

# Advanced degradation of pentachlorophenol from water and process control using carbon nanofibers based composite electrodes

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## Abstract

In the present study, carbon nanofibers-epoxy composite and TiO<sub>2</sub>-modified carbon nanofibers-epoxy composite (TiO<sub>2</sub>-CNF) electrodes were prepared by the two-roll mill procedure and characterized morpho-structurally and electrically in order to degrade pentachlorophenol (PCP) from water. Also, taking into account the dual character of the electrode material and electrochemical techniques, the composite electrodes were tested for PCP detection envisaging the degradation process control. Electrochemical and photoelectrochemical characterization of the electrodes was performed by cyclic voltammetry technique in 0.1 M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte. The degradation process performance was assessed in terms of electrochemical efficiency and a great enhancement of about 25 times was achieved for the photoelectrochemical process in comparison with electrochemical one using TiO<sub>2</sub>-CNF composite electrode. This electrode exhibited useful peculiarities for PCP detection application both under and without UV irradiation. The validity of the proposed CV-based protocol using a TiO<sub>2</sub>-CNF composite electrode was determined by its application in the PCP degradation process control. Good accuracy was found by comparison with the results obtained by UV-VIS spectrophotometry.

*Keywords: pentachlorophenol photoelectrooxidation, electrochemical detection, carbon nanofibers based composite electrode, advanced wastewater treatment.*

## 1 Introduction

Pentachlorophenol (PCP) is a highly toxic persistent organic pollutant present in the environment due to its extensive use as a pesticide in agriculture and in wood



preservation in industries. Its presence in water and soil could also contaminate the groundwater and become a potential risk to humans and animals [1].

Photocatalytic technology has been intensively studied and holds great promise for environmental application [2], and  $\text{TiO}_2$  seems to be the most hopeful photocatalyst for PCP degradation due to its low cost, non-toxicity, high activity and chemical stability [2, 3].  $\text{TiO}_2$  photocatalytic activity is based on the capacity of this semiconductive material to oxidize PCP even to complete mineralization after 16 hours of UV irradiation [4]. Despite the numerous advantages of photocatalysis in PCP removal from water, rapid recombination of photogenerated electrons ( $e^-$ ) and holes ( $h^+$ ) at  $\text{TiO}_2$ -based catalysts along the process raise an important problem. The solution to this problem could be a bias potential application in the photocatalytic degradation as an electrochemically-assisted photocatalytic process [5, 6]. Furthermore, the optimization of the process parameters for practical application that involve combination of electrolysis and heterogeneous photocatalysis as a photoelectrooxidation (PEO) process in order to reach a suitable option for the degradation of persistent organic compounds in a relatively short time [7] continue to be a challenge. One of the most important parameters for this process to be effectively based on the technical-economic criteria is the electrode material.

The preparation and exploitation of new composite electrode materials based on nanostructured carbon for environmental applications represent an intensive preoccupation of a large number of scientists. Carbon based composite electrode materials have been reported to be efficient in the electrochemical and photoelectrocatalytic degradation of organic pollutants from water [8–10].

Functionalization of carbon materials with a  $\text{TiO}_2$  catalyst gives the possibility for specific application in water treatment [11, 12] and development of new sensors [3].

This paper deals with exploiting the dual role of a  $\text{TiO}_2$  modified composite material in advanced degradation of PCP from water and the process control. In order to achieve this goal, a  $\text{TiO}_2$  modified carbon nanofiber composite electrode has been obtained, applied for PEO degradation of PCP from water, and characterized and tested for further detection application in order to control the degradation process.

