Study of an organically modified clay: Selective adsorption of heavy metal ions and voltammetric determination of mercury(II)

Newton L. Dias Filho *, Devaney Ribeiro do Carmo

Departamento de Física e Química, UNESP-Universidade Estadual Paulista, Avenida Brasil, 56-Centro, C.P. 31, 15385-000 Ilha Solteira, SP, Brazil

Abstract

In this work, a hydrophilic clay, Na-montmorillonite from Wyoming, USA, was rendered organophilic by exchanging the inorganic interlayer cations for hexadecyltrimethylammonium ions (HDTA), with the formulae of $[(CH_3)_3N(C_{16}H_{33})]^+$ ion. Based on fact that organo-clay has high affinities for non-ionic organic molecules, 1,3,4-thiadiazole-2,5-dithiol was loaded on the HDTA-montmorillonite surface, resulting in the 1,3,4-thiadiazole-2,5-dithiol-HDTA-montmorillonite complex (TDD-organo-clay).

The following properties of TDD-organo-clay are discussed: selective adsorption of heavy metal ions measured by batch and chromatographic column techniques, and utilization as preconcentration agent in a chemically modified carbon paste electrode (CMCPE) for determination of mercury(II).

The main point of this paper is the construction of a selective sensor, a carbon paste electrode modified with TDD-organo-clay, its properties and its application to the determination of mercury(II) ions, as this element belongs to the most toxic metals. The chemical selectivity of this functional group and the selectivity of voltammetry were combined for preconcentration and determination.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Organo-clay; Carbon paste electrodes; Voltammetry; Mercury; Preconcentration

1. Introduction

Clay minerals consist of silicate layers stacked on one another and are important in many different fields such as agriculture, oil drilling, building industry [1]. In the tetrahedral layers of mineral clays Si^{4+} ions are replaced isomorphously by Al^{3+} ions and, in the octahedral layer Al^{3+} ions are replaced by especially Mg^{2+} ions but also Fe^{3+} ions, and Mg^{2+} ions by Li^+ ions producing layers negatively charged. The negative charges of the layers are compensated by cations Ca^{2+}, Mg^{2+} or alkali-metal ions bounded between the layers. These cations can be exchanged by other inorganic or organic cations [2].

Clays obtained by adsorption of organic molecules, at the maximum degree of hydrophobicity are called organo-clays and are used in a wide range of practical applications

[3–5]. To build up the organic films between the layers of the montmorillonite-type layer silicates, long chain compounds must be introduced. An organophilic surface and interlayer environment can be produced by replacing naturally occurring inorganic exchange cations with a variety of organic cations [6–10].

Numerous studies have been devoted to clay-organic complexes. However, only a small amount of data has been assembled out to study the quantitative aspects of adsorption of heavy metal ions from aqueous solutions by organo-clay minerals [11]. It is known that traditional organo-clay minerals are ineffective sorbents of aqueous phase heavy metal ions. Based on the fact that organo-clays exhibit strong sorptive capabilities for organic molecules, organofunctional groups with potential usefulness in chemical analysis can be incorporated on its surface. The physically adsorbed reagent do not present any restrictions in coordinating with the metal ions on the surface. Quantitative retention of the metal ion complex species on the surface is achieved provided that they

---

* Corresponding author. Tel.: +55 1837431078; fax: +55 1837424868.
  E-mail address: nldias@dfq.feis.unesp.br (N.L. Dias Filho).

are insoluble in aqueous solution. In this context, organofunctional groups loaded on the organo-clay surface can perfectly be used in preconcentration process of metal ions present in water samples as well as in voltammetric determination of mercury at a chemically modified carbon-paste electrode (CMCPE).

Clay modified electrodes (CMEs) have potential use in electrocatalysis and are very promising as sensors in electroanalytical chemistry. CMEs offers advantages over the conventional electrode due to: (i) mercury electrodes presents high toxicity and rapid deterioration of electrode response [12], (ii) the possibility of oxide formation on the platinum and gold electrodes surface, causing complications with analytical applications [13].

The use of organo-clay complex composite material as an electrode modifier has not been explored so far to electroanalysis. In electroanalysis there is a CME category, which concerns mainly in the electrochemical quantification of various inorganic ions or organic species at trace levels after subsequent preconcentration on the clays surface, and naturally have made them especially attractive for the electrochemical detection of environmental pollutants. The voltammetry applied to clay modified electrodes [14–18] belongs to this category. Clays are also potentially candidates to support biomolecules or electrocatalysts that are often employed to modify electrode surfaces for electroanalysis purposes [19]. The application of organically modified clays or "organo-clays", involving a strong covalent bond between the organic and inorganic components, in combination to electrochemistry remains however rare, in spite of the increasingly growing interest for organo-clays and polymer-clay nanocomposites [20–22]. The typical examples include the preparation of organosilasesquioxane-laponite clay films on solid electrodes [23] and their subsequent utilization as electrochemical sensors [24–28]. The speciation of mercury at trace levels in environmental samples is of great importance nowadays because mercury is one of the most contaminants in water, and accumulatable metals in biological systems [29].

In this work, a organo-clay was obtained by replacement of the inorganic cations in Na-montmorillonite for hexadecyltrimethylammonium ions (HDTA), with the formulae of $[(CH_3)_3N(C_{16}H_{33})]^+$, allowing to open up the lamellae and causing profound changes in the sorption and intercalation of organic molecules. In contrast to natural montmorillonites, organic molecules are now freely sorbed between the montmorillonite lamellae and the sorptive capacity is very much increased. 1,3,4-Thiadiazole-2,5-dithiol (TDD) was loaded on the HDTA-montmorillonite surface, resulting in the 1,3,4-thiadiazole-2,5-dithiol-HDTA-montmorillonite complex (TDD-organo-clay).

