

The degradation of phenol derivates from wastewaters by electrochemical treatment

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Abstract

A group of carbon-based electrodes, *i.e.*, glassy-carbon (GC), boron doped diamond (BDD), expanded graphite-polystyrene composite (EG-PS), expanded graphite-epoxy composite (EG-Epoxy) and expanded graphite-carbon nanofiber-epoxy composite (EG-CNF-Epoxy) electrodes were investigated for electrochemical degradation of 4-chlorophenol (4-CP). Based on the investigated electrochemical techniques, *e.g.*, cyclic voltammetry (CV) and chronoamperometry (CA), the operation conditions and the electrode suitable for electrochemical oxidation of 4-CP were selected. In addition, multiple pulsed amperometry (MPA) was applied for the *in-situ* electrochemical cleaning of the electrode surface to improve the electrode efficiency. The BDD electrode exhibited the best features related to the 4-CP electrochemical degradation efficiency.

Keywords: wastewater, electrochemical degradation, 4-CP, carbon-based anodes.

1 Introduction

The phenol derivates are toxic and non-biodegradable organic compounds included in the list of priority phenols, which are used/produced in several industrial processes, being commonly used as preservatives, disinfectants, in pulp processing, in the manufacture of pesticides and intermediars [1–4].

The choice of wastewater treatment method depends on the treatment performance and economic component. Due to the treatment of industrial



effluents requiring costly physical or physicochemical pretreatment, electrochemical is becoming a new alternative for the wastewater treatment and is replacing the traditional processes. The electrochemical wastewater treatment technology can be regarded as environmentally compatible, versatile, safe, because the electrons play the role of a clean reagent, without additional chemicals [5–8].

The practical application of electrochemical oxidation processes to the destruction of organic pollutants in water solution requires the essential features of the anode related to the oxidation process efficiency [9]. Function of the anode type, organic pollutants can be destroyed electrochemically by direct anodic oxidation (DSA type) or by an indirect oxidation process that involves the electrochemical generation of powerful oxidants as hydroxyl radical, peroxodisulfuric acid, etc. [10].

In the electrochemical processes, the aim is the complete oxidation of organics to CO₂ or the conversion of the toxic organics to biocompatible compounds [1]. It has been reported [2, 3] that the phenol electrooxidation produces electrode fouling by electropolymerization that leads to a low rate of oxidation, low permeability and strong adhesion on the electrode. On the other hand, it was shown that for removal of some phenolic compounds from wastewaters, a rather effective way is the adsorption of these compounds in the form of oligomeric and polymeric compounds on a high-surface-area carbon electrode [5].

The objective of the present study is to give an overall comparison of the glassy-carbon (GC), boron doped diamond (BDD), expanded graphite-epoxy composite (EG-Epoxy), expanded graphite-polystyrene composite (EG-PS), expanded graphite-carbon nanofiber-epoxy composite (EG-CNF-Epoxy) electrodes. The cyclic voltammetric behavior was investigated first to reveal the basic electrochemical performance difference. 4-chlorophenol (4-CP) was used as model pollutants to compare the activity of the electrodes under the same conditions by chronamperometry (CA). In order to improve the electrode activity by electrochemical cleaning during the electrochemical treatment, multiple pulsed amperometry (MPA) technique was tested. The results obtained will help to select appropriate electrodes for the anodic oxidation of pollutants.

2 Experimental

The composite electrodes were prepared from low viscosity polystyrene pellets (PS N2000, Crystal from Shell) or two-component epoxy resin (LY5052, Araldite) mixed with two types of conductive carbon fillers: expanded graphite (EG) powder (Conductograph, SGL Carbon) and carbon nanofibers (CNF) (PS-447 BOX). In the case of the EG-Epoxy composite the full amount of EG to the matrix resin was not added directly, due to the high surface area of the graphite flakes, therefore, the mixing was performed in a roll-mill at room temperature. The two parts of the epoxy were mixed together and the full amount of the EG was added in steps forming a thick paste. Then the epoxy was cured in a hot press at 80 °C for 40 minutes. Simultaneously the material was shaped in a plate



of 1 mm thickness. The plate was slowly cooled down (for about 12 h) to the room temperature without removing the applied pressure. The graphite filler EG was mixed with the PS N2000 matrix in a roll-mill at 250 °C for about 30 min. A plate of approximately 1 mm was pressed by a hot press (Fontajne Holland) at the same temperature.

