

## Phenol determination on HDTMA-bentonite-based electrodes

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### ABSTRACT

The partial and complete substitution of cations in the interlayer region of clay with different amounts of hexadecyl trimethylammonium bromide (HDTMABr) was performed. The aim was to synthesize organo-bentonites to be used as constituents of porous electrodes for the electrooxidation of phenol. Domestic clay from Bogovina was subjected to a common procedure of the production of organo-bentonites. It included the following steps: grinding, sieving, Na-exchange, cation exchange and drying. The samples were characterized by X-ray diffraction (XRD) analysis, while the textural properties were evaluated by nitrogen physisorption. The multisweep cyclic voltammetry was applied to analyze the behavior of the clay modified glassy carbon electrode. The influences of the surfactant loading and pH of the support electrolyte were investigated. Rapid deactivation of electrodes occurred in an acidic environment, while good stability of the investigated electrodes was obtained in alkaline medium.

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### 1. Introduction

Phenol is readily absorbed from all media; it is rapidly distributed to all tissues. The liver, lung and the gastrointestinal mucosa are the most important sites of phenol metabolism. Clinical symptoms after short-term exposure are neuromuscular hyperexcitability, necrosis of the skin and mucous membranes, and effects on the lungs, kidneys and liver. The recommendations of the European Union for the limit of phenols in potable and mineral waters is  $0.5 \mu\text{g l}^{-1}$  (0.5 ppb), while the limits for wastewater emissions are  $0.5 \text{ mg l}^{-1}$  (0.5 ppm) for surface waters and  $1 \text{ mg l}^{-1}$  for the sewerage system [1]. The determination of phenol in aqueous solution is of the great importance due to its high toxicity and solubility. Electrochemical techniques using modified electrodes are promising and interesting because they have a number of advantages. Although HPLC [2] and GC [3] techniques have low detection limits, electrochemical methods do not require previous sample treatments and are much simpler. In addition, they can be performed in opaque media, which makes them more advantageous in comparison to UV-Vis spectrophotometry. Different electrodes such as  $\text{PbO}_2$ -CP-E [4], enzyme-based electrodes [5], Nafion-coated glassy carbon electrode (GCE) [6] have been investigated for phenol oxidation. The major disadvantage of these electrodes is electrode passivation due to the formation of polymeric products. Clay modified electrodes received attention since clays are inexpensive materials, easily modified and has the ability to preconcentrate analytes, leading to better sensitivity and lower detection limits.

Electrodes modified by films of a porous material, such as clays, represent a research area of wide interest [7–10]. One of the possible applications of these electrodes is in the reaction of phenol oxidation, used either to detect [11,12] the amount of phenol or to realize complete oxidation of phenol.

Bentonites are clays rich in smectite [13]. The properties of smectites such as: crystal shape and size, cation exchange capacity (CEC), hydration and swelling, thixotropy, bonding capacity, impermeability, plasticity and tendency to react with organic compounds [14], provide them with the possibility for a variety of applications. Smectites are cationic clay minerals that consist of negatively charged aluminosilicate sheets with intercalated exchangeable cations and water molecules [15]. The forces holding the stacks together are relatively weak and hence the intercalation of small molecules between the layers is easy. Smectites can be made organophilic by exchanging the exchangeable cations with alkylammonium ions. Usually quaternary alkylammonium cations of the general form  $[(\text{CH}_3)_3\text{NR}]^+$  or  $[(\text{CH}_3)_2\text{NR}'\text{R}'']^+$ , where R, R' and R'' are hydrocarbon groups, are used in the synthesis of organoclays. The arrangement of the intercalated surfactant cations depends on the alkyl chain length and the quantity of the cation used for the modification. Organobentonite materials with mono-, bi-, pseudotrimolecular and paraffin layers of  $[(\text{CH}_3)_3\text{NR}]^+$  cations within the interlayer region of smectite can be obtained. The formation of paraffin layers is possible if HDTMA cations, with the alkyl chain of 16C atoms, in the quantity of doubled CEC value, is used. An enhanced interaction of these materials with organic molecules is expected due to their high organophily [16]. On the other hand quaternary alkylammonium cations with shorter alkyl chains are unable to form paraffin layers within smectite even if applied in amounts that are several times greater than the CEC values [17].

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Depending on the chain length, organoclays display distinct sorptive properties [18]. The configuration of HDTMA cations within the interlayer of smectite-type clays is expected to create a microstructural environment which can result in either favorable or unfavorable interactions with redox species.

The present work reports the results of the electrochemical oxidation of phenol on organoclay-modified electrodes. The multisweep cyclic voltammetry technique was used to investigate the effect of surfactant loading and pH of the supporting electrolyte on the behavior of the modified electrodes.