This work focuses on the preparation and utilization of the TDD-organo-clay looking at the following properties: (a) selective adsorption towards mercury(II) ions measured by batch and chromatographic column techniques, and (b) utilization as preconcentration agent in a chemically modified

carbon paste electrode (CMCPE) for determination of mercury(II), as this element belongs to the most toxic metals.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical reagent grade unless stated otherwise. The surfactant used in the preparation of the organo-clay was the commercial product hexadecyltrimethylammonium (HDTA) bromide (purum quality). Solutions were prepared from doubly-demineralized water obtained by passing distilled water through a Millipore Milli-Q water purification system. Dilute solutions ($\leq 1 \times 10^{-3}$ mol L^{-1}) of Hg(II) and other ions were prepared fresh daily. Stock standard solutions of Hg(II), Pb(II), Cd(II), Cu(II), and Zn(II) and other ions were prepared by stepwise dilution from 1000 mg L^{-1} Titrisol standards (Merck).

2.2. Preparation of the organo-clay complex

The clay utilized in this work was a sample of montmorillonite (Volclay 325) from Wyoming, USA, supplied by American Colloid Company, Arlington Heights, IL, USA. Clay mineral montmorillonite was converted into the sodium homoionic form by the procedure described in the literature [30].

The sodium form of the clay, homoionic Na-montmorillonite, was treated with an aqueous solution containing an excess of the hexadecyltrimethylammonium (HDTA). Bromide salt, then washed with distilled water until no free bromide was found. The homoionic hexadecyltrimethylammonium-clay (HDTA-montmorillonite) was then dialyzed to remove excess salt, freeze-dried, and stored at room temperature.

Based on the fact that usual organo-clays have high affinities for non-ionic organic molecules, 1,3,4-thiadiazole-2,5-dithiol (TDD) was loaded on the HDTA-montmorillonite surface, by the procedure described as follows.

About 30 g of HDTA-montmorillonite was immersed in 50 mL of TDD pyridine solution (10%, w/v) and shaken for few hours and then the solvent was removed in a rotary evaporator under vacuum. The product obtained, 1,3,4-thiadiazole-2,5-dithiol-HDTA-montmorillonite complex (TDD-organo-clay), was suspended in deionized water with continuous stirring for 2 h, then filtered and washed with deionized water. The material was again washed repeatedly with deionized water to remove any non-adsorbed reagent. Finally the product was dried at 353 K under reduced pressure for about 5 h.

2.3. Adsorption isotherms and preconcentration experiments

The adsorption isotherms of metal ions by TDD-organo-clay were determined for Hg(II), Cd(II), Pb(II), Cu(II), and

Zn(II) metal ions in aqueous solutions at different pH values by batch method. About 0.5 g of the sorbent were immersed in 50 mL solutions of metal ions of 2.5×10^{-3} mol L^{-1} and shaken for 30 min at 298 ± 0.2 K. The quantity of the metal in each flask was determined by AAS.

The quantity of the adsorbed metal, N_f, in each flask was determined by the equation:

$$N_f = \frac{N_a - N_s}{m} \qquad (1)$$

where N_a is the initial mole number of the metal in the solution phase, N_s is the metal mole number under equilibrium condition and m is the mass of the adsorbent.

For the preconcentration of individual metal ions by column method, each metal was quantitatively adsorbed adjusting the pH solutions according to the values found in the previous batch method. For these experiments, a glass column with 20 cm × 0.8 cm i.d. was packed with about 5 g of the sorbent. Initially the column was washed with pure water and then 1000 mL of solution of metal ion of 0.5×10^{-6} mol L^{-1} was percolated through the column with a flow rate of 5.0 mL min^{-1}. In every run, the effluent was collected and a quantity of metal ion analyzed. Elution of the metals from the column were made by passing 25 mL of hydrochloric or nitric acid of different concentrations. Quantitative elution of Hg(II) was possible passing 25 mL of 0.05 mol L^{-1} cysteine solution acidified with 3.0 mol L^{-1} HCl solution.

Adsorption and elution studies of a mixture of the metal ions Hg(II), Cd(II), Pb(II), Cu(II), and Zn(II) as well interference of other metal ions, such as Co(II), Ni(II), Mn(II), Bi(III), Fe(II) and Fe(III) were also carried out. The interference of some anions, such as chloride, nitrate, sulphate, fluoride, thiocyanate, bromide, phosphate, acetate, oxalate, and tartrate have also been investigated in this work. In these studies, a series of aqueous solutions were prepared in which the metal ion concentrations were fixed at 0.25×10^{-6} mol L^{-1} except for one of them fixed at 2.5×10^{-6} or 25.0×10^{-6} mol L^{-1}. For adsorption, 1000 mL of aqueous elution was percolated through the column. The adsorbed metal ions were eluted using solutions previously known from study of preconcentration of individual metal ions.

2.4. Apparatus

The N content of the samples was determined by elemental analysis using an equipment EA 1110 from CE Instruments. The data reported are average of at least three parallel determinations. The basal spacings d_L of the clay samples were measured by X-ray diffraction using a Philips X-ray diffractometer Model XRG 3100. Tubo de Cu $\lambda k\alpha$ 1.5406 Å, 40 kV/20 mA. The specific surface area was obtained by the BET technique using ASAP 2000 Micromeritics apparatus.

