

Halloysite as a Carbon Paste Electrode Modifier for the Detection of Phenol Compounds

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Various modification methods of halloysite and their applications as modifiers of carbon paste electrodes (CPEs) have been presented. CPEs were modified by the addition of different halloysite materials and were prepared for detection of phenol (Ph) and 4-chlorophenol (4-CP). The electrochemical behavior of these materials was investigated employing cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The modifier was found to enhance the electroactive surface area and the peak current in comparison to the bare carbon paste electrodes. The range of observed changes of these parameters significantly depends on method chosen for halloysite modification.

Keywords: Halloysite, Organic modifiers, Carbon paste electrodes, Voltammetry, Phenol compounds

1. INTRODUCTION

As a natural clay mineral, halloysite contains a gibbsite octahedral sheet ($\text{Al}(\text{OH})_3$) and is modified by siloxane groups at the outer surface, consisting in c.a. 30% of hollow cylinders formed by multiple rolled layers. The mineral appears in two different polymorphs: the hydrated form ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) and the anhydrous form ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) [1,2]. What is characterized by is its uncommon and immense amount of pores as well as its large surface area. Furthermore, it transfers ion well and is sensitive to both mechanical and chemical processes. Additionally, due to its crystallite structure, of which about 30% constitutes of rigid straight nanotubes which are placed between layers, it has application as a strengthening nanofiller. Halloysite is mainly used as a nanocontainer for the controlled release of several chemicals. In contrast to kaolin and montmorillonite, it has distinct advantages. The most characteristic feature of halloysite is its inner lumen which has a property to entrap chemical agents such as macromolecules, drugs, DNA, proteins and other chemically active agents [3]. Halloysite-based nanocomposites have been commonly used for catalytic, antibacterial,

electrical, optical and magnetic applications due to their physicochemical properties, hydrophobicity, ion exchange capability, and their tubular structures.

Halloysites which appear in Poland could be altered for applications in the form of active fillers. The implementation of proper modification procedures (ultrasound and chemical) allows to modified its usage in a broad scope of polymers [4-6].

The initial phase of the process includes ultrasounds usage in order to create vacancies of the crystallographic structure. It was predicted that these defects would constitute active places to which would be joined modifying compound. Thanks to this process, one can obtain a filler characterized by organic/inorganic layers. The hybrid structure of the halloysite will ensure better dispersion of this additive in polymers as well as improvement of interactions between the phases [7]. The selection of modified compound was made on the basis of probably active interactions between polymers and hybrid nanofillers [8,9].

Halloysite has also been used for other purposes e.g. in electroanalysis as a modifier of carbon paste electrodes [10,11]. Different methods were used for the determination of organochlorine compounds in water samples. Analytical techniques such as spectrophotometry [12-14], chromatography [15,16] and mass spectrometry [17,18] as well as electrochemical techniques [19-21], which offer a reliable, fast and simple method of analysis without complicated sample preparation procedures, were applied. Due to low cost, low residual current, speed of obtaining a new reproducible surface and possibilities of miniaturization carbon paste electrodes have received great attention in electrochemical studies. Moreover, they are easily prepared and modified by adding the modifier directly to a carbon paste electrode during the paste preparation [10]. Among others, halloysite has also been used as a modifier of carbon-based paste electrodes [11,22].

2. EXPERIMENTAL

2.1. Reagents and materials

The phenol (Ph), 4-chlorophenol (4-CP), glycidyl metacrylate, urea, gelatin and graphite used were from Sigma-Aldrich (St. Louis, USA). The stock standard solutions of Ph and 4-CP (0.5 mmol L^{-1}) were prepared in 0.1 mol L^{-1} sodium sulfate. The working solutions were prepared by dilution with Na_2SO_4 of the appropriate concentration.

2.2. Modification process of halloysite

The preliminary treatment of halloysite using ultrasound of frequency 35 kHz for 2-3 h in an ultrasound bath IS-7S (Intersonic S.A.). The quantity of modifying compound implemented in the process was taken through numerous preliminary experiments. Modified halloysite materials were obtained by mixing an organic compound with halloysite at room temperature in a solvent by using a magnetic stirrer. The modified halloysite was purified of unreacted substances. The names of hybrid modifiers are shown in Table 1.