For CNF-EG-Epoxy composite, CNF and EG have been mixed with the two components of the epoxy in a roll-mill at room temperature and the obtained paste was cured in a hot press at 80 °C for 40 minutes. Simultaneously the material was shaped in a plate of approximately 1 mm thickness. The plate was slowly cooled down (for about 12 h) to the room temperature without removing the applied pressure.

Plates with a surface area of 4 cm² were cut from all compositions put on a glass supports and electrical contacts were made using a silver paint. The electrodes were isolated on the sides by epoxy resin. Prior to use, this working electrode was gradually cleaned, first polished with abrasive paper and then on a felt-polishing pad by using 0.03 µm alumina powder (Metrohm, Switzerland) in distilled water for 5 minutes and rinsing with distilled water. The cylindrical glassy carbon (GC) and boron-doped diamond (BDD) electrodes with the surface areas of 2.81 cm² and respective, 0.07068 cm² were commercial types, provided by Metrohm and respective, Windsor Scientific Ltd, UK.

The electrochemical performances of these electrodes were studied by cyclic voltammetry (CV), chronoamperometry (CA) and multiple-pulsed amperometry (MPA). Subsequently, an electrochemical pretreatment by three repetitive cyclings between -0.5 V to 1.25 V vs. SCE in 0.1 M Na₂SO₄ supporting electrolyte was performed. All measurements were carried out using an Autolab potentiostat/galvanostat PGSTAT 302 (Eco Chemie, The Netherlands) controlled with GPES 4.9 software and a three-electrode cell, with a saturated calomel electrode as reference electrode, a platinum counter electrode and a carbon-based composite, GC or BDD as working electrode.

The concentration of 4-CP before and after the degradation process was determined using a UV-VIS spectrometer by type Jasco V-530, at the wavelength of 226 nm.

4-chlorophenol and sodium sulphate were analytical grade from Merck, and the solutions were freshly prepared with double-distilled water.

3 Results and discussion

Figures 1 a-e show first cyclic voltammograms (CVs) at scan rate of 0.05 Vs⁻¹ of GC, BDD, EG-PS composite, EG-Epoxy composite and CNF-EG-Epoxy composite electrodes in 0.1 M Na₂SO₄ + 0.2 mM 4-CP. The voltammetric parameters of the oxidation of 4-CP at all carbon based material electrodes are gathered in table 1.

It can be noticed for each electrode the potential value at which the oxidation process occurred, and the lowest potential value was recorded for BDD electrode. Starting with second CV the peak current decreased by quite 100% for CNF-EG-Epoxy composite electrode, which is due to the electrode fouling.



