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Evaluation of the SBA-15 materials ability to accumulation of 4-chlorophenol on carbon paste electrode

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Abstract The adsorption of 4-chlorophenol (4-CP) from an aqueous solution on three ordered mesoporous silica materials (commercial unmodified SBA-15-Sigma, synthesized unmodified SBA-15 and amino-functionalized SBA-15-NH$_2$) was studied. The adsorption isotherms were analyzed using the Generalized Langmuir equation taking into account the energetic heterogeneity. The adsorption capacities of the mesoporous silicas increased in order: SBA-15 < SBA-15-Sigma < SBA-15-NH$_2$. The materials were used for the modification of the carbon paste electrodes (CPEs) for detection of 4-CP based on differential pulse voltammetry. Different parameters that affects the DPV signal such as scan rate, accumulation time and paste composition were investigated. Compared with the bare (graphite) CPE, the SBA-15 modified electrodes greatly increased the oxidation peak current of 4-CP, showing strong signal enhancement effects. The SBA-15-NH$_2$ modified CPE showed a larger peak current and higher sensitivity for the 4-CP in comparison with the SBA-15 and SBA-15-Sigma modified carbon paste electrodes. The results showed high usefulness of the ordered mesoporous silica materials as an electrode modifiers in the electroanalytical techniques.

Keywords Mesoporous silica · 4-Chlorophenol · Adsorption · Carbon paste electrode

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1 Introduction

Mesoporous silica materials are characterized by high values of specific surface area, large pore volume and their pore structure consists of uniform canals formed in regular space networks. In this group of materials the SBA-15 silicas with hexagonal symmetry having wider mesopores receive much attention because of the possibility of application in the processes which are controlled by diffusion in pore system of a solid (Zhao et al. 1998). The SBA-15 materials with well organized structure are very useful as adsorbents (Gibson 2014a, b), catalyst supports (Huirache-Acuña et al. 2013), supports of active substances (Vallet-Regi et al. 2007; Wang 2009) or sensors (Melde et al. 2008). Moreover, the surface properties of these types of materials can be easily modified, e.g. by functionalization with various groups (Chong and Zhao 2003) in order to attain the highest effectiveness in a given application. Recently, mesoporous materials (unmodified as well as functionalized) have been used as carbon paste electrode (CPE) modifiers. The advantages of CPEs, are as follows: low cost, low residual current, speed of getting a new reproducible surface and possibilities of miniaturization. CPEs can be employed in connection with various electrochemical techniques such as voltammetry and its variants. The often used method is differential pulse voltammetry (DPV). DPV is extremely useful to detect trace levels of organic and inorganic analytes. In this technique, there are a series of regular voltage pulses superimposed on the potential linear sweep or stair steps. Just before each potential change and late in the pulse life, the currents are recorded. The current difference is then plotted against the applied potential. In the differential pulse voltammogram, the height of the current peak can be directly proportional to the concentration of corresponding

analytes. The peak potential varies with different analytes, which can also be used to distinguish the detected species. DPV can help improve the sensitivity of the detection and the resolution of the voltammogram. Therefore, this technology has also been widely used for the electroanalysis.

Moreover, CPEs are easily prepared and modified by adding the modifier directly to a carbon paste during its preparation step (Švancara et al. 2009). Many applications in electrochemistry using SBA-15 as modifier have been reported. Recently, SBA-15 was used as a modifier of carbon paste electrodes (CPEs) for detection and determination of metal ions (Cesarino et al. 2007a, b; Cesarino et al. 2008; Zhang et al. 2010), cardiac troponin I (Guo et al. 2005), diethylstilbestrol (Xie et al. 2014), epinephrine (Yi et al. 2013), catechol (Dong et al. 2012), hydroquinone (Dong et al. 2012), oxalic acid (Raoof et al. 2015) as well as dihydroxybenzene (Zhang et al. 2011), aminophenol (Duan et al. 2013) and naphthol (Zheng et al. 2015) isomers. On the other hand the amino-functionalized mesoporous silicas have attracted great attention in many fields of science. Some examples include catalysis, adsorption and removal of heavy metals as well as holding of various molecules and bioactive materials (Xie et al. 2009, Zhang et al. 2007). It is known that amine groups are effective for the adsorption of organic molecules because of their possible charge association and great adsorption energy. Some examples relate to the adsorption of chlorophenols like 2-chlorophenol (2CPh) and 2,4-dichlorophenol (2,4-DCPh) on a mesoporous silica functionalized by 3-(trimethoxysilyl)propylamine and tetraethylenepentamine (Ghaffari et al. 2014). Amino modiefied SBA-15 material was used also as an effective nanosorbent for the removal of halophenols from wastewater (Anbia and Amirmahmoodi 2011).

This paper describes the application of SBA-15 mesoporous materials as the modifiers of carbon paste electrodes. In the work presented, two unmodified SBA-15 silicas and one amino-functionalized SBA-15 ordered mesoporous silicas in the preparation of CPEs were used. The best conditions for a differential pulse voltammetric (DPV) procedure were optimized and the modified CPEs were applied in the detection of 4-chlorophenol. 4-CP is known as one of the most cumbersome and harmful water pollutants which toxicity is independent of the environment and type of organism. Moreover, the products of its degradation are toxic similarly as the initial compound. The chlorinated phenol was chosen as the target contaminant because it is poisonous to aquatic life, plants and humans at low level (Igbinosa et al. 2013) and is commonly found in drinking water (Michalowicz 2005). The 4-chlorophenol is harmful by inhalation for human at a level equal to 10,000 mg/m^3 (Gigiena i Sanitariya 1964). LD$_{50}$ (Lethal Dose) test, which suggests the death of 50 % (one half) of a group of test animals, for rat indicates the amount of 4-chlorofenol at a level 260 mg/kg by oral route (Clayton 1967). As an example of poisoning of aquatic species by 4-chlorophenol two types of invertebrate (pink hydra (Hydra vulgaris) and green hydra (Hydra viridissima)) were selected as a model of life organisms. LC test (Lethal Concentration) suggests sensitivity to 4-chlorophenol on a level 32 mg/L and 45 mg/L for pink and green hydra respectively (Pollino and Holdway 1999). The electrochemical determination of 4-CP at CPEs modified with montmorillonite (Yang et al. 2008), TiO$_2$ (Wan et al. 2009) as well as carbonaceous materials including carbon black (Kusmierek et al. 2015), activated carbons (Kusmierek et al. 2015), carbon nanotubes (Lipinska et al. 2014) and reduced graphene oxide (Lipinska et al. 2014) has been described. However, the detection and determination of 4-CP using ordered mesoporous silica SBA-15 modified CPEs has not yet been reported.