Table 1. The symbol of modified halloysite materials and used modifying compounds.

Name	The modifying compound/method	The weight ratio of halloysite/modifying compound
H	-	-
HU	ultrasounds	-
HUGMA	glycydyl metacrylate	1 : 0.15
HUU	urea	1 : 0.05
HUG	gelatin	1 : 0.20

2.3. Instrumentation

The Brunauer-Emmett-Teller (BET) surface areas of the halloysite materials were measured by low temperature nitrogen adsorption using a TriStar II 3020 V1.03 (Micrometrics Company). Measurements of their surface chemical compositions were carried out using the JSM – 6490LV JEOL Company scanning microscope coupled with an energy dispersive X-ray spectrometer (EDS).

All the voltammetric measurements were carried out with an AutoLab PGSTAT 20 (Eco Chemie) potentiostat controlled by GPES 4.9 software. In the three-electrode system that was used, a carbon paste electrode was the working electrode, a saturated calomel electrode was the reference electrode and the counter electrode was a platinum wire. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used in this study. All the DPV voltammograms were registered from 0 to +2.0 V at a sweep rate of 50 mV s⁻¹; the pulse height was 50 mV and width was 50 ms.

A Teflon holder with a hole at one end for filling the carbon paste served as the electrode body. Electrical contact was made with a stainless-steel rod through the center of the holder. Modified CPEs were prepared by thoroughly mixing 10% m/m of modifying compound (H, HU, HUG, HUM, HUGMA) and graphite powder with the subsequently addition of mineral oil. All ingredients were placed in an agate mortar, crushed with a pestle and the mixture was kept at room temperature for 3 days. The prepared paste was then packed into the hole of the electrode body and the carbon paste was smoothed onto a paper until it had a shiny appearance.

3. RESULTS AND DISCUSSION

3.1. Characteristic of modifiers

Initially, the structure and composition of the surface of the halloysite before and after modification were measured by scanning electron microscopy and energy-dispersive X-ray spectroscopy. The SEM images (Fig. 1) connected with EDS microanalysis of the modified halloysite materials expose the modification results. Both particles of these materials glued together as well as separated plates/nanotubes can be observed on the SEM image.

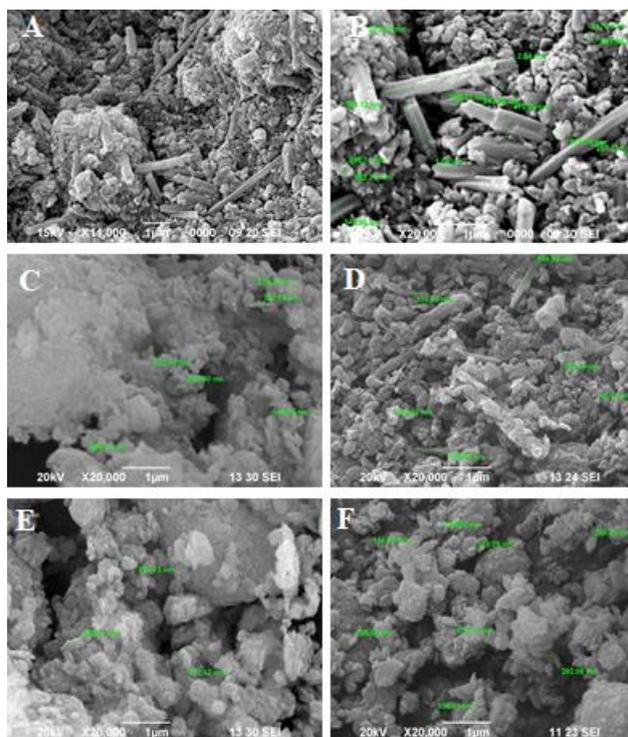


Figure 1. The SEM images of the halloysite (A, B), HU (C), HUGMA (D), HUU (E) and HUG (F)

The results of the EDS analysis of halloysite and halloysite modified by organic compounds are shown in Table 2.

