Talanta 85 (2011) 1357–1363

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Characterization of a carbon paste electrode modified with tripolyphosphate-modified kaolinite clay for the detection of lead

Yoleydis Gómez, Lenys Fernández*, Carlos Borrás, Jorge Mostany, Benjamín Scharifker

Departamento de Química, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

ARTICLE INFO

Article history:
Received 28 March 2011
Received in revised form 8 June 2011
Accepted 9 June 2011
Available online 15 June 2011

Keywords:
Carbon paste electrode
Kaolinite clay
Tripolyphosphate

ABSTRACT

We report about the use of carbon paste electrode modified with kaolinite for analytical detection of trace lead(II) in domestic water by differential pulse voltammetry. Kaolinite clay was modified with tripolyphosphate (TPP) by impregnation method. The results show that TPP in kaolinite clay plays an important role in the accumulation process of Pb(II) on the modified electrode surface. The electroanalytical procedure for determination of Pb(II) comprised two steps: chemical accumulation of the analyte under open-circuit conditions, followed by electrochemical detection of the pre-concentrated species using differential pulse voltammetry. The analytical performance of this system has been explored by studying the effects of preconcentration time, carbon paste composition, pH, supporting electrolyte concentration, as well as interferences due to other ions. The calculated detection limit based on the variability of a blank solution ($3s_b$ criterion) for 10 measurements was 8.4×10^{-8} mol L^{-1}, and the sensitivity determined from the slope of the calibration graph was 0.910 mol L^{-1}. The reproducibility (RSD) for five replicate measurements at 1.0 mg L^{-1} lead level was 1.6%. The results indicate that this electrode is sensitive and effective for the determination of Pb^{2+}.

1. Introduction

Heavy metals are important pollutants in water and they have become a public health concern because of their non-biodegradable and persistent nature. The toxicity of these metals is enhanced through accumulation in living tissues and consequent biomagnifications in the food chain. Particularly, Pb(II) ions can be found in effluents from battery recycling plants, lead mining and electronic assembly plants, and its presence in drinking water is known to cause brain damage, disfunction of kidneys, liver and the central nervous system, with cumulative effects. Major concerns regarding the toxicity of lead have led to the increasing need to monitor traces of lead in a variety of matrices; electrochemical methods may be used for this purpose due to their excellent sensitivity, short analysis time, simplicity, and the low costs involved in the implementation of these powerful tools for measuring trace metals [1–3].

Chemically modified electrodes (CMEs), with surfaces designed for reacting and binding to target analytes, hold great promise for chemical sensing. Electrodes modified by porous material films, such as clays, have been a very active research area [4–10]. Despite their low electrical conductivity, some properties of the clays such as their ionic exchange capacity, good catalytic support, large surface area, mechanical stability and low cost [11,12] make them suitable as electrode surface modifiers. In particular, it has been shown in our laboratory [13–16] that the electrode surface can be advantageously modified by clay-suspensions with the aim of developing novel electrochemical sensors. In these cases the clay suspension has been entrapped by casting onto the surface. Modified electrodes may be also prepared by simply adding the modifier directly to a carbon paste electrode (CPE). CPE is a mixture of an electrically conducting graphite powder and a pasting liquid. It has been widely used as working electrode for electrochemical and electroanalytical applications and shows various advantageous attributes such as stability over a wide potential range with high overpotentials for water decomposition reactions, simple and fast preparation, convenient surface renewal, porous surface and low residual current, besides low cost. However, the sensitivity of bare CPE is relatively poor for determination of inorganic and organic species. An effective way to improve this is by modification of bare CPE through mixing with some other material with unique properties. A particular type of clay material is kaolinite, $Al_2Si_2O_5(OH)_4$, a dioctahedral-layered hydrated aluminosilicate clay of the 1:1 type with two distinct interlayer surfaces: a gibbsite-like with aluminum atoms coordinated octahedrally to corner oxygen atoms and hydroxyl groups, and a silica-like structure, where the silicon atoms are coordinated tetrahedrally to oxygen atoms. The alternating adjacent layers are linked by hydrogen bonds involving aluminol (Al–OH) and siloxane (Si–O) groups. As a consequence of this structure, the silica/oxygen and alumina/hydroxyl sheets

---

* Corresponding author. Tel.: +58 212 9063979; fax: +58 212 9063961.
E-mail address: lfernandez@usb.ve (L. Fernández).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.06.014

are exposed and interact with different molecules. In this paper, we studied the application of a modified kaolinite as modifier of a carbon paste electrode for the determination of lead at trace level concentrations. For this purpose kaolinite clay was modified with tripolyphosphate (TPP) by impregnation method. Our attention was drawn by high complex-forming ability of the polyphosphates with respect to heavy metal ions [17]. Thus it may be expected that kaolinite modified by polyphosphates should exhibit selectivity with respect to heavy metal ions [18,19]. In the electrochemical literature there are numerous scientific reports on the detection of heavy metals by potentiometric electrodes based on ion-selective electrodes [20–22]. However, most of these electrodes show narrow working concentration ranges, long response times and suffer interference from cations. To the best of our knowledge, there are no reports on the application of TPP-kaolinite as modifier of carbon paste electrodes for the chemical accumulation of the analyte, followed by the electrochemical detection of the preconcentrated species. Hence the aim of the present work is the application of such novel strategy for the analytical determination of lead in trace levels.

2. Experimental

2.1. Reagent and materials

The minerals and chemicals used in this investigation were commercial kaolinite from Sigma, tripolyphosphate ($Na_5P_3O_{10}{\cdot}6H_2O$) and ethanol from Aldrich, ammonium acetate and ethanol from Riedel-de Haën; sodium acetate and lithium perchlorate from Sigma. These and all other chemicals of reagent grade were used as received. Solutions were prepared using distilled and demineralized water filtered through a Milli-Q Reagent Water System to a resistance higher than 15 MΩ cm.

