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# Effective determination of clomazone and oxyfluorfen in aqueous samples by differential pulse stripping voltammetry

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**Abstract:** Two novel types of electrochemical sensors were obtained by chemical deposition of Pt and MoO<sub>2</sub> nanoparticles onto multi walled carbon nano tubes (MWCNT) and used for determination of frequently used pesticides clomazone and oxyfluorfen in aqueous media via differential pulse stripping voltammetry (DPSV). Clomazone was determined in 0.1 M phosphate buffer solution at pH 7.0 in the concentration range 0.61-20.56 ng cm<sup>-3</sup>, with LOQ = 0.61 and LOD = 0.38 ng cm<sup>-3</sup>. Oxyfluorfen was determined with good reproducibility (RSD <2.4%) in the concentration range 2.5-34.5 ng cm<sup>-3</sup>, with r = 0.99 and a LOQ of 1.5 ng cm<sup>-3</sup>. Results were in the same range measured by HPLC/DAD, which was used as comparative method. Structural characterization of the doped MWCNT performed by Raman spectroscopy, field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron (HR-TEM), and X-ray crystallography revealed a preserved MWCNT structure decorated with well dispersed species of the platinum and MoO<sub>2</sub> nanoparticles.

**Keywords:** ELECTROCHEMISTRY, SENSOR, VOLTAMMETRY, NANOPARTICLES, PESTICIDES, ENVIRONMENT

## 1. Introduction

In era of rapid industrialization and technological development, the environment is increasingly polluted on daily basis. There are numerous sources of pollution that in many ways emit different groups of pollutants into the immediate environment from where they can migrate to water resources, air, soil, the food chain and ultimately to human beings. Exposure of humans to harmful compounds of anthropogenic origin can have unforeseeable consequences for his health. Therefore, it is necessary to always keep in mind possible sources of pollution and ways of migration of toxic substances in nature and reaching the resources which are in direct contact with humans.

Pesticides are mainly organic artificially synthesized compounds that are nowadays widely used in agriculture to protect plants from insects, fungi, rodents, etc. Their use in the allowed quantities, respecting the time of spontaneous degradation, does not pose a great health risk. However, a major problem with them is that they are in some cases difficult to biodegrade, can accumulate in living organisms while their breakdown products are stable and toxic. The harmful effects of pesticides vary from case to case, but it has been proven that some of them can be carcinogenic, mutagenic, teratogenic or have a number of negative effects on some systems of organs. Therefore, monitoring of pesticides in the environment, and especially in samples that are closest to humans (food, water) is of great importance.

Pesticide concentration is determined mainly by the techniques of liquid or gas chromatography [1]. These techniques are precise but impractical due to the high cost of analysis and the cost of the instrument itself, the need for a highly educated workforce as well as the essential sample preparation steps. Therefore, it is necessary to develop new techniques that with the same levels of reliability, selectivity, accuracy and precision can eliminate these shortcomings.

Voltammetry embraces several electroanalytical methods acknowledged as a sophisticated means for sensitive and rapid determination of a lot of compounds, including pesticides. Electrochemical sensors are a type of sensors where working electrode in three electrode system acts as the transducer. The production and use of these sensors took off in the last decades and found commercial applications in many fields. They are characterized by the few facts: the use of the electron for signal acquisition, which is considered a clean model for analytical applications, with no generation of waste, miniaturization in portable devices (analyses with microvolumes of samples), fast analysis, and low production cost [2].

Multi-walled carbon nanotubes (MWCNTs) are chemically stable material with superior mechanical, electrochemical and optical properties. Their increased sensitivity in sensing platforms is among the rest due to high surface area to volume ratio and pronounced electrical conductivity. Electrochemical sensors based on multi or single walled CNTs can improve electrical and

mechanical properties of composite electrodes which result in higher peak currents and lower overpotential [3]. There are numerous reports where the role of nanocomposites of specific compositions in improvement of electrode response have been elucidated [4,5,6].

This study is based on the fact that immobilization of metallic nanoparticles onto carbon support can boost the advances of electrochemical sensors and lead to enhancements of their performance and application in pesticide determination.

