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Selective Sorption of Mercury(II) from Aqueous Solution with an Organically Modified Clay and its Electroanalytical Application

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Abstract: The organo-clay used in this work was prepared from a Na-montmorillonite (Wyoming-USA deposit) by treatment with water solution of hexadecyltrimethylammonium cations. As organo-clays exhibit strong sorptive capabilities for organic molecules, 2-mercapto-5-amino-1,3,4-thiadiazole organofunctional groups, with potential usefulness in chemical analysis, were incorporated on its solid surface. The physically adsorbed reagent did not present any restrictions in coordinating with several metal ions on the surface. The resultant organo-clay complex exhibited strong sorptive capability for removing mercury ions from water in which other metals and ions were also present. The purpose of this work is to study the selective separation of mercury(II) from aqueous solution using the organo-clay complex, measured by batch and chromatographic column techniques, and its application as preconcentration agent in a chemically modified carbon paste electrode for determination of mercury(II) in aqueous solution.

Keywords: Adsorption, preconcentration, organo-clay, mercury(II), montmorillonite

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INTRODUCTION

Layer silicates intercalated by organic molecules at the maximum degree of hydrophobicity, such as organo-clay complexes, exhibit a wide variety of novel properties which are applicable to various fields (1). The surface-active molecules of cationic surfactants alter the adsorption properties of layer silicates by means of ion exchange, physisorption and surface hydrophobing. Therefore, the interaction between surfactants and clay minerals is of great importance for enviromental, waste disposal, and technical research (2–5).

Many scientists have shown that amines in ionic form can penetrate between the layers of clays, resulting in the production of interlamellar complexes. In these complexes the amine chains are inclined to the plane of the layer. In the interlamellar space adsorption can take place between the organic cations as demonstrated by the expansion of the clay layers which may also be characterized by further increase iof the basal spacing (6–10).

Numerous studies have been devoted for the removal of organic contaminants by clay-organic complexes from water (1–10). 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-clays (11).

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:

1. Mercury electrodes presents high toxicity and rapid deterioration of electrode response (12).
2. 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 is mainly concerned with 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 belongs to this category (14–18). Clays are also potential 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 "organoclays," 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 in organoclays and polymer-clay nanocomposites (20–22). The typical examples include the preparation of organosilasesquioxane-laponite clay films on solid electrodes and their subsequent utilization as electrochemical biosensors (23,24). The speciation of mercury at trace levels in environmental samples is of great importance nowadays because mercury is one of the big contaminants in water, and accumulatable metals in biological systems (25).

In this work, a organoclay 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. Organofunctional groups with potential usefulness in chemical analysis can be incorporated on its surface. In this context, 2-mercapto-5-amino-1,3,4-thiadiazole (MAT) was loaded on the HDTA-montmorillonite surface, resulting in the 2-mercapto-5-amino-1,3,4-thiadiazole-HDTA-montmorillonite complex (MAT-organo-clay). Then, the 2-mercapto-5-amino-1,3,4-thiadiazole (MAT) organofunctional groups loaded on the organo-clay surface can perfectly be used in preconcentration process of metal ions, looking at the selective adsorption towards mercury(II) present in water samples, measured by batch and chromatographic column techniques as well as in voltammetric determination of mercury at a chemically modified carbon-paste electrode (CMCPE), designated as MAT-organo-clay-CPE.

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 obtained by passing distilled water through a Millipore Milli-Q water purification system. Dilute solutions ($\leq 1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$) 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 $1000\,\mathrm{mg\,L^{-1}}$ Titrisol standards (Merck).

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, 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, 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 procedure described as follows.

About 50 g of HDTA-montmorillonite was 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 de 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 solutions of metal ions of $2.5 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ and shaken for 30 min at $298 \pm 0.2\,\mathrm{K}$. 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 (1):

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

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 × 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 $0.5 \times 10^{-6}\,\mathrm{mol\,L}^{-1}$ was percolated through the column with a flow rate of $5.0\,\mathrm{ml\,min^{-1}}$. 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 also possible passing 25 mL of $0.10\,\mathrm{mol\,L^{-1}}$ cysteine solution acidified with $1.0\,\mathrm{mol\,L^{-1}}$ 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 $0.25 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ except for one of them fixed at 2.5×10^{-6} or $25.0 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$. 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. 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 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 were 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 $1.0\,\mathrm{mg\,L^{-1}}$ 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 $0.05\,\mathrm{mol\,L^{-1}}$ KNO_3 solution. After each measurement, the electrode was rinsed for 2 min in $0.10\,\mathrm{mol\,L^{-1}}$ cysteine solution acidified with $1.0\,\mathrm{mol\,L^{-1}}$ HCl solution with open circuit. This conditioning cycle was repeated five times for each new MAT-organo-clay-CPE surface.