2.2. Instrumentation

Voltammograms were obtained using an EG&G Princeton Applied Research (PAR) model 273A potentiostat interfaced to a computer system with PAR M270 software. The experiments were done in a gas-tight three-electrode cell containing a carbon paste electrode as working electrode, a platinum-wire as counter electrode, and a saturated calomel reference electrode (SCE). The solution was purged and blanketed by nitrogen gas during the experiments. X-ray diffraction (XRD) analyses were carried out using a Philips diffractometer with Cu-λα radiation source, $\lambda = 1.542$ Å, 40 kV/20 mA at a scanning rate of 30 min^{-1}. The *d*-spacing was analyzed by using Bragg's equation, $n\lambda = 2d \sin\theta$, where n is an integer (1, 2, 3,. . .), λ is the wavelength, d the distance between atomic planes, and θ the angle of incidence of X-ray beam to the atomic planes. FT-IR spectra were recorded with a Bruker TENSOR 27 spectrometer using fine round samples combined with spectroscopic grade KBr (sample/KBr weight ratio of 1/100) pressed into a disc. The cation-exchange capacity (CEC) of the sample was estimated from NH_4^+ adsorption by using inductively coupled plasma (ICP) to determine the Na^+ concentration. The specific surface area, total pore volume and average diameter of the solids were measured by N_2 adsorption according to the BET-method.

2.3. Procedures

Kaolinite samples were added to tripolyphosphate solutions (0.5 mol l^{-1}); this concentration is thought to be sufficiently high for saturated sorption of phosphate to occur, with a solid/solution ratio of 1 g per 50 ml at 25 °C. pH was measured before and after 24 h of solid/solution contact time, and no significant variation was observed. The suspensions were sonicated for 25 min, then stirred for 24 h and centrifuged. The solid material was filtered and washed three times using distilled water (~50 mL water per gram), then oven-dried at 110 °C for 45 min.

Experiments with modified CPE have been carried out at various kaolinite or TPP-kaolinite to graphite ratios. Keeping the quantity of carbon used fixed at 5 mg, the kaolinite or TPP-kaolinite content was varied as 5, 10, 20, 30 50 and 60%, to obtain the desired paste. Carbon paste was prepared by hand-mixing graphite powder (spectra pure grade, Fluka) with 2–3 mL of nujol oil (McCarthy, Fullerton, CA) in a mortar and pestle. For making modified electrodes, the graphite powder was first mixed with the desired amount of modifier. The modifier was uniformly dispersed through the carbon paste by forming an ethanol slurry of graphite/modifier, and placing the slurry in an ultrasonicator for 10 min until the ethanol was completely evaporated. Electrode assemblies were made by packing the carbon paste into a glass tube containing a hand-made piston, so that the carbon paste could be gradually extruded to prepare a fresh surface. The geometric surface area of the electrodes was 0.6 cm^2.

2.4. Real sample preparation

The TPP-kaolinite/CPE modified electrode was tested in domestic water samples under the optimized conditions. For every sample, four solutions have been prepared by adding the Pb^{2+} ions in the domestic water, and analyzed without any previous treatment.

3. Results and discussion

3.1. Characterization of the kaolinite samples

3.1.1. X-ray diffraction analysis

The X-ray powder diffraction patterns of both TPP-kaolinite clay and the unmodified kaolinite are shown in Fig. 1. The patterns show that both samples contain kaolinite as the major clay mineral, with characteristic peaks at $2\theta = 14°$ ($d_L = 7.16$ Å) and $2\theta = 29°$ ($d_L = 3.57$ Å) [24]. XRD peaks of the modified kaolinite sample (Fig. 1b) became less intense compared to those of the unmodified kaolinite sample (Fig. 1a), suggesting a loss of crystallinity in the clay minerals due to polyphosphate presence. Moreover, the presence of polyphosphate in the samples did not promote valuable change in the kaolinites *d*-spacing (d_L); this suggests that the modification with polyphosphate was effective only on the surface of clay adsorbent and not on the crystal of the clay mineral. This result is in agreement with the literature [23]. Kaolinite has neither swelling nor water sorption properties. Exchange in the interlayer region of kaolinite cannot occur because of strong bonding between the layers.

3.1.2. FT-IR spectroscopy

The infrared spectra of both unmodified and modified TPP-kaolinite sample are shown in Fig. 2. In the spectra of the unmodified kaolinite (Fig. 2a), there are four vibrational regions, which contain characteristic features of the kaolinite spectrum [25]. These are: the four bands characteristic of O–H stretching vibration (3697, 3665, 3653 and 3621 cm^{-1}), Si–O stretching (1115–1123 cm^{-1}), Al–O bending (940 cm^{-1}), and the SiO_2 bending (550–565 cm^{-1}) regions. The major difference between the unmodified kaolinite and TPP-kaolinite is the appearance of strong and broad band of O–H–O at 3456 cm^{-1} in the TPP-kaolinite spectra (Fig. 2B), which indicates adsorption of TPP at the outer surface of the clay. The modification of the kaolinite sample with TPP molecules tends to shift the adsorption bands of Si–O and Al–O from 1115–1123 cm^{-1} and 940 cm^{-1} to 1121–1134 cm^{-1} and 988 cm^{-1}, respectively. This indicates [26,27] that modifications may have taken place on these positions of the surface of the clay minerals, yielding surface complex formation at the SiOH and AlOH sites of the clay. On the other hand, the TPP-kaolinite clay spectra showed the P–OH stretching vibration, O–P=O and O–P–O bending vibration (2362, 815 and 670 cm^{-1}, respectively), which were absent in the unmodified kaolinite clay. These are peaks characteristic for tripolyphosphates (condensed phosphates) [27], suggesting that at 0.5 M of $Na_5P_3O_{10}\cdot 6H_2O$ (tripolyphosphate-grafting experiments were performed using this concentration), the mechanism for binding of polyphosphate to surface of the clay possibly involves a polycondensation reaction which takes place between the polyphosphate initially chemisorbed on $=Al^{+}OH^{-}$ groups existing on the surface and the dissolved polyphosphate. These are the possible sites for the adsorption of metal ions on the TPP-kaolinite clay, while for the unmodified kaolinite it appears that the Si–O and Al–O are the main sites of adsorption of metal ions.