## 2 Experimental

### 2.1 Preparation of ( $\text{TiO}_2$ -modified) nanofiber composite electrode

Carbon nanofibers (CNF) were dispersed into N,N-dimethylformamide (DMF), 99.8% using a Cole-Parmer<sup>®</sup> 750-Watt Ultrasonic Processor for 10 minutes. Then, the  $\text{TiO}_2$  (Degussa) and epoxy resin was added into the solution and sonication was continued for another 10 minutes. The solvent was evaporated from the mixture at 60°C in vacuum oven for 12 hours. In order to achieve a homogeneous mixture with a high level of dispersion and distribution of  $\text{TiO}_2$ -modified-CNF into polymeric matrix a two-roll mill process was applied. The temperature of 70 °C was kept constant along the mixing process, i.e. 40 minutes, alternating the

mixing speed of 10 rpm with 20 rpm. Then, the curing component of epoxy matrix (the ratio between epoxy resin and curing agent was 100:38) was added to the mixture, and for another 20 minutes the mixing was continued. The resulting paste was introduced into PVC tubes, and the electrode contact was made using a copper wire. The resulting electrode was cured into a vacuum oven at 80°C for 24 hours. The cleaning and renewing electrode surface was made mechanically by polishing the surface on ultra-fine sandpaper.

## 2.2 Electrode materials characterization

The morphological, electrical and electrochemical electrode material characterization was performed. Scanning electron microscope (SEM XL20, Philips) was used for the morphological characterization. The electrical characterization was achieved through the four-point probe method, and the electrical resistance was measured using a digital multimeter DMM2000 and a 6221 DC current source, both provided by Keithley. The electrochemical behaviour of the composite electrodes was studied through the cycling voltammetry technique performed with an Autolab potentiostat/galvanostat PGSTAT 302 (EcoChemie, The Netherlands).

## 2.3 Electrochemical and photoelectrochemical applications

Cyclic voltammetry (CV) was applied for the detection protocol elaboration on the carbon based composite electrodes unmodified/modified with TiO<sub>2</sub>. The UV irradiation effect was assessed for PCP degradation and detection using a 6 W UV lamp, with a wavelength of between 254 and 356 nm, at room temperature. The chronoamperometry technique was used to perform the electrochemical and photoelectrochemical degradation, under a potentiostatic regime.

PCP concentration was determined with a Varian Cary 100 UV-VIS spectrophotometer at a wavelength of 218 nm.

The performance of the PCP electrochemical and photoelectrochemical degradation process was assessed in terms of the electrochemical efficiency, expressed by eqn (1) [13]:

$$E_{PCP} = \frac{C_{PCP0} - C_{PCP}}{C \cdot S} \cdot V \quad (1)$$

where  $E_{PCP}$  is the electrochemical efficiency expressed in g/C·cm<sup>2</sup>;  $C_{PCP0}$  is the initial concentration of PCP in solution (mg/L);  $C_{PCP}$  (mg/L) is the PCP concentration after degradation for a charge consumption of C corresponding to a certain time; V is the sample volume, i.e. 50 ml, and S is the area of the electrode surface (cm<sup>2</sup>).

### 3 Results and discussion

#### 3.1 Morphological and electrical characterization

SEM images of CNF and TiO<sub>2</sub>-CNF composite surfaces are shown in table 1 and a good dispersion of CNF and TiO<sub>2</sub> within epoxy matrix was noticed.

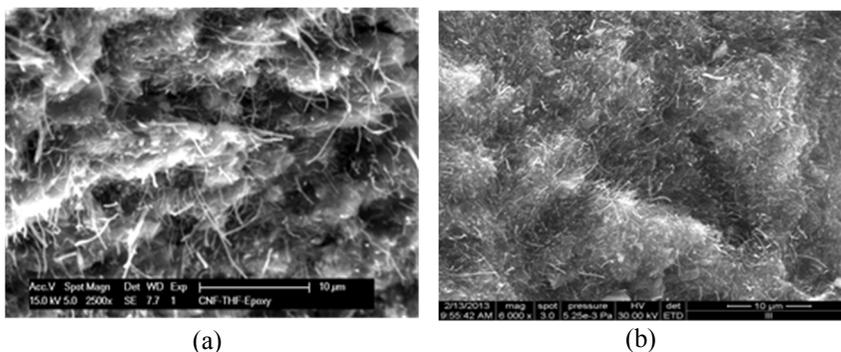


Figure 1: SEM images of (a) CNF and (b) TiO<sub>2</sub>-CNF composite electrode surfaces.

