

Using the Organofunctionalised SBA-15 Nanostructured Silica as a Carbon Paste Electrode Modifier: Determination of Cadmium Ions by Differential Anodic Pulse Stripping Voltammetry

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O desempenho do eletrodo de pasta de carbono (EPC) modificado com a sílica SBA-15 nanoestruturada organofuncionalizada com benzotiazol-2-tiol na determinação de íons Cd(II) em águas naturais é descrito, baseado no processo de DPASV. O Cd(II) apresentou um pico de oxidação por volta de $-0,85$ V (vs. ECS) em tampão fosfato (pH 3,0). Os melhores resultados obtidos foram com as seguintes condições otimizadas: amplitude de pulso 100 mV, 2 min de tempo de acumulação, velocidade de varredura 10 mV s⁻¹ em solução tampão fosfato pH 3,0. Usando tais parâmetros observou-se uma resposta linear para o Cd(II) no intervalo de $1,00$ a $10,0 \times 10^{-6}$ mol L⁻¹ com limite de detecção de $4,5 \times 10^{-7}$ mol L⁻¹. Cd(II) foi adicionado em amostras de águas naturais e determinado com recuperação média de 96,4% em concentrações da ordem de 10^{-6} mol L⁻¹.

The performance of a carbon paste electrode (CPE) modified with SBA-15 nanostructured silica organofunctionalised with 2-benzothiazolethiol in the determination of Cd(II) ions in natural water is described, based in a DPASV procedure. The Cd(II) oxidation peak was observed around -0.85 V (vs. SCE) in phosphate buffer (pH 3.0). The best results were obtained under the following optimised conditions: 100 mV pulse amplitude, 2 min accumulation time, 10 mV s⁻¹ scan rate in phosphate buffer pH 3.0. Using such parameters a linear dynamic range from 1.00 to 10.0×10^{-6} mol L⁻¹ Cd(II) was observed with limit of detection 4.5×10^{-7} mol L⁻¹. Cd(II) spiked in a natural water sample was determined with 96.4% mean recovery at μ mol L⁻¹ level. The results indicate that this electrode is sensitive for determination of Cd(II). Interference of some divalent cations were also evaluated.

Keywords: cadmium, SBA-15 nanostructured silica, carbon paste electrode, 2-benzothiazolethiol

Introduction

The discovery of micelle templated silicas like MCM-41, MCM-48 and SBA-15 first reported in the early 1990's has led to a whole new class of materials with high thermal and mechanical stability.^{1,2} The continuing development of mesoporous silica make the studies on silica-supported nanocomposites very active. Due to their uniform pore size, hexagonal array of one-dimensional cylindrical channels and large surface area, mesoporous

silica are important for applications in emergent areas such as energy storage in doublelayer supercapacitors, catalytic support in fuel cell electrodes, adsorption of bulky molecules in liquid phase, improvement of selectivity and sensitivity in the preparation of electrodes for electroanalysis etc.³⁻⁶ Walcarius^{7,8} present extensive reviews about the preparation and application of silica modified electrodes showing their importance as electroanalytical sensors. Mesoporous silica can be modified and functionalised by incorporation of organic groups in the silica structure via synthesis procedure and the immobilisation of organic substances that can be bonded to the silanol groups on the silica surface.

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Electrochemical sensors based on stripping voltammetry appear to be a promising technique for determining aqueous heavy metal concentrations. These sensors are usually sensitive, compact, low cost and easily integrated into field-deployable units.^{6,9,10} Carbon paste electrodes modified with functional ligands have been more widely used to pre-concentrate and quantify trace metal ions.¹¹⁻¹⁷

The pollution of cadmium is one of the most serious environmental problems because of our stability in contaminated site and complexity of mechanism in biological toxicity. Once absorbed, cadmium can be accumulated in the body and greatly threaten the health of human.^{18,19} Due to its affinity by sulphur, modifiers containing sulphur in their structures are interesting in the preparation of modified electrodes for cadmium detection. Several procedures have been proposed for the determination of cadmium based on adsorptive accumulation.^{20,21} Mercury films and the mercury drop electrodes are the most used electrodes in the determination of Cd(II) in different samples.^{22,23}