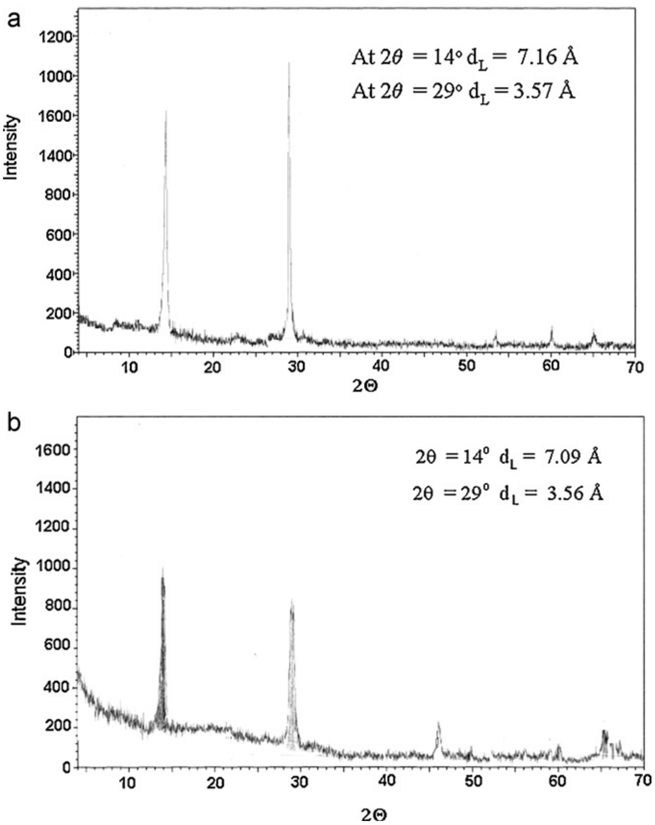

Fig. 1. XRD pattern of kaolinite (a) and TPP-kaolinite (b).

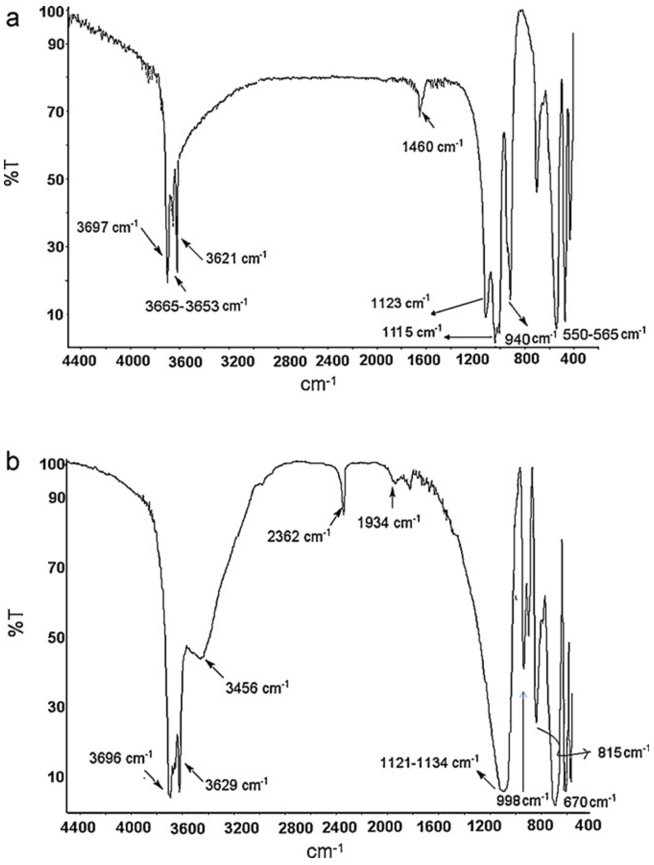

Fig. 2. IR spectra of kaolinite (a) and TPP-kaolinite (b).

3.1.3. *Physical properties of samples studied*

The BET surface areas, total pore volumes, average pore diameters and cation exchange capacities (CEC) obtained were 35.09 $m^2\,g^{-1}$, 0.11 $cm^3\,g^{-1}$, 30 nm, 12.67 mEq/100 g for kaolinite, and 46.77 $m^2\,g^{-1}$, 0.16 $cm^3\,g^{-1}$, 58 Å, 97.86 mEq/100 g for TPP-kaolinite samples.

The surface area and total volume of porous material are the most useful microstructural parameters for defining its properties. These parameters increased with the kaolinite modification, suggesting that modification creates a porous framework that increasing the surface area. According to the IUPAC recommendation, total porosity can be classified into three groups which were macropores ($d > 50$ nm), mesopores ($2 < d > 50$ nm) and micropores ($d < 2$ nm). Based on the average pore diameter values, unmodified kaolinite and TPP-kaolinite fall into the categories of mesopores and macropores, respectively. In addition, it was observed that there was an increase in the CEC in the TPP-kolinite compared to unmodified kaolinite. This promotion should be reflected in the increase of the adsorbent selectivity for cationic species from aqueous solution.