Determination of Mercury

The MAT-organo-clay-CPE electrode was placed in 25 mL of stirred $10^{-6} - 10^{-8}\,\mathrm{mol\,L^{-1}}$ 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 $0.05\,\mathrm{mol\,L^{-1}}$ 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 $0.10\,\mathrm{mol\,L^{-1}}$ cysteine solution acidified with $1.0\,\mathrm{mol\,L^{-1}}$ HCl solution. The chosen supporting electrolyte was changed after each measurement and the electrode was cleaned with $0.10\,\mathrm{mol\,L^{-1}}$ cysteine solution acidified with $1.0\,\mathrm{mol\,L^{-1}}$ HCl solution as in the conditioning step.

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 derivates 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 the clay.

The presence of bound long chain hexadecyltrimethylammonium cations, which form a structure between neighboring lamellae, promotes the accumulation of 2-mercapto-5-amino-1,3,4-thiadiazole (MAT) molecules at the solid

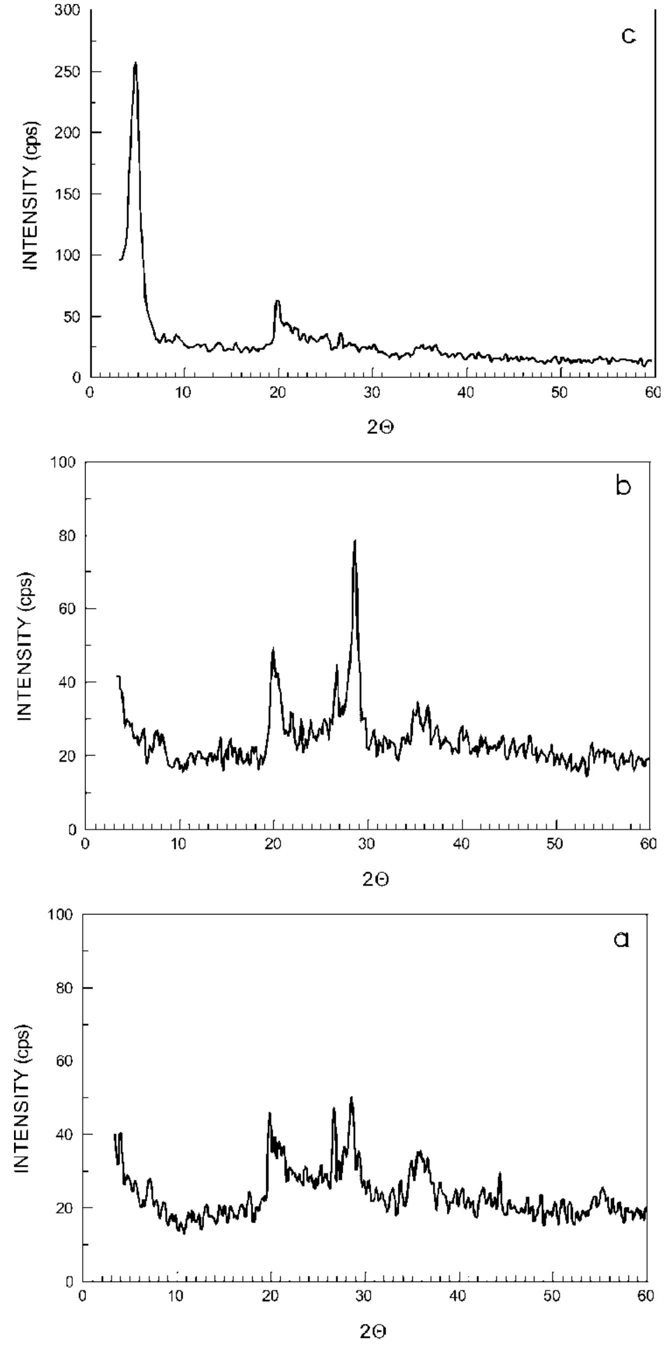

Figure 1. Intensity of the basal reflections after alkylammonium ion exchange and swelling: (a) natural clay; (b) Na-montmorillonite; (c) HDTA-montmorillonite.

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 specifc surface area was of 230 $m^2 g^{-1}$. The MAT-organo-clay was stable up to 280°C and started decomposing above this temperature.

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 than 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 one metal ion, involving sulphur and/or nitrogen atoms of the MAT molecules loaded on HDTA-clay surface.