Electrical characterization of CNF based composite electrodes was achieved by electrical resistance measurements through the four point probe method (FPP), and the recorded results are presented in table 1. These results show that electrode materials are suitable to be applied for electrochemical experiments.

Table 1: Electrical conductivity of carbon based electrode materials.

Electrode material	Electrical conductivity, S·cm <sup>-1</sup>
CNF	0.750
CNF-TiO <sub>2</sub>	0.700

#### 3.2 Electrochemical characterization of the electrode materials

The electrochemical behaviour of potassium ferrocyanide K<sub>3</sub>Fe(CN)<sub>6</sub> in 1 M KNO<sub>3</sub> supporting electrolyte on the electrode surface was studied using CV recorded at different scan rates (0.025; 0.05; 0.1; 0.2; 0.3 Vs<sup>-1</sup>) in the potential range of -1 → +1.5 V vs. SCE. Table 2 shows the electroactive surface areas of the carbon composite electrodes, which were calculated based on the Randles-Sevcik equation:

$$I_p = 2.69 \times 10^5 AD^{1/2} n^{3/2} \nu^{1/2} C \quad (2)$$

where  $A$  represents the area of the electrode (cm<sup>2</sup>),  $n$  the number of electrons participating in the reaction and it is equal to 1,  $D$  the apparent diffusion coefficient of the molecule in solution (cm<sup>2</sup> s<sup>-1</sup>),  $C$  the concentration of the probe molecule in the solution (*i.e.*, 4 mM), and  $\nu$  is the scan rate (V s<sup>-1</sup>).

Table 2: Apparent diffusion coefficients and the electroactive surface areas of the nanostructured carbon-based composite electrodes.

Electrode	$D_{\text{apparent}} [\text{cm}^2 \cdot \text{s}^{-1}]$	$A_{\text{electroactive}} [\text{cm}^2]$	$A_{\text{geo}} [\text{cm}^2]$
CNF	$1.02 \cdot 10^{-5}$	0.242	0.196
CNF-TiO <sub>2</sub>	$2.53 \cdot 10^{-5}$	0.251	0.196

Based on the above presented results, it can be concluded that both tested unmodified and modified carbon based-composite electrodes exhibit an electroactive surface area higher than the geometrical one.

### 3.3 Electrooxidation applications

For an accurate assessment of electrode material performances for PCP degradation through electrooxidation process, cyclic voltammetry was the first technique applied in our study.

#### 3.3.1 Electrode process characterization by cyclic voltammetry

Electrochemical behaviour of the electrode materials in the presence of PCP allowed us to elucidate some aspects regarding the oxidation process, focusing on an overpotential values operating parameter for both electrooxidation and photoelectrooxidation processes.

The CV technique was applied for TiO<sub>2</sub> unmodified/modified carbon nanofibers based composite electrodes in 0.1 mM Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte, without and under UV irradiation.

Fig. 2 presents the cyclic voltammograms recorded on TiO<sub>2</sub> modified /unmodified carbon nanofibers based composite electrodes in 0.1 M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte and in the presence of 60 μM PCP at a scan rate of 0.05 V s<sup>-1</sup>, in the potential range between -0.5 and +1.25 V vs. SCE, without and under UV irradiation.