## 2. Experimental

### 2.1. Synthesis of materials

The commercial glassy carbon (GC) electrode was modified by the following procedure. For a start, 50 mg of MWCNT (carbon > 95%, outer diameter × length: 6–9 nm × 5 μm) purchased from Sigma-Aldrich was dispersed in 20 cm<sup>3</sup> mixture of ethanol and water (50v/v%). Then, 0.5 cm<sup>3</sup> of aniline was introduced into suspension and sonicated for 90 min. In the first case, 26.7 mg of chloroplatinic acid hydrate (H<sub>2</sub>PtCl<sub>6</sub> × H<sub>2</sub>O) was dissolved in 2 cm<sup>3</sup> of water and added to suspension which was then sonicated for the next 5 min and acidified afterwards with 0.5 cm<sup>3</sup> of 5 M HNO<sub>3</sub>. In the second case, 16.3 mg of sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub> × 2H<sub>2</sub>O) was dissolved in 2 cm<sup>3</sup> of water and introduced into sonicated suspension. For the reduction of ions of platinum and molybdenum, excess of 20 mg of sodium borohydride was dissolved in 2 cm<sup>3</sup> of water and then added to the suspension. It was stirred for a while and left for the next 24 h, then filtered and rinsed with deionized water to neutral pH. The obtained materials were dried at 90 °C for a couple of hours and used as the electrode modifier in voltammetric analyses.

### 2.2. Characterization

Field emission scanning electron microscopy (FE-SEM) was used for morphological characterization of the samples on microscope JEOL JXA-8500F. High resolution transmission electron microscope (HR-TEM) images were recorded by JEOL JEM-F200. Diffractometer (Rigaku Corporation, Japan), with CuKα radiation (λ = 1.5406 Å) and a scan speed of 5°/min was employed in X-ray analyses in the range between 0 and 60°2θ, with a step 0.02°.

### 2.3. Electrode preparation

Quantity of 5 mg of doped MWCNT sample was dispersed in 1 cm<sup>3</sup> of ethanol/water mixture (40 v/v%) and homogenized in the ultrasonic bath for 30 min. The surface of the GCE electrodes was polished on fine cloth using alumina powder. A drop which contained 15 mm<sup>3</sup> of the previously prepared suspension was transferred onto the GC electrode (working area was 0.04 cm<sup>2</sup>) and dried under nitrogen stream. After the thin carbon layer was dried, it was covered with 10 mm<sup>3</sup> of 0.05 wt.% Nafion in ethanol. The solvent was removed by evaporation.

### 2.4. Voltammetry

Pesticides were analyzed by the means of differential pulse stripping voltammetry (DPSV). Working solutions with pesticide in 0.1 M phosphate buffer were analyzed in a conventional voltammetric cell with operating volume of 10 cm<sup>3</sup> by using 797 VA Computrace analyzer (Metrohm, Switzerland) controlled by 797 VA Computrace software (version 1.2). A three-electrode system consisted of Ag/AgCl electrode (saturated with KCl) as a reference, platinum wire as auxiliary and dopant-MWCNT modified GCE as working electrode.

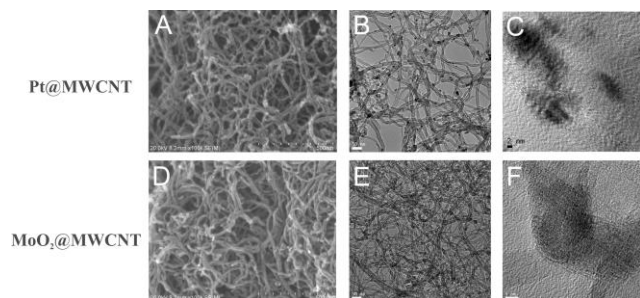
Prior to each run, the working electrode was electrochemically activated by potential cycling in various range with speed 0.1 V s<sup>-1</sup> for 10 cycles. The background voltammograms of the supporting electrolyte were recorded under the same conditions. The blank probe containing only the supporting electrolyte was recorded under the same conditions. Before starting a new set of measurements, the supporting electrolyte was deaerated by suprapure nitrogen for 5 min and then volumes from pesticides stock solutions were added to probes in order to make desired concentrations. The parameters for DPSV differed in the case of two different materials applied. Detailed instructions and descriptions of the working conditions can be found in the referred literature [7,8]. All the measurements were performed at room temperature (23 ± 1 °C).