## 2. Experimental

### 2.1. Materials

Bentonite was obtained from the Bogovina Coal and Bentonite Mine, Serbia. It was crushed, grinded and sieved through a 74  $\mu\text{m}$  sieve. The chemical composition of bentonite was reported previously [19].

HDTMABr [(CH<sub>3</sub>)<sub>3</sub>NC<sub>16</sub>H<sub>33</sub>Br] of chemical purity of 98% was obtained from Alfa-Aesar Chemical Company and phenol p.a. from Lach-Ner.

### 2.2. Preparation of the samples

Na-enriched bentonite was prepared by stirring a dispersion of bentonite powder (<74  $\mu\text{m}$ ) in 1 M NaCl for 24 h. After stirring, the dispersion was filtered through a Buchner funnel. The filtration cake was rinsed with distilled water to remove NaCl and excess of exchangeable cations from the sample. The washing was repeated until the filtrate was Cl<sup>-</sup> free (tested with 0.1 M AgNO<sub>3</sub>). The obtained Na-enriched bentonite was dried at 110 °C and denoted Na-B. The CEC of Na-B was determined by the standard ammonium acetate method [20]. The CEC of bentonite dried at 110 °C was 0.63 mmol l<sup>-1</sup> g<sup>-1</sup>.

The procedure for organobentonite synthesis was performed according to Baskaralingam et al. [21]. First, a suspension of 3.000 g Na-bentonite was dispersed in 150 cm<sup>3</sup> distilled water and homogenized using a magnetic stirrer. The HDTMA-Br to bentonite ratios were 0.127, 0.317, 0.633 and 1.266 mol g<sup>-1</sup> representing 0.2, 0.5, 1.0, and 2.0 times of CEC value, respectively. Therefore, the samples were denoted as 0.2HDTMA-B, 0.5HDTMA-B, 1.0HDTMA-B and 2.0HDTMA-B, respectively.

The preparation of each sorbent consisted of the dropwise addition of 100 cm<sup>3</sup> HDTMA-bromide solution of a defined concentration into a stirred Na-bentonite suspension. The procedure included continuous stirring at room temperature for 24 h. After stirring, the suspension was filtered through a Buchner funnel. The filtration cake was washed with distilled water until AgNO<sub>3</sub> test for bromide anions showed negative. The sample was dried at 80 °C.

The XRD patterns for powders of the Na-enriched and HDTMA-modified clays were obtained using a Philips PW 1710 X-ray powder diffractometer with a Cu anode ( $\lambda = 0.154178$  nm).

Nitrogen adsorption–desorption isotherms were determined using a Sorptomatic 1990 Thermo Finnigan at –196 °C. The samples were outgassed at 160 °C, for 20 h. Various models and appropriate software (WinADP) were used to analyze the obtained isotherms. Specific surface area of the samples,  $S_{\text{BET}}$ , was calculated according to the Brunauer, Emmett, Teller method [22,23]. The total

pore volume was calculated according to the Gurvitch method for  $p/p_0 = 0.98$  [22]. The pore size distribution for mesopores was calculated according to the Barrett, Joyner, Halenda method from the desorption branch of the isotherms [24]. The micropores were analyzed using the Dubinin-Radushkevich method [25].

In order to use the HDTMA-bentonites as electrode materials, the HDTMA-bentonites were homogeneously dispersed in a 5 mass% Nafion solution in a mixture of isopropyl alcohol and water using an ultrasonic bath. The electronic conductivity of the samples were enhanced by adding 10 mass% of carbon black Vulcan XC72 (Cabot Corp.) into the initial suspension. A droplet of each suspension was placed on the surface of a glassy carbon rotating disc electrode. After the solvent removal by evaporation at 90 °C, the HDTMA-bentonite particles were uniformly distributed on the glassy carbon support in the form of a thin layer.

For electrochemical investigations in a three-electrode all glass cell, the clay-modified glassy carbon electrodes was used as a working electrode. The reference electrode was Ag/AgCl in 1 M KCl, while a platinum foil served as the counter electrode. Phenol degradation was investigated for the starting concentration of phenol of 10 mM in either 0.1 M H<sub>2</sub>SO<sub>4</sub> or 0.1 M NaOH at room temperature. The phenol/electrolyte solutions were purged with nitrogen. The electrochemical measurements were performed using 757 VA Computrace Metrohm. The cyclic voltammograms (CV) were recorded at a scan rate of 10 mV s<sup>-1</sup> and rotation rate of 600 rpm. The square wave voltammograms (SWV) were recorded in the potential window of 0 to –0.8 V vs. Ag/AgCl electrode with following parameters: pulse amplitude = 50 mV, scan increment = 10 mV and frequency = 2 Hz.