All electrochemical measurements were recorded with an EG & G Princeton Applied Research Model 273A polarographic analyzer connected to a microcomputer for data collecting. The electrochemical behavior of TDD-organo-clay was monitored by cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV). A three-electrode cell involving a TDD-organo-clay carbon paste as the working electrode, a KCl saturated Ag/AgCl, as the reference electrode, and a Pt-wire as the auxiliary electrode were used for all investigations

2.5. Preparation of the TDD-organo-clay-CPE

The chemically modified carbon paste electrodes (TDD-organo-clay-CPE) was prepared by mixing 22 mg of TDD-organo-clay with 78 mg of graphite (Aldrich) and 50 μL of mineral oil. The TDD-organo-clay-CPE was introduced into the glass cavity with 2 mm inner diameter, connected with of copper wire.

2.6. Procedure

2.6.1. Electrode conditioning
Fresh TDD-organo-clay-CPE surfaces were conditioned by exposure to a 1.0 mg L^{-1} mercury solution at pH 3.00, adjusted with HNO$_3$, for 5 min with open circuit. The speed of stirring was 500 rpm. The electrode was then rinsed with deionized water. The DPASV was recorded over the range −0.2 to +0.8 V in 0.05 mol L^{-1} KNO$_3$ solution. After each measurement, the electrode was rinsed for 2 min in 0.05 mol L^{-1} cysteine solution acidified with 3.0 mol L^{-1} HCl solution with open circuit. This conditioning cycle was repeated five times for each new TDD-organo-clay-CPE surface.

2.6.2. Determination of mercury
The TDD-organo-clay-CPE electrode was placed in 25 mL of stirred 10^{-6} to 10^{-8} mol L^{-1} mercury solution for a pre-determined time. The electrode is then removed from the pre-concentration solution, washed with water, dried with absorbent paper and placed in the measurement cell containing 0.05 mol L^{-1} KNO$_3$ solution. Voltammograms were then recorded over the range −0.2 and +0.8 V. Several "cleaning" solutions were evaluated. Best cleaning efficiency and reproducibility were obtained with 0.05 mol L^{-1} cysteine solution acidified with 3.0 mol L^{-1} HCl solution. The chosen supporting electrolyte was changed after each measurement and the electrode was cleaned with 0.05 mol L^{-1} cysteine solution acidified with 3.0 mol L^{-1} HCl solution as in the conditioning step.

2.6.3. Determination of mercury(II) in natural waters
Successive additions of known concentrations of mercury(II) were introduced into the reference solution of 25 mL sample of river or sea water. The water samples were collected from the Tiete and Pinheiros River and Ubatuba and Santos beach in São Paulo state (Brazil). The mercury was determined by the DPASV method already described to obtain the dependence between peak heights and the concentration

of mercury(II) (calibration plot). Finally, the mercury peaks heights of the spiked water samples were compared with a calibration plot obtained for the reference solution.

3. Results and discussion

3.1. Properties of the TDD-organo-clay: X-ray results

The hydrophilic clay, Na-montmorillonite, was rendered organophilic by exchanging the inorganic interlayer cations for hexadecyltrimethylammonium ions. The total exchange capacity from the N (1.05%) and C (17.15%) content of the alkylammonium derivates is 0.953 and 0.956 mEq/g, respectively.

The intensities of the basal reflections of the montmorillonite after alkylammonium ion exchange and swelling are shown in Fig. 1. Displacement of the Na$^+$ interlayer cations by HDTA cations increased the intensity of the (0 0 1) reflections, and greatly enhanced the structural organization of clay.

The amount of TDD loaded on the organo-clay supporting material was 0.163 mmol of TDD per gram of HDTA-clay. The specific surface area was of 224 m^2 g^{-1}. The TDD-HDTA-clay was stable up to 295 °C and started decomposing above this temperature.

3.2. Isotherms of adsorption: preconcentration and recovery of metal ions

The isotherms of adsorption of metal ions by TDD-organo-clay from aqueous solutions at different pH were determined for Hg(II), Cd(II), Pb(II), Cu(II), and Zn(II) metal ions using the batch method. Fixing the initial concentration of metal ion and changing the pH solutions and plotting N_f versus pH, the set of curves shown in Fig. 2 was obtained. Fig. 2 shows that adsorption of Hg(II) by TDD-HDTA-clay is independent of the pH of the solution. Adsorption of the ion by unmodified clay (natural clay and Na-montmorillonite) and HDTA-clay is negligible in all the pH solutions range (isotherms not shown). The high affinity of TDD-organo-clay in all the pH solutions range by Hg(II) is explained well by the Pearson rule [31] because TDD and Hg(II) are soft base and acid, respectively. It can be observed that adsorption of the remaining metals is dependent of changes in pH solutions and increased when they vary from 1 to 8.

The fraction of surface-attached ligand bonded to Hg(II) ion is given by Eq. (2)

