# PYROPHYLLITE-MODIFIED CARBON PASTE ELECTRODE FOR CARBENDAZIM DETECTION IN WATER AND FOOD

# Jasmina Grbović Novaković, Anđela Mitrović Rajić, Katarina Tošić, Sara Mijaković, Sanja Milošević Govedarević, Ana Vujačić Nikezić, Bojana Paskaš Mamula

Centre of Excellence for Hydrogen and Renewable Energy, "Vinča" Institute of Nuclear Sciences, National Institute of Republic of Serbia Belgrade, Serbia

# Jasmina Kustura, Enita Kurtanović, Belma Halilhodžić

Innovation Science Development Center (INRC), AD Harbi Ltd Sarajevo, B&H

Keywords: pyrophyllite Parsovići, carbon paste electrode, electrochemical sensor

# ABSTRACT

The work aims to design a pyrophyllite-modified carbon paste electrode for pesticide detection in aqueous solutions. The structural and morphological characterization of natural pyrophyllite clay for Parsovići mine, Bosnia and Herzegovina, and mechanically modified pyrophyllite was performed using X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and particle size analysis (PSD). The electrochemical characteristics of the constructed electrode were investigated using cyclic voltammetry in 1 mM  $K_4Fe(CN)_6$  in 0.1 M KCl and 0.5 M  $H_2SO_4$  and differential pulse stripping voltammetry in Britton-Robinson buffer at pH 2-8. It was shown that the maximum at + 0.96 V versus Ag/AgCl originates from oxidation by carbendazim at pH 4 in the Britton-Robinson buffer. The electrode designed in this way showed numerous advantages such as good stability and sensitivity. The developed analytical method is linear over the range of 1 ppm to 10 ppm with r=0.999 and a detection limit of 0.3 ppm.

# **1. INTRODUCTION**

The crystal lattice of 2:1 phyllosilicate mineral pyrophyllite consists of an octahedral sheet of AlO<sub>4</sub>(OH)<sub>2</sub> located between two SiO<sub>4</sub> tetrahedral layers. The bonds between layers are weak van der Walls [1-8], so the layers can easily slide over each other. Pyrophyllite can be used in porcelain, building materials, fire-resistant material, insecticide, textiles, detergents, cosmetics, and as the filler for rubberizing, papermaking, painting, etc. [2,9-15]. Different applications of pyrophyllite starting from various types of ceramics including refractories, enamels, and ceramics membranes [9,10,1,17] to heavy metal and organic pollutant adsorbents [16-20] require different modifications methods [1-22]:

- 1. ion exchange with inorganic and organic cations and cationic complexes;
- 2. reaction with acids;
- 3. pillaring by different types of poly- (hydroxo metal) cation;
- 4. dehydroxylation and calcination, delamination and reaggregation of clay minerals;

One of the possible methods of modification is mechanochemical activation (MCA). MCA is an environmentally friendly green chemistry method that introduces structural disorder, reduces particle size, and increases of chemical reactivity of material [21-23]. It has been shown that in contrast to the high chemical stability of pyrophyllite, mechanochemically

activated pyrophyllite and its ores result in noteworthy structural distortion and reduction of particles and crystallite size [1-5,7,8,18,11,21,24-28]. Therefore in this work, we suggest the use of MCA as a modification technique for pyrophyllite as functionalized material for modified carbon paste electrode (CPE). CPEs are extensively used in the field of electrochemical sensors due to the low cost of materials, simple sample preparation, low background current, and wide potential window [29]. CPEs are a mixture of graphite (carbon) materials, a binder (paraffin oil, silicone oil, or tricresylphosphate), and some functionalization materials. Clay-based electrochemical sensors are used for qualitative and quantitative analysis of various gases and components in aqueous solutions [30-36]. Previous research has been done on clays such as sepiolite, serpentinite, kaolinite, haloysite, montmorillonite [31-36].

According to our best knowledge, there are no scientific studies related to the application of CPE based on mechanically modified pyrophyllite in electroanalytical practice. Therefore, we propose using pyrophyllite as the electrochemical active substance in CPEs as a working electrode for detecting the carbendazim pesticide. Determination of pesticide traces in food and water is of extreme interest since pesticides are highly toxic chemicals with pronounced carcinogenicity and endocrine-disrupting effects.