## 3. Results and discussion

### 3.1. Sample characterization

#### 3.1.1. XRD analysis

The values of smectite basal spacing,  $d_{001}$ , of the Na-B and HDTMA-modified bentonites were calculated from XRD patterns [26] and are listed in Table 1. The incorporation of surfactant molecules into the smectite structure led to a constant increase in the  $d_{001}$  basal spacing up to 2.00 nm for both 1.0HDTMA-B and 2.0HDTMA-B. The obtained values of the  $d_{001}$  basal spacing corresponded to a monolayer, bilayer and pseudotrimolecular layer arrangements of HDTMA between the smectite layers [27].

The thickness of the single TOT layer of smectite (where T stands for tetrahedral sheet, O for octahedral sheet), estimated from the XRD pattern of oriented heat-treated sample was 1.00 nm [28], which is in agreement with literature data [29].

A pseudotrilayer arrangement of intercalated HDTMA can satisfactorily explain the basal reflection at the angle corresponding to 2.00 nm for 1.0HDTMA-B. Beneke and Lagaly [30] and Brindley and Moll [31] proposed a model for the arrangement of alkyl chains based upon their mutual interlocking. It was assumed that a CH<sub>2</sub> group of one chain lies between similar groups of neighboring chains in the parallel packing of the chains. In this case, the height of the bilayer with interlocking chains should be smaller than that without interlocking. The interlayer distance decreases by 0.1 nm for each added interlocking layer. Therefore, the height of pseudotrilayer should be 1.0 nm. This value is similar to the experimental results presented here and those previously reported by

**Table 1**  
The basal spacing  $d_{001}$  of investigated samples.

Sample	Na-B	0.2HDTMA-B	0.5HDTMA-B	1.0HDTMA-B	2.0HDTMA-B
$d_{001}$ (nm)	1.28	1.44	1.52	2.00	2.00

other researchers [32]. With increasing the HDTMA loading, a further raise in the  $d_{001}$  basal spacing was not observed. This result is in the agreement with the work of Xu and Boyd [33] who established that the formation of a vertical configuration (i.e. paraffin complex) did not occur in low charged montmorillonite. Since a further increase of HDTMA loading did not lead to a further raise of the basal spacing, it can be assumed that, after replacing all exchangeable interlayer cations, the additional surfactant molecules were attached to the smectite surface.

### 3.1.2. Adsorption–desorption isotherms

The nitrogen adsorption–desorption isotherms of Na–B and the series of HDTMA-bentonites are shown in Fig. 1.

The adsorption isotherms for Na–B and 0.2HDTMA-B belong to those of the Type II isotherm according to the IUPAC classification. A large uptake of nitrogen was observed close to the saturation pressure, exhibiting multilayer adsorption and implying the presence of mesopores [34]. On the other hand, the isotherms of the samples with higher HDTMA loadings belong to the Type III isotherms. According to the IUPAC classification that is characteristic of systems with weak adsorbate–adsorbent interactions.

The textural properties calculated from the adsorption isotherms data are presented in Table 2.

The BET surface areas of the clay/organoclays decreased in order Na–B  $\gg$  0.2HDTMA-B  $\approx$  0.5HDTMA-B  $>$  1.0HDTMA-B  $>$  2HDTMA-B.

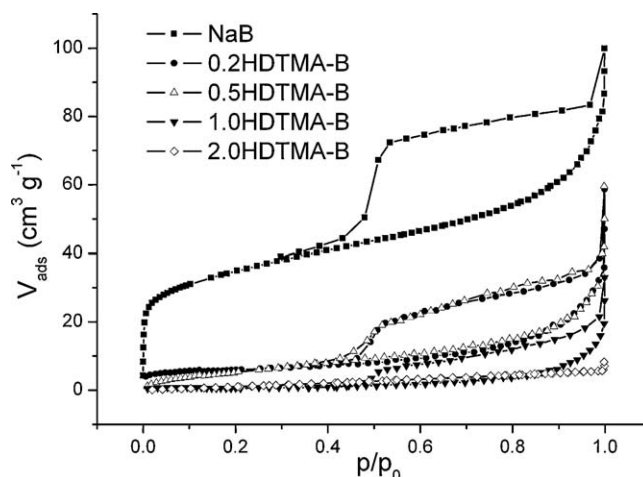


Fig. 1.  $N_2$  adsorption–desorption isotherms for NaB (squares), 0.2HDTMA-B (circles), 0.5HDTMA-B (empty triangles), 1.0HDTMA-B (full triangles) and 2.0HDTMA-B (empty deltoids).