Simultaneous determination of Pb(II), Cd(II) and Cu(II) have been proposed based on differential pulse and adsorptive stripping voltammetry procedures.^{24,25}

In the present work, the use of organofunctionalised SBA-15 silica with 2-benzothiazolethiol in the preparation of carbon paste electrodes is described. SBA-15 silica presented the advantage of no need of surface pre-treatment before modification when compared with silica gel usually employed in such methods. The best conditions for a differential pulse anodic stripping voltammetric procedure were optimised and the electrode was applied in the determination of Cd(II) spiked in a well water sample with good results.

Experimental

Apparatus

All the voltammetric measurements were carried out in a 20 ml capacity thermostated glass cell at 25 °C, using a carbon-paste modified with SBA-15 silica organofunctionalised with 2-benzothiazolethiol (BTPSBA-MCPE) as a working, saturated calomel as reference (SCE) and platinum wire as auxiliary electrodes. High purity nitrogen (FID. 4.9 AGA) was used for deaeration of the electrolyte solution. DPASV were performed in BAS CV-50W Voltammetric Analyzer (Bioanalytical Systems) controlled by the BAS 50W windows control software, v. 2.3 (Bioanalytical Systems).

Reagents and solutions

All the solutions were prepared with water purified in a Millipore Milli-Q system. All the chemicals were of analytical grade and used without further purification. The supporting electrolyte used for most experiments was a 0.10 mol L⁻¹ phosphate buffer pH 3.0. Stock solutions containing 1.0 × 10⁻³ mol L⁻¹ Cd(II) were prepared daily by dissolving an appropriate amount of a 1,000 mg L⁻¹ reference cadmium chloride solution (Merck) in 100 mL of the 0.10 mol L⁻¹ phosphate buffer pH 3.0.

The 3-(chloropropyl)-trimethoxysilane (Aldrich) and 2-benzothiazolethiol (Sigma) were used in the functionalization of the SBA-15 silica.

A 1-2 mm particle size graphite powder (Aldrich) and mineral oil (Aldrich) were used for the preparation of the carbon pastes.

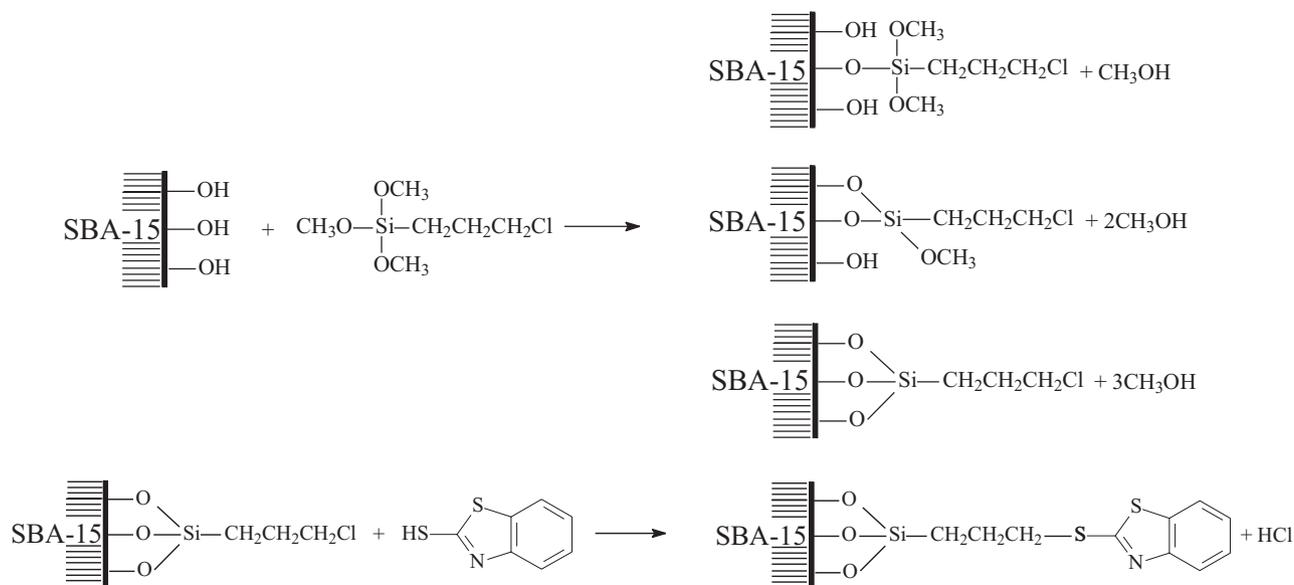
Preparation of the organofunctionalised SBA-15 silica