3.2. *Voltammetric response of a redox probe reactions at modified electrodes*

Usually, modification of electrodes with charged species has remarkable effects on the electrochemical behavior of redox probe reactions. These effects depend on the charge of both the electrode surface and the redox probe. In order to check this suggestion, $Fe(CN)_6{}^{3-}$ and $Ru(NH_3)_6{}^{3+/2+}$ have been used as electrochemical probes. Fig. 3 shows cyclic voltammograms (CVs) at bare CPE, kaolinite/CPE and TPP-kaolinite/CPE electrodes in 0.1 mol L^{-1} $LiClO_4$. Electrodes have been soaked 30 min in an aqueous solution containing 5×10^{-1} mol L^{-1} $Fe(CN)_6{}^{3-}$ (Fig. 3A) or 5×10^{-1} mol L^{-1} $Ru(NH_3)_6{}^{3+/2+}$ (Fig. 3B).

Soaking bare CPE for 30 min in a solution $Fe(CN)_6{}^{3-}$ leads to two well-defined peaks (Fig. 3A – a). The wave shapes, linear dependence of *Ip* on the sweep rate for ν less than 50 mVs^{-1}(data not shown), and the fact that $\Delta E \approx 32$ mV, indicate that incorporated $Fe(CN)_6{}^{3-}$ acts as an adsorbed species. At kaolinite/CPE and TPP-kaolinite/CPE modified electrodes, the electrochemical response to $Fe(CN)_6{}^{3-}$ species is small (Fig. 3A – b and c, respectively); it could be concluded that the modified electrodes concentrate fewer anionic species than CPE, which can be to due to electrostatic repulsions acting from the anionic clay sites. In contrast, the modified electrodes present affinity for cationic $Ru(NH_3)_6{}^{3+/2+}$ (Fig. 3B – c and b). This electroactive probe allowed us to demonstrate that modified electrodes incorporated $Ru(NH_3)_6{}^{3+/2+}$ upon soaking in a solution of the positive active agent, by electrostatic attraction. Soaking bare CPE in a solution $Ru(NH_3)_6{}^{3+/2+}$ (Fig. 3B –

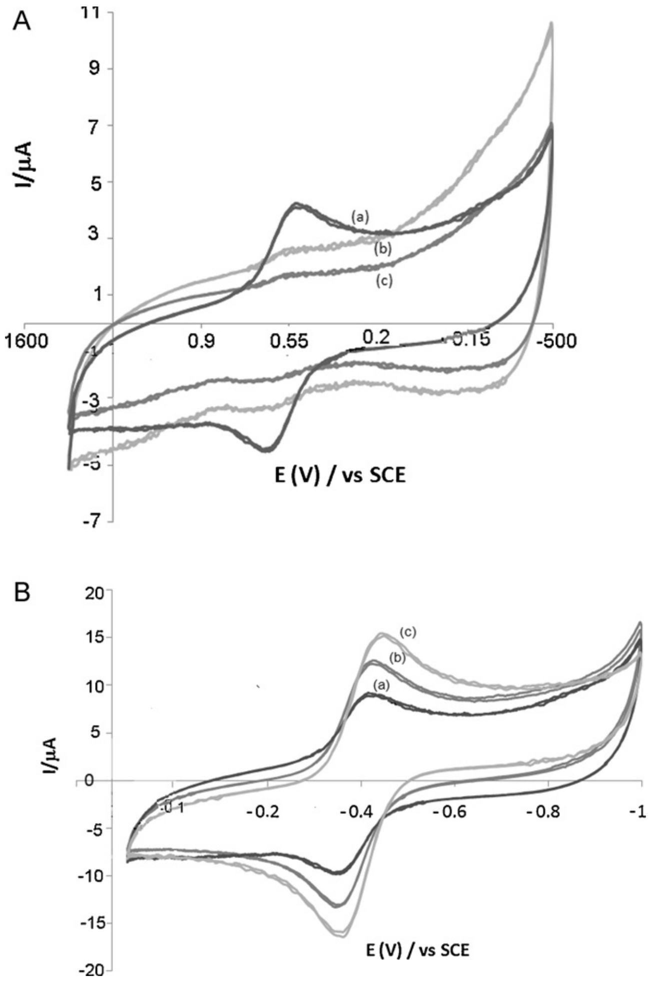

Fig. 3. Cyclic voltammograms (after 3 cycles) at 100 mV/s of the CPE (a), TPP-kaolinite/CPE (b) and kaolinite/CPE (c) modified electrodes in 0.1 M $LiClO_4$ + 0.5 mM $Fe(CN)_6{}^{3-/4-}$ (A) and 0.1 M $LiClO_4$ + 0.5 mM $Ru(NH_3)_6{}^{3+/2+}$ (B).

a), leads to peak currents smaller than those obtained after soaking the modified electrodes in the same solution. At TPP-kaolinite/CPE modified electrode, the peak currents of the oxidation/reduction of $Ru(NH_3)_6{}^{3+/2+}$ (Fig. 3B – c) were 20% higher than those observed at kaolinite/CPE modified electrode (Fig. 3B – b). This means that TPP incorporation in the kaolinite lead to the formation of more negative sites, which are able to concentrate larger amounts of positive $Ru(NH_3)_6{}^{3+/2+}$ species at TPP-kaolinite/CPE as compared with kaolinite/CPE. These results are clear indication of the potential application of TPP-kaolinite/CPE modified electrode for the adsorption of positive species.