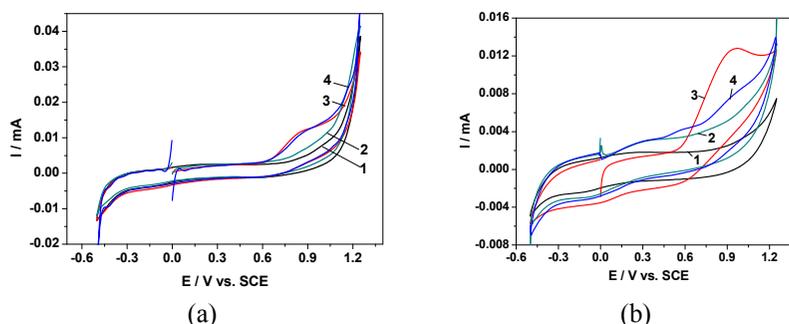


Figure 2: Cyclic voltammograms recorded on (a) CNF; (b) CNF-TiO<sub>2</sub> electrodes in 0.1 M Na<sub>2</sub>SO<sub>4</sub> without (1) and under (2) UV irradiation and in the presence of 60 μM PCP without (3) and under (4) UV irradiation; potential range -0.5 → +1.25 V vs. SCE; scan rate: 0.05 V·s<sup>-1</sup>.

Table 3: Voltammetric parameters of PCP oxidation on carbon based composite electrodes.

Electrode type	Without UV irradiation		With UV irradiation	
	$a \cdot 10^3$ [mA· $\mu$ M <sup>-1</sup> ]	$E_a$ [V]	$a \cdot 10^4$ [mA· $\mu$ M <sup>-1</sup> ]	$E_a$ [V]
CNF	0.13	+ 0.85	0.82	+ 0.85
CNF-TiO <sub>2</sub>	0.35	+ 0.73	2.39	+ 0.80
CNF	–	–	–	+0.57
CNF-TiO <sub>2</sub>	–	–	0.0016	+0.57

The current peak noticed at the potential value of about +0.8 V/SCE showed good direct electrooxidation activity of carbon nanofibers based composite electrodes for PCP oxidation.

Under UV irradiation, an increase in the background current can be observed for both composite electrodes. In the presence of PCP, no influence of UV irradiation was noticed for CNF while for TiO<sub>2</sub>-CNF the signal corresponding to PCP oxidation decreased but a new peak at lower oxidation potential appeared characterized by a lower current height (see curve 4, fig. 2(b)).

### 3.3.2 Electrochemical and photoelectrochemical oxidation

Performances of carbon based composite electrode materials for both electrooxidation and photoelectrooxidation processes have been assessed.

The electrochemical efficiency for PCP electrochemical and photoelectrochemical degradation was calculated based on pollutant concentration measured before and after electrooxidation conducted at an oxidation potential of +1.5 V using chronoamperometry technique. A significant enhancement of the electrochemical efficiency for PCP degradation by PEO process in comparison with EO was noticed. After the first 30 minutes of electrolysis, the electrochemical efficiency for CNF-TiO<sub>2</sub> increased by about 25 times. During the electrolysis process, the efficiencies decreased due to higher charge consumption and also, a possible fouling effect on the electrode surface by the presence of the products. The efficiency decreasing is slower for CNF-TiO<sub>2</sub> because of the photocatalytic effect of TiO<sub>2</sub> that cleans in-situ the electrode surface. The results are presented in table 4.

Table 4: Electrochemical efficiencies recorded after 120 minutes of electrooxidation (EO)/photoelectrooxidation (PEO) at 50 mg·L<sup>-1</sup> PCP, using different electrode types, in 0.1 M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte, at a potential value of 1.5 V through chronoamperometry.

Process type	Electrode type	$E_{PCP}$ , g·C <sup>-1</sup> ·cm <sup>-2</sup>			
		30/min	60/min	90/min	120/min
EO	CNF	6.22	2.99	2.04	2.38
	CNF-TiO <sub>2</sub>	5.85	4.33	3.57	5.73
PEO	CNF	138.30	111.74	72.66	51.92
	CNF-TiO <sub>2</sub>	139.93	123.81	90.87	68.66

Some examples of UV-VIS spectra recorded in the 200–350 nm wavelength range before and after the photoelectrodegradation process using carbon nanofibers composite electrodes are presented in fig. 3. A significant decrease of peak intensity, and also a slight change in spectra shape can be observed. This observation could give information regarding the small amount of intermediate formation into the photoelectrooxidation process.