$$\emptyset^{max} = \frac{N_f^{max}}{N_o} \tag{2}$$

where N_o is the amount of TDD organofunctional groups (mol) per mass of TDD-organo-clay (g), and N_f^{max} is the quantity of the adsorbed metal, N_f, under saturation conditions. The value of $\emptyset^{max}$ for Hg(II) in all the pH solutions range is 2.09. As $\emptyset^{max} \approx 2$ for Hg(II), it is clear that this result
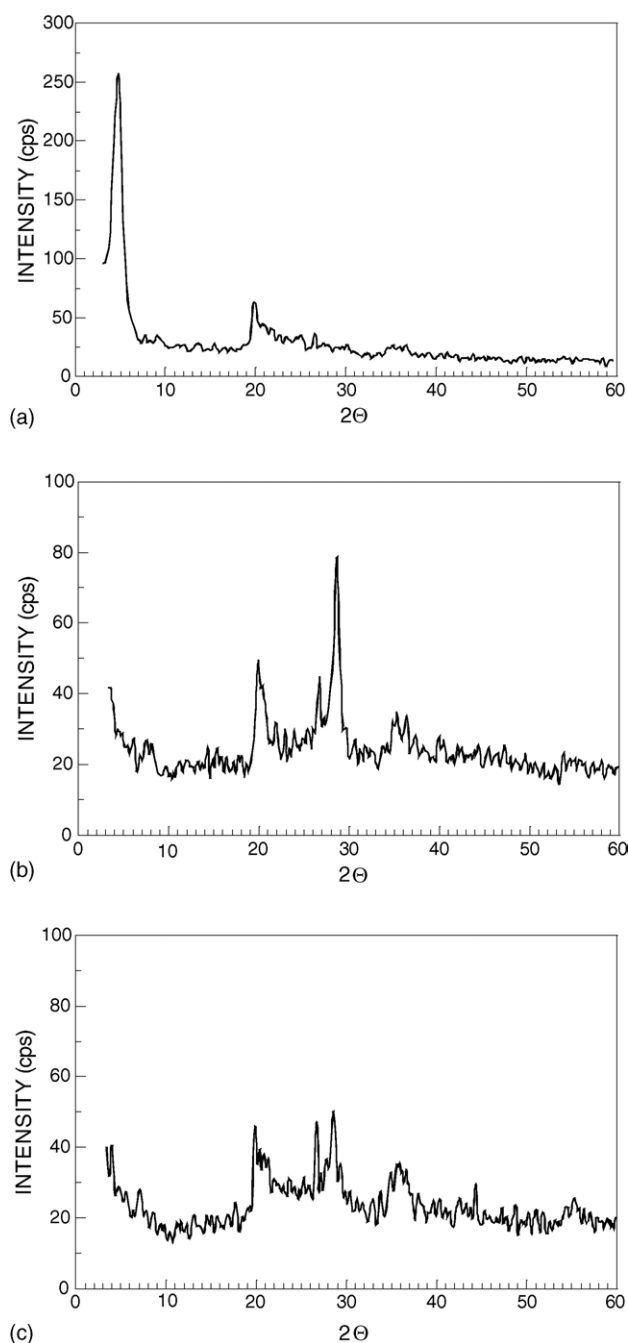

Fig. 1. Intensity of the basal reflections after alkylammonium ion exchange and swelling: (a) natural clay, (b) Na-montmorillonite, (c) HDTA-montmorillonite.

provide good argument that the complexes formed, presumably, are of the type metal/ligand = 2:1. This assumption is reasonably taking into account that the coordination of Hg(II) to five donor sites of the TDD molecule attached to the matrix is possible. The ligand TDD can act as a unidentate towards two Hg(II) ions. The coordination can occur simultaneously through nitrogen and sulphur atoms.

Preconcentration of each metal ion by TDD-organo-clay from an aqueous solution was examined by column method.
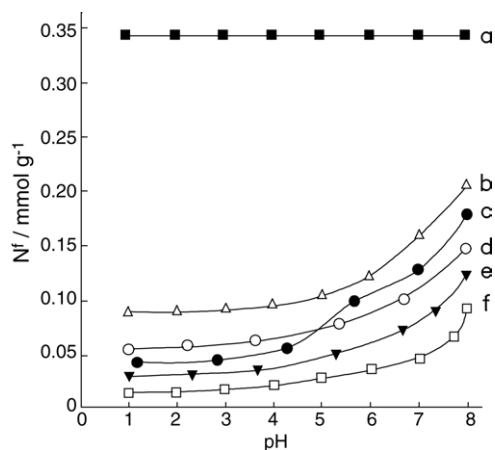
Fig. 2. Isotherms of adsorption of metal ions by TDD-organo-clay from aqueous solutions as function of pH: (a) Hg(II), (b) Cu(II), (c) Pb(II), (d) Cd(II), (e) Ni(II), (f) Zn(II).

In the experiments, each metal was quantitatively adsorbed and was eluted as shown in Fig. 3. It can be observed that, in the experimental conditions used, only Cd(II), Pb(II), Cu(II), and Zn(II) could be quantitatively eluted with until 1.0 M HCl or HNO3. Mercury forms a strong complex on the surface of the sorbent TDD-organo-clay, and therefore a quantitative desorption is possible by using hydrochloric or nitric acid at a high concentration ($\sim$7 M). Quantitative elution of Hg(II) was also possible using 20 mL of 0.05 M solution of cysteine in 3 M HCl (Fig. 4).

In the studies of adsorption and recovery of a mixture of ions, could be observed that recovery of Hg(II) in the presence of other metal ions, such as Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II), Mn(II), Ag(I), Bi(III), Fe(II) and Fe(III), in 10 or a 100 times higher concentrations, was not significantly affected. These metals are sorbed at higher pH values, so that a selective preconcentration of Hg(II) can be carried out in their presence. A 1000-fold excess of chloride, nitrate, sulphate, fluoride, thiocyanate, bromide, phosphate, acetate, oxalate, and tartrate ions also does not interfere with the determination.
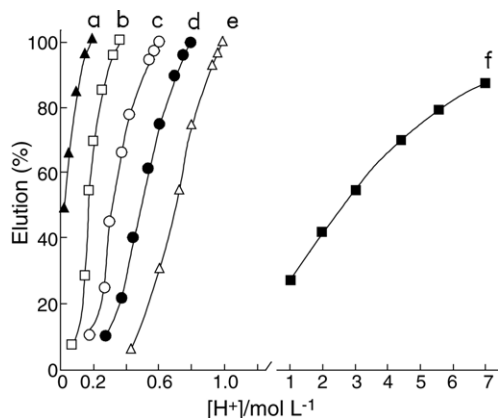