3.3. *Electrochemical detection of Pb(II) at TPP-kaolinite modified electrode*

3.3.1. *Voltammetric behavior of Pb(II) at modified electrodes*

Cyclic voltammograms (CVs) at 20 mV/s of bare CPE, kaolinite/CPE and TPP-kaolinite/CPE modified electrodes in the presence of 0.10 mol L^{-1} acetate buffer (pH 4.5) + 5×10^{-3} mol L^{-1} Pb(II) are shown in Fig. 4, where the preconcentration time was 7 min. The CVs show an increase in current from −583 to −633 mV due to Pb(0) formation, and an anodic peak (≈430 mV) due to Pb(0) redisolution. TPP-kaolinite/CPE modified electrode (Fig. 4c) exhibits an anodic redisolution peak with higher intensity in comparison to that observed at kaolinite/CPE and CPE electrodes (Fig. 4a and b, respectively). This result demonstrates that the kaolinite clay modified with TPP plays an important role in the accumulation process of Pb(II) on the modified electrode surface.

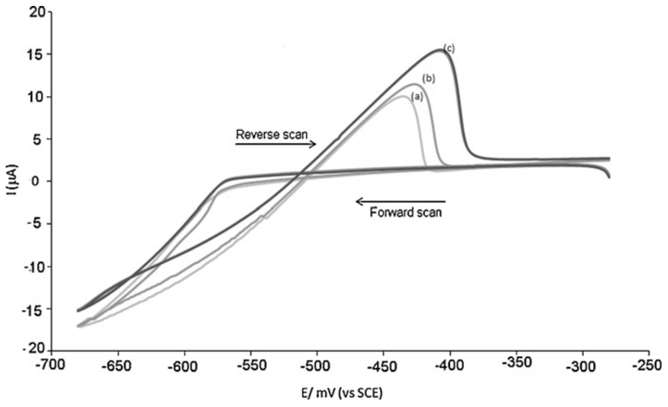

Fig. 4. Cyclic voltammograms (CVs) at 20 mV/s of CPE (a), kaolinite/CPE (b), and TPP-kaolinite/CPE (c) electrodes, in the presence of 0.10 M acetate buffer (pH 4.5) + 5×10^{-5} M Pb(II).

Fig. 5 shows the surface concentration of lead (Γ) at modified electrodes as a function of preconcentration time. The reductive voltammetric currents were obtained after immersion of the freshly modified electrode in lead solution (5×10^{-5} mol L^{-1}), as a preconcentration stage under open circuit condition, followed by rinsing with distilled water and a differential pulse voltammetry of the electrode in a lead free solution containing only supporting electrolyte (0.10 M acetate buffer (pH 4.5). Γ was estimated from the cathodic peak current using the equation $\Gamma = Q/nFA$ [28], where A is the electrode geometric area, nF is the molar charge transferred where F is the Faraday constant and $n = 2$, and Q is the charge obtained from the integration of the cathodic peak current. Q was measured with a recently prepared electrode for each point in Fig. 5, and all voltammograms were corrected for background currents before integration. Γ increases with the preconcentration time in both kaolinite/CPE (Fig. 5a) and TPP-kaolinite/CPE (Fig. 5b) modified electrodes, reaching higher plateau values in the latter. The higher affinity for lead of the TPP-kaolinite/CPE modified electrode is also manifest by faster increase of the lead surface concentration during the initial stages, as compared with the response observed in kaolinite/CPE.

Analysis of the IR spectra shown in Fig. 6 reveals that all peaks related to P–OH, O–P–and O–P=O functional groups, decreased after immersion of the freshly modified electrode in lead solution as a preconcentration stage under open circuit condition, suggest-

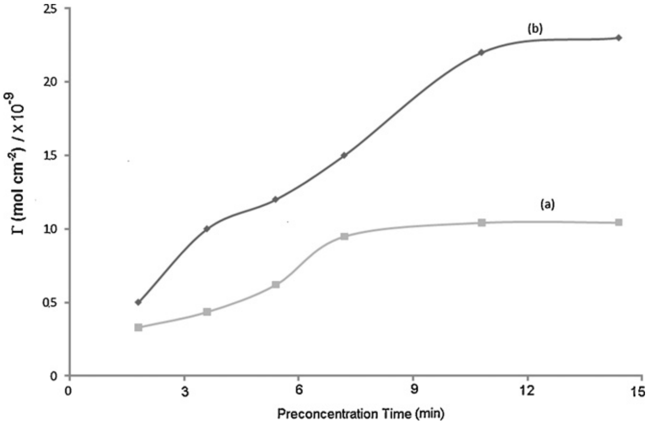

Fig. 5. Surface concentration (Γ) of lead at kaolinite/CPE (a) and TPP-kaolinite/CPE (b) modified electrodes, as a function of preconcentration time in 5×10^{-5} mol L^{-1} lead solution at open circuit.

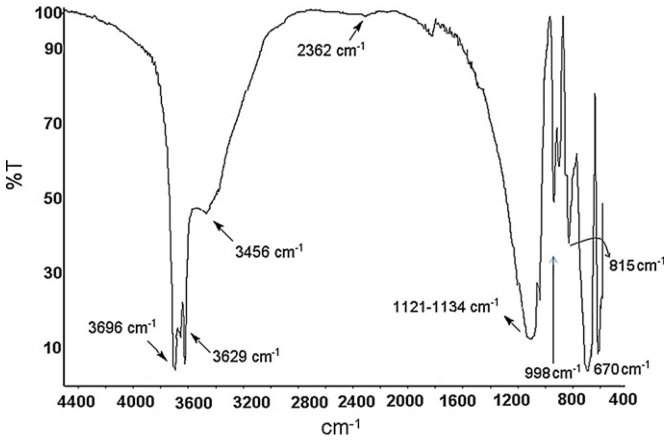

Fig. 6. IR spectra for TPP-kaolinite/CPE after immersion of the freshly modified electrode in 5×10^{-5} mol L^{-1} lead solution under open circuit condition.

ing that these functional groups are possibly responsible for the adsorption of Pb(II) onto TPP-kaolinite/CPE modified electrode.