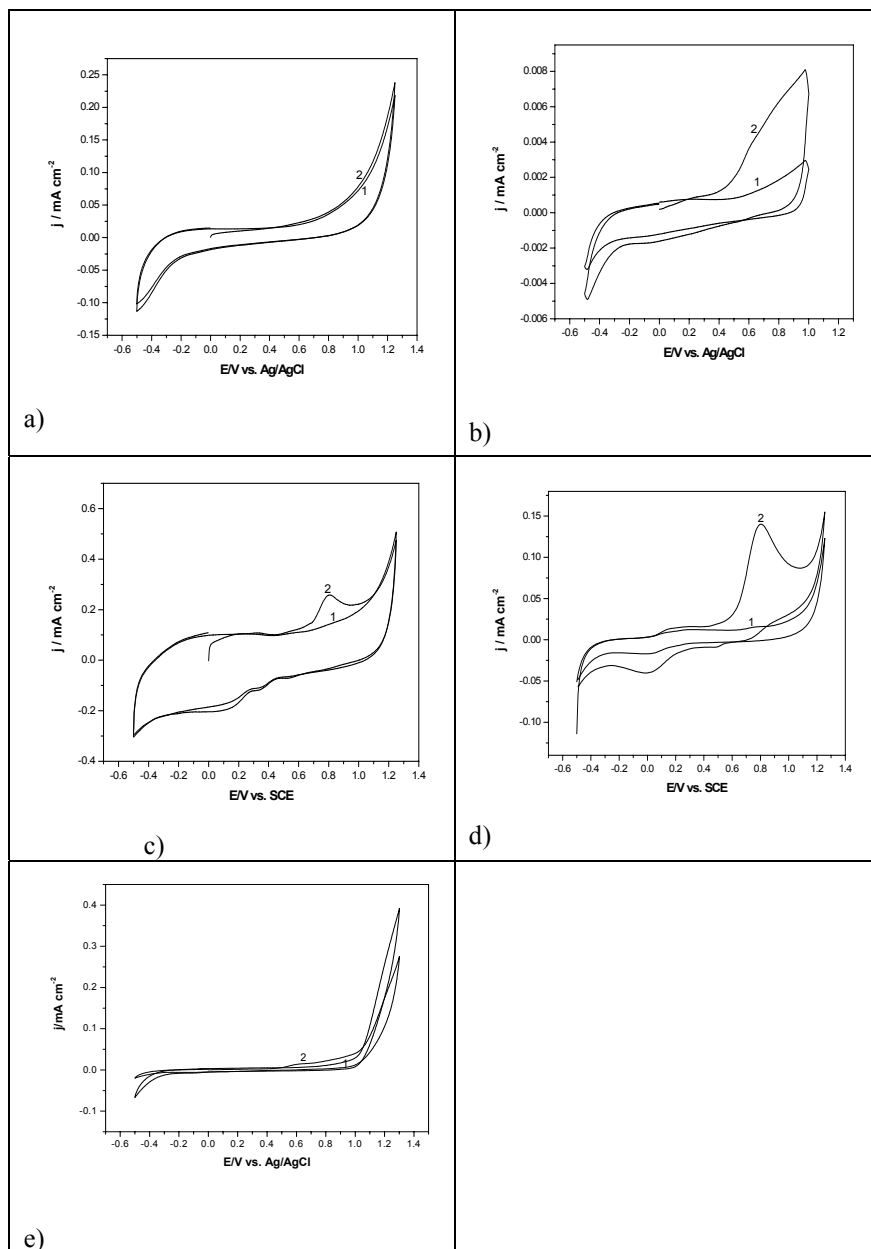


Figure 1: Cyclic voltammograms in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of 0.2 mM 4-CP of: a)-GC, b)-BDD, c)-EG-PS, d)-EG-Epoxy, e)-EG-CNF-Epoxy electrodes; starting potential: 0 V vs. SCE; potential range: $-0.5 \text{ V} \rightarrow +1.25 \text{ V} / 1 \text{ V} \rightarrow -0.5 \text{ V}$ vs. SCE; scan rate: $0.05 \text{ V} \cdot \text{s}^{-1}$.

Table 1: Voltammetric parameters of the oxidation of 4-CP for several carbon based material electrodes.

Material electrodes	Scan number	$j^*(\text{mAcm}^{-2})$	E(V)
GC	1	$2.885 \cdot 10^{-3}$	0.8
	2	$2.477 \cdot 10^{-3}$	0.8
	3	$2.068 \cdot 10^{-3}$	0.8
BDD	1	$2,63 \cdot 10^{-3}$	0.6
	2	$9,42 \cdot 10^{-4}$	0.6
	3	$8,64 \cdot 10^{-4}$	0.6
EG-PS	1	0.115347	0.8
	2	0.052313	0.8
	3	0.043995	0.8
EG-Epoxy	1	$3.633 \cdot 10^{-3}$	0.8
	2	-	0.8
	3	-	0.8
CNF-EG-Epoxy	1	$8,203 \cdot 10^{-3}$	0.8
	2	-	0.8
	3	-	0.8

*The capacitive component has been subtracted from the current densities.

