ELECTROCHEMICAL DETECTION OF PENTACHLOROPHENOL FROM WATER AT CARBON NANOFIBERS-EPOXY COMPOSITE ELECTRODES

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ABSTRACT

In this paper cyclic voltammetry (CV) and linear-sweep voltammetry (LSV) experiments were conducted in order to compare the electroactivity of three types of carbon nanofibers based composite electrodes, *i.e.,* natural and synthetic zeolite modified electrodes and a simple carbon nanofibers electrode for pentachlorophenol (PCP) detection. The enhancement factor of electrode sensitivity for the determination of PCP at the tested electrodes was determined by applying a chemical preconcentration step prior to voltammetric quantification. Synthetic-zeolite modified electrode exhibited a larger electroactivity than the other two electrodes, due to a better ability of synthetic zeolite particles from the electrode surface to retain PCP molecules, without inactivation of electroactive sites.

INTRODUCTION

Electroanalytical techniques have been intensively studied as suitable methods in determination of a large variety of chemicals due to the improvements achieved in electroanalysis, *e.g.,* high performance electrode materials [1,2], optimal detection conditions, application of a preconcentration step prior to their analysis, which allows the attainment of limits of detection compatible with environmental regulations [3]. Releases of highly toxic polychlorinated organic compounds as pentachlorophenol (PCP) into the environment and its persistence in waters at very low concentrations, as a consequence of its low solubility, impose PCP precise determination [4]. By using the electroanalytical techniques it is important to establish a detection scheme which could imply application of a preconcentration step prior to determination of polychlorinated organic compounds at trace levels. In our study, we compare the activity of three types of carbon nanofibers composite electrodes in order to exploit the synergism of carbon nanofibers and natural/synthetic zeolites embedded in an epoxy matrix in order to find a high performance electrode material and an adequate detection scheme for pentachlorophenol determination from water.

MATERIALS and METHODS

Carbon nanofibers (CNFs) with average diameter of 60–150 nm and average length of 30–100 μm were purchased from Pyrograf III (PR24 AGLD). Syntetic A-type zeolite (SZ) was prepared using natural zeolite (NZ) from Mirsid, Romania, with 68% wt. clinoptilolite as a silicon source and sodium aluminate as aluminium source. Dispersion of the CNFs in tetrahydrofuran, 99.9% (THF, Sigma Aldrich) was achieved using a Cole-Parmer® 750-Watt Ultrasonic Processor. The two-component epoxy resin used in the study was Araldite®LY5052/ Aradur®5052, purchased from Huntsman Advanced Materials, Switzerland. PCP and sodium sulphate were purchased from Fluka and Merck, respectively, as analytical grade reagents. Electrochemical 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 the composite working electrode.

The composite electrodes were prepared by dispersion of CNFs in tetrahydrofuran and epoxy resin (Araldite®LY5052) by ultrasonication, followed by the homogenization of the resulting paste with the zeolite particles and also with the hardener using a two-roll mill. The mixture was then poured into PVC tubes and cured at 60°C for 24 h, obtaining discs electrodes with the surface area of 0.196 cm^2. The ratios were chosen to reach 20 % (wt.) CNFs for CNF-Epoxy electrode; 20 % (wt.) CNFs and 20 % (wt.) SZ for SZCNF-Epoxy electrode; and 20 % (wt.) CNFs and 20 % (wt.) NZ for NZCNF-Epoxy electrode, respectively.

RESULTS

Electrochemical behaviour of CNFs based composite electrodes

The electrochemical characterization of the studied electrodes was performed by cyclic voltammetry in 0.1M Na_2SO_4 supporting electrolyte and in the presence of PCP. All three electrodes exhibited a well-defined oxidative response for PCP at the following potential values: +0.73 V/SCE for CNF-Epoxy; +0.84 V/SCE for SZCNF-Epoxy and +0.81 V/SCE for NZCNF-Epoxy, peaks corresponding to the PCP oxidation on carbon nanofibers (see Fig. 1).