#### 2. EXPERIMENTAL PART

X-ray diffraction has been used to determine the phase composition of samples using Rigaku Ultima IV, Japan). Crystallite size and lattice strain are calculated using XRD profile analysis using the Williamson-Hall plot according to Eq. (1) [37]:

$$\beta\cos(\theta) = 2\varepsilon\sin(\theta) + \frac{0.9\lambda}{D}$$
(1)

where k = 0.9 is the shape factor and  $\beta$  is the corrected peak full width at half maximum (FWHM) [33]

The  $\beta \cos(\theta)$  is plotted as a function of  $\sin(\theta)$ , and a straight line is derived using the least squares method with an intercept at 0.9  $\lambda$ /D and a slope of 2 $\epsilon$ . Both crystallite size D and lattice strain  $\epsilon$  are calculated from equation (1). The qualitative analysis of samples was performed on Thermo Scientific Nicolet iS10 Spectrometer using attenuated total reflectance (ATR) sampling technique. The surface modifications, the phase distribution of the MCA-activated clays, material homogeneity, and morphology of the powder particles were investigated by scanning electron microscopy (SEM) using model JOEL JSM6610LV, manufacturer JOEL, USA) equipped with EDS spectrometer model BLACK-Comet CXR-SR-50, manufacturer StellarNet Inc.). A Malvern 2000SM Mastersizer laser scattering particle size analysis system has been used to obtain quantitative clay particle size distributions. The Ag/AgCl electrode (saturated with KCl) was used as a reference electrode, the platinum wire was used as an auxiliary electrode, and different types of pyrophyllite-modified CPE with paraffin oil were used as the working electrodes. Voltametric analyses were done on Gamry potentiostat Interface 1010E.

#### 3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of pyrophyllite ore (P-0) from the Parsovići mine (Bosnia and Herzegovina). The ore contain pyrophyllite, quartz, kaolinite, calcite, and muscovite. Two major phases are pyrophyllite with characteristic reflections at  $2\theta$  9.68 and 29.23 and quartz at  $2\theta$  20.94 and 26.74 [11]. Mechanical modification causes a noticeable increase in the crystallite size of both quartz and pyrophyllite, thus indicating the presence of residual stress in the crystal lattice as shown in Figure 2. After 15 minutes of mechanical milling microstrain and crystallite size decreases.



Figure 1. XRD patterns of pyrophyllite ore from the Parsovići mine, Bosnia and Herzegovina



Figure 2. Microstrain and crystallite size of pyrophyllite samples milled from 0 to 15 minutes

Figure 3. Changes in geometric-specific surface area and particle size during mechanical milling

FTIR spectra are shown in Figure 4. The unmilled sample (P-0) showed a strong band at 3672 cm<sup>-1</sup> which can be assigned to OH vibration from Al-OH linkage [11]. At 1120 cm<sup>-1</sup>, a strong band is observed that can be attributed to Si-O stretching vibration. The bands at 832 cm<sup>-1</sup> and 943 cm<sup>-1</sup> correspond to Al-OH bending vibration. The peak at 518 cm<sup>-1</sup> can be assigned to Si-O-Si bending vibration. The vibration at 1616 cm<sup>-1</sup> corresponds to bending the OH surface group [11]). The band at 802 cm<sup>-1</sup> corresponds to the characteristic bands of silica [38]. The band at 754 cm<sup>-1</sup> indicates the presence of Si–O–Al where Al is in tetrahedral coordination. It also indicates that there is a possible presence of sericite/muscovite minerals. The peak at 532 cm<sup>-1</sup> can be assigned to octahedral AlO<sub>6</sub> sheet vibrations. The band at 1028 cm<sup>-1</sup> can be assigned to the intense Si-O and Si-O-Al stretching vibrations, characteristic of aluminosilicates [9]. The band at 450 cm<sup>-1</sup> corresponds to the bending of Si – O groups [39]. After 5 minutes of grinding, the bands at 779 cm<sup>-1</sup> and 797 cm<sup>-1</sup> appear indicating the presence of quartz [21] and thus confirming the results of XRD analysis. These vibrations are present even after 120 minutes of grinding, indicating that quartz has a more stable structure than pyrophyllite [7]. After 15 minutes of grinding, the vibration at 1120 cm<sup>-1</sup> disappears indicating a breakdown of the Si-O band, which means that the tetrahedral sheets have been destroyed. Also, after 60 minutes of milling, the bands at 3673 cm<sup>-1</sup>, 943 cm<sup>-1</sup>, and 832 cm<sup>-1</sup> disappeared, as a result of the release of OH groups from the Al-centered octahedrons. Therefore, the octahedral sheets are damaged [11]. The intensity of the band at 518 cm<sup>-1</sup> decreases with increasing milling time as a consequence of the collapse of the Si-O-Al band, resulting in a broken link between the tetrahedral and octahedral sheets [11].