For GC, BDD and EG-PS composite, EG-Epoxy composite electrodes the peak current decreases by 64.18%, 13.10%, 58.80%, and respective 54.64%, starting with the second CV. In general, the electrode fouling is owing the complex mechanism of phenols oxidation on carbon based electrode, which involves both the adsorption of reactant/intermediate or final oxidation products and the formation of passive, nonconductive layer of oligomer products of oxidation process on its surface [3, 5, 11, 12].

The effect of initial concentration of 4-CP on the oxidation process for both potential ranges of water decomposition and stabilization, and expressed by the cyclic scanning is shown as example for BDD electrode in Figure 2. It is obvious that increasing initial concentration decreased the rate of 4-CP oxidation due to faster electrode fouling. On the other hand, it is known that increasing the bulk solution concentration should increase the rate of 4-CP oxidation if the process is mass transfer controlled [12]. From Figure 2 it can be see that no significant electrode fouling occurred at BDD electrode for the oxidation of 1mM 4-CP under both potential ranges of water decomposition and stabilization.

The effect of the scan rate on the anodic peak current of the first CV of BDD electrode tested in 0.1 M Na_2SO_4 + 0.2 mM 4-CP is shown in Figure 3. This experiment was performed for each electrode but not all results are presented. The electrode cleaning during CV running at different scan rates was performed. The linear proportionality of the anodic peak current with the square root of the scan rate obtained for all tested electrodes indicated control by mass transport. No intercept of 0 suggested that the adsorption steps and specific surface reaction cannot be neglected (insert a of Figure 3). The most strong adsorption

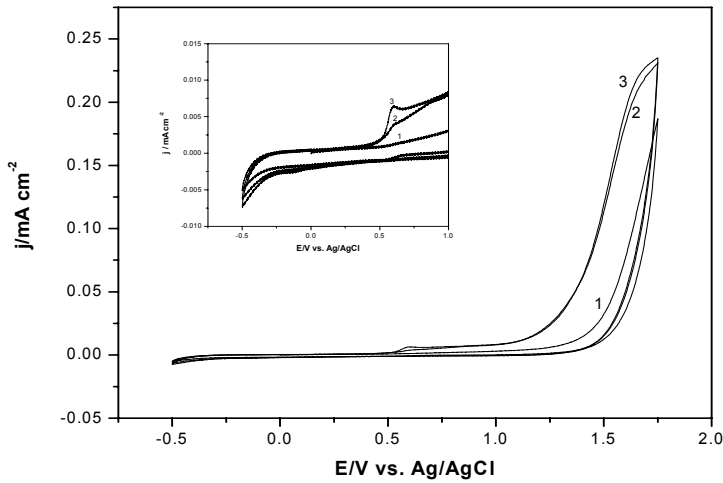


Figure 2: The first scanning of cyclic voltammograms of the BDD electrode in 0.1M Na₂SO₄ solution (curve 1) with 0.2 mM 4-CP (curve 2) and 1 mM 4-CP (curve 3): potential range: -0.5V →+ 1.75 V→- 0.5V vs. Ag/AgCl; scan rate = 0.05 V*s⁻¹. Insert: details of the limited potential range.

