Full Paper

Electrocatalytic Oxidation of 2,4-dichlorophenol (2,4-DCP) at GC Electrode Modified by Nickel Phthalocyanine (NiPc)

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Abstract- The electrochemical oxidation of 2,4-dichlorophenol (2,4-DCP) at a glassy carbon (GC) electrode modified with Nickel phthalocyanine (NiPc), a complex of nickel without any substitutents, was studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The modification of the electrode was performed by repetitive cyclic voltammetric scans in NiPc solution. The number of optimum cycles was obtained 70. Nickel phthalocyanine with different thickness was characterised by electrochemical impedance spectroscopy and it was corresponding to cyclic voltammograms. Also the catalytic activity of the modified electrode (GC/NiPc) was investigated. It was found that, GC/NiPc electrode had significant response for 2,4-DCP oxidation. Therefore, it can be a good candidate for electrooxidation of 2,4-DCP. By using this technique the small amounts of DCP compound in waste waters can be detected.

1. INTRODUCTION

Chlorophenols (CPs) are toxic compounds for human and aquatic organisms and they have been recognized as environmental persistence and their toxicity increase with increasing chlorine substitution. The position of the chlorine atom in the aromatic ring determines the degradation rate of the compound. For example, CPs with a chlorine atom presenting a higher

degradation rate than those with two chlorine atoms in the aromatic ring. The OH group of CPs causes their solubility in water [1-5]. In more recent years the electrochemical detection of CPs has been investigated by several researchers. Up to now, different electrode materials such as Pt, GC and BDD (boron-doped dimond) have been tested. Because of the electrode fouling, electrooxidtion of CPs on these electrodes showed instability [6-9]. It is essential to find stable, easy to use, sensitive and low-cost method for detection of CPs in water and this led to use of macrocompelexes for electrode modification [10-11]. The use of chemically modified electrodes with transition metal complexes, improved the performance of solid electrodes by incorporating catalytic sites [12-13]. Most success in preventing fouling of the electrode has been obtained when nickel macrocycles such as Ni Porphyrins, Ni Cyclamand Phthalocyanines derivatives are employed. These macrocycles have been shown to be good electrocatalysts for the oxidation of CPs [14-15]. The main characteristic of phthalocyanines is their high chemical and thermal stability and their tendency to form aggregates [16-18]. It should be noted that the exact mechanism of the electrocatalytic process involved in the activation reaction is not fully established, one may expect that the nickel complex-based coating structure plays an important role. In most previous work nickel phthalocyanine (NiPc) derivations were used for modification of the electrode (Fig. 1). NiTSPc is the most popular precursor for a very peculiar anodic modification of electrode surface. Interest in this process is caused by a high electrocatalytic activity of the resulting film in oxidation of several compounds such as CPs. For the first time, NiPc without any substituent was used for modification of the electrode (Fig.1). Modification of electrodes can be done in several ways but electro-polymerization forms multilayered polymer coating of the complexes improving the response sensitivity of the electrode. Deposition of NiPc on electrodes in alkaline media leads to acheive a better catalytic effect and this has been suggested to be due to the formation of interconnected O-Ni-O OXO bridges [19-21]. In this research, the activity of NiPc on the electrocatalytic oxidation of 2,4-DCP in NaOH solution is investigated. The electrocatalytic properties of the modified electrode were also reported.
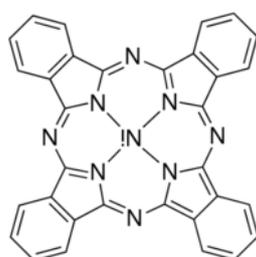

Fig.1. The chemical structure of nickel phthalocyanine (NiPc)

2. EXPERIMENTAL

2.1. Material and equipment

Nickel (II) phthalocyanine, 2,4-dichlorophenol (2,4-DCP) and dichloromethane(DCM) were obtained from Sigma-Aldrich. Tetrabutylammonium tetrafluoroborate (TBABF$_4$), which was used as the electrolyte for electrochemical experiments, and NaOH were obtained from Merck. All solvents were used without any.