The differential pulse stripping voltammetry was used for the quantitative determination of carbendazim. Based on the previous results [40,41], an electrode with a composition of 50P:50C was chosen as the working electrode, where pyrophyllite was mechanochemically activated for a period of 15 minutes. Changes were monitored at pH 4 and 8.



Figure 4. FTIR of pure and milled material from 0 to 15 minutes, P-O (O min), P-5 (5 min), P-10 (10 min), P-20 (20 min)

Figure 5 shows differential pulse voltammograms for the determination of carbendazim in Britton-Robinson buffer at pH 4. (lower) and pH 8 (higher). The maximum occurs at + 0.96 V and 0.73 respectively. The maximum intensity increases with increasing concentration of carbendazim [42]. The peak at around 0.5 V corresponds to the hydrogen evolution reaction.

From peak maxima, we have obtained the calibration curves for carbendazim detection with excellent linearity. The slope and intercept at pH 8 have the following values 0.40 and 8.85, while at pH 4 are 0.31 and 9.22.

The results show that the sensor constructed in this way, carbon paste modified with pyrophyllite where paraffin oil was used as the binding liquid, in Britton-Robinson buffer shows excellent sensitivity and a low detection limit in the range from 1 ppm to 10 pm. Kalijadis et al. used the method of differential pulse stripping voltammetry for qualitative and quantitative detection of carbendazim, where a carbon paste electrode obtained with nitrogen was used as the working electrode, while tricresyl phosphate was used as the binding liquid [43]. Ashrafi et al. investigated a carbon paste electrode with tricresyl phosphate as a binding fluid for the detection of carbendazim [44]. The influence of pH in

the Britton-Robinson buffer on pH in the range from 2 to 8 was also investigated. The maximum oxidation of carbendazim was most intense at pH 4.



Figure 5. Differential pulse voltammograms for the determination of carbendazim in Britton-Robinson buffer at pH 4 (lower) and pH 8 (higher)



Figure 6. Calibration curve obtained for a pyrophyllite-modified carbon paste electrode with paraffin oil as a binding fluid for the detection of carbendazim in Britton-Robinson buffer at pH 4 and pH 8 in the concentration range from 1 ppm to 10 ppm

The influence of the presence of 2-hydroxypropyl- $\beta$ -cyclodextrin on the electrochemical behavior of carbendazim was also investigated. The detection was followed by the method of differential pulse adsorptive "striping" voltammetry. It was found that the analytical performance of the tricresyl phosphate carbon paste electrode could be improved almost

two-fold by the addition of the 2-hydroxypropyl- $\beta$ -cyclodextrin modifier. Guo and coworkers (Guo et al.) used cyclodextrin-graphene hybrid nanosheets as a material for the electrochemical detection of carbendazim [45]. The effect of pH was investigated in the range of 5 to 10 in 0.1 M phosphate buffer. At pH 7, the maximum oxidation by carbendazim was the most intense, so the measurements were performed at this pH value. Differential pulse voltammetry was used for carbendazim detection. The detection limit was 2.0·10–9 mol/L, and the relative standard deviation was 4.67%.