Fig. 3. Elution of metal ions adsorbed on TDD-organo-clay by acid solutions: (a) Ni(II), (b) Zn(II), (c) Cd(II), (d) Pb(II), (e) Cu(II), (f) Hg(II).
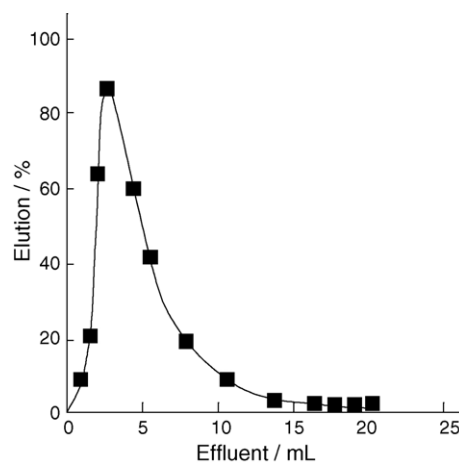

Fig. 4. Elution of Hg(II) adsorbed on TDD-organo-clay by 0.05 M cysteine solution in 3.0 M HCl.

3.3. Optimization of experimental conditions for electroanalytical application

The homoionic hexadecyltrimethylammonium-clay modified by 1,3,4-thiadiazole-2,5-dithiol was employed as the electrode surface modifier due to reason that it has shown to be an effective solid-phase selective sorbent for Hg(II). Preconcentration analyses were performed according to the two-step procedure "accumulation at open circuit followed by quantitative voltammetric detection".

In order to establish the most suitable conditions for retention of mercury on the TDD-organo-clay-CPE, several characteristics were examined. Fig. 5 shows a repetitive cyclic voltammogram of mercury(II) solution in the potential range −0.2 to +0.8 V versus Ag/AgCl, and two peaks were observed. However, the cathodic wave peak, around 0.15 V,
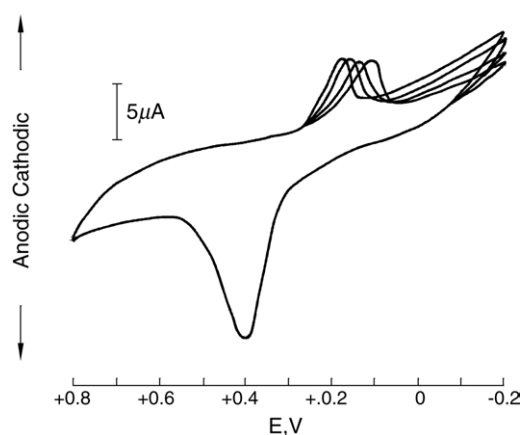

Fig. 5. Repetitive cyclic voltammogram of mercury obtained at a carbon paste electrode modified with 22% (w/w) of TDD-organo-clay-CPE. The reference electrode was KCl saturated Ag/AgCl, and the auxiliary electrode was a platinum wire. Supporting electrolyte, $0.05 \, mol \, L^{-1}$ KNO3 solution. Concentration of Hg(II), $0.5 \, mg \, L^{-1}$. Potential range, −0.2 to +0.8 V; scan rate, $20 \, mV \, s^{-1}$. Arrows indicate scan direction. Current intensity for accumulation at a blank (HDTA-montmorillonite carbon paste electrode) was 0.04 µA.

is irregular and changes its form in each cycle. This peak at about 0.15 V is the reduction current for mercury(II) accumulated in the TDD-organo-clay-CPE. The anodic wave peak at 0.40 V is well defined and does not change during the cycles. This peak is due to oxidation of the mercury metal. The electrode process is then irreversible and the anodic peak was therefore further investigated for analytical purposes. Since the anodic peak at 0.40 V is sharp enough to be used for the determination of mercury, the procedure including reduction of the accumulated mercury(II) is recommended. After the accumulation step made with open circuit, the electrode was placed in the electrochemical cell with the supporting electrolyte and a potential of −0.2 V was applied at the beginning of the scan. When the potential scan reaches the value of 0.40 V, an anodic peak is produced owing the oxidation of mercury as indicate in Eq. (3)

$$Hg^0 \rightarrow Hg^{2+} + 2e^- \tag{3}$$

The scan rate of 10 mV s^{-1} was used in the differential-pulse mode and the scan started immediately after the connection of the electrodes.

For anodic stripping several media were tested (KNO$_3$, KCl, KSCN, KI, KNO$_2$, and KBr). The best developed peaks were recorded in 0.05 mol L^{-1} KNO$_3$. This medium allows the reduction and the anodic stripping to be done in a single electrolyte without decreasing the sensitivity and, moreover, the determination may be carried out in the presence of dissolved oxygen. This was confirmed by comparison of results obtained in aerobic and anaerobic media.

The influence of the pH solution on the accumulation of mercury(II) was examined in the concentration range 0.2–0.8 mg L^{-1}. The signal showed a increasing non-negligible from pH 0.0 to 2.0, a stable signal was obtained for the pH range from 2.0 to 6.0 and then the peak current decreased sharply above pH 6.0 (Fig. 6).