The differences between useful signals recorded in the presence of PCP at the zeolite modified electrodes, having natural clinoptilolitic zeolite or synthetic A-type zeolite in composition, could be partly attributed to the Si/Al ratios, *i.e.,* 4:1 in natural zeolite and 1:1 in synthetic zeolite, because a high content of aluminium in the zeolite structure leads to an increase of zeolite hydrophilicity [5].

Electrochemical detection of PCP

For all tested electrodes, the anodic current response to PCP (first scan, without mechanical cleaning between successive additions of analyte) was linear, with the electrode sensitivities between 0.135 – 0.158 μA / μM and a limit of detection (LOD) varying between 0.2-0.4 μM PCP. The obtained electroanalytical performances were relatively similar for all three electrodes by CV, with slightly better performances for the SZCNF-Epoxy electrode. The presence of zeolites in the electrode material seems to be useful in the control of the surface electrode fouling. At the concentration of 30 μM PCP in Na_2SO_4 (the results are not shown), the CNF-Epoxy electrode surface was partial fouling due to the adsorption of intermediates and products from PCP oxidation and the formation of a non-conductive polymer film. At the other two zeolite-modified electrodes, the partial fouling of the electrode surface occurred at higher concentrations, *i.e.*, 50 μM PCP at SZCNF-Epoxy and 40 μM PCP at NZCNF-Epoxy.

In Fig. 2a, b and c the linear-sweep voltammograms (LSVs) of the CNF-Epoxy, SZCNF-Epoxy and NZCNF-Epoxy electrodes in 0.1 M Na_2SO_4 and in the presence of different PCP concentrations, which were ranged between 2nd and 10 μM are compared. For all situations, a linear dependence between current and PCP concentrations was obtained. Under these working conditions, a slight improvement of electroanalytical performances subjected to electrode sensitivity for PCP detection was achieved for SZCNF-Epoxy, as 0.173 μA/μM, compared with 0.140 μA/μM for NZCNF-Epoxy and 0.169 μA/μM for CNF-Epoxy. In order to enhance the electronalaytical response for PCP detection, the further experiments were carried out to apply a preconcentration-voltammetric detection scheme.

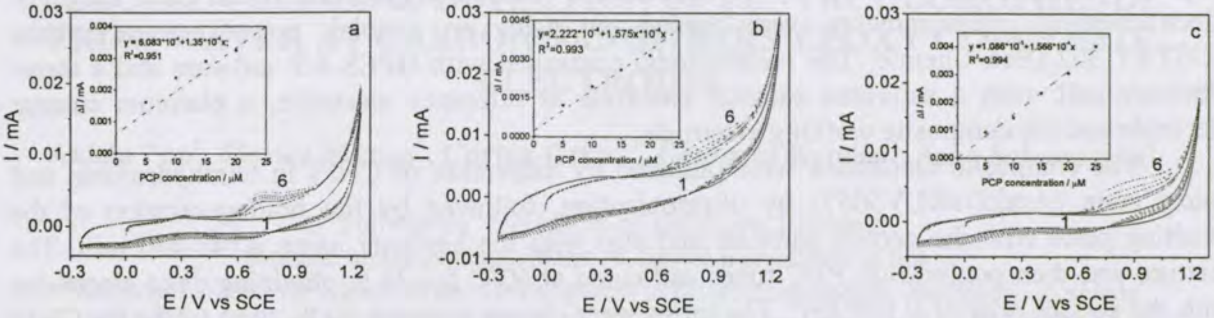

Fig. 1. CVs recorded with a potential scan rate 0.05 Vs^{-1} in a 0.1M Na_2SO_4 supporting electrolyte (1) and in the presence of different PCP concentrations; (2)-5 μM; (3)-10 μM; (4)-15 μM; (5)-20 μM; (6)-25 μM; at CNF-Epoxy (a), SZCNF-Epoxy (b) and NZCNF-Epoxy (c) electrodes.

