EXTENDED ABSTRACT

Contamination of water by priority organic pollutants is very common in industrialized countries and constitutes a serious environmental problem because of their toxicity, carcinogenic effects on human health, and resistance to biodegradation.

In this context, it is imperative that both prevention/treatment of contaminated water and monitoring its quality by quantitative determination of these pollutants occur.

In the past decade, special attention has been given to advanced oxidation processes (AOPs) in water treatment for removal or degradation/mineralization of these pollutants. These processes refer to a set of oxidative water treatments, which primarily involve the generation of very reactive oxygen species, able to attack rapidly and destroy hazardous pollutants. A main innovation is the combination of different advanced oxidation processes and appropriate post-treatment technologies, called hybrid oxidation processes.

The new carbon materials, *i.e.*, carbon nanotubes (CNTs) and carbon nanofibers (CNFs), have similar physicochemical properties in many aspects, such as chemical stability and good electrical conductivity and they are used as a support for dispersion of functional materials in order to obtain a large surface area, better catalyst dispersion, and high electroactivity.

TiO_2 and other n-type semiconductors are applied as photocatalysts for an effective degradation and mineralization of target compounds. The activity of these materials as photocatalysts strongly depends on the preparation method. Sol-gel is an excellent method to prepare TiO_2-based materials, including modification by incorporating metal ions (Ag, Pt, Ti, etc.). However, TiO_2-based photocatalysis exhibits two typical disadvantages, *i.e.*, the difficulty of ultimate separation of TiO_2 particles from water and the limited reaction rate by slow electron transfer from the catalyst to dissolved oxygen.

Photoelectrocatalytic processes using different TiO_2-based electrodes have received a lot of attention, because this technology can reduce the recombination of photogenerated electron-hole pairs using an external bias and solve the separation problem of semiconductor particles from water. Improving the physical and chemical properties of titanium oxide and its modified forms can be realized also by fixing it on different support materials (clay minerals, silica, composite materials, etc.). The natural mineral materials, such as the eco-friendly and low cost zeolites, have excellent properties that can be exploited for electrochemical applications. Due to these properties, *e.g.*, ion-exchange capacity, molecular selectivity,

catalyst-assisted reactivity, microporous structure and electrical conductivity, they are frequently used in composite electrodes.

Development of electrochemical techniques and methods, corroborated with the evolution of nanostructured materials, allowed to obtain electrochemical sensors with improved electroanalytical characteristics.

The main objective of this study is the exploitation of the dual character of these nanostructured carbon-based electrodes, considered as the key of the electrochemical process performance to be applied for both degradation/mineralization of priority organic pollutants from wastewater, as well as their electrochemical detection, allowing integrated control of the degradation process.

To achieve this study aim, pentachlorophenol (PCP) was chosen as a target compound, which is a highly chlorinated phenol that belongs to the “priority organic pollutant” group, listed by the European Commission Legislation and transposed into Romanian legislation through the Water Framework Directive.

Two general objectives of this study have been proposed:

1. Preparation and morphological, as well as electrical and electrochemical characterization of some unmodified/TiO_2-modified nanostructured carbon composite electrodes, which possess electrocatalytic and photoelectrocatalytic activity towards PCP oxidation.
2. Testing and selecting carbon composite electrode materials appropriate for:
    - electrochemical and photoelectrochemical degradation of PCP;
    - PCP detection experiments;
    - dual application in electrochemical and photoelectrochemical degradation of PCP and integrated control of this process by electrochemical monitoring of PCP - considered as a process parameter.

Accomplishing these objectives led to the design of a flowchart comprising the following steps:

- Synthesis of new carbon-based composite electrode materials (carbon nanotubes and nanofibers), unmodified or modified with TiO_2, Ag-doped TiO_2, zeolite, zeolite functionalized with TiO_2 and zeolite functionalized with Ag-doped TiO_2.
- Morphological, electrical and electrochemical characterization of the electrode materials in order to determine specific features, especially their electroactive surface area.
- Electrochemical characterization of the carbon composite electrode materials in 0.1 M Na_2SO_4 supporting electrolyte in the dark and under UV irradiation, which supplies

information about the potential window, O_2 evolution potential, background current and photocurrent, respectively.