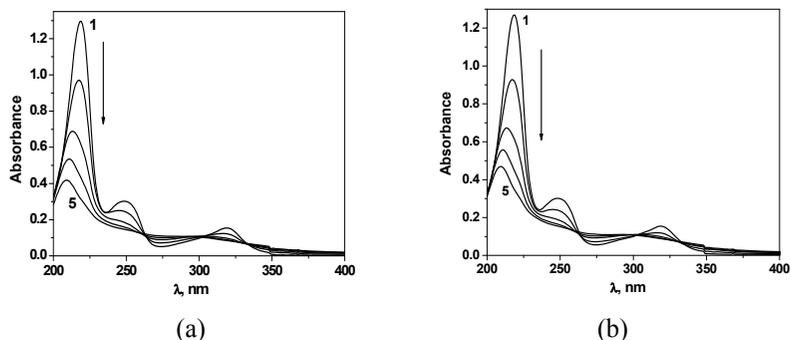


Figure 3: UV-VIS spectra recorded after 50 mg·L<sup>-1</sup> PCP photoelectrooxidation using (a) CNF; (b) CNF-TiO<sub>2</sub> electrodes; 1 – initial; 2 – after 30 minutes; 3 – after 60 minutes; 4 – after 90 minutes; 5 – after 120 minutes reaction time.

### 3.4 PCP electrochemical detection studies using CV technique

#### 3.4.1 PCP electrochemical detection without UV irradiation

Fig. 4 presents the cyclic voltammograms recorded at the scan rate of 0.05 V·s<sup>-1</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte and in the presence of a different PCP concentration (10–60 μM) on carbon nanofibers based composite electrodes (CNF and CNF-TiO<sub>2</sub>). A linear dependence can be observed between the anodic current peak corresponding to PCP oxidation potential and PCP concentration, and from the straight line slope, the sensitivity of the detection method was determined.

Electrocatalytical activity for PCP oxidation is envisaged by anodic peaks corresponding to PCP direct oxidation on the composite electrodes surface recorded around potential value of +0.85 V vs. SCE.

Based on the electroanalytical parameters presented in table 5, it can be noticed the electrocatalytic effect of the TiO<sub>2</sub> improved both sensitivity and the detection potential value for PCP detection.

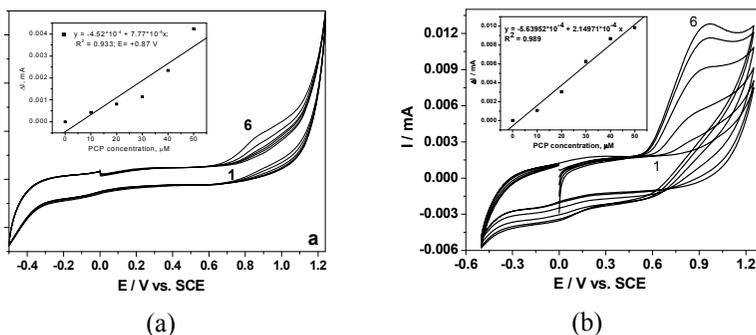


Figure 4: Cyclic voltammograms recorded on (a) CNF, (b) CNF-TiO<sub>2</sub> electrode in 0.1M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte and in the presence of different PCP concentrations: 1–0 μM; 2–10 μM; 3–20 μM; 4–30 μM; 5–40 μM; 6–50 μM; 7–60 μM; potential range: -0.5 V → +1.25 V vs. SCE; scan rate: 0.05 V·s<sup>-1</sup>. Inset: recorded anodic peak currents.

Table 5: Electroanalytical performances of carbon nanofibers based composite electrodes for PCP detection.

Electrode material	Detection potential, V/SCE	Sensitivity (μA/μM)	Correlation coefficient, R <sup>2</sup>
CNF	+0.85	0.0777	0.933
CNF-TiO <sub>2</sub>	+0.90	0.2150	0.989

### 3.4.2 PCP electrochemical detection with UV irradiation

Taking into account the photocatalytic effect of TiO<sub>2</sub>, the detection experiments using CV were carried out under UV irradiation. The cyclic voltammograms recorded in 0.1 M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte and in the presence of different PCP concentrations (10–60 μM) on TiO<sub>2</sub> modified/unmodified composite electrodes under UV irradiation are presented in fig. 5.