# 4. CONCLUSION

Mechanochemically activated pyrophyllite was used for the construction of electrochemical sensors. The microstructural and morphological characterization of the material was performed by X-ray structural analysis, scanning electron microscopy, and infrared spectroscopy with Fourier transform, and the particle size distribution was monitored by the laser diffraction method. The response of the sensor was obtained by differential pulse stripping voltammetry. Based on X-ray structural analysis, it was concluded that the mechanochemical modification leads to a change in the crystal structure of pyrophyllite. The particles change their morphology from lamellar to particles that do not have a characteristic shape already after 5 minutes of grinding while the specific surface area increases with the increase of milling time. Given that mechanical grinding causes the amorphization of soft phases of pyrophyllite ore, further insight into the structure of the material was provided by infrared spectroscopy with Fourier transform. It was shown that after 15 minutes of grinding the tetrahedral structure (SiO4 plate) collapses. Mechanochemically activated pyrophyllite was used to form a modified carbon paste electrode. This electrode is part of the pesticide detection sensor. The electrochemical properties of the obtained electrode were investigated by cyclic voltammetry and differential pulse stripping voltammetry. It was also shown that the reactions at the electrode are fast and reversible and that the electrode is stable. Differential pulse stripping voltammetry showed that this electrode can be used for qualitative and quantitative detection of carbendazim fungicides. The best results were obtained at pH 4, where the limit of detection was 0.3 ppm, the limit of quantification was 1.03 ppm, and the residual standard deviation was 2.3 %.

# 5. ACKNOWLEDGMENT

This work is supported by the Ministry of Science, Technology, and Innovation of The Republic of Serbia under Grant 451-03-68/2022/14/200017.

We thank AD Harbi Ltd for the assignment of mineral raw materials for research purposes.

# 6. REFERENCES

- [1] H. Hayashi, K. Koshi, A. Hamada, H. Sakabe, Structural change of pyrophyllite by grinding, and its effect on the toxicity of the cell. *Clay Science 1*(5) (1962), 99-108
- [2] S. Mohammadnejad, J. L. Provis, J. S. J. van Deventer, Effects of grinding on the preg-robbing behavior of pyrophyllite, *Hydrometallurgy*, 146 (2014), 154–163
- [3] J. L. Pérez-Rodríguez, L. Madrid Sánchez del Villar, P. J. Sánchez-Soto, Effects of dry grinding on pyrophyllite, *Clay Minerals 23* (1988), 399–410
- [4] P. J. Sánchez-Soto, A. Justo, J. L. Pérez-Rodríguez, Grinding effect on kaolinite-pyrophylliteillite natural mixtures and its influence on mullite formation, *Journal of Materials Science 29(5)* (1994), 1276–1283