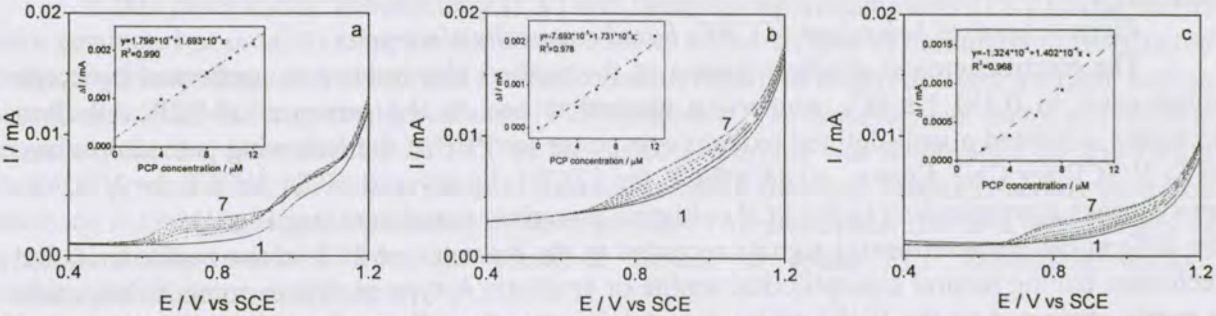

Fig. 2. LSVs recorded in a 0.1M Na_2SO_4 supporting electrolyte (1) and in the presence of different PCP concentrations; (2)-2 μM; (3)-4 μM; (4)-6 μM; (5)- 8 μM; (6)-10 μM; (6)-12 μM at CNF-Epoxy (a), SZCNF-Epoxy (b) and NZCNF-Epoxy (c) electrodes.

Influence of accumulation time

For a preconcetration-voltammetric detection scheme the accumulation time is very important, because it could influence the degree of adsorption on the electrode surface. CNFs are materials with a good adsorption capacity for PCP. Also, an important role that may be played by the zeolite is its availability to concentrate species within its porous structure. To determine the enhancement factor as the ratio of peak current after and before sorption process, the effect of accumulation time on anodic peak current was investigated by LSV. Fig. 3 shows the dependence of the anodic peak current corresponding to the PCP oxidation and the enhancement factor on the accumulation time for 10 μM PCP. The differences between accumulation times required to reach the equilibrium for the each tested electrode reveals the presence of a diffusion effect of solution in the bulk of the electrode, which is in relation with the electrode surface porosity [6]. In the case of the CNF-Epoxy and NZCNF-Epoxy electrodes a slight enhancement of anodic peak current was achieved, while for the SZCNF-Epoxy electrode for an increasing accumulation time up to 30 minutes the amount of PCP at the electrode surface increased, leading to the enhancement of anodic peak current with 2.3 times.

The optimum accumulation time for this electrode was settled at 20 minutes, and a better electroanalytical performance was obtained by using preconcentration – linear-sweep voltammetric detection scheme, *i.e.*, a sensitivity of 0.358 μA/μM, in good correlation with the calculated value for enhancement factor. Also, a LOD of 0.16 μM gives the perspective of the potential application of this electrode to determine PCP traces from water.

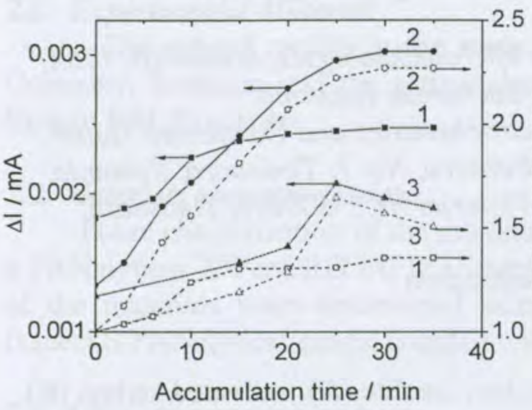

Fig. 3. Peak current responses (–) and enhancement factor (---) for the oxidation of 10 μM PCP for (1) CNF-Epoxy, (2) SZCNF-Epoxy, (3) NZCNF-Epoxy electrodes, as a function of the accumulation time, with background current subtraction.

CONCLUSIONS

All tested electrodes exhibited useful features for the voltammetric determination of very low PCP concentrations, related to their electrode composition, simple preparation and easy renewal of the active electrode surface, with better performance of the SZCNF-Epoxy composite electrodes and a good fouling electrode control. By applying a chemical preconcentration step prior to the voltammetric determination of PCP an enhanced response signal was achieved.

Acknowledgement

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