2 Experimental

2.1 Chemicals and instruments

The 4-chlorophenol (2,4-D, ≥99 %), triblock copolymer Pluronic P123 (M$_n$ ∼ 5800), tetraethoxysilane (TEOS, 98 %), aminopropyltriethoxysilane (APTES, ≥98 %) and graphite powder were from Sigma-Aldrich (St. Louis, USA). The ethanol (96 %), hydrochloric acid (35 %), sodium sulfate (≥99 %), potassium hexacyanoferrate(III) and potassium nitrate were obtained from Avantor Performance Materials (Gliwice, Poland). Three mesoporous silica materials were used in this studies - commercially available mesoporous silica received from Sigma-Aldrich (SBA-15-Sigma), and the two silicas (unmodified SBA-15 and amino-functionalized SBA-15-NH$_2$) synthesized according to the procedure described in Sect. 2.2. Stock standard solutions of 4-CP (0.5 mmol/dm^3) were prepared in 0.1 mol/dm^3 sodium sulfate for electrochemical studies and in distilled water for adsorption studies. The working solutions were prepared by dilution as needed.

The porous structure characteristics were obtained on the basis of low temperature nitrogen adsorption–desorption isotherms (Micromeritics ASAP 2020 volumetric adsorption analyser, Norcross, USA). The X-ray diffraction measurements were performed using an Empyrean X-ray diffractometer from PANalytical 2014 over the 2θ range from 0.3° to 5° with step size of 0.01°. Attenuated Total Reflectance (ATR-FTIR) spectra were recorded using an IR spectrometer TENSOR 27 (Brucker, 2014, Germany) equipped with diamond crystal. The spectra were recorded in the spectral range of 400–4000 cm^{-1}. Thermal analysis was carried out on a TG–DTA/DSC apparatus (STA 449 Jupiter F1, Netzsch, Germany). The samples were heated

from 4 to 900 °C in Al_2O_3 crucibles under oxidative (synthetic air) atmosphere with flow rate 25 mL min^{-1}. The heating rate was 10 °C·min^{-1}. The analysis of structure ordering of the investigated samples was conducted by electron microscopy in high resolution transmission electron microscope S/TEM Titan3 G2 60-300 (FEI Company). The Elemental CHN analysis was performed by Perkin Elmer 2400 Elemental Analyzer (1997). Cary 3E UV–Vis spectrophotometer (Varian Inc., USA) was used for absorbance measurement. Cyclic voltammetry (CV) and DPV were performed in an analytical system (Autolab, Eco Chemie, Netherlands), potentiostat/galvanostat connected to a three electrode cell, linked with a computer and with software (Eco Chemie). The system was run on a PC using GPES 4.9 software. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and the saturated calomel electrode as a reference electrode was used. The working electrode was either an unmodified carbon paste electrode or a carbon paste electrode modified with mesoporous material (SBA-15-Sigma, SBA-15 or SBA-15-NH$_2$).

2.2 Preparation of SBA-15 materials

Pure SBA-15 support was prepared by sol–gel technique (Zhao et al. 1998). In a typical preparation, 8.0 g of tri-block copolymer Pluronic P123 as a structure directing agent was dissolved in 240 cm^3 of HCl (2 mol/L) and 60 cm^3 of H$_2$O. Mixture was stirred at 40 °C for 3 h. Afterwards 18.32 cm^3 of tetraethoxysilane (TEOS) was added dropwise. The solution was stirred for 24 h at the same temperature. The precipitated mixture was aged at 80 °C for 48 h without stirring and next the solid product was washed with distilled water and organic components were removed by calcination at 550 °C for 4 h in muffle furnace under an air atmosphere.

The amino-functionalized SBA-15 was prepared by post-synthesis basic treatment by aminopropyltriethoxysilane (Wang et al. 2007). For post-synthesis modification. 2.0 g of as-synthesized SBA-15 powder without organic template was added into a mixed solution of APTES and ethanol (50 cm^3 ethanol (96 %) and 3 cm^3 of APTES). After stirring at 25 °C for 6 h, the powder (denoted as SBA-15-NH$_2$) was filtered, washed with distilled and gently dried at 35 °C for 24 h.

2.3 Adsorption studies

The adsorption experiments were carried out in Erlenmeyer flasks containing 0.15 g of silica materials and 10 cm^3 of the solutions of a known concentration of 4-CP (from 50 to 500 µmol/dm^3). The flasks were agitated for 6 h at a constant speed of 200 rpm at 25 °C. At the end of this

period, the mixtures were filtered through a 0.2-µm pore size filter and analyzed by using UV–Vis spectrophotometry at 274 nm. The equilibrium amount of 4-CP adsorbed per unit mass of SBA-15, q$_e$ (µmol/g), was calculated by the equation:

$$q_e = \frac{(C_0 - C_e)V}{m_a} \tag{1}$$

where C_O and C_e are the initial and the equilibrium concentration of 4-chlorophenol (µmol/dm^3), V is the volume of the solution (dm^3) and m_a is the mass of the adsorbent (g). All the experiments were carried out in duplicate, and average values were used for further calculations.

2.4 Preparation of the electrodes

A Teflon holder with a hole at one end (2.5 mm diameter and 3.5 mm deep) for the carbon paste filling served as the electrode body. Electrical contact was made with a stainless steel rod through the center of the holder. This rod can move up and down by screw movement to press the paste down when renewal of the electrode surface is needed. Modified CPEs were prepared by thoroughly mixing 5 or 10 mg of mesoporous material (SBA-15-Sigma, SBA-15 or SBA-15- NH2) with, respectively, 95 or 90 mg of graphite powder (diameter >45 µm) and, subsequently, adding 15 mg of mineral oil (13 % m/m). Homogenization was then achieved by careful mixing using agate pestle and mortar and afterwards rubbed by intensive pressing with the pestle. The mixture was kept at room temperature for 2 days. The ready 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. Unmodified carbon paste electrode was prepared in a similar manner, with the addition of only 100 mg of the same graphite powder and 15 mg of mineral oil (Nujol).

3 Results and discussion

3.1 Characterization of SBA-15 materials

The physical properties of mesoporous silica materials were characterized using low temperature nitrogen adsorption–desorption isotherm, small-angle X-ray powder diffraction, ATR-FTIR infrared spectroscopy, thermogravimetry, SEM and TEM techniques.