Table 2. The EDS analysis results of halloysite materials.

Modified halloysite	Element content (wt.%)					
	O	Al	Si	Fe	C	N
H	63.57	16.05	18.46	1.92	-	-
HU	65.57	17.05	15.03	2.35	-	-
HUGMA	37.70	12.61	16.68	0.72	31.41	-
HUU	31.68	17.61	14.68	0.60	33.42	2.01
HUG	35.68	11.61	12.68	0.60	34.42	5.01

The SEM-EDS analysis shows O, Al, Si, Fe for all halloysite materials; carbon for HUGMA, HUU, HUG and; nitrogen for HUU and HUG. Organic/nonorganic structure of halloysite was confirmed thanks to the presence of carbon in EDS spectrum of halloysite after the modification process.

The Brunauer–Emmett–Teller (BET) specific surface areas and pore volumes of halloysite materials are presented in Table 3.

Table 3. Surface area, pore volume, pore size and particle size of the halloysite materials.

Halloysite materials	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Particle size (nm)
H	61	0.18	11.22	93
HU	78	0.22	11.17	77
HUGMA	46	0,18	15.24	130
HUU	47	0.17	14.53	128
HUG	44	0.19	16.82	134

The BET surface area decreased significantly in the case of the halloysite modified by organic compounds, which is consistent with the adsorption capacity of the tested samples. The particle size increased depending on the type of organic compound applied to the modification. According to the International Union of Pure and Applied Chemistry (IUPAC), pores are classified into three types: macropores (≥ 50 nm), mesopores (2-50 nm) and micropores (≤ 2 nm) [10]. Therefore, for all halloysite materials, it would be appropriate to classify the pore size in the range of 2 nm to 50 nm, as mesopores.

3.2. Electrochemistry of phenol compounds

First of all, the electrochemical characterization of the carbon paste electrodes (containing 10% of modifier) was tested in order to estimate their active areas. These studies were performed using the well-characterized inner-sphere redox probe ferro-/ferricyanide (5 mmol L⁻¹) in 0.5 mol L⁻¹ KCl according to the procedure described elsewhere [23]. The results are presented in Fig. 2.

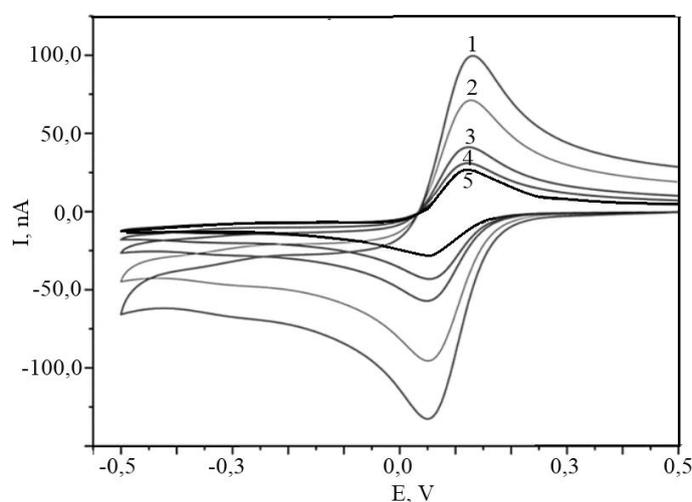


Figure 2. Cyclic voltammogram of 5 mmol L⁻¹ potassium ferrocyanide in 0.1 mol L⁻¹ KCl recorded on 1- CPE/HUG, 2- CPE/HUU, 3- CPE/HU, 4- CPE/H, 5- CPE/HUGMA.

The peak current for a reversible process is described by the Randles-Sevcik equation:

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

where: A represents the area of the electrode (cm^2), n is the number of electrons participating in the reaction (equal to 1), D is the diffusion coefficient of the molecule in solution, C is the concentration of the probe molecule in the solution and ν is the scan rate (V s^{-1}).

Based on the results presented in Fig. 2, the values of the active electrode areas were found to be 0.0613; 0.0466; 0.0215; 0.0166 and 0.0157 cm^2 for HUG, HUU, HU, H and HUGMA respectively.

