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

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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 $AlO_4(OH)_2$ located between two SiO_4 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]:

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

where k = 0.9 is the shape factor and β 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 λ/D and a slope of 2ε. Both crystallite size D and lattice strain ε 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 2θ 9.68 and 29.23 and quartz at 2θ 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.

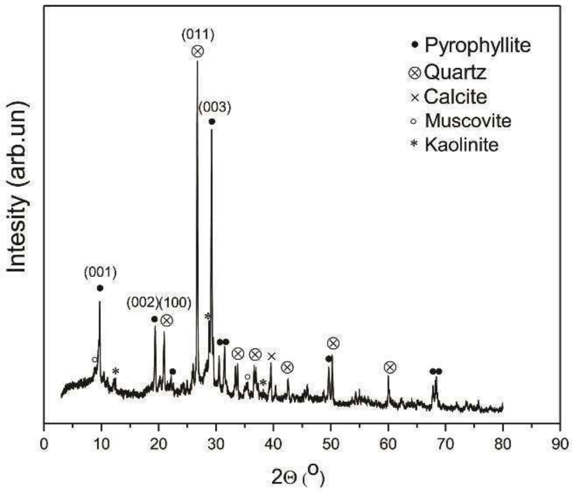

Figure 1. XRD patterns of pyrophyllite ore from the Parsovići mine, Bosnia and Herzegovina

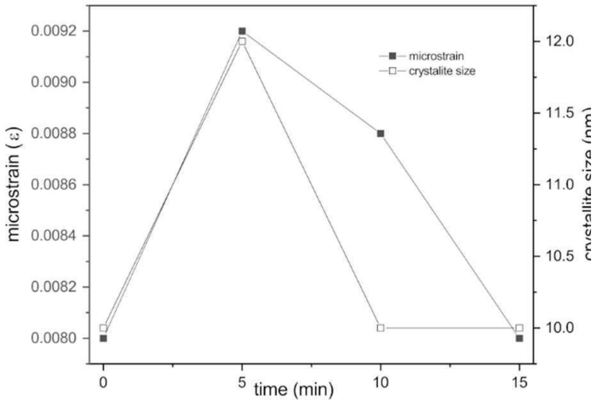

Figure 2. Microstrain and crystallite size of pyrophyllite samples milled from 0 to 15 minutes

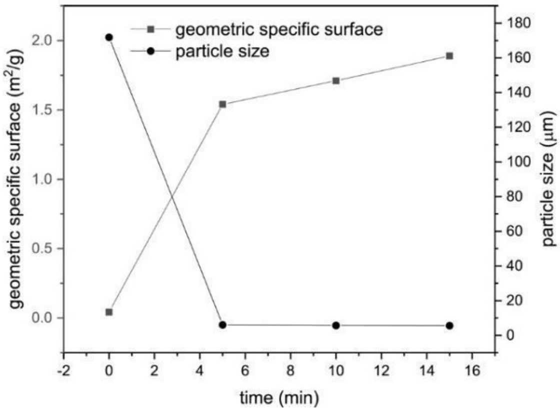

Figure 3. Changes in geometric-specific surface area and particle size during mechanical milling

FTIR spectra are shown in Figure 4. The unmilled sample (P-0) showed a strong band at 3672 cm^{-1} which can be assigned to OH vibration from Al-OH linkage [11]. At 1120 cm^{-1}, a strong band is observed that can be attributed to Si-O stretching vibration. The bands at 832 cm^{-1} and 943 cm^{-1} correspond to Al-OH bending vibration. The peak at 518 cm^{-1} can be assigned to Si-O-Si bending vibration. The vibration at 1616 cm^{-1} corresponds to bending the OH surface group [11]). The band at 802 cm^{-1} corresponds to the characteristic bands of silica [38]. The band at 754 cm^{-1} 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^{-1} can be assigned to octahedral AlO_6 sheet vibrations. The band at 1028 cm^{-1} can be assigned to the intense Si–O and Si–O–Al stretching vibrations, characteristic of aluminosilicates [9]. The band at 450 cm^{-1} corresponds to the bending of Si – O groups [39]. After 5 minutes of grinding, the bands at 779 cm^{-1} and 797 cm^{-1} 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^{-1} 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^{-1}, 943 $cm^{-1,}$ and 832 cm^{-1} 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^{-1} 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.