As we already noticed in the previous subsection dedicated to the degradation experiments, the sensitivity recorded at +0.9 V/SCE decreased for CNF-TiO<sub>2</sub> but a good sensitivity recorded at +0.7 V/SCE was achieved, which was better than those reached for CNF.

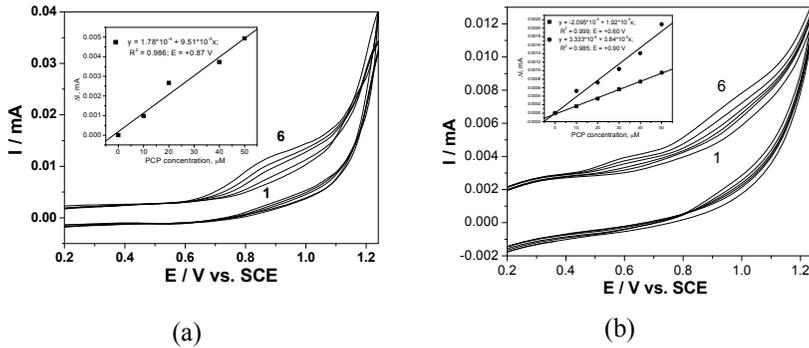


Figure 5: Cyclic voltammograms recorded on (a) CNF, (b) CNF-TiO<sub>2</sub> electrode in 0.1M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte and in the presence of different PCP concentrations: 1–0  $\mu\text{M}$ ; 2–10  $\mu\text{M}$ ; 3–20  $\mu\text{M}$ ; 4–30  $\mu\text{M}$ ; 5–40  $\mu\text{M}$ ; 6–50  $\mu\text{M}$ ; 7–60  $\mu\text{M}$ ; potential range: -0.5 V  $\rightarrow$  +1.25 V vs. SCE; scan rate: 0.05 V $\cdot$ s<sup>-1</sup>, under UV irradiation. Inset: Dependence between anodic peak current recorded at potential of +0.85 V vs. SCE on CNF electrode; and +0.9 and +0.6 V vs SCE on CNF-TiO<sub>2</sub> electrode and PCP concentration.

Table 6: Electroanalytical performances of carbon nanofibers based composite electrodes for PCP detection recorded under UV irradiation.

Electrode material	Detection potential, V/SCE	Sensitivity ( $\mu\text{A}/\mu\text{M}$ )	Correlation coefficient, $R^2$
CNF	+0.85	0.0951	0.986
CNF-TiO <sub>2</sub>	+0.90	0.1384	0.985
	+0.70	0.1192	0.999

## 4 Conclusions

TiO<sub>2</sub> modified/unmodified composite electrodes were successfully obtained by the two-roll mill procedure. A good distribution of the carbon nanofibers and TiO<sub>2</sub> within epoxy matrix was evidenced. The photoelectrochemical degradation process of PCP performed under potentiostatic condition at +1.5 V/SCE using TiO<sub>2</sub>-CNF electrodes was assessed in term of electrochemical efficiency. This process exhibited 25 times higher efficiency than the corresponding electrochemical one.

Both carbon nanofibers composite electrodes presented dual functionality as voltammetric detector and the electrode material for PCP degradation application, but TiO<sub>2</sub>-CNF was more efficient.

The validity of this detection method was checked by its application for the assessment of the photoelectrochemical process applied for the degradation of 50 mg·L<sup>-1</sup> PCP. The results were compared with those obtained by UV-VIS spectrophotometry and a good accuracy was reached.

It can be concluded that TiO<sub>2</sub>-CNF composite electrode is very promising for the practical application of PCP degradation process and its control.

## Acknowledgements

This work was partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013, and partially by the Romanian National Research Programs PN-II-ID-165/2011 and PNII-60/2012 (WATUSER).