Nitrogen adsorption/desorption isotherms for all silica mesoporous materials were determined at 77 K. Figure 1 shows the nitrogen adsorption–desorption isotherms and functions of pore size distribution (PSD) (Barrett, Joyner and Halenda (BJH) procedure 1951) obtained for the investigated samples. The shape of the sorption isotherms
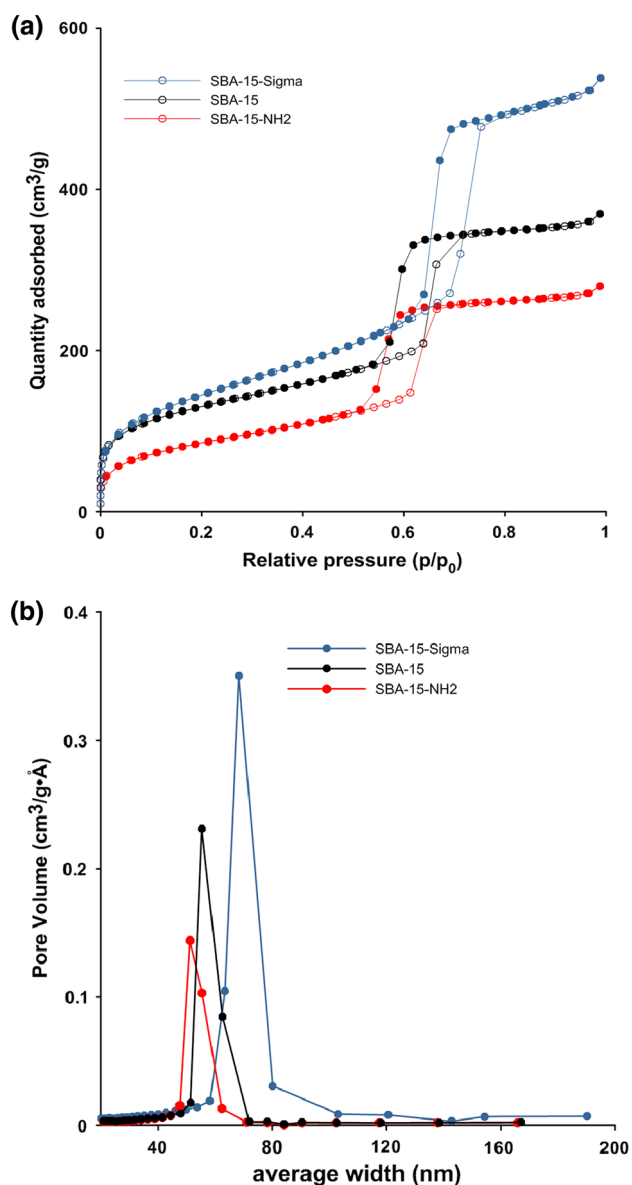
Fig. 1 a Nitrogen adsorption–desorption isotherms on SBA-15-Sigma, SBA-15 and SBA-15-NH$_2$ at 77.4 K; **b** pore size distribution calculated according BJH method from the adsorption branch of isotherm

are typical for SBA-15 materials with ordered mesoporosity. All samples yield IV type of isotherm with H1 hysteresis loop in the p/p$_0$ range 0.55 ∼ 0.75. This well-defined hysteresis loop of H1 type rendering to the IUPAC classification (Gregg and Sing 1982) shows parallel branches of adsorption and desorption. This type of hysteresis loops is related with capillary condensation of nitrogen in similar, uniformly ordered and opened cylindrical mesopores. The presence of such structures was confirmed by BJH pore size calculations. As a result narrow functions characterized by a maximum at 50 Å (SBA-15-NH2), 55 Å (SBA-15) and 70 Å (SBA-15-Sigma) what suggest

presence of comparable mesopores, were obtained. After grafting of the aminopropyltriethoxysilane, the PSD decreased by 5 Å. The BET surface area as well as the total pore volume decreased for sample after modification. Consequently, the modification leads to a decrease of BET surface area by 210 m^2/g and 157 m^2/g for SBA-15-Sigma and SBA-15 respectively. Similarly, the total pore volume decreased by 0.26 cm^3/g and 0.15 cm^3/g. A decrease of textural parameters was observed as an effect of attaching the amino groups and agrees with the other literature references (Ziarani et al. 2012). The values of specific surface areas (S_{BET}) of the materials, as well as the total pore (V_t) and micropore (V_{mic}) volumes calculated from the adsorption isotherms are presented in Table 1. In Table the mesopore diameter (w) calculated from adsorption branch of nitrogen isotherm is also given.

The ordering of porous structure of SBA-15 materials before and after modification by NH$_2$ groups were evaluated by X-ray diffraction measurements in range of small angles 2θ. The XRD patterns of SBA-15 materials are displayed in Fig. 2. In all cases the SBA-15 supports exhibit structural ordering according to hexagonal symmetry p6 mm characteristic for this type of materials. Three first and well-resolved reflections registered at small diffraction angles can be indexed as (100), (110) and (200) reflections of the hexagonal lattice and still observed after post synthesis modification. It can be observed that the three first reflections of SBA-15-Sigma sample (commercial SBA-15) are shifted slightly to lower angles. This indicates that the dimension of unit cell becomes higher than as-prepared mesoporous ordered silica. The unit cell parameters calculated from these three peaks were 10.1 nm, 10.3 nm and 11.0 nm in the case of SBA-15, SBA-15-NH$_2$ and SBA-15-Sigma, respectively.

