

Voltammetry of Mercury(II) Based on an Organo-Clay Modified Graphite Electrode

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Abstract

Organo-clay complex of ligand-hexadecyltrimethylammonium with montmorillonite was made for the purpose of application as a preconcentration agent in a chemically modified carbon paste electrode for determination of mercury (II) in aqueous solution. It was found out that the adsorption of Hg(II) by organo-clay complex is independent of the pH of the solution. It was also found out that the adsorption of the remaining metals Cd(II), Pb(II), Cu(II), Zn(II), and Ni(II) was dependent on the changes in pH solutions and increased when it varies from 1 to 8. The resultant material was characterized by cyclic and differential pulse anodic voltammetry using a modified graphite paste electrode in different supporting electrolytes. The mercury response was evaluated with respect to pH, electrode composition, preconcentration time, mercury concentration, possible interferences and other variables.

Keywords: adsorption, preconcentration, clay, carbon paste electrode, voltammetry.

Introduction

In recent years there has been an increased interest in natural materials likely to be of use in purifying industrial wastes polluted by heavy metals [1-11]. The exchangeable cations present on montmorillonites can be replaced by long-chain quaternary ammonium cations, the resulting clays having some useful properties, e.g., they are able to adsorb organic molecules.

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Clays modified by adsorption of ionic surfactants enhance their sorption capacity and selectivity for a variety of organic molecules. Increasing the surfactant concentration, an increase in the organic molecule aggregation on the clay is observed, followed by a migration of the organic molecules to the internal domains of the clay particles [6-11].

Clay modified electrodes have potential use in electrocatalysis and they are very promising as sensors in electroanalytical chemistry [12-22]. The typical examples include the preparation of organosilasesquioxane-laponite clay films on solid electrodes and their subsequent utilization as electrochemical biosensors [23-24]. However, application of 2-mercapto-5-amino-1,3,4-thiadiazole-hexadecyltrimethylammonium bromide-montmorillonite complex as a preconcentration agent in a chemically modified carbon paste electrode for determination of mercury (II) in aqueous solution has not yet been explored.

The speciation of mercury at trace levels in environmental samples is of great importance nowadays because mercury is one of the most important contaminants in water and accumulative metals in biological systems [25].

The objective of this work was to place an ionic surfactant and a ligand (organic base) within the interlamellar spaces of layer lattice silicates, such as montmorillonite, for the purpose of adsorption of heavy metal ions in aqueous medium, as well as for the application in voltammetric determination of mercury at a chemically modified carbon-paste electrode.

Experimental

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 (conductivity of 18.2 M Ω -cm) 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).

Preparation of the organo-clay complex

The clay used 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, Na-montmorillonite, by the procedure described in the literature [26].

The sodium form of the clay, homoionic Na-montmorillonite, was treated with an aqueous solution containing an excess of the hexadecyltrimethylammonium (HDTA) bromide salt, with the formulae of $[(\text{CH}_3)_3\text{N}(\text{C}_{16}\text{H}_{33})]^+$, 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 nonionic organic molecules, 2-mercapto-5-amino-1,3,4-thiadiazole (MAT) was loaded on the HDTA-montmorillonite surface, by the usual procedure [6-10] described as follows.

About 50 g of HDTA-montmorillonite were immersed in 50 mL of MAT pyridine solution (10 w/v%) and shaken continuously at room temperature. After 72 h the solution was removed, and the solid was washed several times with deionized water, re-dispersed in a fresh MAT pyridine solution, and allowed to react again for 72 h at 70 °C. Then, the solvent was removed in a rotary evaporator under vacuum. The product obtained, 2-mercapto-5-amino-1,3,4-thiadiazole-HDTA-montmorillonite complex, hereafter denominated as MAT-organo-clay, was suspended in deionized water with continuous stirring for 8 h, then filtered and washed with deionized water. The material was again washed repeatedly with deionized water to remove any non-adsorbed reagent and dialysed at 70 °C until the C/N content was virtually constant. Finally, the product was dried at 353 K under reduced pressure for about 8 h.