The SBA-15 silica was synthesized according to a previously described procedure.³ SBA-15 silica with a large surface area (> 1500 m² g⁻¹) and large pore volumes (> 1 cm³ g⁻¹) was used without further treatment, in a procedure described earlier.^{6,26} Thus 3.0 g of SBA-15 silica was refluxed with 2 mL of the 3-(chloropropyl)-trimethoxysilane in 40 mL dry xylene for 24 h. The solid was filtered and washed with xylene, ethanol, acetone and ether, successively.

In the organofunctionalization procedure, a sample of 3-chloropropyl SBA-15 silica was suspended in a *N,N'*-dimethylformamide solution containing 2-benzothiazolethiol kept under constant stirring and reflux during 24 h. The suspension was filtered and washed successively with *N,N'*-dimethylformamide, ethanol, acetone and ether. The solid was treated with hot ethanol in a Soxhlet extractor during 8 h for elimination of the excess of organoalcoxysilane. Finally, the product was dried in air at 80 °C for 12 h. Scheme 1 shows the silica modification procedure. The organofunctionalised SBA-15 silica was characterised by elemental analysis, IR spectroscopy, thermal analysis (TG and DSC), NMR in solid phase (¹³ C and ²⁹ Si) and scanning electron microscopy.

Preparation of the modified carbon paste electrodes

Modified carbon paste electrodes (MCPE) were prepared by mixing the graphite powder with BTPSBA at varying ratios (10, 15, 20, 25 %, m/m). Exactly 0.750 g of this mixture was subsequently added to 0.250 g of mineral oil (25%, m/m) and mixed in a mortar for at least



Scheme 1. Covalent modification of SBA-15 silica surface by silanization reaction with 3-(chloropropyl)-trimethoxysilane and conversion to organofunctionalised SBA-15 silica with 2-benzothiazolethiol.

20 min to produce the final paste. The carbon paste electrode was finally obtained by packing the paste into a plastic tube 4.5 mm i.d. (geometrical area 0.16 cm²) and arranged with a copper wire serving as an external electric contact. Appropriate packing was achieved by pressing the electrode surface against a bond paper until a smooth surface was obtained.

Sample preparation and analysis of cadmium in well water

A well-known amount of cadmium was spiked to an aliquot of 10.0 mL of well water in order to reach a final concentration of 2.0×10^{-5} mol L⁻¹ in Cd²⁺. This sample was mixed with 10.0 ml of 0.1 mol L⁻¹ phosphate buffer pH 3.0.

The Cd(II) content in these samples was determined by four successive addition of a standard cadmium(II) solution. The optimised parameters of differential pulse anodic stripping voltammetry for cadmium determination in the sample were: potential interval -1.10 to -0.60 V (vs. SCE); scan rate of 10 mV s⁻¹, 100 mV pulse amplitude; accumulation time 120 s at -1.10 V. All measurements were performed in solutions deaerated by bubbling N₂ for 15 min.

The contents of the metals present in the well water sample was determined in an Intralab AA12/1475 (Gemini) using air or acetilene flame and appropriated hollow cathode lamps. The wavelength and concentration intervals were defined according to the manufacturer of the instrument.