The 0.2HDTMA-B showed a dramatic decrease of the surface area, micropore and mesopore volume in comparison to the Na–B. Further increase of the surfactant loading led to further decrease of the textural properties, but less pronounced. With the increase

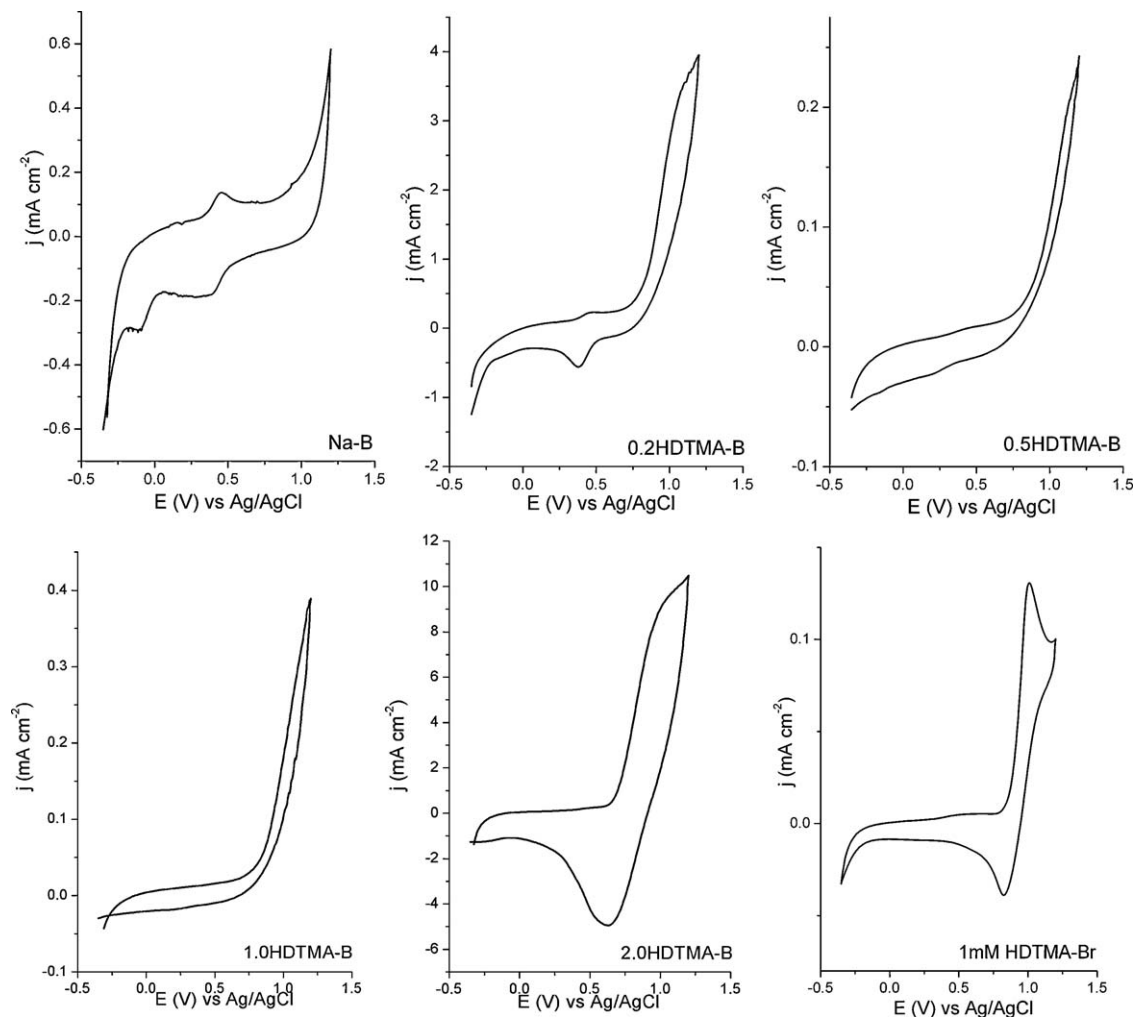


Fig. 2. Cyclic voltammograms in 0.1 M  $H_2SO_4$  recorded at a polarization rate of  $10 \text{ mV s}^{-1}$  for Na–B electrode (a), 0.2HDTMA-B electrode (b), 0.5HDTMA-B electrode (c), 1.0HDTMA-B electrode (d), 2.0HDTMA-B electrode (e) and 1 mM HDTMA-Br solution (f).