Adsorption isotherms and preconcentration experiments

The adsorption isotherms of metal ions by MAT-organo-clay were determined for Hg(II), Cd(II), Pb(II), Cu(II), Zn(II), and Ni(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 solution of metal ions of $2.5 \times 10^{-3} \text{ mol L}^{-1}$ and shaken for 30 min at $298 \pm 0.2 \text{ K}$. 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 Equation 1:

$$N_f = (N_a - N_s) / m \quad (1)$$

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 x 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 $0.5 \times 10^{-6} \text{ mol L}^{-1}$ were 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 analysed. Elution of the metals from the column was made by passing 25 mL of hydrochloric or nitric acid of different concentrations. Quantitative elution of Hg(II) was also possible passing 25 mL of 0.10 mol L^{-1} cysteine solution acidified with 1.0 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 has also been investigated in this work. In these studies, a series of aqueous solutions was prepared in which the metal ion concentrations were fixed at $0.25 \times 10^{-6} \text{ mol L}^{-1}$, except for one of them fixed at 2.5×10^{-6} or $25.0 \times 10^{-6} \text{ mol L}^{-1}$. 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.

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, with a tube of $\text{Cu } \lambda_{\text{K}\alpha} \text{ } 1.5406 \text{ \AA}$, 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 behaviour of MAT-organo-clay-CPE was monitored by cyclic voltammetry and differential pulse anodic stripping voltammetry (DPASV). A three-electrode cell involving a MAT-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 was used for all investigations

Preparation of the MAT-organo-clay-CPE

The chemically modified carbon paste electrode, hereafter designated as MAT-organo-clay-CPE, was prepared by mixing 20 mg of MAT-organo-clay with 80 mg of graphite (Aldrich) and 50 μL of mineral oil. The MAT-organo-clay-CPE was introduced into the glass cavity with 2 mm inner diameter, connected with of copper wire.

Procedure

Electrode conditioning

Fresh MAT-organo-clay-CPE surfaces were conditioned by exposure to a 1.0 mg L^{-1} mercury solution at pH 2.00, adjusted with HNO_3 , for 3 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 $0.05 \text{ mol L}^{-1} \text{ KNO}_3$ solution. After each measurement, the electrode was rinsed for 2 min in 0.10 mol L^{-1} cysteine solution acidified with $1.0 \text{ mol L}^{-1} \text{ HCl}$ solution with open circuit. This conditioning cycle was repeated five times for each new MAT-organo-clay-CPE surface.

Determination of mercury

MAT-organo-clay-CPE electrode was placed in 25 mL of stirred 10^{-6} - 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 KNO₃ 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 0.10 mol L⁻¹ cysteine solution acidified with 1.0 mol L⁻¹ HCl solution. The chosen supporting electrolyte was changed after each measurement and the electrode was cleaned with 0.10 mol L⁻¹ cysteine solution acidified with 1.0 mol L⁻¹ HCl solution as in the conditioning step.

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.

Results and discussion

Properties of the MAT-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 derivatives is 0.953 and 0.956 mEq/g, respectively. Three decimal digits are given only to reveal the variation in layer charge more clearly. 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 (001) reflections, and greatly enhanced the structural organization of clay.

The presence of bound long chain hexadecyltrimethylammonium cations, which form a structure between neighbouring lamellae, promotes the accumulation of 2-mercapto-5-amino-1,3,4-thiadiazole (MAT) molecules at the solid surface. The amount of MAT loaded on the organo-clay supporting material was 0.235 mmol of MAT per gram of HDTA-clay. The amount of MAT supported on the organo-clay was determined by difference between the N contents of the HDTA-clay and MAT-HDTA-clay (MAT-organo-clay). The specific surface area was of 230 m² g⁻¹. The MAT-organo-clay was stable up to 280 °C and started decomposing above this temperature.