Results and Discussion

Characterization of the chemically modified SBA-15 silica

Figure 1 presents the IR spectra of unmodified SBA-15 silica (curve a), 3-chloropropyl SBA-15 silica (curve b) and BTPSBA (curve c).

IR spectroscopy is employed for accompanying the functionalisation steps of SBA-15 silica. In the region of 1300-2000 cm⁻¹, it was possible to observe the most significant changes, when the spectra of SBA-15 silica is compared with the functionalised SBA-15 silica one. The infrared spectra shown in Figure 1 confirm the presence of 2-benzothiazolethiol groups bound to the silica surface. The bands in the 1600-1700 cm⁻¹ region

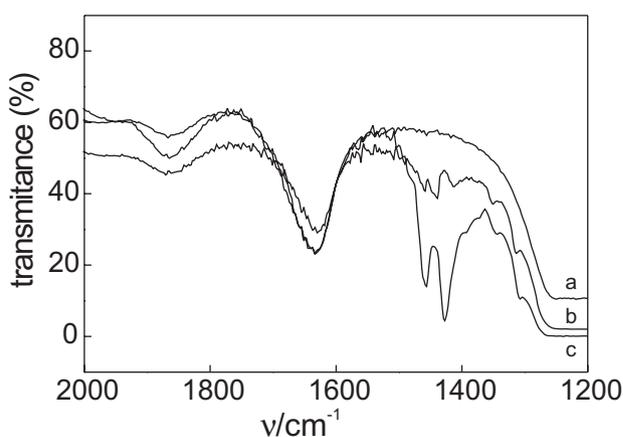


Figure 1. IR spectroscopy the functionalised SBA-15 silica steps: a) unmodified silica SBA-15, b) 3-chloropropyl SBA-15 silica and c) BTPSBA.

represents the OH bending and stretching vibration of Si-OH groups and physisorbed water. The bands in the 1435-1410 cm^{-1} region correspond to the stretching vibration of $\text{CH}_2\text{-S}$ group and at 1540 cm^{-1} relative to the stretching of Si-NH₂ groups.

Differential Pulse Anodic Stripping Voltammetry (DPASV)

DPASV of 3.85×10^{-5} mol L⁻¹ Cd(II) solution in 0.1 mol L⁻¹ phosphate buffer pH 4.0, showed one anodic peak around -0.86 V (*vs.* SCE). Parameters such as accumulation potential, pre-concentration time, scan rate, supporting electrolyte, pH, electrode composition that affects the voltammetric peak current were optimized as described below.

Effect of scan rate and pulse amplitude

The anodic peak currents for cadmium in DPASV were evaluated as a function of scan rate between 5 and 50 mV s^{-1} and pulse amplitudes from 15 to 100 mV. For this purpose pre-concentration of Cd(II) from a 3.85×10^{-5} mol L⁻¹ solution in 0.1 mol L⁻¹ phosphate buffer pH 4.0 were performed for 10 s, potential interval -1.10 to -0.60 V (*vs.* SCE) and a carbon-paste composition of 15% (m/m) modified SBA-15 silica, 60% (m/m) graphite and 25% (m/m) mineral oil. ⁶ The scan rate of 10 mV s^{-1} was chosen because it presented more anodic peak current. Higher scan rates caused loss in peak definition and lower anodic peak current.

The peak current increased in higher pulse amplitude, hence the better pulse amplitude was 100 mV.

Effect of accumulation potential

Accumulation potentials between -1.40 and -1.00 V were investigated, under the same conditions as above. Then Cd(0) was oxidized by differential pulse voltammetry at 10 mV s^{-1} and pulse amplitude of 100 mV. It was observed that for an accumulation potential in -1.00 V, a decrease in the anodic peak current occurs caused by an inefficient reduction of Cd(II) to Cd(0) at the electrode surface. In -1.40 and -1.10 V interval higher anodic peak current was observed in -1.10 V. Thus -1.10 V was chosen as the accumulation potential in further studies, with the advantage of minimising the possibility of reducing interfering species at higher potentials.