2.2. Electrode preparation

Prior to each experiment, the GC electrode was polished with emery paper (1200 grit) to obtain a mirror-like surface, rinsed with distilled water and sonicated in ethanol and 50/50 mixture water for 10 minutes and finally rinse with distilled water. In a typical experiment, deposition of NiPc complex on GC electrode was performed by repetitive scanning (70 cycles) on the bare surface of the electrode in 1 mm the complex solution with DCM/TBABF$_4$ at the potential range of -0.5 to 1.2 V v.s. SCE followed by repetitive scanning (60 cycles) in the anodic potential rang of -0.5 to 0.8 V v.s. SCE in NaOH solution. The scan rate was 100 mV.S^{-1} for both of processes.

2.3. Electrochemical methods

Electrochemical studies were carried out in a conventional three-electrode cell system powered by an electrochemical system comprising of Ivium Compact Stat. For impedance measurements, a frequency range of 100 kHz to 10 mHz was employed. The AC voltage amplitude was 5 mV. Fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was performed using the Z-View software package. Saturated calomel electrode (SCE), a Platinum wire and a GC electrode modified with NiPc complex with a surface area of 0.03 cm^2 were used as the reference, counter and working electrodes, respectively. All the experiments were carried out at 298±2 K. A JEOL Scanning Microanalyzer JXA-840 was used to examine the topography of NiPc on the surface of the electrode.

3. RESULTS AND DISCUSSION

3.1. Scanning electron microscopy (SEM) of graphite electrode

The SEM images of the surface of unmodified GC (A) and GC/NiPc modified electrode (B) were presented in Figs. 2A and 2B. As shown, the film of catalyst was covered the entire surface of the electrode. It is obvious that the films were fairly compact with virtually no pores and cavities.
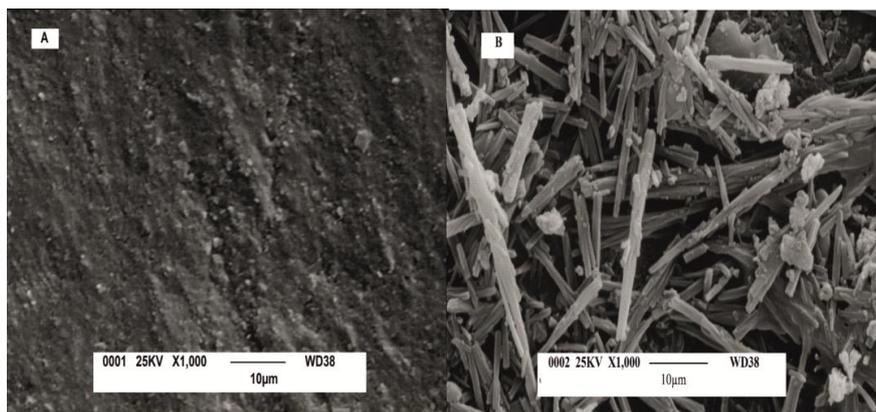
Fig. 2. The surface morphology (SEM) of (A) unmodified GC and (B) GC/NiPc modified electrodes