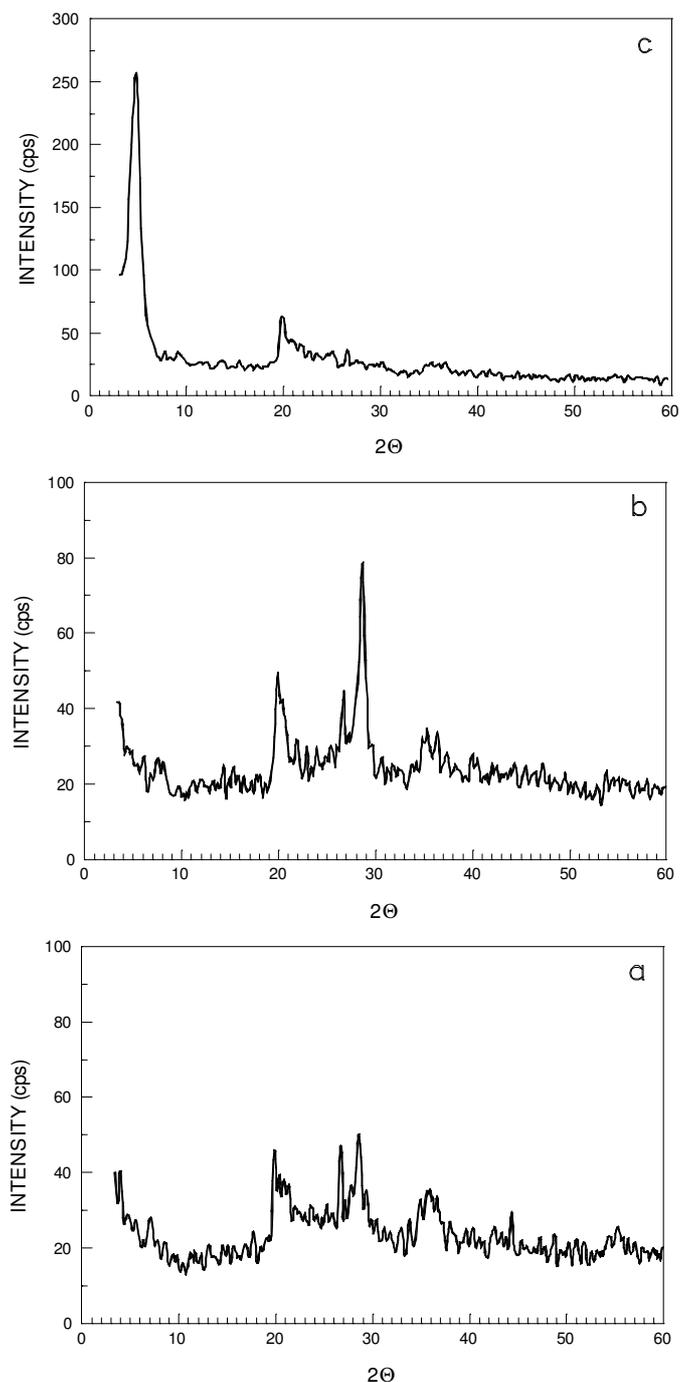


Figure 1. Intensity of the basal reflections after alkylammonium ion exchange and swelling: (a) natural clay; (b) Na-montmorillonite; (c) HDTA-montmorillonite.

Isotherms of adsorption. Preconcentration and recovery of metal ions

Adsorption of metal ions from solution by a solid phase can occur by formation of a surface complex between the adsorbed ligand and the metal [27-31]. The sorptive capacity is very much increased relative to the same material before loading with the ligand.

The complexation of mercury at the surface MAT-organo-clay is achieved by direct coordination with the ligand acting possibly as a unidentate towards two metal ions, involving sulphur and/or nitrogen atoms of the MAT molecules loaded on HDTA-clay surface.