Effect of pre-concentration time

The dependence of anodic peak current with the pre-concentration time for 3.85×10^{-5} mol L⁻¹ Cd(II) was also investigated. The anodic peak current increases with the increasing in the pre-concentration time between 0 and 120 s above which it became nearly constant due to the

surface saturation.^{27,28} Hence for all subsequent measurements pre-concentration time of 120 s was employed.

Electrode composition effect

The effect of the carbon paste composition in the voltammetric response of the electrode modified with BTPSBA was evaluated by DPASV of 3.85×10^{-5} mol L⁻¹ Cd(II) in 0.1 mol L⁻¹ phosphate buffer pH 4.0 in the better conditions above. The anodic peak current increased with the amount of organofunctionalised SBA-15 silica in the paste up to 15% (m/m), decreasing significantly when more modified silica is used in the electrode preparation. This probably occurs due to the a decrease in the conductive area at the electrode surface. According to these results a carbon-paste composition of 15% (m/m) modified SBA-15 silica, 60% (m/m) graphite and 25% (m/m) mineral oil was continue to be employed.

Effect of supporting electrolyte and pH

The voltammetric behavior was examined in different supporting electrolytes as 0.10 mol L⁻¹ sodium hydrogen-phosphate, 0.10 mol L⁻¹ sodium acetate, 0.10 mol L⁻¹ potassium chloride and 0.10 mol L⁻¹ potassium nitrate solution with pH adjusted to 2.0, 3.0, 4.0, 5.0 and 6.0. Voltammetric peaks were observed in sodium hydrogen-phosphate, sodium acetate and potassium chloride, however, in phosphate buffer the anodic peak currents was higher and better defined peak shapes were observed, and this supporting electrolyte was continue to be employed in next experiments.

The effect of pH on the voltammetric response of BTPSBA-MCPE was studied in a pH range between 2.0 and 6.0 in a solution containing 3.85×10^{-5} mol L⁻¹ Cd(II) in 0.1 mol L⁻¹ phosphate buffer and is presented in Figure 2. The anodic peak current increased as the pH is changed from 2 to 3, reaching a maximum at the last. In the pH range 4.0-6.0 the current decreased.

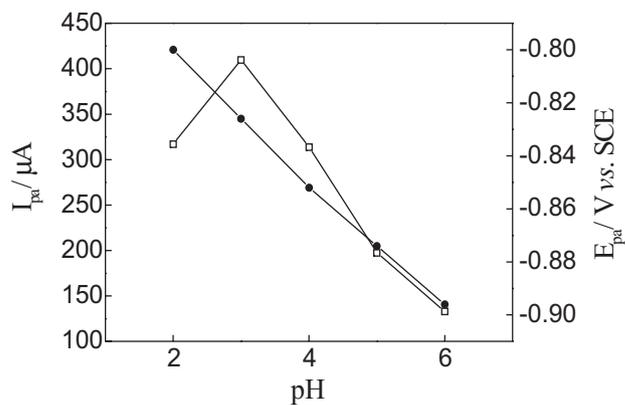


Figure 2. Effect of pH on anodic peak current (\square) and potential (\bullet) of BTPSBA-MCPE of 3.85×10^{-5} mol L⁻¹ Cd(II) in 0.1 mol L⁻¹ phosphate buffer. Potential interval: -1.10 to -0.60 V (*vs.* SCE); accumulation time 120 s, scan rate of 10 mV s^{-1} and pulse amplitude of 100 mV.

Probably in more acidic medium the ligand is preferentially in the protonated form, since the estimated $pK_{a1} = 0.85 \pm 0.30$ at 25°C is described for the free 2-benzothiazolethiol.²⁹ At higher pH the metal hydrolysis seems to prejudice accumulation at the electrode surface.