3.2. Electropolymerization

Modification of GC electrode was performed by electropolymerization process. Fig.3. shows the selected cyclic voltammograms during electropolymerization of 1mM NiPc complex in dichloromethane (DCM) solution on GC electrode within the potential range -0.5 to 1.2 V. Since NiPc is insoluble in water, dichloromethen was used as suitable solvent for electropolymerization. Increasing the number of scans led to increase the current density and form new peaks.
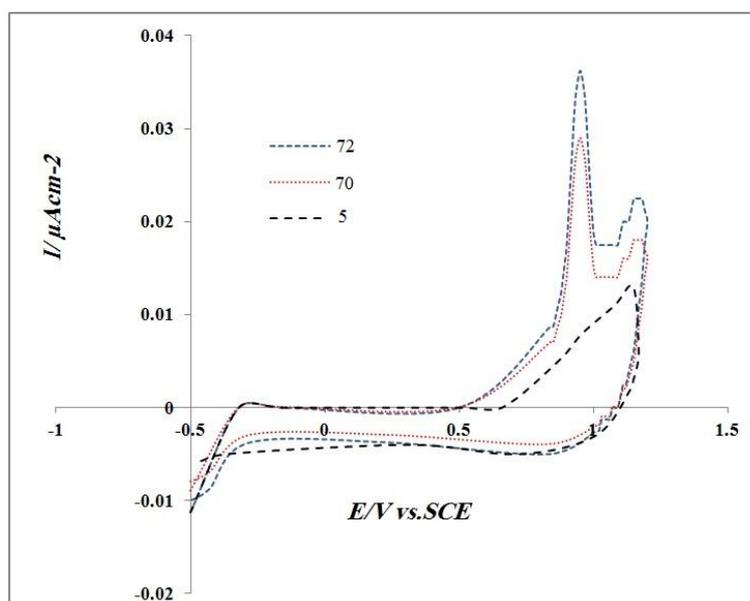

Fig. 3. Selected voltammograms of 1 mM NiPc in DCM containing 0.1 M TBABF4 at GC electrode, the numbers indicate the scan number. Scan rate: 100 mV.S^{-1}

The regulary increase of the current density testifies in favor of the layer-by-layer deposition of the electroactive film. There is a formation of a polymer peak at 0.9-1.0 V versus SCE and the related peak shifts to posittive potentials with increase in the number of scans, this is an indication of an increase in the electrical resistance of the polymer film.
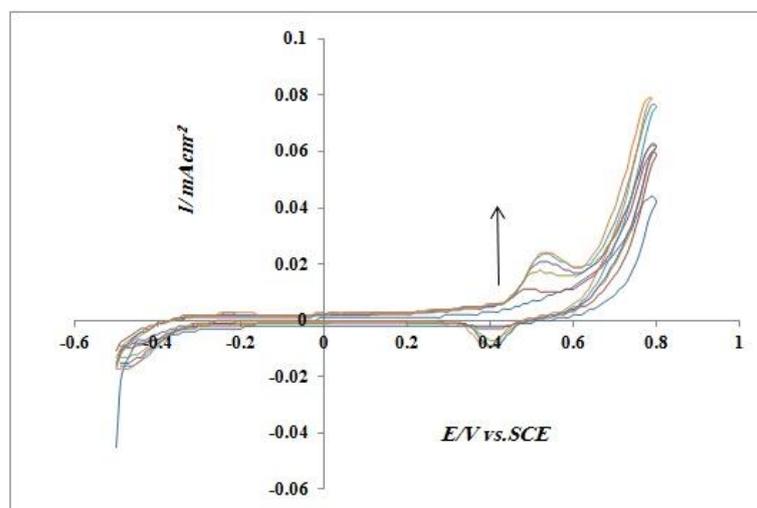

Fig. 4. Repetitive cyclic voltammograms of GC/NiPc modified electrode in 0.1 M NaOH (Scan rate: 100 mV.S^{-1})
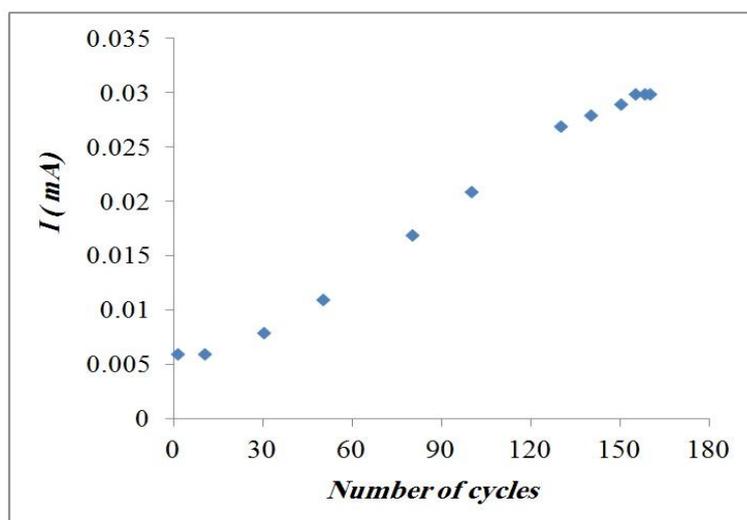

