

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

Newton L. Dias Filho\*, Devaney Ribeiro do Carmo

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

Received 28 February 2005; accepted 14 June 2005

Available online 25 July 2005

## Abstract

In this work, a hydrophilic clay, Na-montmorillonite from Wyoming, USA, was rendered organophilic by exchanging the inorganic interlayer cations for hexadecyltrimethylammonium ions (HDTA), with the formulae of  $[(\text{CH}_3)_3\text{N}(\text{C}_{16}\text{H}_{33})]^+$  ion. Based on fact that organo-clay has high affinities for non-ionic organic molecules, 1,3,4-thiadiazole-2,5-dithiol was loaded on the HDTA-montmorillonite surface, resulting in the 1,3,4-thiadiazole-2,5-dithiol-HDTA-montmorillonite complex (TDD-organo-clay).

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

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

© 2005 Elsevier B.V. All rights reserved.

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

## 1. Introduction

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

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

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

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

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

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

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

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

In this work, a organo-clay was obtained by replacement of the inorganic cations in Na-montmorillonite for hexadecyltrimethylammonium ions (HDTA), with the formulae of  $[(\text{CH}_3)_3\text{N}(\text{C}_{16}\text{H}_{33})]^+$ , allowing to open up the lamellae and causing profound changes in the sorption and intercalation of organic molecules. In contrast to natural montmorillonites, organic molecules are now freely sorbed between the montmorillonite lamellae and the sorptive capacity is very much increased. 1,3,4-Thiadiazole-2,5-dithiol (TDD) was loaded on the HDTA-montmorillonite surface, resulting in the 1,3,4-thiadiazole-2,5-dithiol-HDTA-montmorillonite complex (TDD-organo-clay).

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

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

## 2. Experimental

### 2.1. Chemicals and reagents

All chemicals were of analytical reagent grade unless stated otherwise. The surfactant used in the preparation of the organo-clay was the commercial product hexadecyltrimethylammonium (HDTA) bromide (purum quality). Solutions were prepared from doubly-demineralized water obtained by passing distilled water through a Millipore Milli-Q water purification system. Dilute solutions ( $\leq 1 \times 10^{-3} \text{ mol L}^{-1}$ ) 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  $1000 \text{ mg L}^{-1}$  Titrisol standards (Merck).

### 2.2. Preparation of the organo-clay complex

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

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

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

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

### 2.3. Adsorption isotherms and preconcentration experiments

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

Download English Version:

<https://daneshyari.com/en/article/1247417>

Download Persian Version:

<https://daneshyari.com/article/1247417>

[Daneshyari.com](https://daneshyari.com)