The FTIR spectra of all silica materials are presented in Fig. 3. The ATR-FTIR spectra of investigated samples display the typical bands of mesoporous silica materials. In all cases the absorption peaks at wavenumbers of 1042, 800 and 445 cm^{-1} correspond to the vibrations of Si–O-Si (SiO$_4$) (more specifically, Si–O–Si stretching vibrations, Si–O bending vibrations and Si–O out of plane deformation vibrations respectively). Moreover, on the IR spectrum of investigated samples small but characteristic bands appear at about 3745 cm^{-1} which are assigned to isolated silanol groups on silica surface (Morrow et al. 1976). In general after modification of mesoporous silica by amine groups, reduction of the peak intensity at 1042 cm^{-1} of Si–O–Si group and at 970 cm^{-1} of stretching Si–OH group as well as the presence of typically hardly discernible bands of NH group at about 1510 cm^{-1} (Chong and Zhao 2003) for SBA-15-NH$_2$ should indicate the successful modification of the silica surface. In the obtained ATR–FTIR spectra the intensity of the stretching peak of Si–O–Si as well as Si–O

Table 1 Porous structure parameters obtained from nitrogen adsorption isotherms (77.4 K)

Silica material	S_{BET} (m²/g)	C	w (nm)	V_t (cm³/g)	V_{mi} (cm³/g)
SBA-15-Sigma	517	110	6.25	0.83	0.020
SBA-15	464	183	5.23	0.57	0.061
SBA-15-NH$_2$	307	97	5.01	0.42	0.011
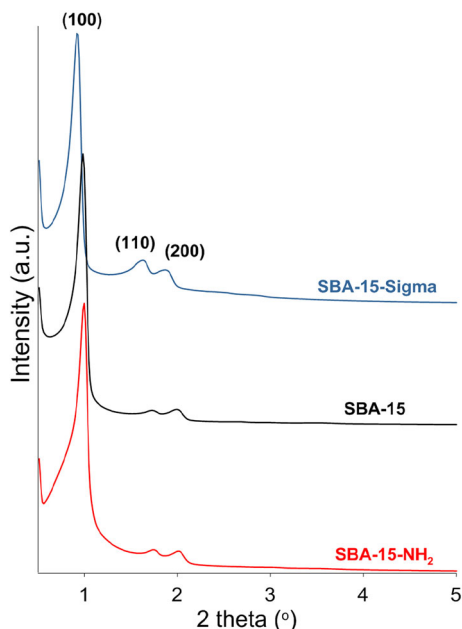
Fig. 2 The small-angle XRD patterns of mesoporous silica materials
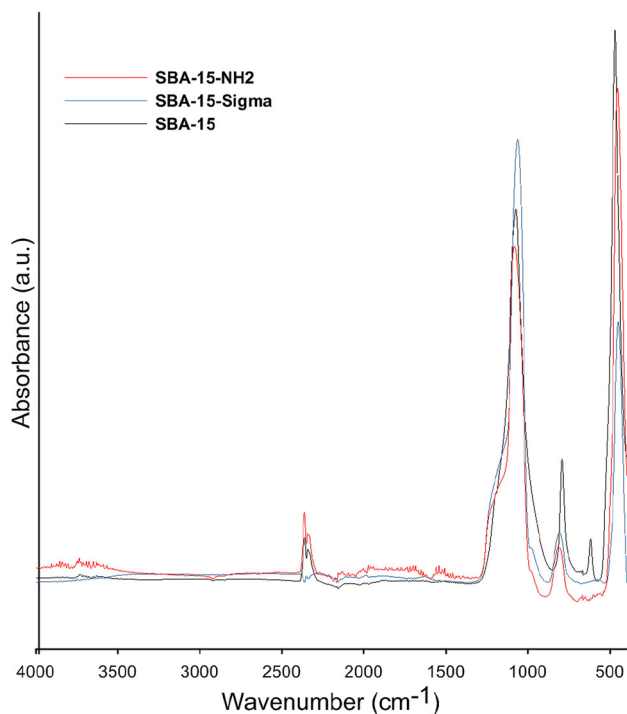
Fig. 3 ATR-FTIR infrared spectra of mesoporous ordered silica samples

bending vibrations and stretching Si–OH groups of functionalized SBA-15 decreased significantly which correlates well with the mechanism of its reaction with aminopropyltrimethoxysilane. Unfortunately, in this case an additional peak directly related to the amine groups (located at about 1542 cm^{-1} and describing the bending vibrations of –NH groups) is not clearly observed. In other words, some changes of the baseline were observed for modified sample, which may suggested presence of –NH bending vibrations, but the presence of a new, well-formed signal was far from obvious. It may be explained by the fact that the unequivocal characterization of this type of materials modified by amine groups using FTIR spectrometry sometimes is not so simple. Very often, these signals are very weak, even at significant content of surface localized functional groups. Regrettably, sometimes ATR-FTIR technique may be not sensitive enough to observe well-defined signals from modifiers.

Elemental analysis of carbon, hydrogen and nitrogen was performed to characterize the elemental composition of SBA-15-NH2 sample. Mass percentage of CHN elements was determined for this sample as 2.83, 1.06 and 1.14 %, respectively.

Figure 4 shows the results of thermogravimetric analysis of unmodified and amine functionalized SBA-15 silicas as the mass loss curves and the differential thermal analysis curves. The TGA and DTA analyses of investigated samples show no significant changes in the case of unmodified mesoporous silica (SBA-15-Sigma and SBA-15). SBA-15-Sigma and SBA-15 show a small weight loss whereas the SBA-15-NH$_2$ display significantly larger weight losses due to the incorporation of amine groups.

The observed total weight loss for SBA-15-Sigma and SBA-15 are small (4.22 and 1.99 % for SBA-15-Sigma and SBA-15 respectively). In this case the total weight loss can be associated with water molecules (physisorbed water and molecules eliminated by condensation of surface silanols). The observed total weight loss for SBA-15-NH$_2$ sample was significantly higher (6.9 %) and is related to a sum of physisorbed water and grafted ammine groups. All samples were compared in Fig. 4d.

The SEM and TEM images (Fig. 5) show that the prepared SBA-15 as well as SBA-15-NH$_2$ samples exhibit a well-ordered mesoporous channels arranged in 2D hexagonal structure according p6 mm symmetry. This structural

