

Electrooxidation of 2- and 4-chlorophenols on Glassy Carbon and ITO Electrodes Modified with Ni-tetrasulphthalocyanine

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Degradation of water pollutants such as chlorophenols (CPs) is important due to their high toxicity. The high stability of these compounds makes their degradation difficult. The oxidation of CPs at solid electrodes is not simple since several reaction pathways are possible, leading to different reaction products [1]. The reaction produces phenoxy radicals, which can be coupled, forming a passivating film on the electrode. Thus, the development of electrodes that inhibit the CPs polymerization is of vital importance for achieving the CPs mineralization. In this sense, the use of chemically modified electrodes with metal-phthalocyanines (M-Pcs) gives an interesting possibility for reaching these objectives.

Numerous methods for preparing Pcs/solid electrodes have been described [2]. Films of Ni-tetraazamacrocyclic complexes have been deposited on gold electrodes [3] and with Ni-porphyrin and Ni-cyclam complexes on vitreous carbon [4]. Characterized the film by *in situ* surface-enhanced Raman spectroscopy show that the complexes do not decompose in the procedure of modification and that they are attached to the electrode surface and interconnected via the oxo-bridges [3]. The use of Ni-tetrasulpho-phthalocyanine (Ni-TSP) offers the advantage that is a water-soluble.

In this work, Ni-TSP was electropolymerized on glassy carbon (Ni-TSP/GC) or ITO (Ni-TSP/ITO) electrodes by cyclic voltammetry (CV), at different scan rates, in 0.1 M NaHCO₃ + 0.1 M Na₂CO₃ + 1 mM Ni-TSP (pH 11) solutions. The films were characterized by CV and by ultraviolet-visible (UV-vis) spectroscopy for Ni-TSP/ITO electrodes. The spectroscopic properties for the Ni-TSP film electropolymerized on ITO are not very different from those observed in aqueous NiTSP solutions. Both the Soret (329 nm) and Q (602 nm) bands are slightly shifted (319 and 615 nm, respectively). The differential spectra, obtained subtracting the first spectrum from those obtained during the growth of the film, show a decrease in the absorbance of both bands (Q and Soret) and the appearance of a new band between 400 and 500 nm. This band has been attributed to a metal-ligand charge-transfer in the case of CoPc films adsorbed on carbon substrates [5].

Voltammetry curves show only one oxidation peak that appears during the positive scan whereas in the reverse scan only 2-CP shows a reduction peak ca. 0.15 V (SCE). Both the oxidation of 4-CP and 2-CP are diffusional processes on both GC and Ni-TSP/GC electrodes (I_p vs. $v^{0.5}$ plot are linear) An increase in the peak current upon modification of GC with Ni-TSP is not observed. The presence of the NiTSP catalysts has two effects namely: the oxidation wave is shifted to more negative potentials and ii) the polymerization rate is decreased. The catalysts then has two beneficial effects, it lower the overpotential of phenol oxidation and decreases the passivation of the electrode. Both effects are more pronounced for 4PC.

UV-vis spectroscopy was used to evaluate the polymerization rate during consecutive scanning the potential because in the presence of CP a new band with absorption peaks at 400 nm is observed in the differential spectra. The polymerization rate was concomitant with the increase of electrical charged consumed during the process and measured with cyclic voltammetry. The effect of the thickness of the poly-Ni-TSP film on the CP oxidation was evaluated by CV and polarization curves (0.002 V s⁻¹). Two reaction zones can be observed. The respective Tafel slopes for Ni-TSP/CV electrodes obtained during 7 and 17 potential cycles at 0.002 V s⁻¹ and different 2- and 4-CP concentration are tabulated in Table I.

Table I: Tafel slopes in mV decade⁻¹ for 2- and 4-CP oxidation on Ni-TSP/GC electrode.

[CP] mM	2-CP		4-CP		
	Zone I	Zone II	Zone I	Zone II	
1	125	62	114	64	7 CV
10	126	55	126	61	
50	107	61	124	57	
1	97	53	118	63	17 CV
10	100	62	128	56	
50	81	73	114	58	

These results do not show an effect of the Ni-TSP film thickness on the reaction mechanism. Very thick films show ohmic components in the CV (results are not shown here). The two reaction zones observed with different Tafel slopes, probably are related with a change in the reaction mechanism when a critical phenoxy radical concentration is reached and the polymerization reaction (where at least two radical are coupled to form oligomers that can be deposited on the electrode surface) increase its reaction rate. A Tafel slope near 120 mV decade⁻¹ is expected for a first one electron rate determining step involving the formation of phenoxy radicals. The dispersion in the values of Tafel slopes can also be attributed indirectly to polymerization of phenolic species that block reaction sites on the electrode surface. The second reaction zone (Tafel slope ca. 59 mV) suggests that a chemical step is rate determining, preceded by a fast one electron transfer. This fast e transfer step probably involves the Ni(III/II) couple on the polyNiTSP since this process is observed at potentials not far from those attributed to the Ni(III/II) couple. The slow step could be attributed to the chemical oxidation of phenolic species bound to Ni(III) centers on the catalyst.

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