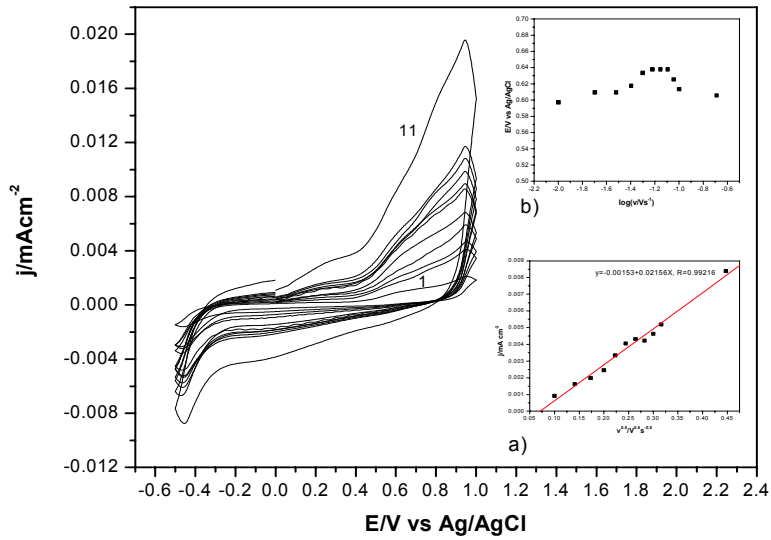


Figure 3: Cyclic voltammograms of the BDD electrode in 0.1M Na₂SO₄ solution and 0.2 mM 4-CP at different scan rates, curves 1-11: 0.01-0.2Vs⁻¹. Insert: a)-Plot of the anodic peak current recorded at 0.6V vs. Ag/AgCl versus the square root of scan rate, b)-Plot of the anodic peak potential versus the logarithm of the scan rate.

effects were noticed for EG-CNF-Epoxy electrode, these results being in concordance with those obtaining by three consecutive scanning using CV. Even the oxidation potential value is almost constant (inset b of Figure 3) the 4-CP oxidation is not reversible because no corresponding reduction cathodic peak appeared by backward scanning.

In order to obtain information about electrode fouling under the anodic potential range of oxygen evolution and of limiting current (1.1 and respective, 0.6 V vs. Ag/AgCl) chronoamperometric measurements were performed. The chronoamperograms recorded for each electrode during 2 h are presented in Figure 4.

The shapes of the chronoamperograms indicated GC electrode as most suitable for 4-CP oxidation under the potential range of oxygen evolution. However, it is necessary to take into account that for all electrodes, except BDD electrode the major process is oxygen evolution, which hamper the electrode fouling. Depending on the applied current density/potential, two different operating regimes have been identified [3, 5] *i.e.*, $j_{\text{appl}} < j_{\text{lim}}$ the electrolysis is under current control with the current efficiency of 100% and $i_{\text{appl}} > i_{\text{lim}}$ the electrolysis is under mass-transport control and the secondary reactions of oxygen evolution are involved with a decreasing of current efficiency. Except BDD, the electrode fouling occurred after a few minutes when $j_{\text{appl}} < j_{\text{lim}}$ (the results are not shown).

Figure 5 shows an example of multiple pulsed amperogram recorded for BDD electrode in 0.1 M Na_2SO_4 and in the presence of 0.2 mM 4-CP. After the time duration of 900 seconds, the electrode fouling started to occur.

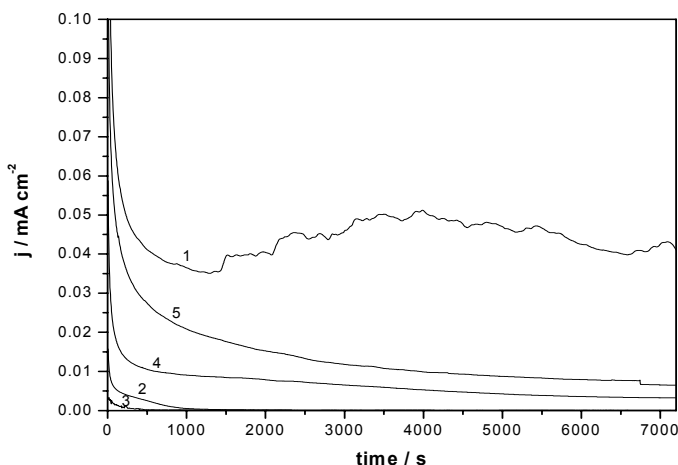


Figure 4: Chronoamperograms recorded at +1.1 V vs. Ag/AgCl for: 1-GC, 3-EG-PS, 4-EG-Epoxy, 5-CNF-EG-Epoxy electrodes, respective at +0.6V vs. Ag/AgCl for-BDD electrode (curve 2), in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of 0.2 mM 4-CP.