The effect of the amount of TDD-organo-clay on the accumulation of mercury(II) was investigated by altering the
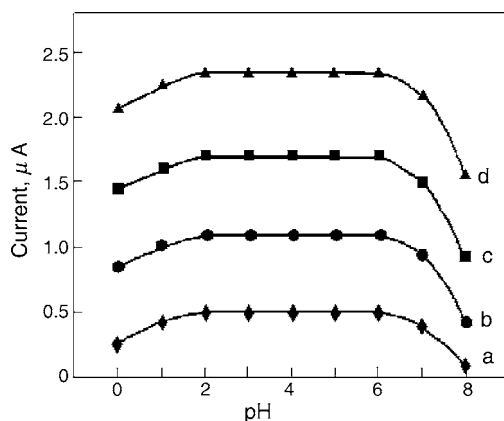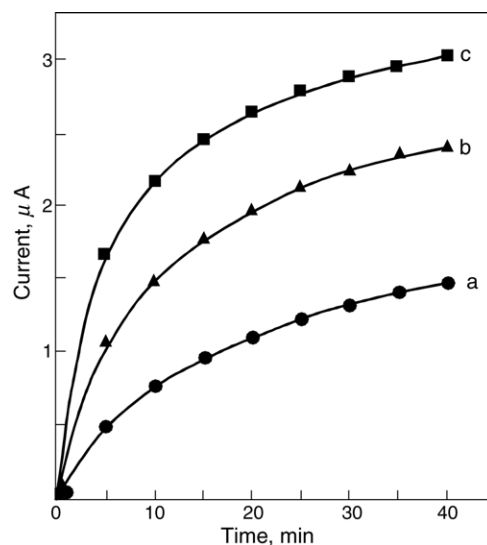

Fig. 7. Dependence of the anodic peak current on preconcentration time at different mercury concentrations: (a) 0.2; (b) 0.4; (c) 0.6 mg L^{-1}.

weight ratio of TDD-organo-clay to graphite powder in carbon paste. The ratio of TDD-organo-clay to graphite in the paste was fixed at 22% (w/w) so that the peak current was constant. A CMCPE with 22% TDD-organo-clay was used for most of this work.

Several "cleaning" solutions were evaluated and the best cleaning efficiency and reproducibility were obtained with 0.05 M solution of cysteine in 3 M HCl.

A final parameter expected to be of primary importance to the mercury(II) preconcentration was the length of time allowed for the deposition process to take place. The results obtained as a function of accumulation time for three different mercury(II) concentrations are shown in Fig. 7. For each of the three concentrations, the steady-state quantity of mercury(II) deposited was different. Larger signals were obtained for higher concentration, though the dependence was not linear. In all three cases, the greatest increase in current occurred in the first 5 min and this time was chosen for the preconcentration step. Compared to previously reported rates of uptake of metal ions at various CMCPE surfaces, the present process was very fast [32–40].

3.4. Calibration graph, precision, and detection limit

The calibration graph of current versus mercury concentration in the range 0.01–2 mg L^{-1} in 0.05 mol L^{-1} KNO$_3$ solution for a preconcentration time of 5 min is shown in Fig. 8. Fig. 9 shows some voltammograms of points on this graph. The calibration graph was linear over the range 0.01–1.0 mg L^{-1} mercury(II) and obey the straight-line

$$I\,(\mu A) = 2.92[Hg^{2+}] + 0.060 \tag{4}$$

Fig. 6. Dependence of the anodic peak current of Hg(II) on the pH of the preconcentration solution of Hg(II). Differential pulse anodic stripping voltammetry with 10 mV s^{-1} scan rate, 50 mV amplitude and 5 min preconcentration time. Hg(II) concentration: (a) 0.2; (b) 0.4; (c) 0.6; (d) 0.8 mg L^{-1}.
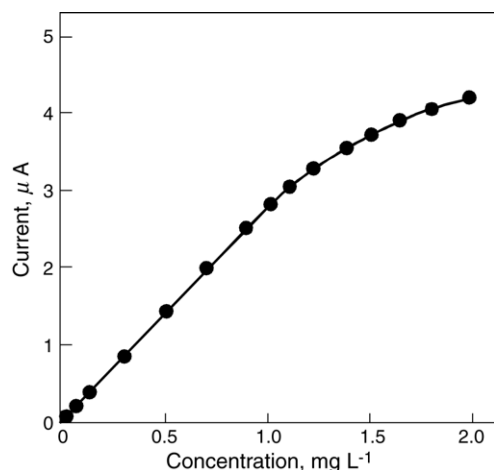
Fig. 8. Calibration graph of current vs. mercury concentration.

with a correlation coefficient of 0.998. For points between 1.0 and 2.0 mg L^{-1}, the plot shows non-linear behavior, which requires the use of a calibration graph in this concentration range.
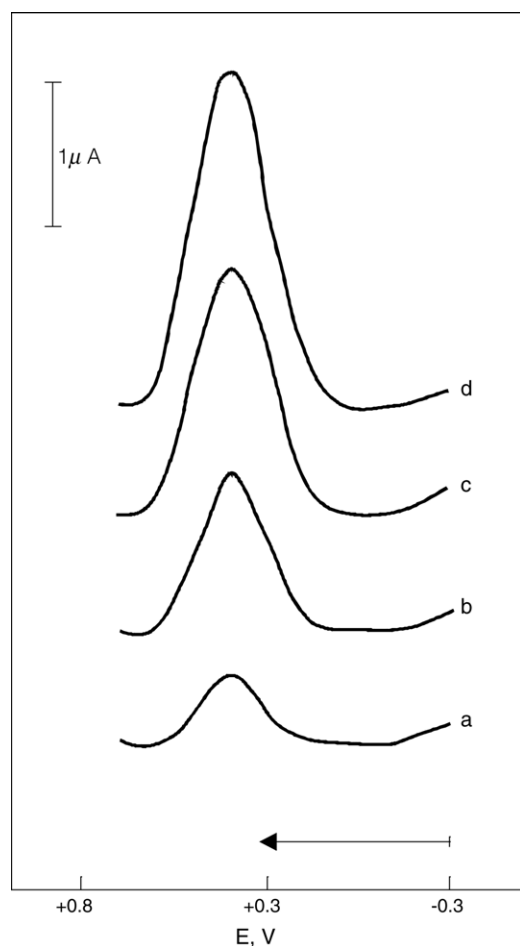

Fig. 9. Differential pulse anodic stripping voltammograms for different mercury(II) concentrations obtained after 5 min accumulation: (a) 0.2; (b) 0.4; (c) 0.6; (d) 0.8 mg L^{-1}.