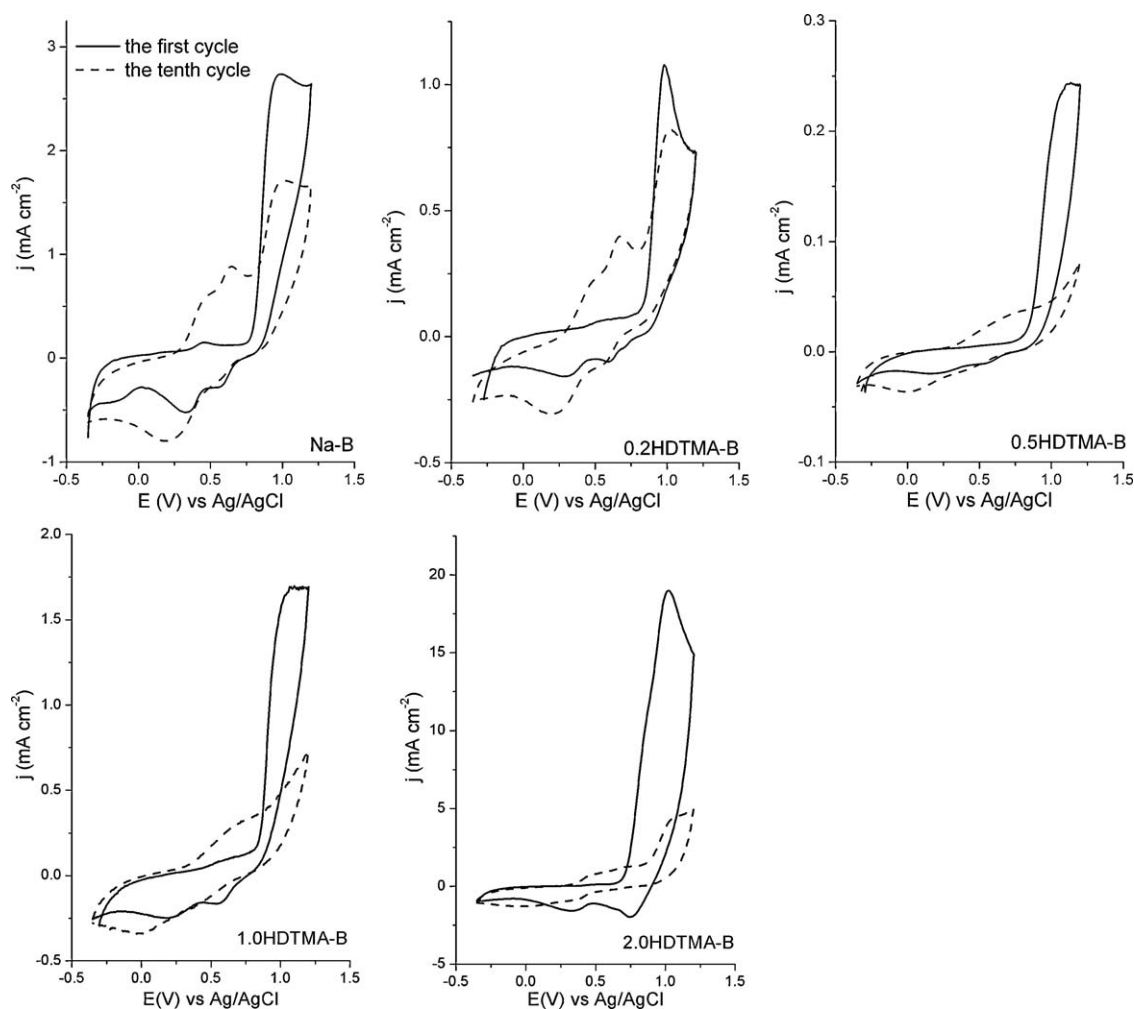


Fig. 3. Cyclic voltammograms of the investigated electrodes in 10 mM phenol + 0.1 M  $H_2SO_4$ , recorded at a polarization rate of  $10 \text{ mV s}^{-1}$ .

of HDTMA loading the microporosity disappeared. The presence of HDTMA cations in the interlamellar layer apparently resulted in pore blockage that inhibited the passage of the nitrogen molecules.

### 3.2. Electrochemical behavior

In a previously published paper, phenol electrooxidation on an aluminosilicate electrode in acidic, alkaline and neutral media was investigated [35]. The highest current for phenol oxidation was obtained in the acidic electrolyte. Therefore, the electrochemical response of phenol on the HDTMA-bentonite electrode was investigated in 0.1 M  $H_2SO_4$  that served as the supporting electrolyte.

Table 2

The textural properties of samples based on the analysis of nitrogen adsorption isotherms.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) <sup>a</sup>	$V_{0.98}$ ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>b</sup>	$V_{\mu}^{\text{D}}$ ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>c</sup>	$D_{\text{BJH}}$ (nm) <sup>d</sup>
Na-B	120	0.117	0.045	4.0
0.2HDTMA-B	20	0.047	0.010	4.6
0.5HDTMA-B	20	0.046	0.008	4.6
1.0HDTMA-B	3	0.021	–	7.1
2.0HDTMA-B	1	0.016	–	6.0

<sup>a</sup>  $S_{\text{BET}}$ , specific surface area.

<sup>b</sup>  $V_{0.98}$ , total pore volume.

<sup>c</sup>  $V_{\mu}^{\text{D}}$ , micropore volume.

<sup>d</sup>  $D_{\text{BJH}}$ , the mesopore diameter calculated according to Barrett, Joyner, Halenda method.