- The assessment of the behaviour of the electrode materials in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of PCP in the dark and under UV irradiation, which allows to establish the relationship between the electrode material and the type of oxidation reaction (direct, indirect, or mediated).
- The evaluation of photolysis and photocatalysis processes performance for PCP degradation and mineralization.
- The evaluation of electrode materials performance in electrooxidation and photoelectrooxidation processes, in order to select the suitable operating conditions for degradation experiments.
- The accomplishment of PCP detection experiments, which provides specific informations, *i.e.*, concentration ranges, detection potential value, electrode sensitivity, stability, and detection limits.
- Testing dual character of the selected electrode materials by simultaneous application for both degradation and detection of PCP from wastewater.

The original contributions of this PhD thesis are related to the elaboration and preparation of several unmodified/TiO_2-modified-carbon-epoxy composite electrode materials, which involved both the detailed characterization of the electrode materials and their application, either in the advanced photoelectrooxidation /mineralization of PCP from wastewater or its detection.

In this context, the main goal of this PhD thesis was to exploit the dual character of carbon-based composite electrode materials and electrochemical techniques in order to use them in both degradation processes of organic pollutants and water quality control by electrochemical detection.

Several unmodified/TiO_2-modified carbon epoxy composite electrodes were successfully obtained by a two-roll mill procedure: CNT, CNT-TiO_2(sol-gel), CNT-$TiO_{2,}$ CNT-TiO_2/Ag, CNT-ZN, CNT-Z-TiO_2(sol-gel), CNT-Z-$TiO_{2,}$ CNT-Z-TiO_2/Ag, CNF, CNF-$TiO_{2,}$ CNF-Z-$TiO_{2,}$ CNF-Z-TiO_2/Ag.

The morphological, structural and electrical characterization results of the above-presented compositions of the carbon based composite electrode conclude:

- the conductive fillers, *i.e.*, carbon nanotubes and carbon nanofibers are well-distributed and dispersed within the epoxy matrix taken into account the specific preparation method involving method dispersion within suitable solvent by sonication, evidenced by SEM images;
- the presence of TiO_2 did not modified significantly the morphology of the electrodes surfaces, while TiO_2-modified zeolite conferred them a porous structure;
- the electrical conductivity values in the case of CNF based electrodes were higher than those obtained for CNT based electrodes, which should be explained by the more uniform distribution of CNF versus CNT within epoxy matrix;
- all prepared carbon based composite electrode are characterized by the electrical conductivities suitable for the electrochemical applications;
- the electrochemical behavior of the well-known ferri/ferrocyanide standard redox system allowed determining the electroactive surface area of these electrodes. All tested carbon-based composite electrode exhibited the electroactive surface area higher than the geometrical one.
- the presence of TiO_2 did not modified significantly the electroactive surface area, while zeolite within the composite composition led to its slight decrease.
- a significant difference was noticed between the electroactive surface areas obtained for electrode materials based on CNT, which were much higher than those obtained for electrode materials based on CNF;
- the best electroactive surface area was determined for the electrode materials: CNT-TiO_2/Ag, CNT-Z-TiO_2/Ag and CNF-Z-TiO_2/Ag.

In order to evaluate the performance of electrode materials in photoelectrooxidation processes, preliminary study of individual advanced degradation processes (photolysis, photocatalysis and electrooxidare) was required.

The application of both photolysis and photocatalysis led to maximum PCP degradation efficiency of 100% for an initial concentration of 10 $mg \cdot L^{-1}$ PCP, after 120 minute reaction time. Increasing initial PCP concentration (20, 50 $mg \cdot L^{-1}$) decreased the degradation efficiency of PCP up to 55%. Photolysis is suitable for PCP degradation, but does not allow an effective mineralization of this compound (k_{TOC}/k_{app}=0,26). Due to the very small surface area of fixed catalyst, its contribution to improve the degradation/mineralization processes was insignificant (k_{TOC}/k_{app}=0,35).