3.3.2. *Effect of pH*

Fig. 7 shows the variation of the peak currents obtained by differential pulse voltammetry of reduction of the Pb(II) adsorbed on the modified electrodes, with solution pH during the preconcentration stage. At kaolinite/CPE modified electrode (Fig. 7a), the cathodic peak currents increased slightly with pH, up to pH 8. This behavior can be rationalized by the fact that at moderately low pH, the edges of kaolinite flakes contain positively charged sites, resulting from coordination of aluminum ions at the edges with water at low hydroxyl ion concentrations, repelling cations from solution. The continuous increase of pH (up to pH 12) led to a decrease of the peak current due to hydrolysis of Pb^{2+} in alkaline solution. With the TPP-kaolinite/CPE modified electrode (Fig. 7b) the cathodic peak current also increased slightly from pH 3 onwards with a steeper increase at pH values close to 7, followed by decreasing currents at higher pH. Since TPP leads to the neutralization of the kaolinite active sites, then Pb(II) ions have to compete with protons for the adsorption sites (negatively charged phosphate groups) on the TPP-kaolinite adsorbent surface at low pH. Upon increasing the pH, the active sites on the adsorbent surface deprotonate, assisting Pb(II) uptake. As observed with the kaolinite/CPE modified electrode, further increase of pH led to a decreasing peak currents due to hydrolysis of Pb^{2+} in alkaline solution.

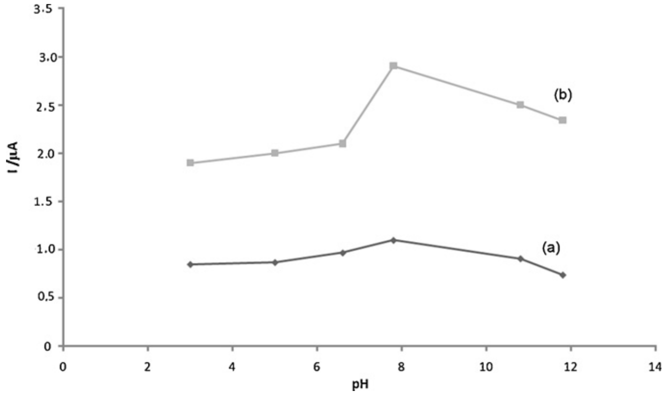

Fig. 7. Variation of peak current obtained by differential pulse voltammetric of the Pb(II) reduction adsorbed on the modified electrodes, with solution pH during preconcentration. (a) kaolinite/CPE and (b) TPP-kaolinite/CPE modified electrode.

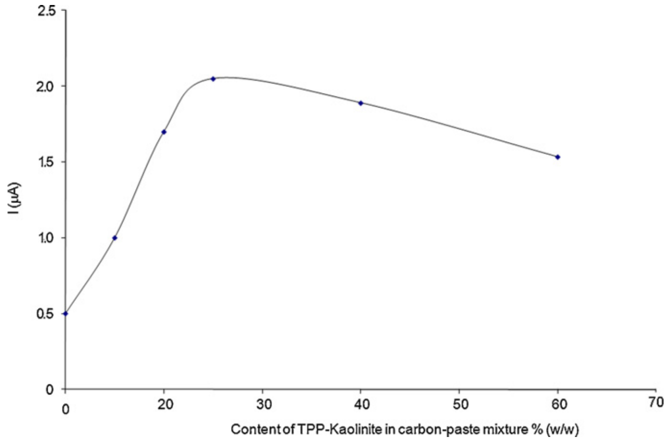

Fig. 8. Effect of the carbon paste composition on the differential pulse voltammetric response for Pb(II) reduction of the electrode modified with TPP-kaolinite.

3.3.3. *Effect of carbon paste composition*

The efficiency of the TPP-kaolinite/CPE modified electrode for lead detection depends strongly on the number of anionic sites available. In order to study the influence of this parameter, the effect of the carbon paste composition on the voltammetric response of the electrode modified with TPP-kaolinite was evaluated by differential pulse voltammetry. The amount of carbon was fixed at 5 mg while the TPP-kaolinite content was varied as 5, 10, 20, 30 50 and 60% to obtain the desired paste. Electrodes with different percent of modifier were prepared and examined for their voltammetric signals under identical conditions. The cathodic peak current (Fig. 8), increased with the amount of TPP-kaolinite in the paste, up to 25% (w/w). The cathodic peak current however decreased when more than 30% (TPP, w/w) was used in the electrode preparation, probably due to decreasing conductive area at the electrode surface. According to these results, a carbon-paste composition of 30% modified kaolinite, 70% graphite and 0.1 mL mineral oil was used in further studies.

3.3.4. *Effect of supporting electrolyte concentration*

The increase in supporting electrolyte concentration had a negative impact on the adsorption of TPP-kaolinite/CPE modified electrode. The cathodic peak current increased at low supporting electrolyte concentration, from 0.02 mol L^{-1} to 0.1 mol L^{-1}, but drastically decreased at higher concentrations (data not shown). As discussed above in relation to the influence of pH on the responses observed, the decrease of cathodic currents with increasing concentrations of electrolyte may be primarily due to competition between cation of the electrolyte and lead ions for the permanent negatively charged sites on TPP-kaolinite modified faces. The increased ionic strength may also screen the surface negative charges, thus decreasing the cathodic currents due to reduction of metal Pb(II) ions.