#### 3.2.1. Behavior in 0.1 M $H_2SO_4$

First, the electrochemical behavior of the Na-B and the HDTMA-modified clays in acidic media was investigated. The shape of the obtained CVs depended on the amount of surfactant on the clay (Fig. 2).

All the bentonite based electrodes showed hydrogen evolution at the potential of  $-0.3 \text{ V}$  and oxygen evolution at potentials  $>1.1 \text{ V}$ . A vertical shift between the curves corresponding to the opposite polarization directions was very pronounced. Such behavior is a characteristic of electrodes with enhanced surface area that gives rise to the interfacial capacitance. With increasing of the surfactant loading the vertical shift decreased indicating a lower surface area of the electrode.

The cyclic voltammogram recorded for the Na-B and 0.2HDTMA-B electrodes had a pair of peaks at the potential of about  $0.5 \text{ V}$  vs. Ag/AgCl. This pair of peaks was ascribed to the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  oxidation/reduction process [36]. Bearing in mind the high percentage of iron in the Na-B [37], it was reasonable to expect that this oxidation/reduction process would occur on every bentonite-based electrode. No peak at the potential of  $0.5 \text{ V}$  was present in the CVs of the 0.5HDTMA and 1.0HDTMA-bentonite electrodes. Furthermore, the currents obtained for the 0.5HDTMA and 1.0HDTMA-bentonite electrodes were one order of magnitude lower than the currents obtained for the 0.2HDTMA-B electrode.

It could be expected that, at higher HDTMA loadings, all the sodium cations between smectite layers were exchanged by HDTMA ions. The presence of HDTMA blocked the pores and

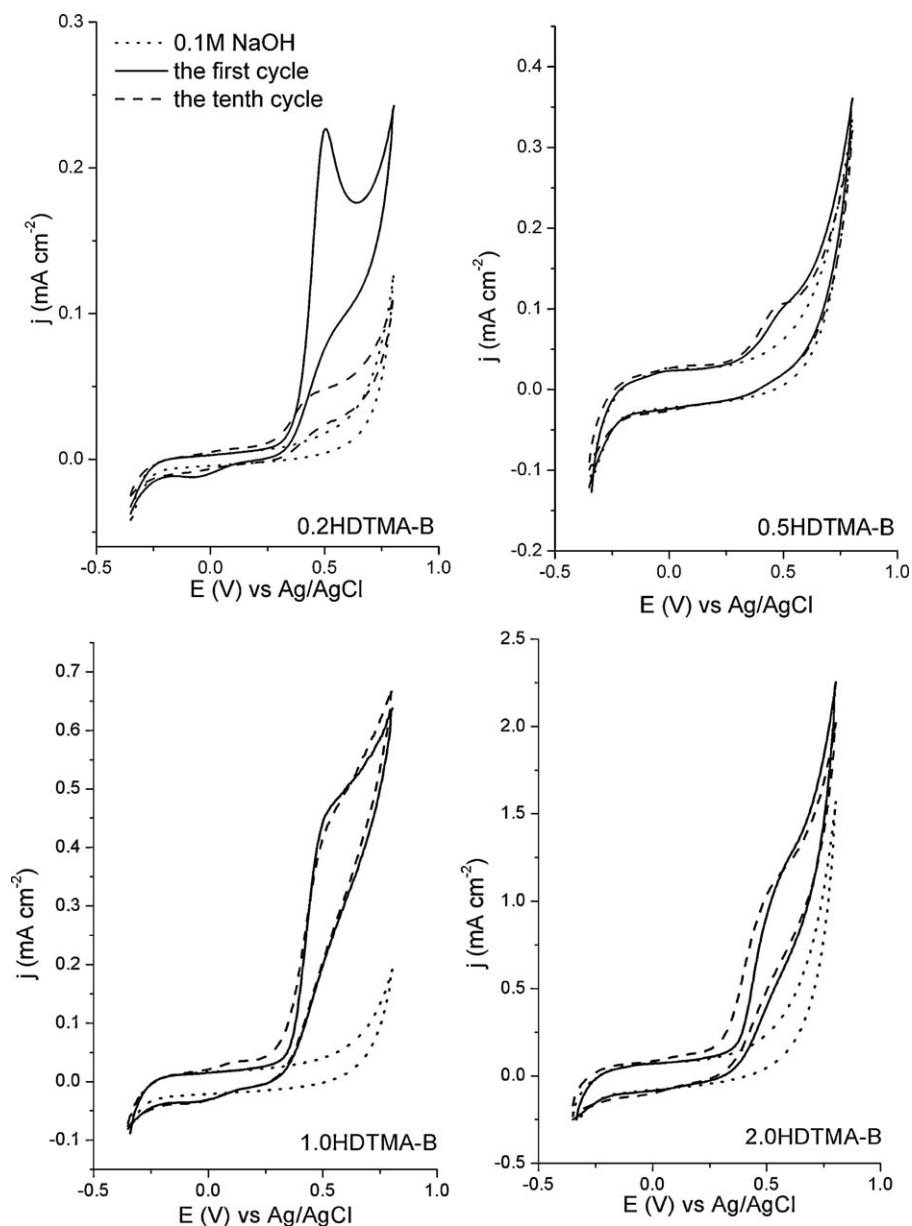


Fig. 4. Cyclic voltammograms in NaOH (solid line) and in 10 mM phenol + 0.1 M NaOH, the first scan (circles) and the tenth scan (squares) of the investigated electrodes.