- [5] J. M. Filio, K. Sugiyama, F. Saito, Y. Waseda, Effect of Dry milling on the Structures and Physical Properties of Pyrophyllite and Talc by a Planetary Ball Mill, *International Journal of* the Society of Materials Engineering for Resources 1(1) (1993), 140-147
- [6] H. Sayılkan, S. Erdemoğlu, Ş. Şener, F. Sayılkan, M. Akarsu, M. Erdemoğlu, Surface modification of pyrophyllite with amino silane coupling agent for the removal of 4-nitrophenol from aqueous solutions, *Journal of Colloid and Interface Science* 275(2) (2004), 530–538
- [7] J. Temuujin, K. Okada, T.S. Jadambaa, K.J.D. MacKenzie, J. Amarsanaa, Effect of grinding on the leaching behaviour of pyrophyllite, *Journal of the European Ceramic Society 23(8)* (2003), 1277–1282
- [8] J. L. Pérez-Rodríguez, A. Wiewiora, V. Ramirez-Valle, A. Durán, L. A. Pérez-Maqueda, Preparation of nano-pyrophyllite: Comparative study of sonication and grinding, *Journal of Physics and Chemistry of Solids* 68(5-6) (2007), 1225–1229
- [9] T. K. Mukhopadhyay, S. Ghatak, H. S. Maiti, Pyrophyllite as raw material for ceramic applications in the perspective of its pyro-chemical properties, *Ceramics International 36(3)* (2010), 909–916
- [10] G. Li, J. Zeng, J. Luo, M. Liu, T. Jiang, G. Qiu, Thermal transformation of pyrophyllite and alkali dissolution behavior of silicon, *Applied Clay Science 99* (2014), 282–288
- [11] J. Zhang, J. Yan, J. Sheng, Dry milling effect on pyrophyllite–quartz natural mixture and its influence on the structural alternation of pyrophyllite, *Micron 71 (2015)*, 1–6
- [12] H. Heller, R. Keren, Anionic polyacrylamide polymer adsorption by pyrophyllite and montmorillonite, *Clays and Clay Minerals* 51(3) (2003), 334–339
- [13] A. Goswami, M. K. Purkait, Kinetic and Equilibrium Study for the Fluoride Adsorption using Pyrophyllite, *Separation Science and Technology* 46(11) (2011), 1797–1807
- [14] S. Saxena, M. Prasad, S. S. Amritphale, N. Chandra, Adsorption of cyanide from aqueous solutions at pyrophyllite surface, *Separation and Purification Technology 24(1-2)* (2001), 263– 270
- [15] Gücek, S. Şener, S. Bilgen, M. A. Mazmancı, Adsorption and kinetic studies of cationic and anionic dyes on pyrophyllite from aqueous solutions, *Journal of Colloid and Interface Science* 286(1) (2005), 53–60
- [16] Y. Jeong, S. Lee, S. Hong, C. Park, Preparation, characterization and application of low-cost pyrophyllite-alumina composite ceramic membranes for treating low-strength domestic wastewater, *Journal of Membrane Science* 536 (2017), 108–115
- [17] R. Ahmad, M. Aslam, E. Park, S. Chang, D. Kwon, J. Kim, Submerged low-cost pyrophyllite ceramic membrane filtration combined with GAC as fluidized particles for industrial wastewater treatment, *Chemosphere 206* (2018), 784–792
- [18] J. B. Dixon, D. G. Schulze, L. W Zelazny, P. J Thomas, C. L. Lawrence, Chapter 13-Pyrophyllite-Talc Minerals, in: J. B. Dixon, D. G. Schulze (Ed.) Soil Mineralogy with Environmental Applications, Soil Science Society of America, (2002), 415-430
- [19] X. Qin, J. Zhao, J. Wang, M. He, Atomic Structure, Electronic and Mechanical Properties of Pyrophyllite under Pressure: A First-Principles Study, *Minerals* 10(9) (2020), 778.
- [20] R. Wardle, G. W. Brindley, The crystal structures of pyrophyllite, 1Tc, and of its dehydroxylate, *American Mineralogist* 57 (1972), 732-750.
- [21] I. Tole, K. Habermehl-Cwirzen, A. Cwirzen, Mechanochemical activation of natural clay minerals: an alternative to produce sustainable cementitious binders – review, *Mineralogy and Petrology 133* (2019), 449-462
- [22] P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J. M. Criado, F. J. Gotor, Hallmarks of mechanochemistry: from nanoparticles to technology, *Chemical Society Reviews* 42(18) (2013), 7571–7637