3.3.5. *Analytical characterization*

Fig. 9A shows differential pulse voltammetries for calibration experiments, using the optimum conditions found in this study as described above, 0.5:1 TPP/kaolinite to graphite ratio, 5 min preconcentration time and 0.10 mol L^{-1} acetate buffer (pH 4.5) as electrolyte. Good linearity was observed in the concentration range between 3×10^{-7} mol L^{-1} and 2×10^{-5} mol L^{-1}, with slope and correlation coefficient values of 0.910 μA/mol L^{-1} and 0.9987, respectively (Fig. 9B). The data points shown in the calibration plots for this concentration range were obtained with five independent

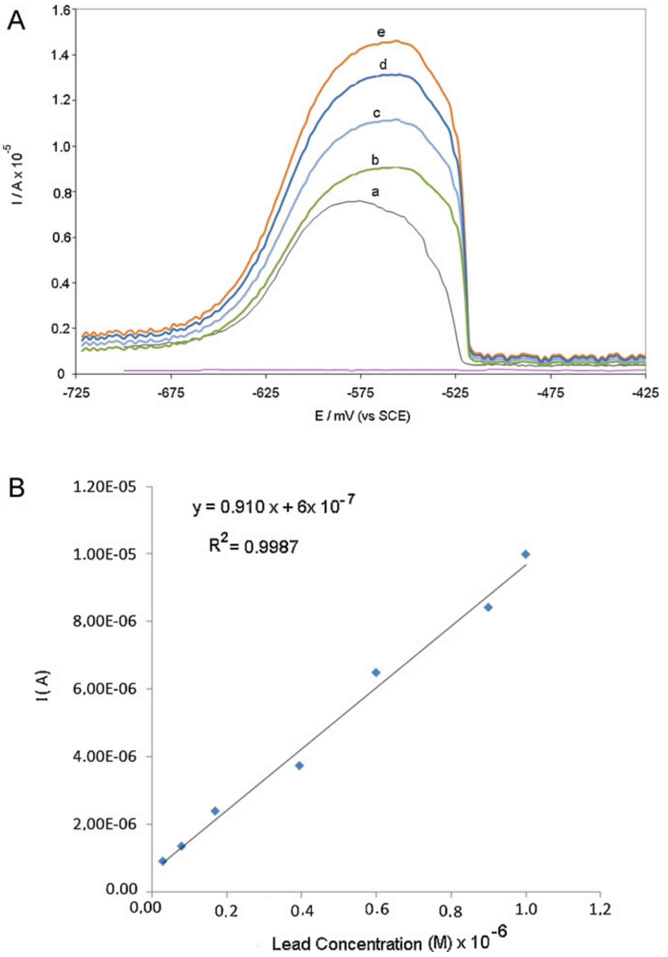

Fig. 9. (A) Differential pulse voltammetry of 3×10^{-7} (a), 8×10^{-7} (b), 2×10^{-6} (c), 4×10^{-6} (d), and 7×10^{-6} (e) mol L^{-1} lead, at TPP-kaolinite/CPE, pH 7.0, with 5 min of preconcentration time in 0.10 M acetate buffer (pH 4.5). (B) Calibration curve for lead at TPP-kaolinite/CEP modified electrode. Conditions as in A.

measurements at each concentration. The detection limit may be estimated as:

Detection limit = $3SN$

where S is the standard deviation of repeated measurements of the lowest detectable concentration, and N is the slope of the calibration plot. From this equation and the data obtained, the detection limit has been estimated as 8.4×10^{-8} mol L^{-1}.

Kaolin-like clay modified electrodes have been employed in the electrochemical detection of diquat [29] phenol [15], cadmium(II) [30], lead [31] and cyanide [32]. To the best of our knowledge, application of modified kaolinite as modifier of carbon paste electrode for the determination of Pb(II) ions has not been hitherto reported.

3.4. Interference

The selectivity of modified electrode TPP-kaolinite/CPE for Pb^{2+} was investigated in the presence of some common metal ion interferents Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, Ag^{+}, Hg^{2+} and Co^{2+}. For this purpose the modified electrode was immersed in a solution of Pb^{2+} (5×10^{-5} mol L^{-1}) and interferent ion (5×10^{-4}mol L^{-1}) for 5 min. The results show that Pb^{2+} interfered with Hg^{2+}, Ni^{2+}, Zn^{2+}and Co^{2+} ions. However, we observed an improvement in selectivity with the TPP-kaolinite/CPE modified electrode, compared with the unmodified CPE for Pb^{2+} in the presence of Cu^{2+}, Cd^{2+} and Ag^{+} ions, as shown in Fig. 10.

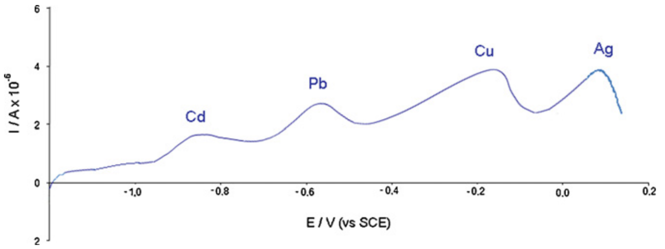

Fig. 10. Differential pulse voltammetry of 1.2×10^{-6} mol L^{-1} lead, in the presence of 3.6×10^{-6} mol L^{-1} cadmium, silver and copper at TPP-kaolinite/CPE, pH 7.0, 5 min of preconcentration time, in 0.10 M acetate buffer (pH 4.5).

Table 1
Analytical results of lead in domestic samples and recovery studies.

Sample	Lead added (mg L^{-1})	Lead found (mg L^{-1})	Recovery (%)
Domestic water	0.01	0.0085	85.40
	0.02	0.0205	102.5
	0.03	0.0308	102.6
	0.04	0.0412	103.0

3.5. Application

The TPP-kaolinite/CPE modified electrode was tested in domestic water samples under the optimized conditions. The recoveries found are satisfactory, and the relative standard deviation obtained after five measurements was 3.45%. As reported in Table 1, the percentage recovered obtained represent satisfactory values for the proposed electroanalytical method, thus indicating the suitability of the proposed method for use in natural water samples although the recovery may be somewhat lower than 100% at lead concentrations lower than 7.0×10^{-8} mol L^{-1}.

