



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

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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 $8.4 \times 10^{-8} \text{ mol L}^{-1}$, 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+} .

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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 sur-

face 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, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, 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

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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 ($\text{Na}_5\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$) 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 $15\text{ M}\Omega\text{ cm}$.

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 $\text{Cu}-\lambda\alpha$ radiation source, $\lambda = 1.542\text{ \AA}$, $40\text{ kV}/20\text{ mA}$ 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 ($\sim 50\text{ mL}$ 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 $2\theta = 14^\circ$ ($d_L = 7.16\text{ \AA}$) and $2\theta = 29^\circ$ ($d_L = 3.57\text{ \AA}$) [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

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