To test the electrode materials in electrochemical and photoelectrochemical processes, electrode prosesses were characterized by cyclic voltammetry (CA). The electrocatalytic properties of carbon based composite electrodes for direct oxidation of PCP on their surfaces were evaluated based on the obtained results in terms of direct electrooxidation activity (a) and direct oxidation potential value (E_a) for each type of electrode materials comparative with boron doped dioamond (BDD) commercial electrode. From the point of view of the potential value corresponding to anodic oxidation peak BDD electrode showed superior electrocatalytic properties, but from the point of view of the electrocatalytic activity, CNT-TiO_2/Ag electrode showed the best performance. CNF-based electrodes exhibited slightly smaller direct electrooxidation activity than CNT-based electrodes, but also better than BDD electrode. In addition, the potential value corresponding to electrooxidation peak was lower.

Under UV irradiaton, the carbon based electrodes (CNF and CNT) behaviour was different versus irradiation absence, the oxidation process is slightly influenced by appearance of a new oxidation peak prior to that recorded without UV irradiation. In this case, the oxidation process of PCP occurred earlier, the electrocatalytic activity is enhanced by photocurrent contribution corresponding to this peak.

The studies regarding to the influence of the scan rate on the voltamogramms shape allowed elucidating some aspects about the PCP oxidation mechanism on the electrode surfaces. The direct oxidation process of PCP using different electrodes (CNT, CNT-TiO_2, CNT-Z-TiO_2, CNT-Z-TiO_2/Ag, CNF-Z-TiO_2 and CNF-Z-TiO_2/Ag) was diffusion-controlled and the adsorption processes were not negligible. Under UV irradiation, the oxidation process of PCP occurred earlier (photoelectrochemical process), and it was also diffusion-controlled.

The chronoamperometry (CA) and multiple-pulsed amperometry (MPA) technique were used to achieve the electrochemical oxidation under potentiostatic conditions at different applied potential values. Taking into consideration the charge consumption the best electrochemical efficiency was obtained by applying CA technique at the applied potential value of +1.5 V *vs*. SCE.

After application the electrochemical process for 50 $mg \cdot L^{-1}$ initial concentration of PCP, using chronoamperometry technique at the applied potential value of +1.5 V *vs*. SCE, higher process efficiencies were noticed in the case of CNF-based electrodes, especial for CNF-Z-TiO_2 electrode in comparison with CNT-based electrodes. Also, BDD electrode showed a higher electrochemical efficiency even if the process efficiency was quite lower than for carbon based composite electrodes. This aspect can be explained by the very low background current of the BDD electrode.

However, the electrode performances for PCP electrodegradation expressed by process efficiency were very low, this aspect may be explained by the very small surface area of the electrodes (0.196 cm^2) and the other hand by the possibility of electrode fouling.

Electrochemical performances of the electrode materials were not improved significantly by applying MPA technique, due to the limitation of *in-situ* cleaning potential values, following the economic aspects of specific energy consumption.

The results concerning the evaluation of photoelectrooxidation processes in terms of process efficiency and electrochemical efficiency showed that all tested electrode materials allow the photoelectrooxidation of PCP under potentiostatic conditions characterized by the water decomposition potential range (potential value of oxygen evolution and generation of hydroxyl radicals), corresponding to the diminution of electrode fouling.

Comparing the process efficiencies obtained after electrooxidation and photocatalysis, also the appearence of a synergetic effect was noticed by applying photoelectrooxidation process.

Based on these results, it was proposed a series of photoelectrocatalytic activity for degradation of PCP, namely: CNF < CNF- TiO_2 < CNF-Z-TiO_2 < CNT < CNT-TiO_2/Ag < CNT-TiO_2 < CNF-Z-TiO_2 < CNT-Z-TiO_2 < CNT-Z-TiO_2/Ag.

It should be noticed that although photoelectrocatalytic activities determined for composite electrodes based on carbon nanofibers were much lower (about 10 times), neverthless the process efficiencies were comparable to those obtained using electrodes based on carbon nanotubes. This is explained by the fact that the process is conducted in operating conditions characterized by oxygen evolution and generation of hydroxyl radicals and not by direct photoelectrooxidation.