Fig. 4 TGA and DTA measurements of different samples. **a** SBA-15-Sigma, **b** SBA-15, **c** SBA-15-NH$_2$, **d** comparison of all investigated samples
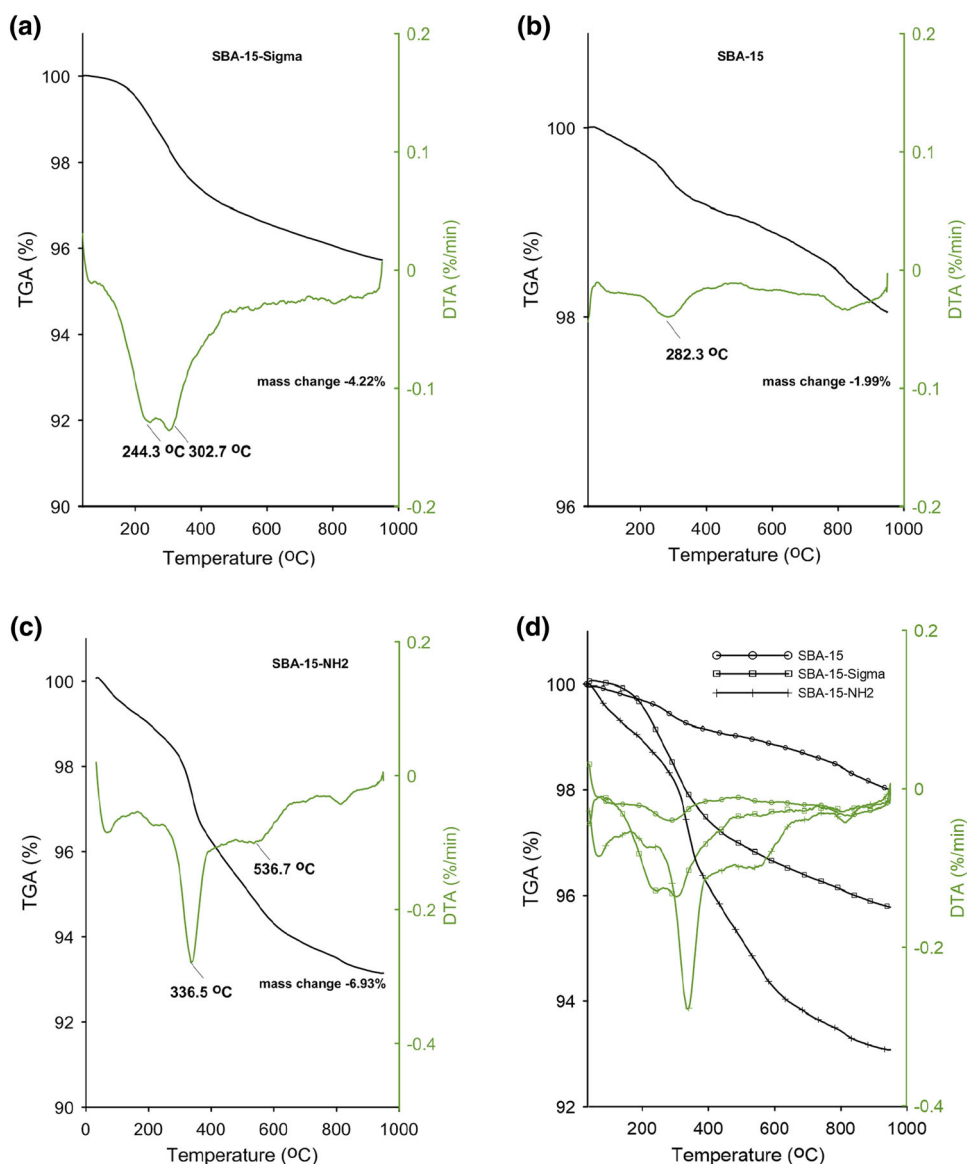
ordering of mesopores is visible in the two directions to pore axis (parallel in Fig. 5b, f and perpendicular in Fig. 5c, d). The distances between two cylindrical mesopores in SBA-15 sample (Fig. 5b) estimated from the TEM images are about 10.2 nm. The diameter of mesopores and thickness of walls are about 6.2 and 4.0 nm respectively. In the case of SBA-15-NH$_2$ sample the distances between two mesopores is greater (10.5 nm) and the diameter and thickness of walls are identified as 7.3 and 3.2 nm respectively.

3.2 Adsorption of 4-CP on SBA-15

The experimental adsorption isotherms of 4-CP on the SBA-15-Sigma, SBA-15 and SBA-15-NH$_2$ are presented in

Fig. 6. For their analysis the Generalized Langmuir (GL) isotherm equation (Marczewski and Jaroniec 1983) derived in terms of the general theory of adsorption on energetically heterogeneous solids was applied:

$$q_e/q_m = \left[\frac{(KC_e)^m}{1 + (KC_e)^m} \right]^{m/n} \qquad (2)$$

where q_e is the equilibrium adsorbed amount, q_m is the adsorption capacity, the heterogeneity parameters m and n characterize the shape (width) and asymmetry of adsorption energy distribution function ($m, n \in (0, 1\rangle$), and the equilibrium constant, K, describes the position of distribution function on energy axis. The GL equation is reduced to simpler isotherms for specific vales of heterogeneity parameters, e.g., for $m = n$ it becomes the well-known Langmuir–Freundlich isotherm corresponding to