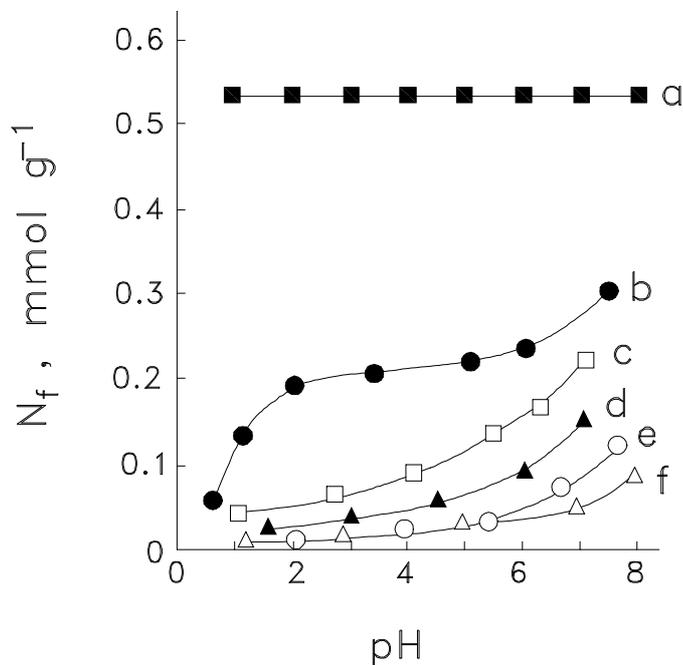


Figure 2. Isotherms of adsorption of metal ions from solutions by MAT-organo-clay as function of pH. (a) Hg(II), (b) Cd(II), (c) Pb(II), (d) Cu(II), (e) Zn(II), and (f) Ni(II).

Isotherms of adsorption of metal ions by MAT-organo-clay from aqueous solutions at different pH were determined for Hg(II), Cd(II), Pb(II), Cu(II), Zn(II), and Ni(II) metal ions using the batch method. Fixing the initial concentration of metal ion and changing the pH solutions and plotting N_f vs. pH, the set of curves shown in Fig. 2 was obtained. Fig. 2 shows that adsorption of Hg(II) by MAT-organo-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 MAT-organo-clay in all the pH solutions range by Hg(II) is well explained by the Pearson rule because MAT and Hg(II) are soft base and acid, respectively [32]. It can be observed that adsorption of the remaining metals is dependent on 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

$$\varnothing^{\max} = N_f^{\max} / N_0 \quad (2)$$

where N_0 is the amount of MAT organofunctional groups (mol) per mass of MAT-organo-clay (g), and N_f^{\max} is the quantity of the adsorbed metal, N_f , under

saturation conditions. The value of \varnothing^{\max} for Hg(II) in all the pH solutions range is 2,21. As $\varnothing^{\max} \approx 2$ for Hg(II), it is clear that this result provides 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 MAT molecule attached to the matrix is possible. The ligand MAT can act as a unidentate towards two Hg(II) ions. The coordination can occur simultaneously through nitrogen and sulfur atoms.

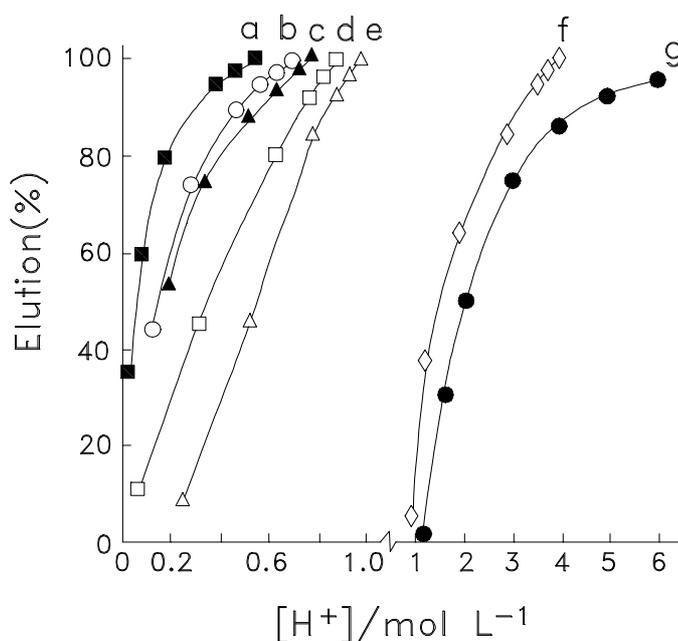


Figure 3. Elution of metal ions adsorbed on MAT-organo-clay by acid solutions. (a) Ni(II), (b) Zn(II), (c) Pb(II), (d) Cu(II), (e) Cd(II), (f) Hg(II) eluted with HNO₃, and (g) Hg(II) eluted with HCl.

Preconcentration of each metal ion by MAT-organo-clay from an aqueous solution was examined by column method. In the experiments, each metal was quantitatively adsorbed and eluted according to Fig. 3. It can be observed that, in the experimental conditions used, only Cd(II), Pb(II), Cu(II), Zn(II), and Ni(II) could be quantitatively eluted with until 1.0 M HCl or HNO₃. Mercury forms a strong complex on the surface of the sorbent MAT-organo-clay, and therefore a quantitative desorption is possible by using hydrochloric or nitric acid at a high concentration (4 to 6 M). Quantitative elution of Hg(II) was also possible using 25 mL of 0.10 M solution of cysteine in 1.0 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 ten or a hundred 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.