The anodic peak potentials are also pH dependent. As the pH increased the peak potentials moved towards more anodic values. The slope of $-26\text{ mV per pH unit}$ suggests a $2e^-$ oxidation process in the 2-4 pH range. For pH from 4-6 the slope changed to 24 mV pH^{-1} suggesting that some acid-base property change is occurring with the modifier, may be the pK_a of the specie is reached. Scheme 2 shows representation of the pre-concentration mechanism and stripping of Cd(II) on the modified electrode surface.

Comparison of the voltammetric behaviour of Cd(II) on carbon paste and silica modified electrodes

Figure 3 presents the differential pulse anodic stripping voltammograms obtained with unmodified carbon paste electrode, SBA-15 silica and organofunctionalised SBA-15 silica modified carbon paste electrodes in 0.10 mol L^{-1} phosphate buffer pH 3.0. No peaks were observed in the potential range -1.40 to -0.60 V (vs. SCE) in the phosphate buffer at the BTPSBA-MCPE (curve a).

However, when the accumulation process was carried out for 120 s at -1.10 V in a solution containing 3.85×10^{-5}

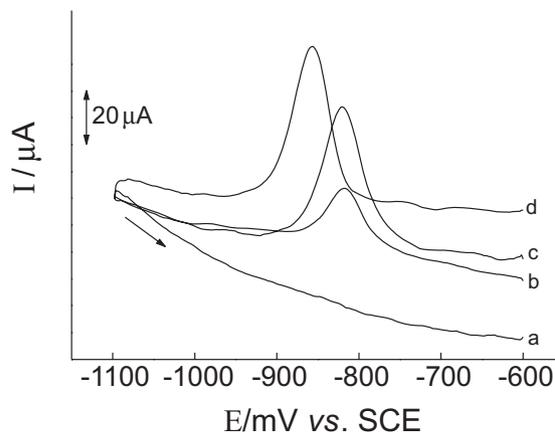
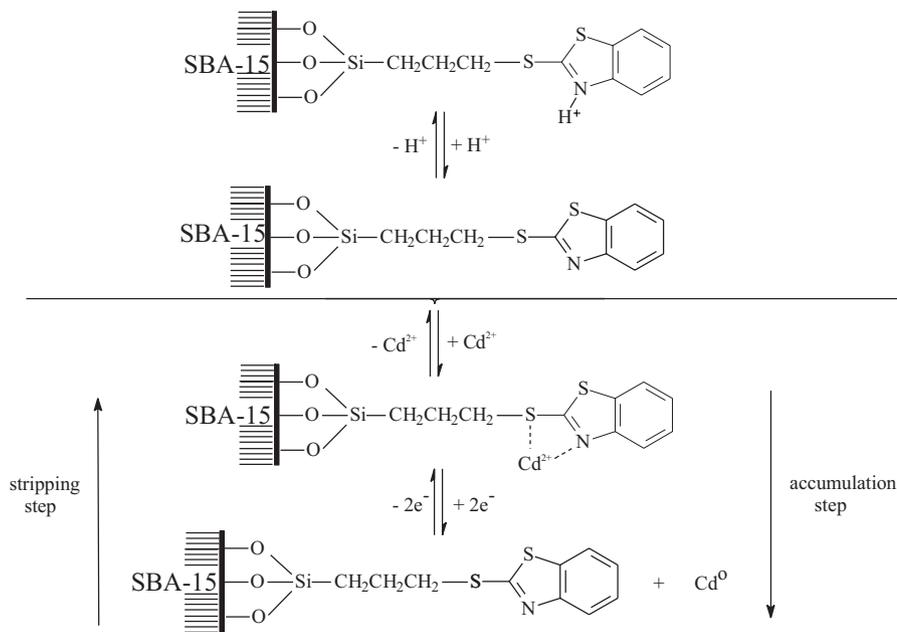


Figure 3. Differential pulse anodic stripping voltammograms obtained at 25.0°C , scan rate of 10 mV s^{-1} and pulse amplitude of 100 mV for (a) BTPSBA-MCPE in the presence only the 0.10 mol L^{-1} phosphate buffer solution pH 3.0, (b) unmodified electrode in the presence of $3.85 \times 10^{-5}\text{ mol L}^{-1}$ Cd(II), (c) SBA-15-MCPE in the presence of $3.85 \times 10^{-5}\text{ mol L}^{-1}$ Cd(II) and (d) BTPSBA-MCPE in the presence of $3.85 \times 10^{-5}\text{ mol L}^{-1}$ Cd(II). Potential interval -1.10 to -0.60 V (vs. SCE) and accumulation time 120 s.