As comparative analysis, concentrations of pesticides were determined by Shimadzu Prominence high performance liquid chromatography (HPLC) system (Shimadzu, Japan).

## 3. Results and discussion

### 3.1. Structure of doped MWCNTs

The microstructure of the materials can be seen in the SEM micrographs (Fig. 1A and Fig. 1D) at magnifications of 100,000 times. Morphology typical for MWCNT is noticed at both images. It is seen that MWCNT bundles are randomly orientated. Diameter of carbon nanotubes is in range of 10 nm while the length can reach more than several micrometers. However, the exact length is difficult to be measured because bundle is always in the meandering form. Pt nanoparticles are observed as light spots or clusters on the surface of MWCNT with diameter of up to 30 nm. In the case of MoO<sub>2</sub> doped MWCNT the dimensions of doping particles is estimated to be in the range mainly of 10 to 20 nm.



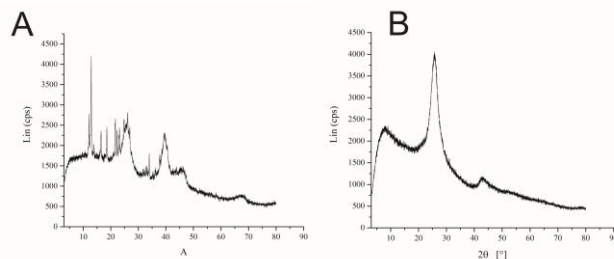
**Fig.1.** FE-SEM and HR-TEM images of Pt@MWCNT and MoO<sub>2</sub>@MWCNT

The TEM image of Pt doped MWCNT given in Fig. 1B indicates that Pt nanoparticles are well dispersed and successfully deposited on the carbon support. There is no evidence that the interior of the MWCNT is filled by Pt phase. Additionally, a higher magnification TEM image reveals that Pt nanoparticles intrinsically agglomerate and form aggregates with an average diameter of ~10 nm (Fig. 1C). It should be noted that Pt nanoparticles are firmly attached to the surface of CNTs since there is no single observation of freely (detached) Pt nanoparticles after analysis a large numbers of samples.

HR-TEM microphotographs of MoO<sub>2</sub> doped MWCNTs given in Fig. 1E and 1F display a hybrid structure consisting of MoO<sub>2</sub> nanoparticles firmly attached to the surface of MWCNT, forming a hairy morphology with discrete dark spots of MoO<sub>2</sub> nanoparticles. Such distribution of nanoparticles was achieved by in situ reduction of dissolved Na<sub>2</sub>MoO<sub>4</sub> in a suspension containing well-dispersed MWCNT according to reaction (Eq. 1):



Higher magnification (Fig. 1F) provides a better view on MoO<sub>2</sub> nanoparticles revealing their polyhedral or round morphology and diameter of the particles in the range from 7 to 50 nm. Larger particles are agglomerates composed of smaller ones which are stacked together. Aniline is used for obtaining stable nanoparticles of MoO<sub>2</sub>. It is assumed that most of aniline present on the surface of MWCNT was washed out during the rinsing step and that the remained surface concentration was not significant for electrocatalytic effects.

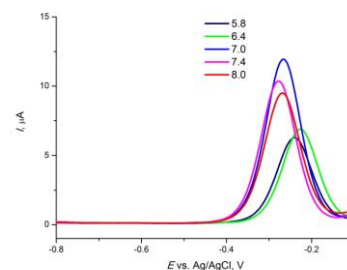


**Fig.2.** XRD patterns A) Pt@MWCNT and B) MoO<sub>2</sub>@MWCNT

The powder XRD technique was used to investigate the crystal structure of the platinum and molybdenum oxide modified MWCNT. As seen from Fig. 2A, the XRD profile of Pt@MWCNT contains peaks for MWCNTs at 26 and 43° 2θ which correspond to the planes of (220), (301) and (002), respectively. These peaks represent the graphitic reflections. In the case of MoO<sub>2</sub> doped MWCNTs (Fig. 2B), a strong intensity at 26° and a weak intensity at 44° are noticed, which correspond to the (002) and (100) planes of the graphite crystal structure as in previous case.