4. Conclusion

The determination of lead using a carbon-paste electrode modified with TPP-kaolinite was improved when compared to unmodified CPE and modified kaolinite/CPE. The range for quantitative detection was 3×10^{-7} mol L^{-1} to 2×10^{-5} mol L^{-1} with a preconcentration time of 7 min. TPP-kaolinite modified electrode has a great potential to be used in the development of portable analyzers for monitoring lead ions, its analytical utility has been demonstrated by measuring Pb^{2+} in water samples. The selectivity of the TPP-kaolinite/CPE modified electrode, compared with the unmodified CPE toward Pb^{2+} analysis, is quite good in the presence of Cu^{2+}, Cd^{2+} and Ag^{+} ions, and the response characteristics of the proposed electrode are in a good comparison with those previously reported electrodes. Evaluation of other modifiers combined with a flow injection is the main aim of our forthcoming studies, to identify ways of improving the detection limit and resolving the negative interferences found.

Acknowledgments

The authors would like to thank Universidad Simón Bolívar (USB), Caracas, Venezuela, for financial support, as well as the members of the Laboratorio de Electroquímica at USB for valuable technical assistance.

References

[1] G. Marino, M.F. Bergamini, M.F.S. Teixeira, E.T.G. Cavalheiro, Talanta 59 (2003) 1021–1028.
[2] P. Gonzalez, V.A. Cortınez, C.A. Fontan, Talanta 58 (2002) 679–690.
[3] D. Dragoe, N. Spataru, R. Kawasaki, A. Manivannan, T. Spataru, D.A. Tryk, A. Fujishima, Acta Electrochim. 51 (2006) 2437–2441.

[4] P.K. Ghosh, A.J. Bard, J. Am. Chem. Soc. 105 (1983) 5691–5693.
[5] D. Ege, P.K. Ghosh, J.R. White, J.F. Equey, A.J. Brad, J. Am. Chem. Soc. 107 (1985) 5644–5652.
[6] K. Itaya, A.J. Bard, J. Phys. Chem. 89 (1985) 5565–5568.
[7] J.R. White, A.J.J. Bard, Electroanal. Chem. Interfacial Electrochem. 197 (1986) 233–244.
[8] K. Itaya, H. Chang, I. Uchida, Inorg. Chem. 26 (1987) 624–626.
[9] E. Scavetta, M. Berrettoni, M. Giorgetti, D. Tonelli, Electrochim. Acta 47 (2002) 2451–2461.
[10] E. Scavetta, D. Tonelli, M. Giorgetti, F. Nobili, R. Marassi, M. Berrettoni, Electrochim. Acta 48 (2003) 1347–1355.
[11] C.H. Song, G. Villemure, J. Electroanal. Chem. 462 (1999) 143–149.
[12] J. Qiu, G. Villemure, J. Electroanal. Chem. 142 (1997) 165–172.
[13] L. Fernández, H. Carrero, Electrochim. Acta 50 (2005) 1233–1240.
[14] L. Fernández, C. Borrás, H. Carrero, Electrochim. Acta 52 (2006) 872–884.
[15] M. Hernández, L. Fernández, C. Borras, J. Mostany, H. Carrero, Anal. Chim. Acta 597 (2007) 245–256.
[16] Y. Gómez, L. Fernández, C. Borrás, J. Mostany, B. Scharifker, Electroanalysis 21 (2009) 1354–1362.
[17] E.A. Prodan, L.I. Prodan, N.F. Ermolenko, Tropolifosfaty. W Tripolyphosphatesx, Nauka Tekh., Minsk, 1969 (in Russian).
[18] K. Okada, K. Nishimuta, Y. Kameshima, A. Nakajima, J. Colloid Interface Sci. 286 (2005) 447–454.
[19] Yu I. Tarasevich, G.M. Klimova, Appl. Clay Sci. 19 (2001) 95–101.
[20] V.K. Gupta, M. Al Khayat, A.K. Singha, M.K. Pal, Anal. Chim. Acta 634 (2009) 36–43.
[21] V.K. Gupta, R. Mangla, S. Agarwal, Electroanalysis 14 (2002) 1127–1132.
[22] V.K. Gupta, A.K. Jain, G. Maheshwari, Int. J. Electrochem. Sci. 2 (2007) 102–112.
[23] J. Wilson (Ed.), Clay Mineralogy: Spectroscopic and Chemical Determinative Methods, Chapman and Hall, London, 1994, Chapter 3.
[24] V.C. Farmer, The Infrared Spectra of Minerals, Mineralogical Society, London, 1974.
[25] J. Madejova, P. Komadel, Clays Clay Miner. 49 (2001) 410–432.
[26] W.E. Van der Linden, J.W. Dleker, Anal. Chim. Acta 119 (1980) 1–24.
[27] H. Karina, F. Mokhtar, T.A. Malika, Mater. Res. Bull. 36 (2001) 897–903.
[28] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, NY, 1980.
[29] M.A. El Mhammedi, M. Bakasse, R. Najih, A. Chtaini, Appl. Clay Sci. 43 (2009) 130–134.
[30] M.A. El Mhammedi, M. Achak, M. Hbidd, M. Bakassee, T. Hbidd, A. Chtaini, J. Hazard. Mater. 170 (2009) 590–594.
[31] M.A Mhammedi, M. Achak, M. Bakasse, A. Chataini, Langmuir 8 (1992) 1908–1918.
[32] S. Letaief, I.K. Tonle, T. Diaco, C. Detellier, Appl. Clay Sci. 42 (2008) 95–101.