Fig. 5 **a** SEM image of the as synthesized SBA-15, **b–d** TEM images of as synthesized SBA-15, **e** SEM image of SBA-15-NH2 sample, **f** TEM mage of SBA-15-NH2 sample
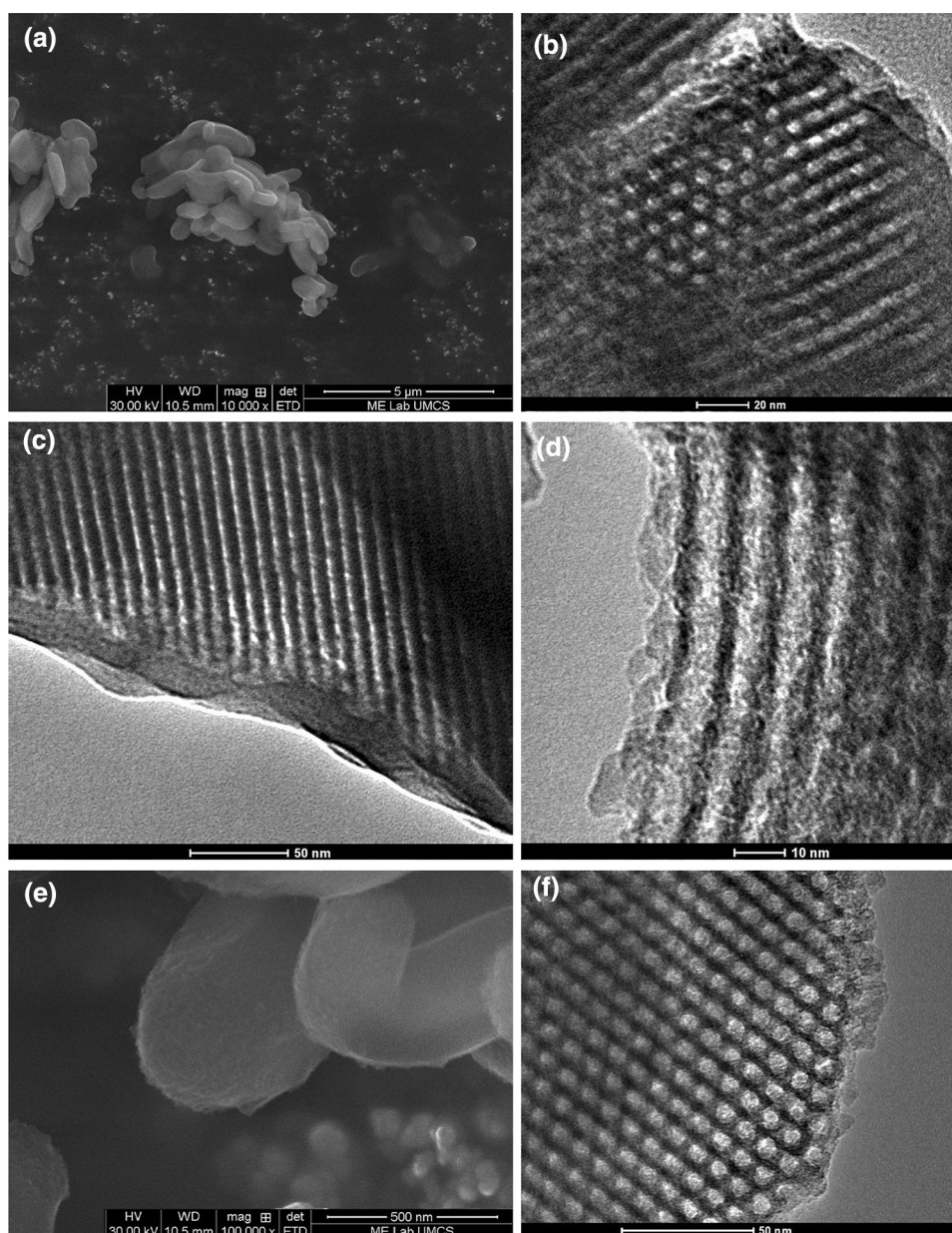
the symmetrical energy distribution, and for $m = n = 1$ it is Langmuir isotherm.

The Generalized Langmuir equation was fitted to experimental data and in the case of all adsorption systems the simplest Langmuir model was found to be the best one ($m = n = 1$). The obtained isotherm parameters and the coefficients of determination R^2 for the adsorption of the 4-CP onto the mesoporous silica materials are presented in Table 2. The high R^2 values indicate that the equilibrium data obtained for all adsorption systems are well described by the Langmuir equation. Though typically adsorption isotherms of organics on porous solids show at least some effects of energetic heterogeneity, however, in our case due to low range of concentration, the adsorption corresponds

to the high energy sites only and may be described by the Langmuir isotherm. Such a result may be also explained by a possible compensation (or even cancelling-out) of the effects of lateral interactions in adsorption space and the system nonhomogeneity (Marczewski et al. 1986, 2013). Moreover, it may be the additional effect of well-organized structure of adsorbent which diminishes the energetic and structural heterogeneity of adsorption system. The estimated adsorption capacities (q_m) decrease in order: SBA-15-NH$_2$ > SBA-15-Sigma > SBA-15. The q_m values for 4-CP adsorption on unmodified SBA-15 and SBA-15-Sigma were lower in comparison to the adsorption capacity obtained for modified SBA-15-NH$_2$. The commercial SBA-15-Sigma was found to be slightly better adsorbent than
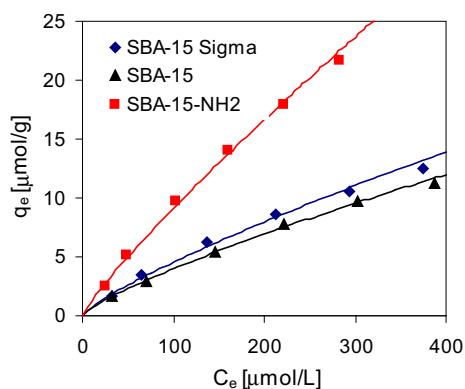
Fig. 6 Adsorption isotherms of 4-chlorophenol on mesoporous silica materials

Table 2 The Generalized Langmuir adsorption isotherm parameters and correlation coefficients R^2 for adsorption of 4-chlorophenol onto mesoporous silica materials

Silica material	Langmuir		
	q_{eq} (μmol/g)	K (dm^3/μmol)	R^2
SBA-15-Sigma	29.3	0.00196	0.99933
SBA-15	28.4	0.00161	0.99933
SBA-15-NH$_2$	71.6	0.00152	0.999933

SBA-15 which is probably due to its the greater specific surface area (517 vs. 464 m^2/g). The higher adsorption capacity of SBA-15-NH$_2$ in comparison to the unmodified silicas is a result of a more favorable interaction between 4-CP and the adsorbent due to the presence of a free electron pair and the more alkaline properties of the mesoporous silica surface. These results are consistent with the results of other authors (Anbia and Amirmahmoodi 2011; Toufaily et al. 2013; Moritz 2015) who also found that amino-functionalized SBA-15 showed higher adsorption capacities for 4-CP than the untreated SBA-15.

The adsorption of 4-CP on mesoporous SBA-15 was previously studied by Anbia and Amirmahmoodi (2011), Toufaily et al. (2013) and Moritz (2015) but the obtained results vary significantly. The adsorption isotherms of 4-CP were better described by the Freundlich equation (Anbia and Amirmahmoodi 2011) and sometimes by the Langmuir equation (Toufaily et al. 2013; Moritz 2015). The Langmuir maximum adsorption capacity values obtained for 4-CP adsorption on unmodified SBA-15 were 57.5 mg/g (Anbia and Amirmahmoodi 2011), 0.3 mg/g (Toufaily et al. 2013) and 9.6 mg/g (Moritz 2015), respectively. These differences are very large, although the specific surface areas of the materials tested are comparable (812 m^2/g (Anbia and Amirmahmoodi 2011), 678 m^2/g

(Toufaily et al. 2013), 828 m^2/g (Moritz 2015)). Recently, Qin et al. (2012) described adsorption of 2-chlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol on mesoporous SBA-15 (S_{BET} = 744 m^2/g). The q_m value for 2-CP adsorption was found to be 2.6 mg/g. The adsorption of 4-chlorophenol was not tested but, based on the other studies of the adsorption of monochlorophenols on the carbonaceous materials (Jung et al. 2001; Hamdaoui and Naffrechoux 2007; Liu et al. 2010; Kusmierek et al. 2014) the adsorption properties of 4-CP and 2-CP are very similar.

