayaprakash, B. K. Swamy, S. Rajendrachari, S.C. Sharma, R. Flores-Moreno, Dual descriptor analysis of cetylpyridinium modified carbon paste electrodes for ascorbic acid sensing applications, J. Mol. Liq., 334 (2021) 116348. https://doi.org/10.1016/j.molliq.2021.116348.

[37] K. I. Alabid, H. N. Nasser, Study of the behavior and determination of phenol based on modified carbon paste electrode with nickel oxide-nitrogen carbon quantum dots using cyclic voltammetry, Anal. Methods in Environ. Chem. J., 6 (2023) 58-68. https://doi.org/10.24200/amecj.v6.i01.227

[38] K. I. Alabid, H. N. Nasser, An analytical method based on a modified carbon paste electrode by nanoparticles in optimal conditions for determining phenol in the liquid solutions and comparing it to high-performance liquid Chromatography, Anal. Methods in Environ. Chem. J., 6 (2023) 55-70. https://doi.org/10.24200/amecj.v6.i02.240

[39] K. I. Alabid, H.N. Nasser, Synthesis and characterization of nickel oxide with nitrogen quantum carbon dots as nanoadsorbent (NiO-NCQD) nanocomposite. Int. J. Nano Dimens., 14 (2023) 227-237. https://doi.org/10.22034/IJND.2023.1984570.2217

[40] W. Boumya, H. Hammani, F. Laghrib, S. Lahrich, A. Farahi, M. Achak, M. E.Mhammedi, Electrochemical study of 2, 4-dinitrophenylhydrazine as derivatization reagent and aldehydes at carbon glassy electrode, Electroanal., 29 (2017) 1700-1711. https://doi.org/10.1002/elan.201700019