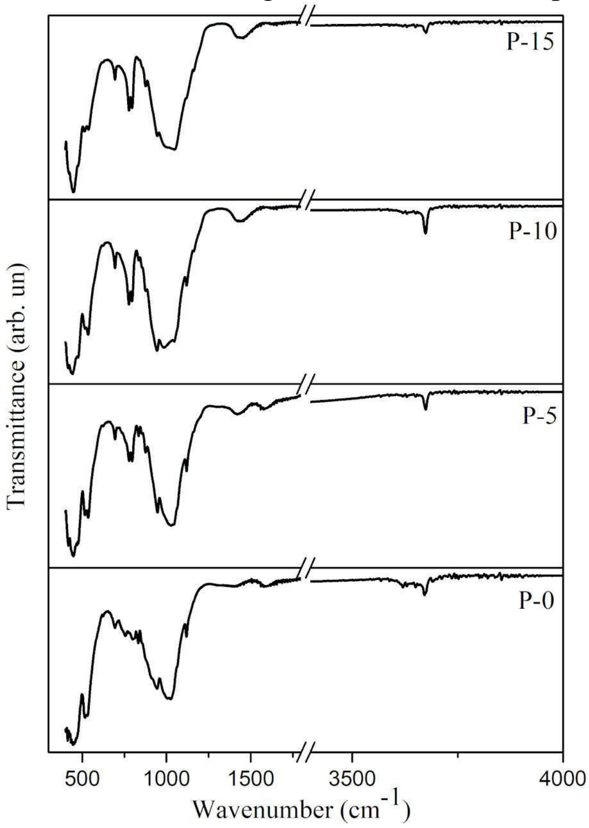

Figure 4. FTIR of pure and milled material from 0 to 15 minutes, P-O (O min), P-5 (5 min), P-10 (10 min), P-20 (20 min)

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.

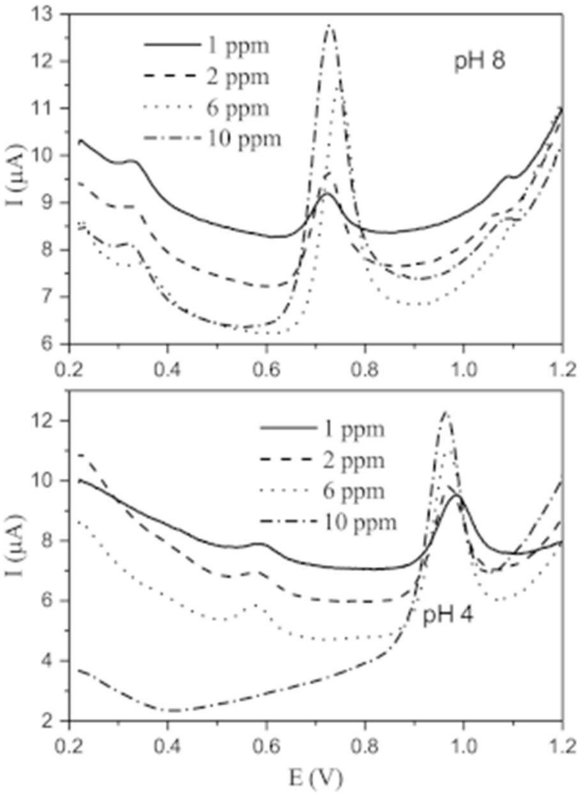

Figure 5. Differential pulse voltammograms for the determination of carbendazim in Britton-Robinson buffer at pH 4 (lower) and pH 8 (higher)

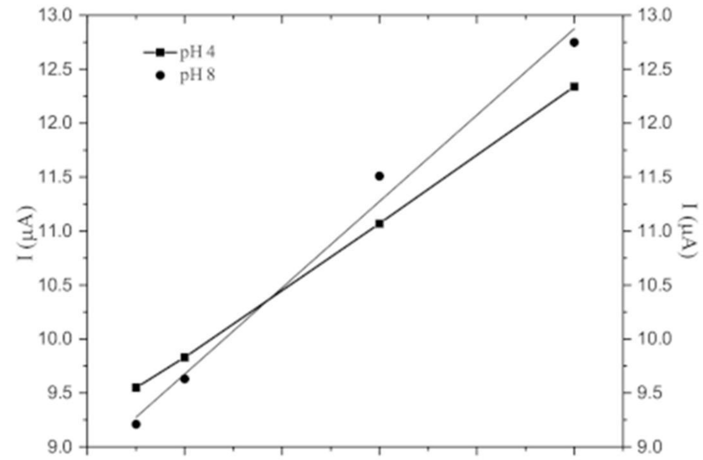

Figure 6. Calibration curve obtained for a pyrophyllite-modified carbon paste electrode with paraffin oil as a binding fluid for the detection of carbendazim in Britton-Robinson buffer at pH 4 and pH 8 in the concentration range from 1 ppm to 10 ppm

The influence of the presence of 2-hydroxypropyl-β-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-β-cyclodextrin modifier. Guo and co-workers (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 $2.0 \cdot 10^{-9}$ 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 (SiO_4 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

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