### 3.2. Electrochemical analysis

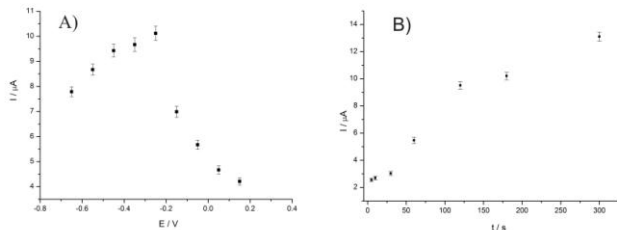
The cathodic response of clomazone by the Pt modified MWCNT was evaluated with respect to the several supporting electrolytes including potassium chloride, phosphate buffer and Britton–Robinson (B-R) buffer. Phosphate buffer was found to be the most suitable medium while in case of MoO<sub>2</sub>@MWCNT it was B-R solution. For the first case, the DPSV curves were recorded in 0.1 M phosphate buffer (pH range 5.8 – 8.0) to study the effect of pH on the voltammetric behavior of clomazone. As clearly noticeable from Fig. 3, there is no linear relationship between DP peak potential and pH. It is indicated that mechanism of clomazone reduction is complex with no common electrochemical behaviour involving addition of hydrogen. It has been ascertained from experimental data that the best peak shape and the maximum peaks current occurred in the 0.1 M phosphate buffer at pH 7.0. This is the reason why it was chosen for further investigation as optimal parameter from the analytical point of view. For comparison, there was no electrochemical response of clomazone with bare GC or MWCNT/GC electrodes. The optimal value of -0.25 V was chosen for deposition potential which coincides with the reduction potential for clomazone at selected conditions.



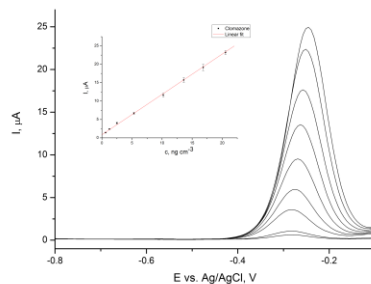
**Fig.3.** DPSV curves for 10.2 ng cm<sup>-3</sup> of clomazone at Pt@MWCNT/GCE

Enhanced adsorption and accumulation of clomazone on the Pt@MWCNT/GC electrode after its pretreatment at -0.25 V can be exploited here to significantly increase sensitivity of DPSV. Fig. 4B shows that the signal has hyperbolic shape with prolongation of the deposition time to 900 s. The peak current increased rapidly with

the increasing of deposition time and almost reached a platform after 120 s. For analytical purpose, Pt@MWCNT/GC electrode was initially pretreated during 900 s into the solution of  $10.2 \text{ ng cm}^{-3}$  of clomazone  $0.1 \text{ M}$  phosphate buffer solution before it was used for measuring its concentration to achieve down to the low ppb level. The additional preconcentration time of 120 s was employed before each measurement. The calibration graph for an accumulation time of 120 s was linear in the range from  $0.61$  to  $20.56 \text{ ng cm}^{-3}$ . Clomazone could be determined by DPSV in the concentration range of  $0.61 - 20.56 \text{ ng cm}^{-3}$  (Fig.3). Thereby, the relative standard deviation does not exceed 1.85%.