The reproducible accumulation and effective cleaning was illustrated by the precision obtained for a series of six repetitions ($n = 6$), with 0.03 and 0.12 mg L^{-1} mercury(II) during a continuous 48 min period. Such series yielded a relative standard deviation of 3.3 and 1.8%, respectively. The initial preconditioning scheme (described in the Section 2) is essential for achieving such good precision. Reproducible results were obtained with different batches of the same modified carbon paste electrode.

The detection limit was estimated as 0.15 µg L^{-1} mercury(II) by means of 3:1 current-to-noise ratio in connection with the optimization of the various parameters involved and using the highest-possible analyzer sensitivity. This detection limit is similar or lower and the concentration range with a linear response is wider than those obtained with other CMCPEs [34–40]. For instance, the detection limits for the determination of Hg(II) on the carbon paste electrode modified with clay [34], diphenylcarbazone [35], diphenylcarbazide [36], humic acid [37], amberlite LA2 [38], and amberlite IRC [40], are 10, 10, 1.0, 1.0, 1.0, and 25 µg L^{-1}, respectively, and for a glassy carbon electrode modified with polypyrrole derivative [40] is 2.0 µg L^{-1}. As other electrode materials like Au and Pt and other techniques, such as ICP-AES or AAS often in connection with a preconcentration step, are not the subject of this work, they are not considered here.

3.5. Influence of foreign ions

The selectivity of the chemically modified carbon-paste electrode containing TDD-organo-clay evaluated by intentionally introducing concentrations of other metal ions into Hg(II) solutions during preconcentration. The ions chosen for study were Ag(I), Zn(II), Co(II), Pb(II), Cu(II), Ni(II), Mn(II), Cd(II), Bi(III), Fe(II) and Fe(III). These ions were chosen because they might reasonably be expected to exhibit redox activity in roughly the same potential range as Hg(II)–TDD-organo-clay-CPE. The interference of some anions and organic compounds have also been investigated in this work.

When Hg(II) preconcentration was performed from solutions containing known concentrations of the test ions, an appreciable effect on the analyte signal was observed only for Ag(I) and this only when the interferent was present in distinct excess. A 100-fold excess of Zn(II), Co(II), Pb(II), Cu(II), Ni(II), Mn(II), Cd(II), Bi(III), Fe(II) and Fe(III), a 1000-fold excess of chloride, nitrate, sulphate, fluoride, thiocyanate, bromide, phosphate, acetate, oxalate, and tartrate and had no influence on the determination of 0.05 mg L^{-1} Hg(II).

Intentional spiking of the sample solution with Ag(I) produced more serious effects. Overlapping peaks of mercury and silver occur at a concentration ratio of 30:1 ([Ag]/[Hg]), as usually occurs in the voltammetric determination of mercury in presence of silver [35]. A 50-fold excess of Ag(I) produced a >40% increase in Hg response under the same preconcentration conditions that had been employed above

Table 1
DPASV determination in natural waters containing $60 \, \mu g \, L^{-1}$ mercury(II) (added)

Sample (place)	Hg content found ($\mu g \, L^{-1}$)	R.S.D. (%) ($n = 7$)
River water		
Pinheiros River, São Paulo State	63	3.6
Tiete River, São Paulo State	58	2.5
Sea water		
Santos Beach, São Paulo State	55	4.7
Ubatuba Beach, São Paulo State	56	3.9

for the other interferents. No significant effects were found in the case of molar ratio Ag(I):Hg(II) = 1–20.

The effect of humic acid (HA) on the analyte signal was also considered. A 100-fold excess of HA had no influence on the determination of $0.05 \, mg \, L^{-1}$ Hg(II).

In the presence of EDTA, cysteine, thiourea, SO_3^{2-}, $S_2O_3^{2-}$, and SCN^- a gradual suppression of the Hg signal became evident. Strong chelates probably do not release Hg(II) ions even in acidic solution and the bound fraction of mercury is not accessible to determination.

The results obtained are of great importance, for instance for the analysis of natural waters. The electrode is capable of measuring mercury(II) bound in labile (halide, sulphate and hydroxide) complexes.

3.6. Determination of mercury(II) in natural waters

The determination of mercury(II) was carried out in both river and sea water. Hence, the determinations were carried out in "spiked" water samples. No pretreatment of samples to remove any matrix component was carried out. The results of these analyses are given in Table 1.

Both water samples were made $60 \, \mu g \, L^{-1}$ in mercury(II), assuming that the original content of these ions was negligible compared to the concentration that was spiked in. The mercury was determined by the DPASV method (standard addition technique) already described.

The responses of the mercury peaks in both river and sea water samples were essentially the same size. The procedure of successive additions was applied for both solutions of samples, and it was observed that linear calibration plots had practically the same slopes. These observations and results have confirmed that the DPASV method reported in this paper can be used for practical analysis. This method can also be used as a relatively simple and quick method to determine mercury(II) in polluted and industrial waste water.