$\text{mol L}^{-1}\text{Cd(II)}$, at the unmodified carbon paste electrode (curve b), the Cd(II) oxidation peak appears at -0.81 V , the SBA-15-MCPE (curve c) exhibits an anodic peak at -0.82 V and the BTPSBA-MCPE (curve d) the Cd(II) oxidation peak appears at -0.85 V , with higher intensity of the anodic current in comparison to that observed at another electrodes. The increase in anodic current at the modified electrode demonstrates that the BTPSBA plays an important role in the accumulation process of Cd(II) on the electrode surface with some advantages in sensitivity.



Scheme 2. Tentative representation of the pre-concentration mechanism and stripping of Cd(II) on the modified electrode surface.

Analytical curve, precision, detection limit and recovery in buffer solutions

Analytical curve for Cd(II) is presented in Figure 4 under the set of optimum conditions resumed in Table 1. The anodic peak current at the BTPSBA-MCPE was linearly proportional to the concentration of the Cd(II) in a range from 1.00 to 10.0×10^{-6} mol L⁻¹ with a limit detection of 4.5×10^{-7} mol L⁻¹ (three times the signal blank/slope).³⁰ The linear regression equation (see detail in Figure 4) is:

$$I_{pa} = -2.27 \times 10^{-6} + 12.12[\text{Cd}^{2+}]; r = 0.998; n=6 \quad (1)$$

From concentrations of Cd(II) higher than 2.0×10^{-5} mol L⁻¹ a deviation of linearity occurred probably due to saturation of the active sites on the electrode surface.

The present electrode can be used without resurfacing or activation and with a relatively low pre-concentration time, when compared with other methods.

Interferences

The influence of Zn(II), Pb(II), Cu(II), Co(II) and Mn(II) in the Cd(II) anodic peak current has been evaluated and the results are presented in Table 2. Severe suppression of the Cd(II) current is observed in the presence of Cu(II), Co(II) and Pb(II), which presence diminished the signal but the influence was constant in any concentration investigated. For Zn(II) and Mn(II) presented a smaller negative interference. The strong negative effect of Cu(II) can be related to a preferential interaction with the 2-bezothiazolethiol groups in the silica. A less intense interaction between the other cations and the modifier could explain the effect for the rest of the interferants investigated.

However the separation of the peaks suggests that a simultaneous analysis of some of these cations can be performed.

Analysis of cadmium in well water

The proposed electrode was applied for DPASV determination of Cd(II) spiked in a well water sample. The results obtained using the standard addition method are presented in Table 3. Recoveries between 95.6 and 97.7% of Cd(II) from well water samples (n=3) was obtained, for 2.99, 4.96, 8.92, 14.78 $\mu\text{mol L}^{-1}$ of Cd(II) added to each sample, shown in the Table 4. Statistical calculations for the assay results showed suitable precision of the proposed method. According to the *F*-test, there were no significant differences between the calculated and added concentrations at the 95% confidence level, indicating that BTPSBA-MCPE can be used for voltammetric determinations of Cd(II) in water samples.