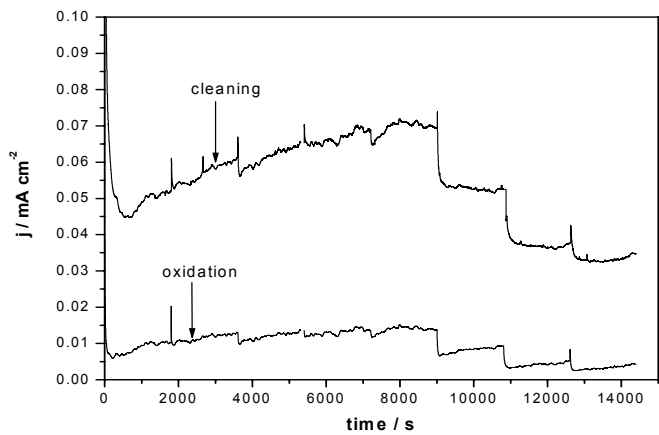


Figure 5: Multiple pulsed amperogram of the BDD electrode in 0.1M Na₂SO₄ supporting electrolyte and in the presence of 0.2 mM 4 – CP; E_{oxidation} was +0.6 V and E_{cleaning} was +1.5V vs. Ag/AgCl; t_{oxidation} was 0.05 seconds and t_{cleaning} was 0.2 seconds.

For all electrodes application in the 4-CP degradation by using both CA and MPA techniques for 2 hours, after each measurement the final concentration of 4-CP was determined spectrophotometrically and the electrochemical efficiency for 4-CP oxidation was obtained based on the equation [13]:

$$E_{CP} = \frac{(CP_0 - CP)}{C \cdot S} V \text{ (g/C}\cdot\text{cm}^2\text{)}$$

where CP₀-CP is the change in the 4-CP concentration during chronoamperometric test for a charge consumption of C corresponding to 2h, V is the sample volume (50 ml) and S is the area of the electrode (cm²).

The electrochemical performance for 4-CP oxidation of the tested electrodes using CA and MPA techniques are gathered in table 2.

Table 2: The electrochemical efficiency (E_{CP}) for the 4-CP degradation.

Electrode material	CA-E _{CP} (g·C ⁻¹ ·cm ⁻²)	MPA-E _{CP} (g·C ⁻¹ ·cm ⁻²)
GC	0.12·10 ⁻⁴	0.45·10 ⁻⁴
BDD	67.30	70.70
EG-PS	3.20·10 ⁻²	0.86
EG-Epoxy	4.74·10 ⁻⁴	16.10·10 ⁻⁴
CNF-EG-Epoxy	2.73·10 ⁻⁴	12.00·10 ⁻³

MPA technique improved the electrochemical performance for 4-CP oxidation for all tested electrodes. It is clear that BDD exhibited the best electrochemical activity for 4-CP oxidation. The electrochemical performances



of the composite electrodes were better than conventional GC electrode but worse than BDD electrode.

4 Conclusions

The performances of GC, EG-Epoxy, EG-PS, EG-CNF-Epoxy and BDD electrodes were compared under the same conditions in order to apply them for the electrochemical degradation of 4-CP. Experimental results indicate that BDD was a much better anode than the other electrodes in terms of electrochemical activity. MPA application improved the electrochemical performance for all tested electrodes. The electrochemical efficiency for 4-CP degradation for the BDD anode was very high compared with other ones, and conventional GC electrode gave the worst results.

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