prevented contact between the electrolyte and the active sites on the surface of the smectite layers. The currents obtained for the 2.0HDTMA-B electrode were one order of magnitude higher than those obtained for the 0.2HDTMA-B electrode. The CV registered using the 2HDTMA-B electrode exhibited a new anodic wave at 0.9 V and cathodic peak at 0.6 V. This oxido-reduction pair of peaks resembled those obtained for 1 mM HDTMA-Br solution in the supporting electrolyte (Fig. 2). This result confirmed the conclusion of the XRD analysis that additional surfactant molecules, after replacing all exchangeable interlayer cations, were attached to the smectite surface. The current obtained for the oxidation of HDTMA adsorbed on the clay surface was two orders of magnitude higher than the current obtained for the same process in solution. This is the consequence of the increased roughness of the clay modified electrode in comparison to a bare carbon glass electrode.

The 2.0HDTMA-B clay deteriorated with cycling due to HDTMA diffusion from the electrode surface. According to the investigation by Ngameni et al. [38], HDTMA-modified bentonite electrodes were stable at potentials below 0.2 V vs. SCE. However, phenol

oxidation commences at higher anodic potentials where these electrodes were not stable. Nevertheless, the first voltammograms of these electrodes in phenol containing solution could provide some valuable information on the investigated materials.

### 3.2.2. Behavior in 0.1 M $H_2SO_4$ containing phenol

Freshly prepared electrodes were cycled in phenol containing supporting electrolyte. The first and the tenth cycle obtained for each examined electrode are presented in Fig. 3. The phenol oxidation wave was registered at the Na-B electrode at a potential around 0.9 V. The tenth cycle evidenced the formation of phenol oxidation products. The corresponding peaks at 0.47 V and 0.64 V vs. Ag/AgCl can be ascribed to hydroquinone and benzoquinone oxido-reduction processes [39]. The same behavior was observed in the case of the 0.2HDTMA-B electrode, with lower currents in comparison to the Na-B electrode. A further increase of the surfactant loading (0.5HDTMA) led to a weak phenol response and the absence of peaks of phenol oxidation products.

The organoclays prepared at lower surfactant concentrations are mainly composed of randomly intercalated layers. In these samples a portion of exchangeable Na cations most probably remained in the smectite interlayer since the amount of the introduced surfactant is not sufficient for their quantitative exchange [27]. The electrochemical behavior of redox species at clay modified electrodes is expected to be affected by three main parameters: the concentration of the analyte, the accessible area of the working electrode and the speed of mass transfer for the probe within the film [40]. Therefore, it might be concluded that the presence of surfactant in the smectite interlayer blocked the active sites for phenol electrooxidation.

Further increase in the amount of surfactant (1.0HDTMA) led to the increase of the phenol oxidation current. The current increase was more obvious in the case of the 2.0HDTMA-B electrode. A minor current at the potential of the oxidation of phenol oxidation products indicated that some phenol oxidation occurred. However, we believe that the increased adsorption of phenol is responsible for the current increase. As concluded from the XRD analysis and the behavior of the 2.0HDTMA-B electrode in 0.1 M H<sub>2</sub>SO<sub>4</sub>, the excess of HDTMA molecules could be attached to the outer smectite surface. This leads to more suitable environment for the phenol adsorption (namely, more organophilic). The weak phenol oxidation response at the 1.0HDTMA-B electrode indicated that certain fraction of surfactant might be present at the outer surface of this sample as well. The investigated electrodes showed short-lived activity for phenol oxidation due to surface fouling, which was expressed as a sudden decrease in the oxidation current during cycling.

A straightforward correlation between the textural properties and electrochemical activity could not be drawn. Although textural properties of organobentonites are generally important, it is the nature of electrode surface (organophilicity) that apparently plays the key role in the electrooxidation of phenol.

### 3.2.3. Behavior in 0.1 M NaOH containing phenol

The CVs obtained for each examined electrode in 0.1 M NaOH with and without the presence of phenol are presented in Fig. 4.