All this observations show that the mesoporous SBA-15 materials reveal varying adsorption capacity towards 4-chlorophenol. In addition, despite the high specific surface areas their adsorption capacity, compared to the activated carbon, is often lower for this and other chlorophenols. For comparison, the adsorption capacity of activated carbon (S_{BET} = 925 m^2/g) for 4-CP was 255 mg/g (Kusmierek et al. 2015). Of course, for other adsorbates situation may be different (heavy metals for example).

3.3 Electrochemical studies

3.3.1 Effect of instrumental parameters

In order to obtain the optimum experimental conditions, some variables affecting the peak current and peak potential were studied for the 4-CP solution of 500 μmol/dm^3 on the carbon paste electrode (CPE) by the proposed voltammetric technique. The effects of the scan rate from 10 to 90 mV/s on the peak potential and the 4-chlorophenol
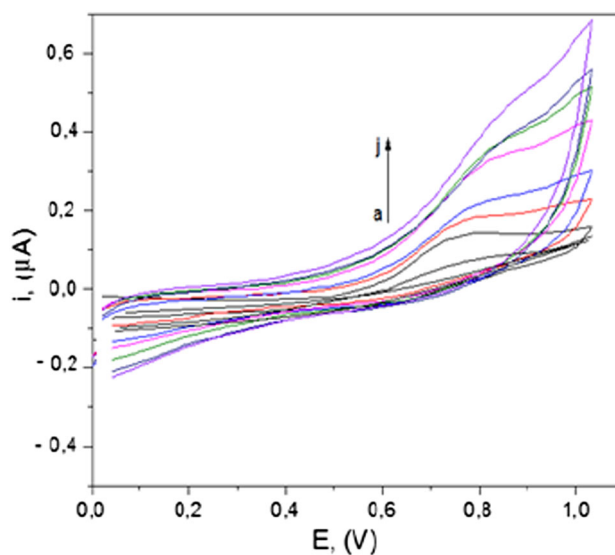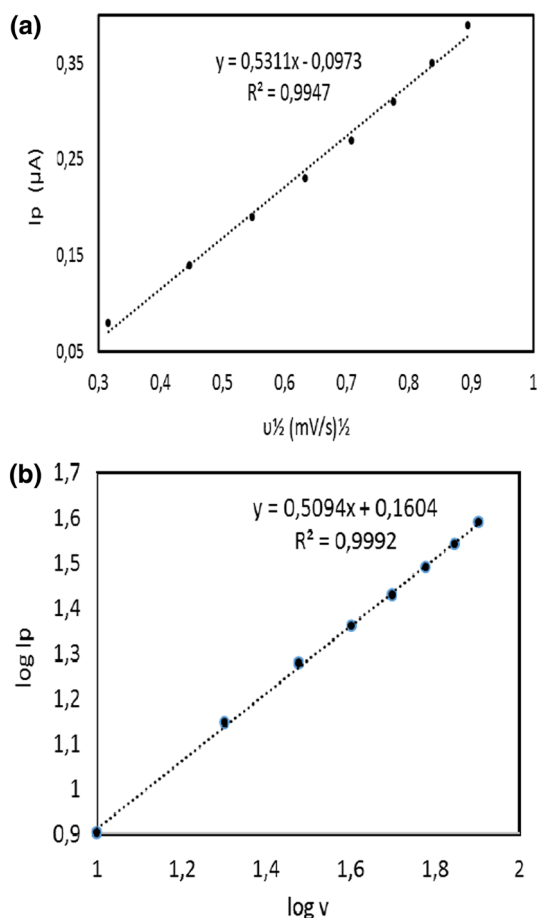

Fig. 7 The cyclic voltammograms of 500 μmol/dm^3 4-CP in 0.1 mol/dm^3 Na$_2$SO$_4$ on a CPE. Scan rate: **a** blank, **b** 10, **c** 20, **d** 30, **e** 40, **f** 50, **g** 60, **h** 70, **i** 80, **j** 90 (mV/s)

peak current were evaluated (Fig. 7). With increasing scan rate, the anodic peak current increased. The electrochemical oxidation process was carried out using cyclic voltammetry techniques (CV). The CV voltammogram of 4-CP exhibited only one anodic peak, with no peak on the reverse scan, indicating the totally irreversible nature of the electrode reaction. In addition, for an irreversible oxidation process, the peak potential E_p shifts to less positive values with the increase in scan rate.

The correlation coefficient of anodic peak current and square root of the scan rate 0.9947 (expected about 1.0) $(I_p = 0.5311v^{1/2} - 0.0973)$, and 0.5094 which is almost close to the theoretical value of 0.5 $(logI_p = 0.5094 \cdot logv + 0.1602)$ slope of plot of logarithm of peak current versus logarithm of scan rate indicated that the oxidation process is predominantly diffusion-controlled (showed in Fig. 8a, b).
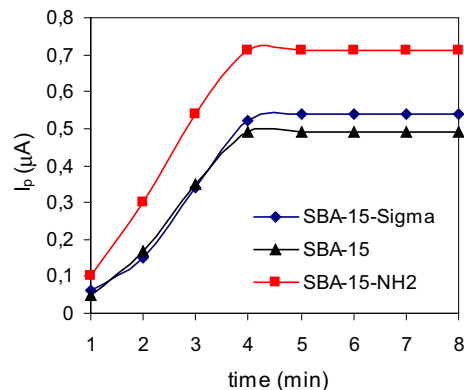
3.3.2 Effect of accumulation time

Before the DPV measurements, the influence of the accumulation time on the peak current was determined. Accumulation time was varied from 1 min to 8 min and the corresponding current value was measured using all concentrations of 4-CP solution (50–500 μmol/dm³). The experiments were conducted at the CPEs containing 10 % of mesoporous materials. The effect of accumulation time on the peak current of 4-CP (500 μmol/dm³) is shown in Fig. 9. The peak current increased with increasing of accumulation time up to about 3–4 min and then became stable.