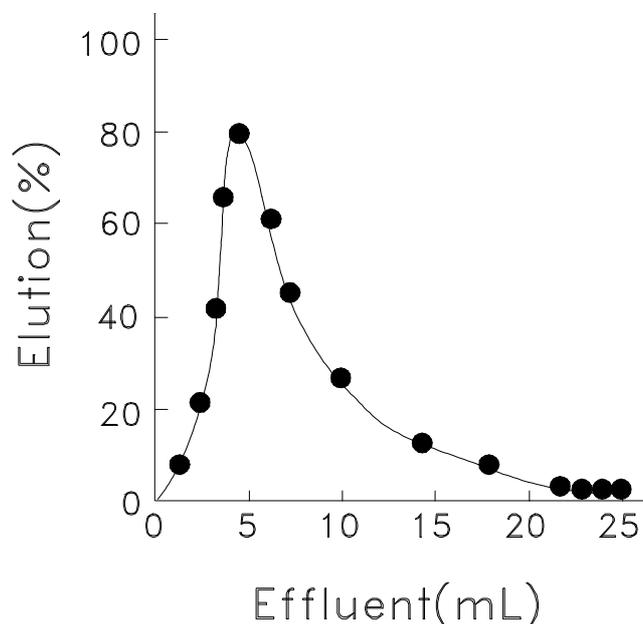


Figure 4. Elution of Hg(II) adsorbed on MAT-organo-clay by 0.10 M cysteine solution in 1.0 M HCl.

Optimization of experimental conditions for electroanalytical application

The homoionic hexadecyltrimethylammonium-clay modified by 2-mercapto-5-amino-1,3,4-thiadiazole (MAT-organo-clay) was employed as the electrode surface modifier due to the 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 MAT-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 vs. Ag/AgCl, and two peaks were observed. However, the cathodic wave peak, around 0.1 V, is irregular and changes its form in each cycle. This peak at about 0.1 V is the reduction current for mercury(II) accumulated in the MAT-organo-clay-CPE. The anodic wave peak at 0.375 V is well defined and does not change during the cycles. This peak is due to the 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 0.375 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 0.375 V, an anodic peak is produced owing the oxidation of mercury as indicates Eq. 3

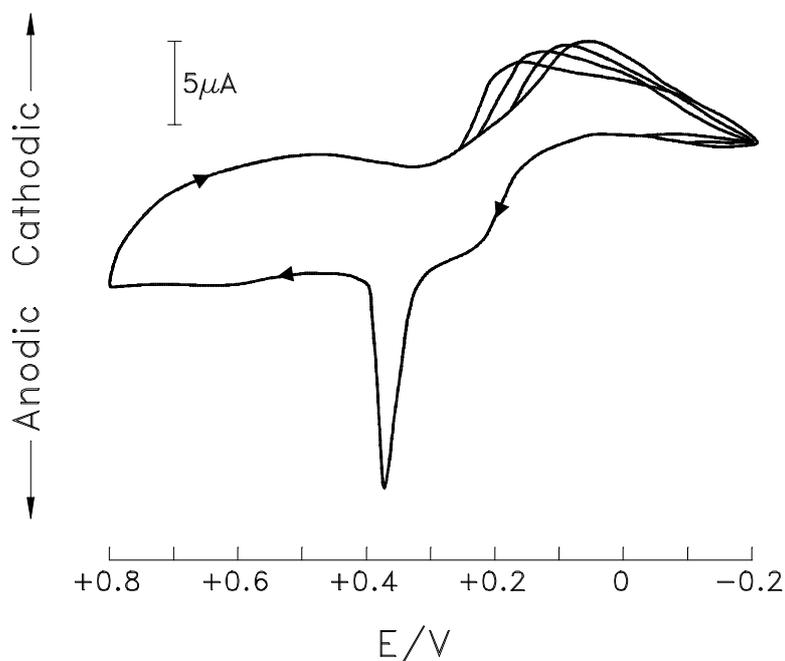
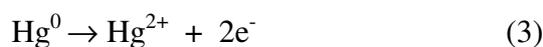


Figure 5. Repetitive cyclic voltammogram of mercury obtained at a carbon paste electrode modified with 20 % (w/w) of MAT-organo-clay. The reference electrode was KCl saturated Ag/AgCl, and the auxiliary electrode was a platinum wire. Supporting electrolyte, 0.05 mol L⁻¹ KNO₃ solution. Concentration of 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.