Fig. 5. Dependence of anodic peak of the GC/NiPc modified electrode on the number of cycles

The electropolymerization process is proven by changing the shape of the voltammogram. As shown, no peak was observed during first scans. On the 70th scan the maximum current density is clearly observed and after that it decreases. Therefore, the optimum scan number was obtained equal to 70.

In order to stabilize the surface of the modified electrode, the GC/ NiPc electrode was transformed to NaOH solution in a potential range of -0.5 to 0.8 V *vs*.SCE (Fig. 4). At the initial stage (up to 5th cycles) the film grows slowly (Fig. 5). This can be related to the difficulties in nucleation of a new phase formed by nickel compounds. As shown the current density of anodic and cathodic waves continuously increased with increase in the number of scans and a set of peaks appears. These results exhibit the conventional Ni(II)/Ni(III) chemically reversible redox transition [22].

3.3. Electrooxidation of 2,4-DCP

Fig. 6 shows the CVs of bare GC electrode (a) and GC/NiPc modified electrode (b) in the absence (1) and presence (2) of 1 mM 2,4-DCP in 0.1 M NaOH solution with 1 V.S^{-1} scan rate been employed. It can be observed that the modified electrode shows better catalytic behavior than unmodified electrode.
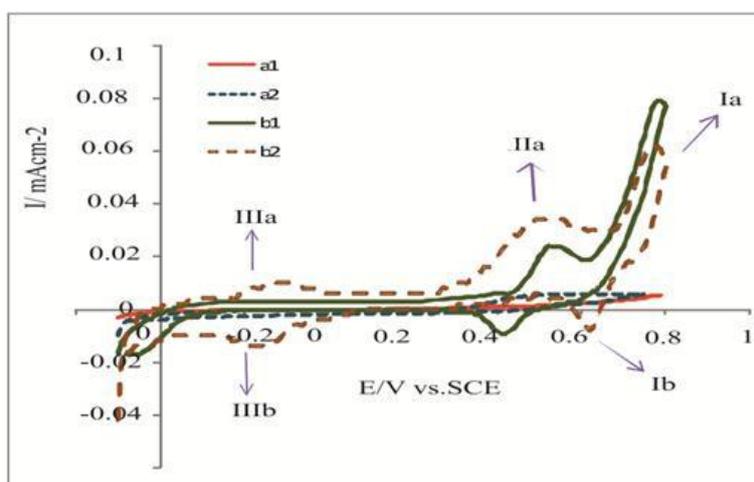

Fig. 6. Cyclic voltammograms of (a) unmodified GC electrode (b) GC/NiPc modified electrodein 0.1 M NaOH solution; (1) before electrooxidation and (2) after electrooxidation of 2,4-DCP (1 mM)

The oxidation of 2,4-DCP was first studied at the bare GC electrode. As shown, the addition of 1 mM 2,4-DCP to the alkaline solution has not significant effect on the electrochemical response of the bare GC electrode. In plot b1, the anodic and cathodic half cycles are observed at 0.55 and 0.44 V versus SCE which are known to be correspond to Ni(II)/Ni(III) redox process. In plot b2, an increase in the anodic current density of GC/NiPc electrode is observed by adding 2,4-DCP to the supporting electrolyte. It shows a remarkable electrocatalytic activity toward the oxidation of 2,4-DCP. The maximum of I$_a$ and I$_b$ peaks which are observed at 0.63 and 0.75 V, correspond to the Ni(II)/Ni(III). II$_a$ peak which is observed at 0.50 V versus SCE corresponds to the oxidation of Ni(II) together with 2,4-DCP,

which is postulated to occur by a chemical reaction with Ni(II) followed by a reoxidation of Ni(II). The oxidation process involves the intermediate/products and the formation of passive layer on the surface of the electrode which is observed at 0 to -0.20 V (III$_a$ and III$_b$).