The effect of the potential scan rates in the range 10-100 mV s^{-1} on the peak current for 0.5 mmol L^{-1} phenol as well as 4-chlorophenol solutions (in 0.1 mol L^{-1} Na_2SO_4) were evaluated for CPEs containing 10% of modifier is presented in Fig. 3. With an increase of the scan rate from 10 to 100 mV s^{-1} under the same experimental conditions, a linear relationship was observed between the peak current and square root of the scan rate with a correlation coefficient ($R^2 = 0.98$), demonstrating that the process is diffusion controlled. The electrochemical oxidation process was carried out using the CV technique.

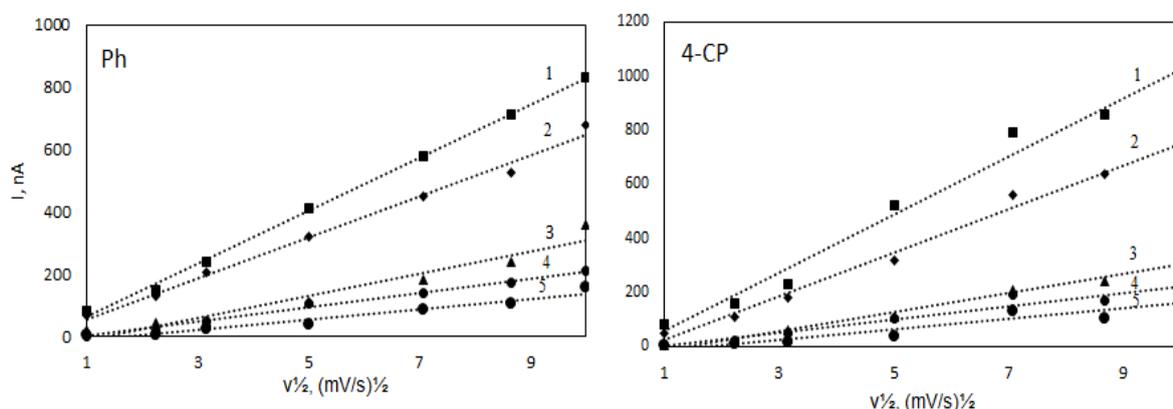


Figure 3. Plots of I_{pa} versus $\nu^{1/2}$ for the oxidation of phenol (a) and 4-CP (b) at carbon paste electrode modified: 1- CPE/HUG, 2- CPE/HUU, 3- CPE/HU, 4- CPE/H, 5- CPE/HUGMA.

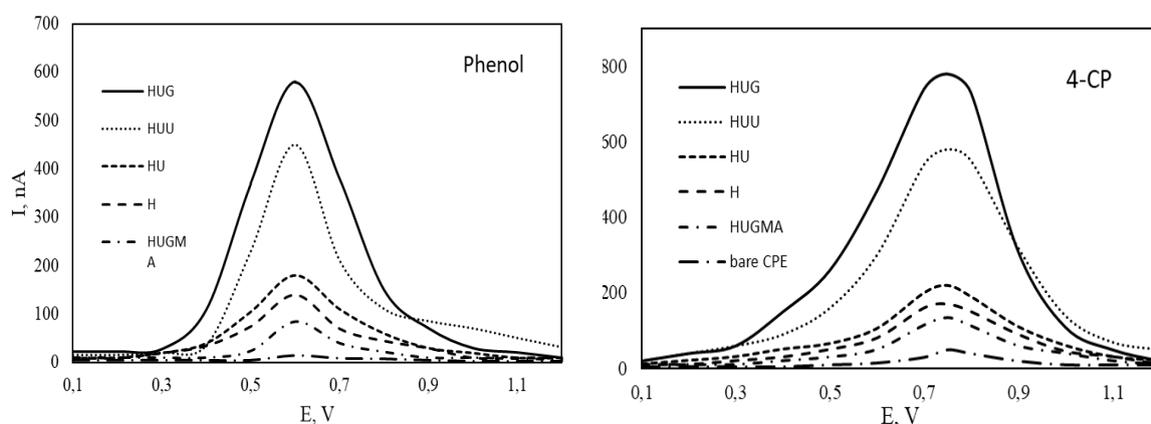


Figure 4. DPV registered for 0.5 mmol L^{-1} Ph and 4-CP solutions using carbon paste electrodes containing 10% by mass of tested materials. Modifiers: 1- CPE/HUG, 2- CPE/HUU, 3- CPE/HU, 4- CPE/H, 5- CPE/HUGMA, 6- bare CPE.