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, such as KNO₃, KCl, KSCN, KI, KNO₂, and KBr. The best developed peaks were recorded in 0.05 mol L⁻¹ KNO₃. 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.

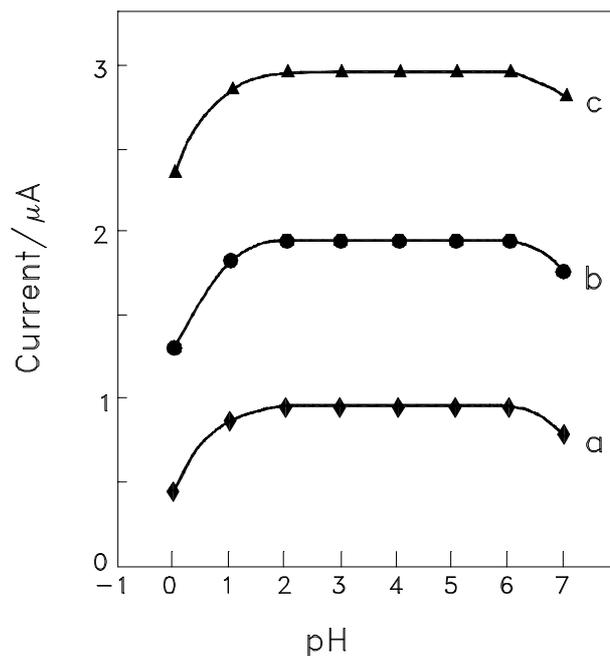


Figure 6. Dependence of the anodic peak current of Hg(II) on the pH of the preconcentration solution of Hg(II). Differential pulse anodic stripping voltammetry with 10 mV s^{-1} scan rate, 50 mV amplitude and 3 min preconcentration time. Hg(II) concentration; (a) 0.2 ; (b) 0.4 ; (c) 0.6 mg L^{-1} .

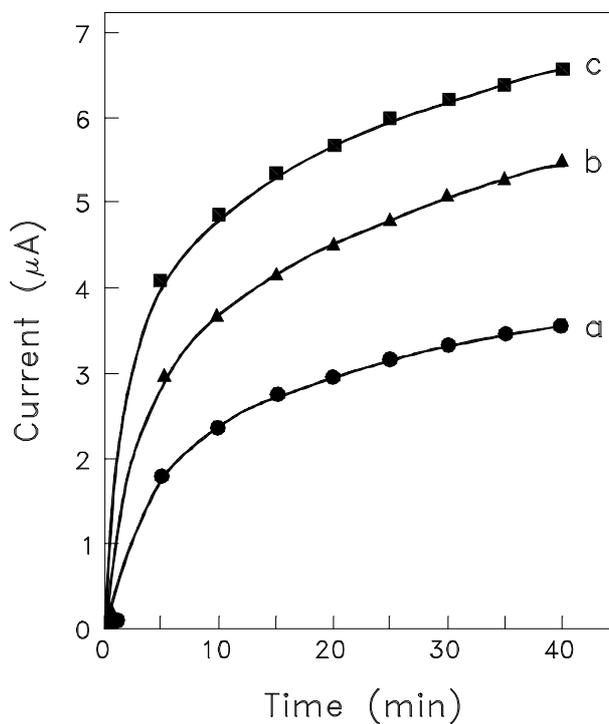


Figure 7. Dependence of the anodic peak current on preconcentration time at different mercury concentrations: (a) 0.2 ; (b) 0.4 ; (c) 0.6 mg L^{-1} .

The influence of the pH solution on the accumulation of mercury(II) was examined in the concentration range $0.2\text{-}0.6 \text{ mg L}^{-1}$. The signal showed a sharp

increase 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 lightly from pH 6.0 to 7.0 (Fig. 6).