## References

- [1] Yu, L., Yang, X., Ye, Y., Peng, X., Wang, D., Silver nanoparticles decorated anatase TiO<sub>2</sub> nanotubes for removal of pentachlorophenol from water, *Journal of Colloid and Interface Science*, **453**, pp. 100–106, 2015.
- [2] Zhang, X., Tang, Y., Li, Y., Wang, Y., Liu, X., Liu, C., Luo, S., Reduced graphene oxide and PbS nanoparticles co-modified TiO<sub>2</sub> nanotube arrays as a recyclable and stable photocatalyst for efficient degradation of pentachlorophenol, *Applied Catalysis A: General*, **457**, pp. 78–84, 2013.
- [3] Zhou, Q., Fang, Z., Li, J., Wang, M., Applications of TiO<sub>2</sub> nanotube arrays in environmental and energy fields: A review, *Microporous and Mesoporous Materials*, **202**, pp. 22–35, 2015.
- [4] Gunlazuardi, J., Lindu, W.A., Photocatalytic degradation of pentachlorophenol in aqueous solution employing immobilized TiO<sub>2</sub> supported on titanium metal, *Journal of Photochemistry and Photobiology A: Chemistry*, **173**, pp. 51–55, 2005.
- [5] Shen, Y., Li, F., Li, S., Liu, D., Fan, L., Zhang, Y., Electrochemically enhanced photocatalytic degradation of organic pollutant on β-PbO<sub>2</sub>-TNT/Ti/TNT bifunctional electrode, *International Journal of Electrochemical Science*, **7**, pp. 8702–8712, 2012.
- [6] Li, G., Yip, H., Wong, K.H., Hu, C., Qu, J., Wong, P.K., Photoelectrochemical degradation of Methylene Blue with PbO<sub>2</sub> electrodes driven by visible light irradiation, *Journal of Environmental Science (China)*, **23**, pp. 998–1003, 2011.
- [7] da Silva, S.W., Bordignon, G.L., Viegas, C., Rodrigues, M.A.S., Arenzon, A., Bernardes, A.M., Treatment of solutions containing nonylphenol ethoxylate by photoelectrooxidation, *Chemosphere*, **119**, pp. S101–S108, 2015.
- [8] Liu, W., Quan, X., Ciu, Q., Ma, M., Chen, S., Wang, Z-J., Ecotoxicological characterization of photoelectrocatalytic process for degradation of

- pentachlorophenol on titania nanotubes electrode, *Ecotoxicology and Environmental Safety*, **71**, pp. 267–273, 2008.
- [9] Zhang, W.Q., Zhu, G.B., Ma, J.Y., Zhang X.H., Chen J.H., A new electrochemical sensor based on W-doped titania-CNTs composites for detection of pentachlorophenol, *Indian Journal of Chemistry*, **50A**, pp. 15–21, 2011.
- [10] Motoc, S., Remes, A., Pop A., Manea, F., Schoonman, J., Electrochemical detection and degradation of ibuprofen from water on multi-walled carbon nanotubes-epoxy composite electrode, *Journal of Environmental Sciences*, **25(4)**, pp. 838–847, 2013.
- [11] Asmussen, R.M., Tian, M., Chen, A.C., A new approach to wastewater remediation based on bifunctional electrodes, *Environmental Science and Technology*, **43**, pp. 5100–5105, 2009.
- [12] Ratiu, C., Manea, F., Lazau, C., Orha, C., Burtica, G., Grozescu, I., Schoonman, J., Photocatalytically-assisted electrochemical degradation of p-aminophenol in aqueous solutions using zeolite-supported TiO<sub>2</sub> catalyst, *Chemical Papers*, **65(3)**, pp. 289–298, 2011.
- [13] Vlaicu, I., Pop, A., Manea, F., Radovan, C., Degradation of humic acid from water by advanced electrochemical oxidation method, *Water Science and Technology: Water Supply*, **11(1)**, pp. 85–95, 2011.