Table 2. Effect of some divalent cations in the 3.85×10^{-5} mol L⁻¹ Cd(II) signal under the optimized DPASV conditions, when compared with the solution that do not contains the interferant

Interferent	Concentration/(10^{-5} mol L ⁻¹)	(%) of Cd(II) signal*
Cu ²⁺	1.0	30.3
	2.0	15.3
	4.0	7.85
Pb ²⁺	1.0	75.4
	2.0	64.0
	4.0	58.4
Zn ²⁺	1.0	94.9
	2.0	80.3
	4.0	77.0
Mn ²⁺	1.0	95.9
	2.0	91.1
	4.0	87.9
Co ²⁺	1.0	78.3
	2.0	71.0
	4.0	62.8

* in relation to a 3.85×10^{-5} mol L⁻¹ Cd(II) in 0.1 mol L⁻¹ phosphate buffer solution pH 3.0, without interferent.

Table 3. Determination of Cd(II) in water sample by proposed method

Repetition	Cadmium ions/($\mu\text{mol L}^{-1}$)		<i>E_r</i> (%)
	Added	Found	
1	2.00	2.03	+1.5
2	2.00	1.91	-4.5
3	2.00	1.95	-2.5
Mean = 1.96 ± 0.06			

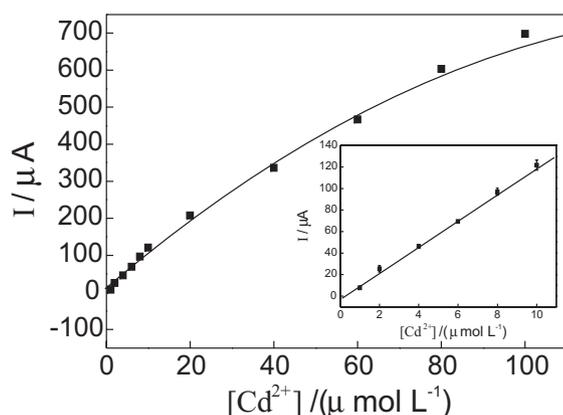
E_r = relative error = added vs. found using the voltammetric proposed method.

Table 1. Optimized parameters for cadmium determination using the carbon paste electrode modified with BTPSBA in differential pulse anodic stripping voltammetry

Parameter	Optimized value
Scan rate	10 mV s ⁻¹
Pulse amplitude	100 mV
Accumulation potential	-1.10 V (vs. SCE)
Pre-concentration time	120 s
Electrode composition	15% (m/m) modified SBA-15 silica, 60% (m/m) graphite and 25% (m/m) mineral oil
Supporting electrolyte and pH	0.10 mol L ⁻¹ phosphate buffer and pH 3.0

Table 4. Results of the recovery experiment in well water for four standard additions of Cd(II)

Added/($\mu\text{mol L}^{-1}$)	Found/($\mu\text{mol L}^{-1}$)	Recovery % = Found/Added \times 100
2.99	2.92 ± 0.05	97.7
4.96	4.74 ± 0.06	95.6
8.92	8.55 ± 0.08	95.9
14.78	14.74 ± 0.03	96.4
		Mean = 96.4 ± 0.93

**Figure 4.** Analytical curve obtained under the conditions describe in the Table 1.**Table 5.** Trace metal concentration in natural water

Metallic cation	Concentration/(mol L^{-1})
Fe^{3+}	3.52×10^{-7}
Zn^{2+}	3.01×10^{-7}
Al^{3+}	-
Cu^{2+}	-
Na^+	1.40×10^{-4}
K^+	2.60×10^{-5}
Mg^{2+}	4.90×10^{-5}
Ca^{2+}	3.33×10^{-4}

Although interferences were found for the cations investigated above it seems that the species naturally occurring in the well water did not interfered in Cd(II) determination in the naturally matrix. The amount of metallic cations found in the water by flame atomic absorption analysis is presented in Table 5.

Conclusions

This work shows that the SBA-15 silica organofunctionalised with 2-benzothiazolethiol can be used in the preparation of modified carbon paste electrodes as one of the applications of the modified nanostructured material, being the determination of Cd(II) presented here as an example of such possibility.

Although the modified electrode signal showed to be severely influenced by interferants e pH, a reproducible and accurate determination can be achieved using the DPASV procedure in natural water sample.

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