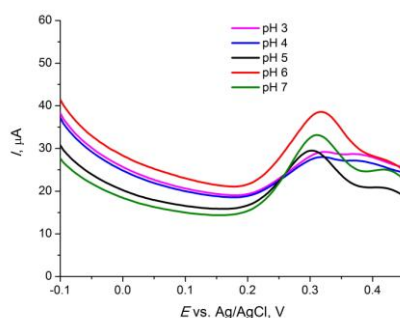


**Fig.4.** Key parameter optimized for DPSV of clomazone: A) Influence of deposition potential B) Effect of deposition time



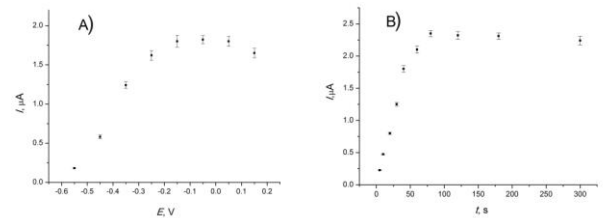
**Fig.5.** DPSV recorded at Pt@MWCNT/GCE for different concentrations of clomazone in  $0.1 \text{ M}$  phosphate buffer solution

In case of  $\text{MoO}_2$  modified MWCNTs, the sharpest and most favorably developed oxidation peak of oxyfluorfen was obtained at pH 6.0. For DPSV analysis, the current intensity of the signal of interest was found to be dependent upon the deposition potential ( $E$ ) between  $+0.15$  and  $-0.55 \text{ V}$ . As shown in Fig.7, the peak current increased to a potential of  $-0.15 \text{ V}$  and then started to decrease. The optimal value of  $-0.15 \text{ V}$  was chosen for deposition potential. Another optimized parameter was the deposition time ( $t$ ). Figure 7B shows that the signal has increased with the prolongation of the deposition time to 300 s. As the optimum, a period of 80 s was selected to achieve down to the ppb level.

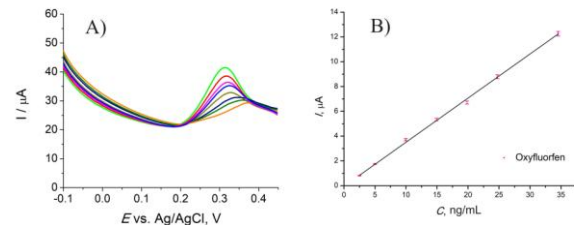


**Fig.6.** DPSV recorded at  $\text{MoO}_2$ @MWCNT/GCE for  $24.7 \text{ ng cm}^{-3}$  of oxyfluorfen in Britton-Robinson buffer

The quantitative DPSV determination of oxyfluorfen is based on the linear relationship between the peak current intensity at  $+0.3 \text{ V}$  and pesticide concentration. As it can be seen, it could be determined by DPSV in the concentration range from  $2.5$  to  $34.5 \text{ ng cm}^{-3}$ , with  $r = 0.99$  (Fig.8A) and the limit of detection (LOD) of  $1.5 \text{ ng cm}^{-3}$ , while the RSD did not exceed 2.4%. The RSD value indicates a relatively good precision of the developed method.



**Fig.7.** Key parameter optimized for DPSV of oxyfluorfen: A) Influence of deposition potential B) Effect of deposition time



**Fig.8.** DPSV recorded at the  $\text{MoO}_2$ @MWCNT/GCE for different concentrations of oxyfluorfen in B-R buffer (pH 6.0)

The interference of some common ions such as  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ag}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$  along with common pesticides such as clomazone, carbendazim, tebufenozide, and glyphosate have not influenced significantly the peak potential nor peak current intensity of the determined pesticides.

#### 4. Conclusions

In this study, decoration of MWCNTs with nanoparticles of elemental platinum and molybdenum oxide of various dimension ranges was proved as important factor in enhancing electrochemical/sensing response of GC electrode. The obtained nanohybrid materials possess a favorable morphology with fast electron-transport throughout MWCNT network which enables advantageous electrocatalytic behavior in clomazone and oxyfluorfen detection in water solutions. DPSV have shown to be fairly efficient technique for rapid and sensitive determination of these pesticides, especially in comparison to robust HPLC technique. DPSV attained relatively low limits of detection and quantification which in comparison to concurrent HPLC method leads to conclusion that DPSV can be acknowledged as handy and fast alternative for pesticide determination especially for on-site applications.

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