The 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. Figure 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 explained well 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 Equation (2)

$$\text{Ø}^{max} = N_f^{max}/N_o \qquad (2)$$

where N_o 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 Ø^{max} for Hg(II) in all the pH solutions range is 2,21. As $\text{Ø}^{max} \approx 2$ for Hg(II), it is clear that this result provides a good argument that the complexes formed, presumably, are of the type metal/ligand = 2:1. This assumption is reasonable 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

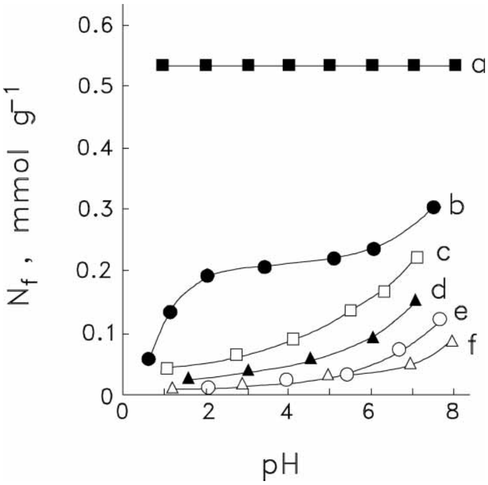

Figure 2. Isotherms of adsorption of metal ions from solutions by MAT-organo-clay as function of pH. (a) Hg(II), (b) Cd(II), (c) Pb(II), (d) Cu(II), (e) Zn(II), and (f) Ni(II).

an unidentate towards two Hg(II) ions. The coordination can occur simultaneously through nitrogen and sulfur atoms.

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 as shown in 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 HNO_3. 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, it was 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.

Electroanalytical Application

The homoionic hexadecyltrimethylammonium-clay modified by 2-mercapto-5-amino-1,3,4-thiadiazole (MAT-organo-clay) was employed as the electrode

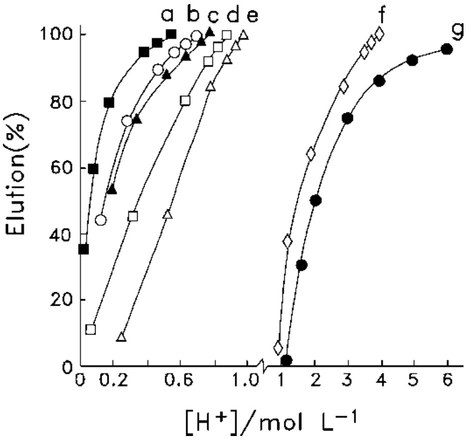

Figure 3. Elution of metal ions adsorbed on MAT-organo-clay by acid solutions. (a) Ni(II), (b) Zn(II), (c) Pb(II), (d) Cu(II), (e) Cd(II), (f) Hg(II) eluted with HNO_3, and (g) Hg(II) eluted with HCl.

surface modifier because it has been 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. Figure 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

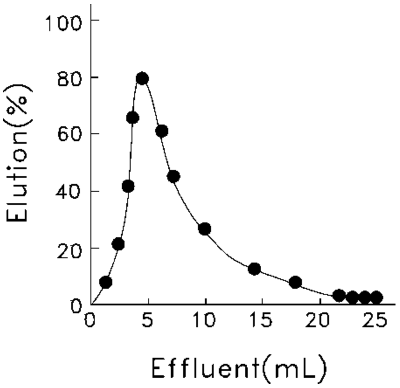

Figure 4. Elution of Hg(II) adsorbed on MAT-organo-clay by 0.10 M cysteine 1solution in 1.0 M HCl.

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 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 indicated in Equation (3).

$$Hg^0 \rightarrow Hg^{2+} + 2e^- \qquad (3)$$

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, such as 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.

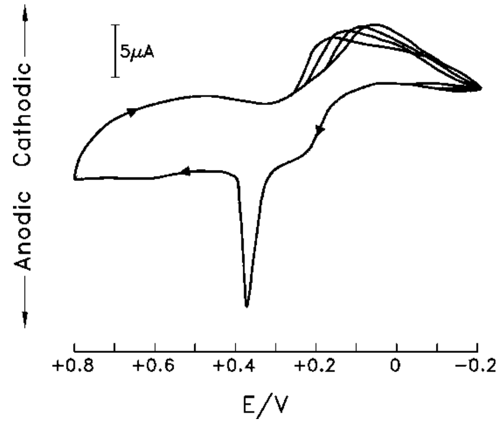

Figure 5. Repetitive cyclic voltammogram of mercury obtained at a carbon paste electrode modified with 20% (w/w) of MAT-organo-clay. The reference electrode was KCl saturated Ag/AgCl, and the auxliliary eletrode was a platinum wire. Supporting electrolyte, 0.05 mol L^{-1} KNO_3 solution. Concentration 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.

However, the carbon paste electrode modified by MAT-organo-clay could be a simple and selective sensor for the determination of mercury(II) in the trace concentration range.

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 of 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 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 HNO_3. 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 with 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 KNO_3; vs Ag/AgCl). The anodic peak at 0.375 V presents a excellent selectivity for Hg(II) ions in presence of foreign ions. MAT-organo-clay modified electrodes have potential use as a sensor in electroanalytical chemistry.

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