In Fig.7 all the CVs of 2,4-DCP show a chemically irreversible oxidation peak. As shown, the peak currents of I$_a$, I$_b$ and II$_a$ decreases with growing voltammetric scan number indicating the fouling of the electrode and diminishing the number of active sites. At (0.00) to (-0.2) V versus SCE a chemically reversible process, which can be attributed to the dichlorohydroquine/dichloroquinone reaction, appears. According to literature fouling of electrode can be explained by the formation of phenoxy radicals [23].
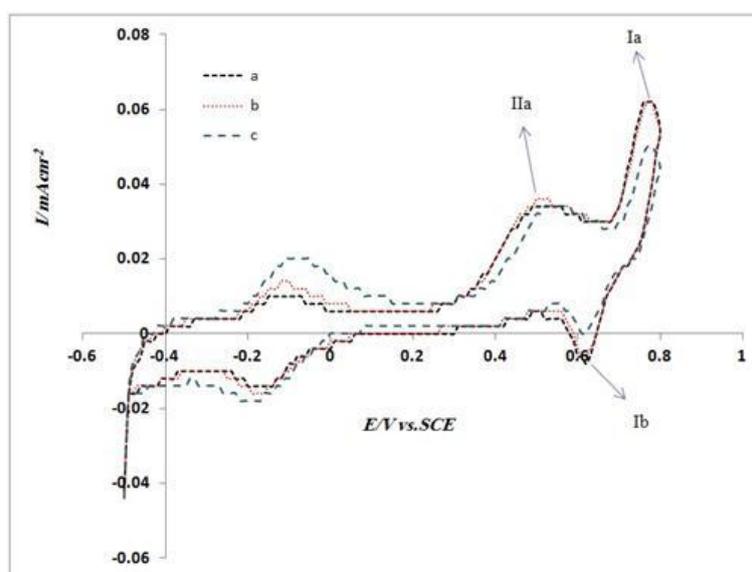

Fig. 7. The first (a), second (b) and tenth (c) CVs at 100 mV.S[1] of GC electrode in 0.1 M NaOH solution

3.4. Electrochemical impedance spectroscopy

The effect of film thickness on the electrocatalytic efficiency of the modified electrode was investigated. Fig. 8 illustrates the Nyquist plot of GC electrode at various scan numbers at DC-offset potential in 1 mM NiPc complex in dichloromethane (DCM) solution. The plot for bare electrode exhibits an almost straight line because electrochemical reactions at such electrodes surface are expected to be a mass diffusional limiting electron-transfer process [24-25]. The Nyquist plot exhibit a semicircle pattern due to barrier to the interfacial electron-transfer. The film thickness is expected to increase with the number of scans. There are two slightly depressed capacitive semicircles: a small one in the high frequency region and a large one in the low frequency region. The large semicircle at low frequency region could be detected. The semicircle in the high frequency region exhibits a slight increase in diameter while the other shows a steady increase which indicates increase resistance of the