- [23] T. K. Achar, A. Bose, P. Mal, Mechanochemical synthesis of small organic molecules, Beilstein Journal of organic chemistry 13(1) (2017), 1907-1931
- [24] J. L. Pérez-Rodriguez, P. J. Sánchez-Soto, The influence of the dry grinding on the thermal behaviour of pyrophyllite, *Journal of Thermal Analysis 37(7)* (1991), 1401–1413
- [25] K. Sugiyama, J. M. Filio, F. Saito, Y. Waseda, Structural change of kaolinite and pyrophyllite induced by dry grinding, *Mineralogical Journal 17(1)* (1994), 28–41
- [26] P. J. Sánchez-Soto, J. L. Pérez-Rodríguez, I. Sobrados, J. Sanz, Influence of grinding in pyrophyllite-mullite thermal transformation assessed by <sup>29</sup>Si and <sup>27</sup>Al MAS NMR Spectroscopies, *Chemistry of Materials 9(3)* (1997), 677–684
- [27] P. J. Sánchez-Soto, M. d. C. Jiménez de Haro, L. A. Pérez-Maqueda, I. Varona, J. L. Pérez Rodríguez, Effects of dry grinding on the structural changes of kaolinite powders, *Journal of American Ceramic Society* 83(7) (2000), 1649–1657
- [28] A. Wiewióra, P. J. Sánchez-Soto, M. A. Avilés, A. Justo, J. L. Pérez-Rodríguez, Effect of dry milling and leaching on polytypic structure of pyrophyllite, *Applied Clay Science 8(4)* (1993), 261–282
- [29] I. Švancara, K. Kalcher, A. Walcarius, K. Vytřas, Electroanalysis with Carbon Paste Electrodes, CRS Press: Boca Raton, FL, 2012
- [30] U. Guth, S. Brosda, J. Schomburg, Applications of clay minerals in sensor techniques, *Applied Clay Science 11(2-4)* (1996), 229–236
- [31] M. Pekin, D. E. Bayraktepe, Z. Yazan, Electrochemical sensor based on a sepiolite clay nanoparticle-based electrochemical sensor for ascorbic acid detection in real-life samples, *Ionics 23(12)* (2017), 3487–3495
- [32] M. Z. Momčilović, M. S. Ranđelović, M. M. Purenović, J. S. Đorđević, A. Onjia, B. Matović, Morpho-structural, adsorption and electrochemical characteristics of serpentinite, *Separation* and Purification Technology 163 (2016), 72–78
- [33] S. P. Akanji, O. A. Arotiba, D. Nkosi, Voltammetric Determination of Pb(ii) Ions at a Modified Kaolinite-Carbon Paste Electrode, *Electrocatalysis 10(6)* (2019), 1–10
- [34] E. S. Goda, M. A Gab-Allah, B. S. Singu, K. R. Yoon, Halloysite nanotubes based electrochemical sensors: A review, *Microchemical Journal* 147 (2019), 1083-1096
- [35] B. J. Sanghavi, G. Hirsch, S. P. Karna, A. K. Srivastava, Potentiometric Stripping Analysis of Methyl and Ethyl Parathion Employing Carbon Nanoparticles and Halloysite Nanoclay Modified Carbon Paste Electrode, *Analytica Chimica Acta* 735 (2012), 37–45
- [36] P. Kula, Z. Navrátilová, P. Kulová, M. Kotoucek, Sorption and determination of Hg(II) on clay modified carbon paste electrodes, *Analytica Chimica Acta 385(1-3)* (1999), 91-101
- [37] G. K. Williamson, W. H. Hall, X-ray Line Broadening from Filed Aluminium and Wolfram, *Acta Metallurgica et Materialia 1(1)* (1953), 22-31
- [38] S. S. Amritphale, S. Bhasin, N. Chandra, Energy efficient process for making pyrophyllitebased ceramic tiles using phosphoric acid and mineralizers, *Ceramics International 32(2)* (2006), 181–187
- [39] M. Erdemoğlu, S. Erdemoğlu, F. Sayılkan, M. Akarsu, Ş. Şener, H.S Ayılkan, Organofunctional modified pyrophyllite: preparation, characterization and Pb(II) ion adsorption property, *Applied Clay Science* 27(1-2) (2004), 41–52
- [40] A. Mitrović, T. Pantić, S. Dimitrijević, A. Ivanović, N. Novaković, S. Kurko, S. Milošević Govedarović, J. Grbović Novaković, Electrochemical sensors based on pyrophyllite – Parsovic, MCM2019, 14th Multinational Congress on Microscopy, September 15-20, 2019, Belgrade, Serbia, Program and the book of abstracts. 494-497.
- [41] J. Milićević, S. Kurko, B. Paskaš Mamula, T. Trtić-Petrović, T. Pantić, S. Milošević Govedarević, A. Hođžić, J. Grbović Novaković, Electrochemical behaviour of pyrophyllite

carbon paste composite electrode, 3rd International Symposium on Materials for Energy Storage and Conversion, September 10-12th, 2018, Belgrade, Serbia, P 14, Program and the book of abstracts, 95

- [42] A. I. Mitrović Rajić, J. S. Milićević, J. D. Grbović Novaković. Development of modified pyrophyllite carbon paste electrode for carbendazim detection, *Materials and Manufacturing Processes* (2022), 1-7
- [43] A. Kalijadis, J. Djorđević, Z. Papp, B. Jokić, V. Spasojević, B. Babić, T. Trtić-Petrović, A novel carbon paste electrode based on nitrogen-doped hydrothermal carbon for electrochemical determination of carbendazim", Journal of Serbian. Chemical Society, 82 (11) (2017), 1259– 1272
- [44] A. M. Ashraf, J. Đorđević, V. Guzsvány, I. Švancara, T. Trtić-Petrović, M. Purenović, K. Vitřas, Trace determination of carbendazim fungicide using adsorptive stripping voltammetry with a carbon paste electrode containing tricresyl phosphate, *International Journal of Electrochemical Science* 7(10) (2012), 9717-9731
- [45] Y. S. Guo, S. Guo, J. Li, E. Wang, S. Dong, Cyclodextrin-graphene hybrid nanosheets as enhanced sensing platform for ultrasensitive determination of carbendazim, *Talanta 84(1)* (2011), 60–64.