The differential pulse voltammograms registered for 0.5 mmol L⁻¹ solutions of phenol and 4-chlorophenol (in 0.1 mol L⁻¹ sodium sulfate) using carbon paste electrodes containing 10% by mass of tested materials are presented in Fig. 4.

From all of the DPV curves (Fig. 4) the peak currents and the peak potentials were determined and are presented in Table 4.

Table 4. Peak currents and potentials determined from DPV curves recorded in 0.5 mmol L⁻¹ Ph and 4-CP.

CPEs	Ph		4-CP	
	I (nA)	E (V)	I (nA)	E (V)
unmodified CPE	21	0.58±0.02	41	0.75±0.02
CPE/H	150	0.59±0.02	175	0.75±0.02
CPE/HU	175	0.57±0.02	205	0.77±0.02
CPE/HUGMA	85	0.59±0.02	124	0.74±0.02
CPE/HUU	462	0.58±0.02	580	0.75±0.02
CPE/HUG	595	0.59±0.02	810	0.75±0.02

The peak currents determined from the recorded DPV curves for Ph as well 4-CP solutions of various concentrations in the range 0.01-0.5 mmol L⁻¹ are presented in Fig. 5.

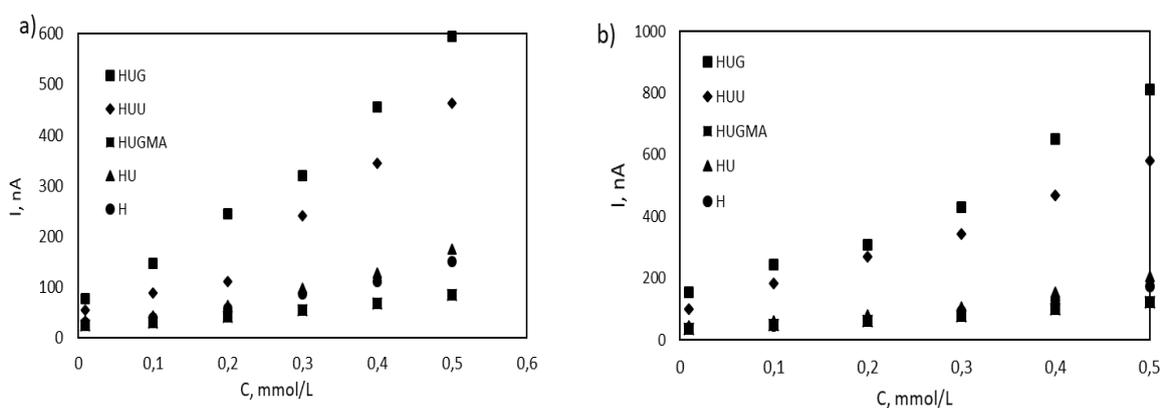


Figure 5. Dependence of peak current from DPV curves of modified CPEs (10% of modifiers content) on Ph (a) and 4-CP (b) solutions concentrations.

The order of peak currents for all the modified CPEs is the same for all applied Ph as well as 4-CP solution concentrations: CPE/HUG > CPE/HUU > CPE/HU > CPE/H > CPE/HUGMA. For all systems of modified CPE, in both solutions, an increase of peak current with an increasing solution concentration was observed.

The peak potentials reveal similar values for all Ph concentrations (~0.58 V) and for 4-CP solutions (~0.76 V). The recorded DPV curves show the dependence of the peak current on the kind of modifiers used. The observed signal for HUG as a CPE modifier (with a 10% content) in 0.5 mmol L⁻¹ phenol solution is about 30 times higher compared to an electrode containing only graphite (Table 4).

A similar relationship (about a 20 times higher peak current) was observed in the electroanalysis of 0.5 mmol L⁻¹ 4-CP using a CPE modified with the same material.