4. Conclusions

TDD-organo-clay has been shown to be an effective solid-phase selective sorbent for Hg(II) and can also be applied in the preparation of a chemically modified carbon paste electrode (CMCPE). Formation of a stronger metal-to-sulphur

donor atom bond accounts for the high affinity shown by TDD for Hg(II) on basis of the Pearson hard-soft acid/base rule.

The carbon paste electrode modified by TDD-organo-clay shows two peaks; one cathodic peak at about 0.15 V and other anodic peak at 0.40 V scanning the potential from −0.2 to 0.8 V ($0.05 \, M \, KNO_3$ versus Ag/AgCl). The anodic peak at 0.40 V presents a excellent selectivity for Hg(II) ions in presence of foreign ions. The detection limit was estimated as $0.15 \, \mu g \, L^{-1}$. The precision of determination is satisfactory for the respective concentration level.

The carbon paste electrode modified by TDD-organo-clay proved to be a simple and selective sensor for the determination of mercury(II) in the trace concentration range. The considerable sensitivity and selectivity towards mercury(II) can also be useful for routine analysis.

References

[1] H. Van Olphen, An Introduction to Clay Colloid Chemistry, 2nd ed., Wiley, New York, 1963.
[2] B.K.G. Theng, The Chemistry of Clay Organic Interactions, Wiley, New York, 1974.
[3] G. Lagaly, Clay Miner. 16 (1981) 1.
[4] R. Bongiovanni, M. Chiarle, E. Pelizzetti, J. Dispersion Sci. Technol. 14 (1993) 255.
[5] T.R. Jones, Clay Miner. 18 (1983) 399.
[6] G. Lagaly, Angew. Chem. Int. Ed. 15 (1976) 575.
[7] R.M. Barrer, Clays Clay Miner. 37 (1989) 385.
[8] J.F. Lee, M.M. Mortland, C.T. Chiou, D.E. Kile, S.A. Boyd, Clays Clay Miner. 38 (1990) 113.
[9] K.R. Srinivasan, H.S. Fogler, Clays Clay Miner. 38 (1990) 287.
[10] K.R. Srinivasan, H.S. Fogler, Clays Clay Miner. 38 (1990) 277.
[11] N.L. Dias Filho, Y. Gushikem, W.L. Polito, Anal. Chim. Acta 306 (1995) 167.
[12] R.F. Bergstrom, D.R. Kay, J.G. Wagner, J. Chromatogr. A 222 (1981) 445.
[13] M.E. Johll, D.G. Williams, D.C. Johnson, Electroanalysis 9 (1997) 1397.
[14] P. Ugo, L. Sperni, G.A. Mazzocchin, Ann. Chim. 92 (2002) 301.
[15] J.M. Zen, P.J. Chen, Electroanalysis 10 (1998) 12.
[16] A. Fitch, J. Electroanal. Chem. 284 (1990) 237.
[17] Z. Navratilova, P. Kula, J. Solid State Electrochem. 4 (2000) 342.
[18] M. Pecorari, P. Bianco, Electroanalysis 10 (1998) 181.
[19] A. Walcarius, in: H.S. Nalwa (Ed.), Encyclopedia of Nanoscience and Nanotechnology, American Scientific Publishers, Stevenson Ranch, CA, 2004.
[20] S.K. Dentel, A.I. Jamrah, M.G. Stapleton, Environ. Sci. Pollut. Contr. Ser. 7 (1994) 525.
[21] S.-Y. Jeong, D.J. Martin, G.Q. Lu, Curr. Top. Colloid Interf. Sci. 5 (2002) 69.
[22] K.A. Carrado, Adv. Polym. Mater. (2003) 349.
[23] L. Coche-Guérente, S. Cosnier, V. Desprez, P. Labbe, D. Petridis, J. Electroanal. Chem. 401 (1996) 253.

[24] L. Coche-Guérente, V. Desprez, P. Labbe, J. Electroanal. Chem. 458 (1998) 73.

[25] B. Brahimi, P. Labbe, J. Reverdy, J. Electroanal. Chem. 267 (1989) 343.

[26] P. Falaras, D. Petridis, J. Electroanal. Chem. 337 (1992) 229.

[27] I.K. Tonle, E. Ngameni, D. Njopwouo, C. Carteret, A. Walcarius, Phys. Chem. Chem. Phys. 5 (2003) 4951.

[28] I.K. Tonle, E. Ngameni, A. Walcarius, Electrochim. Acta 49 (2004) 3435.

[29] M. Morita, J. Yoshinaga, J.S. Edmonds, Pure Appl. Chem. 70 (1998) 1585.

[30] F. Gessner, C. Schmitt, M.G. Neumann, Langmuir 10 (1994) 3749.

[31] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533.

[32] I.G. Svegl, M. Kolar, B. Ogorevc, B. Pihlar, Fresenius J. Anal. Chem. 361 (1998) 358.

[33] Z. Navratilova, P. Kula, Electroanalysis 15 (2003) 837.

[34] P. Kula, Z. Navratilova, P. Kulova, M. Kotoucek, Anal. Chim. Acta 385 (1999) 91.

[35] J. Labuda, V. Plaskon, Anal. Chim. Acta 228 (1990) 259.

[36] Z. Navratilova, Electroanalysis 3 (1991) 799.

[37] Z. Navratilova, P. Kula, Electroanalysis 4 (1992) 683.

[38] X. Cai, K. Kalcher, W. Diewald, C. Neuhold, R.J. Magee, Fresenius J. Anal. Chem. 345 (1993) 25.

[39] R. Agraz, M.T. Sevilla, L. Hernandez, J. Electroanal. Chem. 390 (1995) 47.

[40] P. Ugo, L. Sperni, L.M. Moretto, Electroanalysis 9 (1997) 1153.