The effect of the amount of MAT-organo-clay-CPE on the accumulation of mercury(II) was investigated by altering the weight ratio of MAT-organo-clay-CPE to graphite powder in carbon paste. The ratio of MAT-organo-clay-CPE to graphite in the paste was fixed at 20 % (w/w) so that the peak current was constant. A CMCPE with 20 % MAT-organo-clay-CPE was used for most of this work.

Several "cleaning" solutions were evaluated and the best cleaning efficiency and reproducibility were obtained with 0.10 M solution of cysteine in 1.0 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 3 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 [33-40].

Calibration graph, precision, and detection limit

The calibration graph of current vs. mercury concentration in the range 0.01 - 2 mg L⁻¹ in 0.05 mol L⁻¹ KNO₃ solution for a preconcentration time of 3 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 - 0.7 mg L⁻¹ mercury(II) and obeys the straight-line equation

$$I(\mu\text{A}) = 4.94 [\text{Hg}^{2+}] - 0.020 \quad (4)$$

with a correlation coefficient of 0.999. For points between 0.7 and 2.0 mg L⁻¹, the plot shows non-linear behaviour, which requires the use of a calibration graph in this concentration range.

The reproducible accumulation and effective cleaning was illustrated by the precision obtained for a series of six repetitions (n=6), with 0.03 and 0.09 mg L⁻¹ mercury(II) during a continuous 48-min period. Such series yielded a relative standard deviation of 4.3 and 3.5 %, respectively. The initial preconditioning scheme (described in the experimental section) is essential for achieving such good precision. Reproducible results were obtained with different batches of the same modified carbon paste and MAT-organo-clay-CPE.

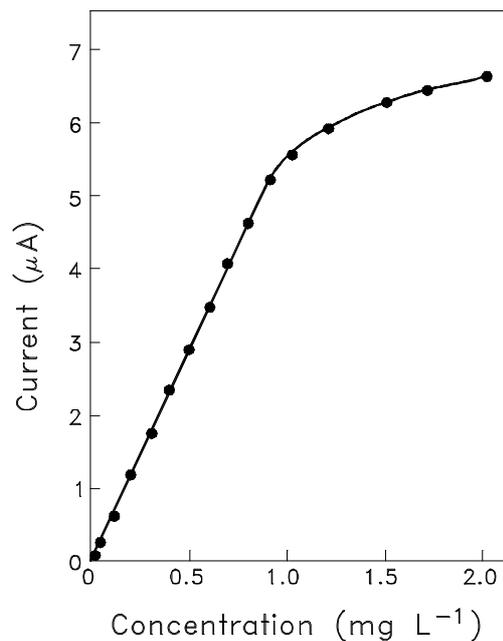


Figure 8. Calibration graph of current versus mercury concentration.

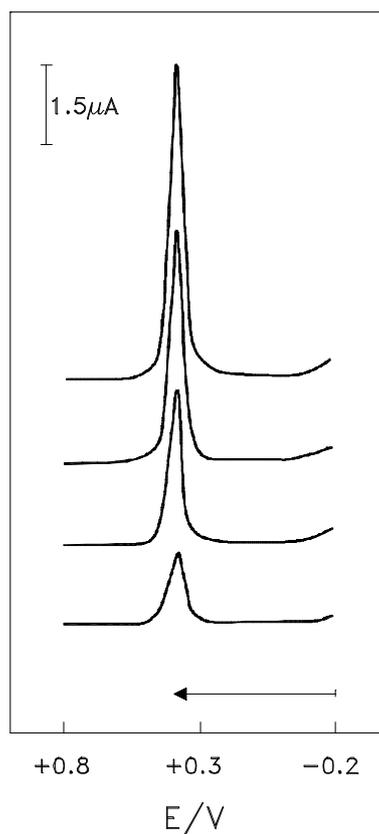


Figure 9. Differential pulse anodic stripping voltammograms for different mercury(II) concentrations obtained after 5-min accumulation: (a) 0.2; (b) 0.4; (c) 0.6; (d) 0.8 mg L⁻¹.