It can be observed that the increase in the peak current for halloysite materials as CPE modifiers HUGMA, H, HU follows the same order as their surface area values 46, 61 and 78 m² g⁻¹, respectively. A analogous dependence was observed in the case of activated carbon materials as CPE modifiers [24]. Increasing surface area caused the enhancement of peak currents for CPE in phenol as well as 4-chlorophenol solutions. The second important factor influencing the peak current of modified CPE was the nitrogen content on the surface of the modifier. For organic substances (deposited on the halloysite surface) of GMA, U and G with increasing nitrogen content in the order: 0, 2.01 and 5.01% wt, can be observed significantly increasing peak currents for the modified CPEs in the same order. A similar relation was observed earlier for SBA-15 silica with and without -NH₂ groups bonded to its surface when these materials are used as CPE modifiers [25].

The characteristics of the calibration plots (Fig. 5) are presented in Table 5. The limits of detection (LOD) were calculated from the calibration curves as $3\sigma/a$ where: a is a slope of the calibration curve and σ is a standard deviation of the blank signal. As can be seen, all of the calibration curves for phenol as well as 4-chlorophenol measurements were linear in the studied ranges (the squares of correlation coefficients were more than 0.98).

Table 5. Linearity results for the modified carbon paste electrode.

Analytical method	Linear regression equation $y = ax + b$	R^2	LOD [$\mu\text{mol L}^{-1}$]
Ph			
bare CPE	$y = 0.13x + 0.020$	0.997	76.6
CPE/H	$y = 0.29x - 0.001$	0.992	34.7
CPE/HU	$y = 0.36x - 0.003$	0.989	27.6
CPE/HUGMA	$y = 0.2x - 0.002$	0.987	39.6
CPE/HUU	$y = 1.00x - 0.038$	0.995	9.9
CPE/HUG	$y = 1.14x + 0.011$	0.991	8.07
4-CP			
bare CPE	$y = 0.16x - 0.004$	0.989	62.2
CPE/H	$y = 0.34x - 0.001$	0.992	29.3
CPE/HU	$y = 0.39x - 0.003$	0.993	24.9
CPE/HUGMA	$y = 0.29x + 0.004$	0.984	32.4
CPE/HUU	$y = 1.12x + 0.038$	0.995	8.89
CPE/HUG	$y = 1.52x + 0.028$	0.987	6.55

The best sensitivity was observed for the carbon paste electrode modified with HUG; the LOD was found to be 8.07 $\mu\text{mol/L}$ in the case of phenol and was over 9 times lower than for the bare electrode (Table 5). The same relationship was observed for the 4-CP solution. The best sensitivity was obtained with the carbon paste electrode modified HUG, while the worst modified with HUGMA.

Compared with other electrodes and electrochemical sensors (Table 6), the cheap and facile fabricated CPEs exhibited relatively good sensitivity. The sensitivity of these methods is comparable to, or slightly worse than those of electrochemical methods for 4-CP detection described by others authors.

Table 6. Comparison for the detection of 4-CP at different electrodes.

Electrode	LOD [$\mu\text{mol/L}$]	Reference
CPE/H	29.3	this study
CPE/HU	24.9	this study
CPE/HUGMA	32.4	this study
CPE/HUU	8.89	this study
CPE/HUG	6.55	this study
expanded graphite-epoxy electrode	20.0	[26]
GCE modified with horseradish peroxidase	15.2	[27]
CNT/Pt nanoparticles/rhodamine B modified GCE	3.70	[28]
SBA-15-NH ₂ modified CPE	1.40	[25]
MWCNT-Ni(OH) ₂ modified GCE	0.50	[29]

4. CONCLUSIONS

This paper describes the properties of CPEs modified by an addition of five different halloysite materials used for detection of phenol and 4-chlorophenol. Different parameters that affect DPV signal such as accumulation time and scan rate were investigated. The measured peak currents were strongly dependent on halloysite modification. Two properties of CPE modifiers played significant roles: their specific surface area and the nitrogen content in the organic substance deposited on the halloysite surface.

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