The stable CV obtained in alkaline solution is presented together with the first and the tenth cycle registered in the phenol containing solution. The formation of polymeric products is favored reaction pathway for phenol electrooxidation in the alkaline solution on aluminosilicate electrodes [35]. The decrease of the electrode activity due to the formation of polymeric products was visible only at the 0.2HDTMA-B electrode. The CVs of the other investigated samples exhibited only one wave at the potential around 0.5 V. The current of this wave increased with an increase of the amount of surfactant present in the clay. Neither peaks related to phenol oxidation products, nor current decrease due to electrode failure was observed. The current increase with the increase of surfactant loading is consistent with the conclusion that adsorption of the phenolate anion is favored due to the presence of surfactant ions at the surface of the clay.

### 3.2.4. Detection of phenol using square wave voltammetry

Square wave voltammetry is a method that provides well-defined peaks at very low concentration levels, which makes it one of the most sensitive electroanalytical techniques. The investigation of the sensitivity toward phenol of the 2.0HDTMA-B electrode was performed by this technique. This sample was chosen since it showed the highest activity toward phenol oxidation. Phenol was successively added to a 0.1 M NaOH solution and the SWV were recorded without preconcentration (Fig. 5).

The carbon glass electrode, bare and covered with Nafion, was also investigated under the same conditions (Fig. 5). Nafion coating improved the sensitivity of the GCE in the detection of phenol [41]. Wang et al. [6] showed that in the presence of cationic surfactants

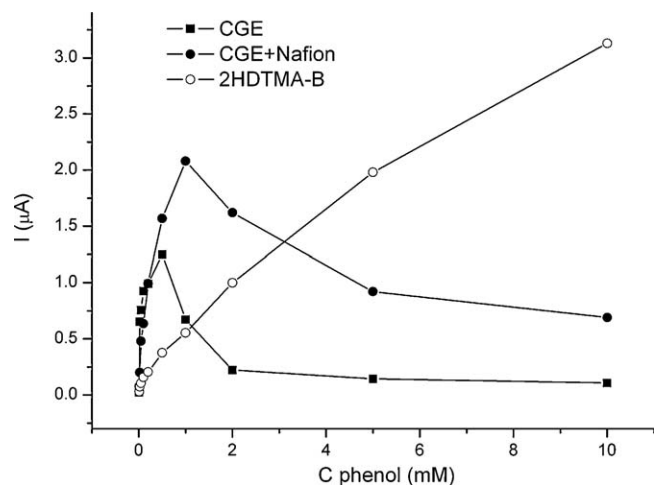


Fig. 5. Current response of different electrodes by successive addition of phenol to 0.1 M NaOH.

with a long hydrophobic chain, the voltammetric signals of phenols could be enhanced by 40–300%, and the detection sensitivity significantly improved. However, the electrochemical response vanishes once the polyphenol covers the bare or the modified GCE surface. The 2.0HDTMA-B electrode retained electroactivity up to high phenol concentrations (100 mM), but linear behavior was obtained only for a narrower concentration range (0.1–5 mM of phenol). A limit of detection of 18 μM was evaluated from the data obtained from the resulting calibration plot using the 3 sigma method. This detection limit is significantly below the European Union limits for wastewater. The repeatability of the responses was checked by performing a series of subsequent calibrations with 5 different solutions. The average slope of three different calibration curves was  $3.8 \times 10^{-5} \mu\text{A} \mu\text{M}^{-1}$ . The results showed good reproducibility and sensitivity of the 2.0HDTMA-B electrode in the oxidation of phenol.

## 4. Conclusion

HDTMA-modified bentonites were synthesized in order to be tested as electrode materials in the electrooxidation of phenol in acidic and alkaline solutions. According to XRD analysis the incorporation of surfactant molecules into the smectite structure led to a constant increase of the  $d_{001}$  basal spacing until 1.0HDTMA-B. A further increase in the surfactant loading had no effect on the basal spacing. A decrease in the specific surface area was observed with increasing surfactant loading.

Experiments in 0.1 M H<sub>2</sub>SO<sub>4</sub>, taken as reference, showed rapid deactivation of HDTMA-bentonite electrodes. The shape of voltammograms changed with the increasing surfactant loading. The voltammogram of 2.0HDTMA-B resembled the voltammogram obtained for HDTMA solution in 0.1 M H<sub>2</sub>SO<sub>4</sub>. The activity of the HDTMA-bentonite electrodes for phenol electrooxidation decreased with surfactant loading up to 2.0HDTMA-B, which showed a significantly higher activity than Na-B. However, due to the deterioration of the electrodes in acidic media, this activity was short-lived.

In alkaline solution, phenol oxidation led to the electrode deactivation only for the 0.2HDTMA-B electrode and the other electrodes retained their initial activity. The CVs of the other investigated samples exhibited only one wave at the potential around 0.5 V. We concluded that the sensitivity toward phenol and stability of the electrodes was markedly improved with increasing HDTMA loading.

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