In order to optimize the photoelectrodegradation process, studies regarding to influence of applied potential on the process efficicency were carried out. The photoelectrooxidation processes were conducted at three different applied potential values (+1; +1.5 and +2 V *vs.* SCE), using CNT-Z-TiO_2 electrode, for 120 minutes reaction times. By increasing the applied potential value charge consumption increased, while current efficiency decreased. Taking into account this economic aspect that limits the application of a very high potential. In addition, the close values of the apparent rate constants for PCP degradation, indicated that from the kinetic point of view is not justify the applying of the potential value higher than +1 V *vs.* SCE. The optimum operating conditions for PCP photoelectrodegradation under potentiostatic conditions assume the use of TiO_2 modified carbon composite electrodes at E = +1 V *vs.* SCE.

The electrochemical behaviour of the electrode materials was determinated in 0.1 M Na_2SO_4 supporting electrolyte, in order to use them in further electrochemical and photoelectrochemical detection of PCP. The potential window and background current were determined by cyclic voltammetry for each type of electrodes.

Almost all studied electrodes showed a large potential window (E > +1.1 V), except these electrodes: CNT-TiO_2(sg), CNT-TiO_2/Ag şi CNT-Z-TiO_2/Ag, which exhibited a narrow potential window, specific aspect of the electrocatalytic behaviour. In addition, the presence of TiO_2 in the electrode composition improved the electrocatalytic properties of both CNF/CNT-based elecetrodes. Under UV irradiation, higher background current is noticed, the difference between the dark and light current being the photocurrent and the potential value of oxygen evolution is less, indicating that the electrode materials exhibit photo-electrochemical acvtivity.

Based on the studies regarding to electrochemical bahaviour of electrode materials in the presence of different concentration of PCP, it was concluded that CNT-based electrodes displayed higher electrocatalytic activity towards CNF-based electrode materials. These results are in according with those obtained for electrode characterization, *i.e.*, low background current that means lower detection limit but less sensitivity in comparison with electrode materials characterized by high background current, characteristics for improved electrocatalytic properties.

Photoelectrocatalytic activity towards PCP oxidation, for the electrochemical detection, is evidenced by the anodic oxidation peak corresponding to direct oxidation of PCP on the electrode surface recorded at about 0.90 V *vs.* SCE. A linear dependence between anodic current and PCP concentration was achieved for all studied electrodes, which gives information about a possible diffusion-controlled process, very desired for detection.

Under UV irradiation, the oxidation process is slightly influenced by appearance of a new oxidation peak prior to that recorded in UV absence. This new small oxidation peak recorded at about +0.65 V *vs.* SCE for almost all composite electrodes depends linearly on the PCP concentration, but inform that under UV irradiation the oxidation process of PCP occurred earlier. The appearance of this new oxidation peak, whose anodic current depended linearly on the PCP concentration at the lower potential value is a positive aspect with a very high potential for exploitation for selective detection of PCP.

The fact that this small peak appears only under UV irradiation, depending linearly on the concentration of PCP and the scan rates, also shows that this peak is due to the PCP photoelecrtooxidation process.

This new oxidation peak recorded at lower potential values for all CNT-based electrodes and for all TiO_2-modified-CNF-based electrodes, except the electrode based CNF in epoxy matrix. This result shows that carbon nanotubes possess photocatalytic properties while carbon nanofibers do not exhibit these properties.

By applying cyclic voltammetry in the presence of UV irradtiation for detection of PCP using carbon nanutubes based composite electrodes, led to enhanced detection parameters, in particular to the detection sensivity and the possibility of detection at a lower potential value. Better photoelectrocatalytic performance have shown by the electrode materials consisted of Ag-doped TiO_2, due to its photocatalytic activity. In the case of CNF-based electrodes without TiO_2, the application of photoelectrochemical detection method is not adequate, because carbon nanofibers do not exhibit photocatalytic activity

All tested composite electrodes based on CNT and CNF are suitable for voltammetric detection of PCP.

The best electroanalytical performance was obtained for the electrode materials: CNT-TiO_2(sg), CNT-TiO_2(Ag), CNT-Z-TiO_2, CNT-Z-TiO_2(Ag), CNF-TiO_2 şi CNF-Z-TiO_2(Ag).