### 3.3.3 Effect of modifier content

Differential pulse voltammograms for the modified CPE and as an example with 500 μmol/dm³ solutions are shown in Fig. 10. From all the DPV curves (without as well as with 5 and 10 % modifiers content) the peak currents and the peak potentials were determined. All the obtained values are presented in Table 3. The peak potentials reveal similar values 0.79 ± 0.01 V for all the 4-CP concentrations and both modifier's contents or the unmodified CPE. The recorded DPV curves show the dependence of the peak current on the 4-CP solution concentration. The I_p exhibit increasing values with an increasing 4-CP concentration for the given CPEs modifier. The peak currents in the case of each CPEs were about two times higher when the 4-CP concentration was increased two times. The results collected in Table 3 show also the other dependence. The increase of the CPE modifier content gives an increase in the peak current. When the modifier content was enhanced (from 5 to 10 %) one could observe a peak current increase of about 1.5 times.

The results showed also that the properties of the modifier have a significant impact on the peak currents.

Fig. 8 The plots of square root of scan rate versus peak current (a) and logarithm of peak current versus logarithm of scan rate (b)

Fig. 9 Effect of accumulation time on the peak current of the 4-CP in 0.1 mol/dm³ Na₂SO₄ solution

Fig. 10 DPV registered for 500 µmol/dm³ 4-CP solutions using carbon paste electrodes containing 5 (**a**) and 10 % (**b**) by mass of tested materials. Modifiers: 1—SBA-15-NH₂, 2—SBA-15-Sigma, 3—SBA-15, 4—unmodified carbon paste electrode
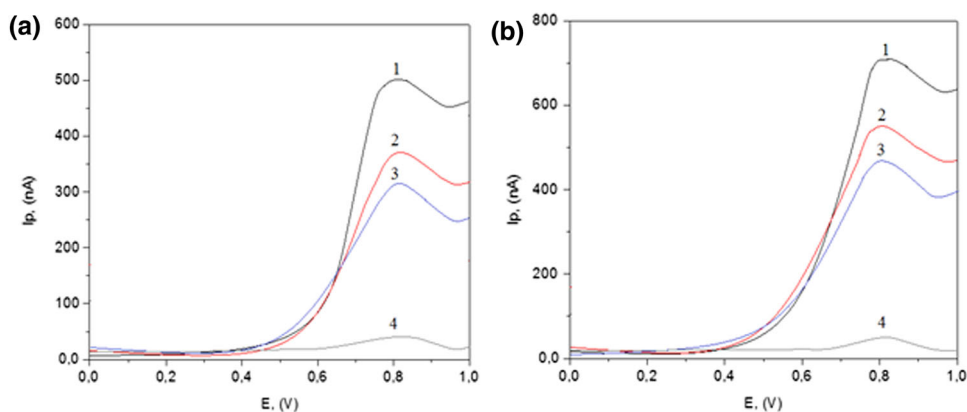
Table 3 Peak currents and potentials determined from DPV curves for carbon paste electrodes modified by adding various quantity of mesoporous materials

Carbon paste electrode	Modifier cont. (%)	Concentrations of 4-CP (µmol/dm³)				
		Peak current (nA)				Peak potential (V)
		500	250	100	50	
SBA-15-Sigma/CPE	5	380	200	75	55	0.80
	10	540	290	135	80	0.80
SBA-15/CPE	5	340	170	72	40	0.80
	10	490	240	110	75	0.79
SBA-15-NH₂/CPE	5	520	250	110	70	0.79
	10	710	400	185	90	0.79

Under the same measurement conditions, the SBA-15-Sigma was a better modifier than the SBA-15, which may be associated with its higher specific surface area and higher adsorption capacity. The positive correlation between the peak current and the specific surface area/adsorption capacity of the modifier has also been observed for carbonaceous materials (Kusmierek et al. 2015). Significantly the best modifier of the CPEs was amino-functionalized mesoporous silica (SBA-15-NH₂). As in the case of adsorption (Table 2) it was due to the better adsorption capacity of the SBA-15-NH₂. The increase in peak current resulting from the amino-functionalization of the SBA-15 was observed also for aminophenols (Duan et al. 2013), dihydroxybenzene (Zhang et al. 2011) and naphthol isomers (Zheng et al. 2015). The higher ability to accumulate 4-chlorophenol and other phenolic derivatives results from the formation of hydrogen interaction between them and the SBA-15-NH₂. In the case of 4-CP (a weak acid) it can be treat as a proton donor for -NH₂ group.

3.3.4 Validation of the method

The limit of detection was calculated using the equation: LOD = 3σ/a where "σ" is a standard deviation of the blank signal and "a" is a slope of the calibration curve. The LOD observed for CPE modified with SBA-15/CPE was 1.4 µmol L⁻¹ and SBA-15-NH2 0.4 µmol L⁻¹. The limit of detection at a CTAB-MMT-modified carbon paste electrode was 0.02 µmol L⁻¹ for 2 min accumulation (Yang et al. 2008). However, the detection and determination of 4-CP using ordered mesoporous silica SBA-15 modified CPEs has not yet been reported.

4 Conclusions

This paper describes the adsorptive properties of three ordered mesoporous silicas SBA-15 and their usefulness as modifiers of the CPEs for detection of 4-chlorophenol. The adsorption isotherms of the 4-CP on the mesoporous silicas were analyzed using the Generalized Langmuir model, and its simplest form—Langmuir equation was found as the best model for analysis of the studied experimental systems. The adsorption capacities (q_m) estimated from the Langmuir equation decreased in the order: SBA-15-NH₂ > SBA-15-Sigma > SBA-15. All three materials were applied as the modifiers of carbon paste electrodes. The influences of the instrumental parameters, the accumulation time and the amount of the modifier were examined. The results showed that the peak current increased with the increasing of the accumulation time up to about 3–4 min and along with the amount of added modifier. Compared with the bare

(graphite) CPE, all the mesoporous silica modified CPEs greatly increased the oxidation peak current of 4-CP, showing strong signal enhancement effects. The results demonstrated that the SBA-15-NH$_2$ modified CPE exhibited better electroanalytic performance and higher sensitivity toward 4-CP than those at the SBA-15/CPE and SBA-15-Sigma/CPE. The existence of amino groups in the channels facilitated the electron transfer between the mesoporous silica material and the electrode surface (Zhang et al. 2011). In our study for the first time such adsorption and electrochemical measurements are carried out in parallel. We have shown that the increase in sorption capacity of SBA-15 samples is accompanied by growth in the peak current recorded by DPV for the CPEs containing different amounts of added SBA-15 as a modifier. The increase of BET surface of silica and the presence of NH$_2$ groups is accompanied by the proportional increase of both adsorption and peak current.

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