polymer film. The semicircle in the high frequency region likely results from a combination of charge transfer resistance and double layer capacitance. The low frequency semicircle is attributed to the adsorption of reaction intermediates on the electrode surface.
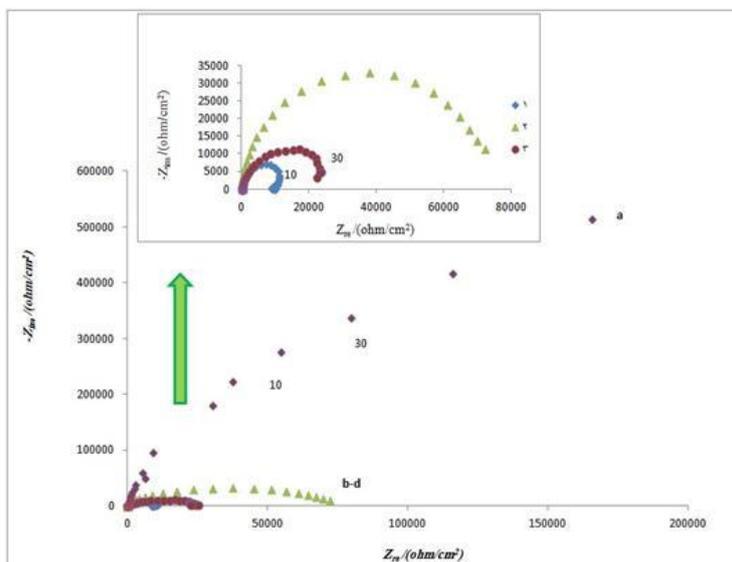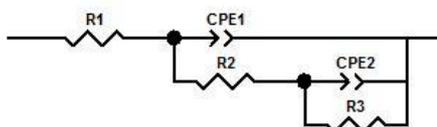

Fig. 8. Nyquist diagrams of (a) bare GC (b-d) GC/NiPc electrode in 0.1 M NaOH solution with different scan numbers (The numbers indicate the scan number). DC potential is 0.55 V *vs*. SCE. Inset shows zoomed main panel

Scheme 1. Equivalent circuit compatible with the Nyquist diagrams in Fig. 8 for different scan numbers on the GC/NiPc electrode

Table 1. Equivalent circuit parameters of different scan numbers on the GC/NiPc electrode in 1mM NiPc complex in dichloromethane (DCM) solution obtained from Fig. 8

Scan number	R_s	R_{ct}	CPE_{dl}	n_1	R_{ads}	CPE_{ads}	n_2
	$(\Omega.cm^{-2})$	$(\Omega.cm^{-2})$	$(mF.cm^{-2})$		$(\Omega.cm^{-2})$	$(mF.cm^{-2})$	
10	122.5	5	0.611	0.85	9615.5	0.847	0.85
30	120.9	5.4	0.643	0.79	22329.1	0.961	0.91
70	119.6	5.6	0.653	0.75	72180.4	1.537	0.89

Increasing the number of scans led to increase the resistance of the polymer film, a trend that agrees with the cyclic voltammetry.

An equivalent circuit compatible with these results is presented in Scheme 1. In this electrical equivalent circuit, R1 and CPE1 are the solution resistance and constant phase element, respectively. CPE2 represents the double layer capacitance. To corroborate the equivalent circuit, the experimental data were fitted to equivalent circuit and the circuit elements were obtained. Table 1 shows the values of the equivalent circuit elements obtained by fitting the experimental results for different scan numbers.

4. CONCLUSIONS

In this paper, the oxidation of 2,4-DCP in NaOH solution at GC electrode modified with NiPc, a complex of Nickel without any substitutents, was investigated. The modification of the electrode was performed by repetitive cyclic voltammetric scans in NiPc solution. The number of optimum cycles was obtained 70. NiPc with different thickness was prepared and characterised by electrochemical impedance and it was corresponding to cyclic voltammograms. The results showed that modification of GC electrode with NiPc enhanced its electro-catalytic activity and the bare GC electrode presents no activity. The GC/NiPc-modified electrode behaved as an efficient catalyst for the electro-oxidation of 2,4-DCP in alkaline medium. It was found that in the presence of 2,4-DCP, GC/NiPc has a significant response for 2,4-DCP oxidation. Therefore, it can be a good candidate for electrooxidation of 2,4-DCP.

Acknowledgments

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