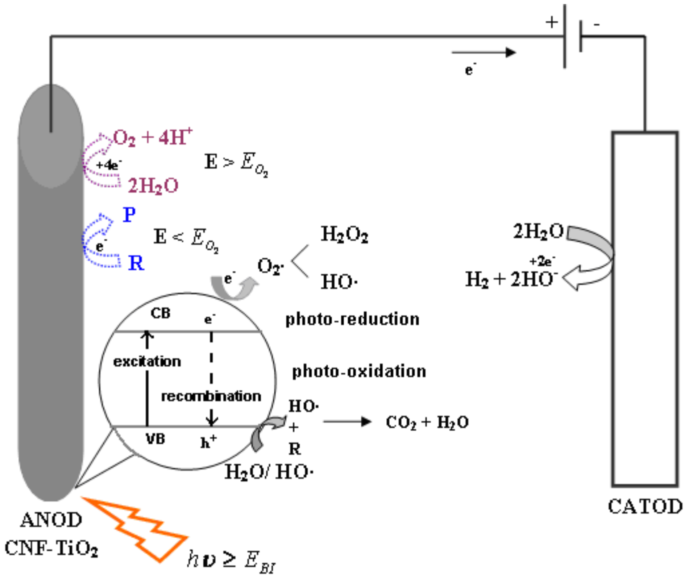
Selection of the method and the electrode in order to develop a specific detection protocol is performed according to the specific requirements for each type of application, that require detailed studies (for example, interference).

Based on the obtained results, it can be concluded that Ag-doped TiO_2-zeolite-modified carbon composite electrodes are suitable for dual applications in photoelectrocatalytic degradation of PCP and its concentration monitoring by voltammetric method.

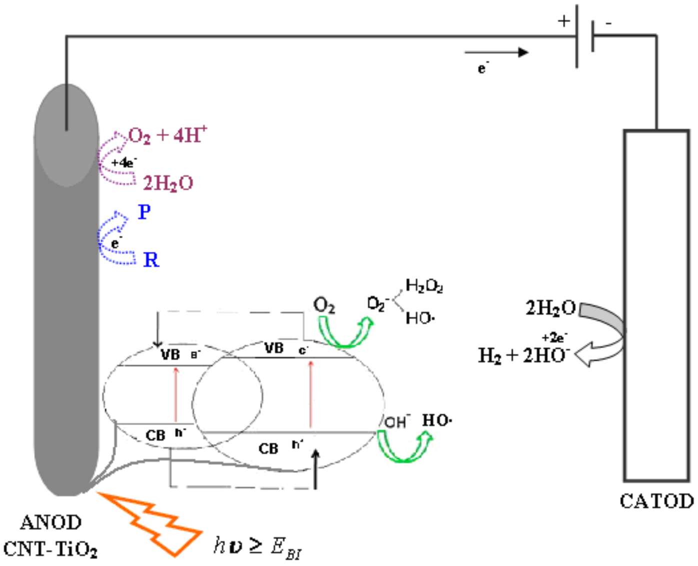
It has been demonstrated that increasing applied anodic potential in photocatalytic process by operating photoelectrocatalytic process, did not improve the process efficiency, even lower electrochemical efficiencies were obtained.

However, the mineralization process is favored by higher applied electric field, which increases the concentration of hydroxyl radicals and prevents the recombination of e^-/h^+, O_2 being an electron acceptor.

Taking into account the reported datas in the literature and the obtained results, may be proposed the following mechanism of PCP photoeletrooxidation using CNF-TiO_2 composite electrode:



In the case of CNT-TiO_2 composite electrode is proposed the following photoelectrooxidation mechanism, the difference consisting in the photocatalytic activity exhibited by CNT:



Selection the type of electrode material and the electrode potential in photoelectrooxidation process will be accomplish according to concrete application, either in conversion processes by incomplete degradation of PCP to less toxic biodegradable intermediate compounds, when the applied potential is lower, or in mineralization processes by complete degradation of PCP, when requires higher potential, but it is economically disadvantageous.