The detection limit was estimated as $2.0 \mu\text{g L}^{-1}$ mercury(II) by means of 4:1 current-to-noise ratio in connection with the optimization of the various parameters involved and using the highest-possible analyser sensitivity. This detection limit is similar or lower and the concentration range with a linear response is wider than those obtained with other CMCPes [35-40]. For instance, the detection limits for the determination of Hg(II) on the carbon paste electrode modified with clay [35], diphenylcarbazone [36], amberlite LA2 [38], and amberlite IRC [39], are $10 \mu\text{g L}^{-1}$, $10 \mu\text{g L}^{-1}$, $1.0 \mu\text{g L}^{-1}$, and $25 \mu\text{g L}^{-1}$, respectively, and for a glassy carbon electrode modified with polypyrrole derivative [40] is $2.0 \mu\text{g L}^{-1}$. As other electrode materials, e.g., 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.

Influence of foreign ions

The selectivity of the chemically modified carbon-paste electrode containing MAT-organo-clay was 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)-MAT-organo-clay-CPE. The interference of some anions and organic compounds have also been investigated in this work.

A 100-fold excess of Zn(II), Co(II), Pb(II), Cu(II), Ni(II), Mn(II), Cd(II), Ag(I), 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).

In the presence of EDTA, cysteine, thiourea, SO_3^{-2} , $\text{S}_2\text{O}_3^{-2}$, 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.

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 $20 \mu\text{g L}^{-1}$ 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.

Table 1. DPASV determination in natural waters containing 20 $\mu\text{g L}^{-1}$ mercury(II) (added).

Sample (place)	Hg content found / ($\mu\text{g L}^{-1}$)	R.S.D. / (%) (n = 7)
River water		
Pinheiros River, Sao Paulo State	21	4.2
Tiete River, Sao Paulo State	20	3.9
Sea Water		
Santos Beach, Sao Paulo State	18	7.3
Ubatuba Beach, Sao Paulo State	19	5.1

The responses of the mercury peaks in both river and sea water samples were essentially of 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.

Conclusions

MAT-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.

The adsorption of Hg(II) by MAT-organo-clay is independent of the pH of the solution. The adsorption of the remaining metals is dependent on changes in pH solutions and increased when they vary from 1 to 8. Formation of a stronger metal-to-sulphur donor atom bond accounts for the high affinity shown by 2-mercapto-5-amino-1,3,4-thiadiazole (MAT) for Hg(II) on the basis of the Pearson hard-soft acid/base rule.

In the experimental conditions used, only Cd(II), Pb(II), Cu(II), Zn(II), and Ni(II) could be quantitatively eluted with until 1.0 M HCl or HNO₃. Mercury forms a strong complex on the surface of the sorbent MAT-organo-clay, and therefore a quantitative desorption is possible by using hydrochloric or nitric acid at a high concentration (4 to 6 M). Quantitative elution of Hg(II) was also possible using 25 mL of 0.10 M solution of cysteine in 1.0 M HCl.

The carbon paste electrode modified by MAT-organo-clay shows two peaks; one cathodic peak at about 0.1 V and other anodic peak at 0.375 V scanning the potential from -0.2 to 0.8 V (0.05 M KNO₃ vs. Ag/AgCl). The anodic peak at 0.375 V presents an excellent selectivity for Hg(II) ions in the presence of foreign ions. The detection limit was estimated as 0.2 $\mu\text{g L}^{-1}$. The precision of determination is satisfactory for the respective concentration level.

The carbon paste electrode modified by MAT-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.

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Resumo

Argila organo complexada de ligante-hexadeciltrimetilammonium com montmorillonite foi preparada com a finalidade de aplicação como um agente de pré-concentração em um eléctrodo de pasta de carbono quimicamente modificado para determinação de mercúrio (II) em solução aquosa. A adsorção de Hg(II) através de complexo da argila organo modificada foi independente do pH da solução. A adsorção dos metais restantes Cd(II), Pb(II), Cu(II), Zn(II), e Ni(II) foi dependente de mudanças do pH das soluções e aumentou quando ele varia de 1 a 8. O material resultante foi caracterizado por voltametria cíclica e de pulso diferencial anódico empregando um eletrodo modificado de pasta de grafite em diferentes eletrólitos de suporte. A resposta do mercúrio foi avaliada relativamente ao pH, composição de eléctrodo, tempo de pré-concentração, concentração de mercúrio, possíveis interferentes e outras variáveis.

Palavras-chave: adsorção, pré-concentração, argila, eléctrodo de pasta de carbono, voltametria.

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