Available online at www.sciencedirect.com

SCIENCE DIRECT

Analytica Chimica Acta 567 (2006) 152–159

ANALYTICA CHIMICA ACTA

www.elsevier.com/locate/aca

Development of a new analytical approach based on cellulose membrane and chelator for differentiation of labile and inert metal species in aquatic systems

André Henrique Rosa[a,∗], Iramaia C. Bellin[a,b], Danielle Goveia[a,b], Luciana C. Oliveira[a,b], Roberto W. Lourenço[a], Newton L. Dias Filho[c], Peter Burba[d]

[a] *UNESP, Universidade Estadual Paulista, Department of Environmental Engineering, 18087-180, Sorocaba, SP, Brazil*
[b] *UNESP, Universidade Estadual Paulista, Institute of Chemistry, 14800-900, Araraquara, SP, Brazil*
[c] *UNESP, Universidade Estadual Paulista, Department of Physics and Chemistry, 15385-000, Ilha Solteira, SP, Brazil*
[d] *ISAS, Institute of Analytical Science, D-44013, Dortmund, Germany*

Received 4 November 2005; received in revised form 10 March 2006; accepted 10 March 2006

Abstract

A new procedure was developed in this study, based on a system equipped with a cellulose membrane and a tetraethylenepentamine hexaacetate chelator (MD–TEPHA) for in situ characterization of the lability of metal species in aquatic systems. To this end, the DM–TEPHA system was prepared by adding TEPHA chelator to cellulose bags pre-purified with 1.0 mol L^{-1} of HCl and NaOH solutions. After the MD–TEPHA system was sealed, it was examined in the laboratory to evaluate the influence of complexation time (0–24 h), pH (3.0, 4.0, 5.0, 6.0 and 7.0), metal ions (Cu, Cd, Fe, Mn and Ni) and concentration of organic matter (15, 30 and 60 mg L^{-1}) on the relative lability of metal species by TEPHA chelator. The results showed that Fe and Cu metals were complexed more slowly by TEPHA chelator in the MD–TEPHA system than were Cd, Ni and Mn in all pH used. It was also found that the pH strongly influences the process of metal complexation by the MD–TEPHA system. At all the pH levels, Cd, Mn and Ni showed greater complexation with TEPHA chelator (recovery of about 95–75%) than did Cu and Fe metals. Time also affects the lability of metal species complexed by aquatic humic substances (AHS); while Cd, Ni and Mn showed a faster kinetics, reaching equilibrium after about 100 min, and Cu and Fe approached equilibrium after 400 min. Increasing the AHS concentration decreases the lability of metal species by shifting the equilibrium to AHS–metal complexes. Our results indicate that the system under study offers an interesting alternative that can be applied to in situ experiments for differentiation of labile and inert metal species in aquatic systems.

Keywords: Water; Natural organic matter; Metals; Lability; Humic substances

---

1. Introduction

The main mass of organic carbon distributed in natural aquatic environments and soils is concentrated in humic substances (HS). In general, HS can be considered the product of a very complex process called humification, which involves physical, chemical and microbiological processes of organic matter in soils and waters. This organic matter is not only restricted to plant remainders but also to animal, microbiota and xenobiotic components (i.e., CO_2, carbons and coals, and organic compounds derived from industrial activities) [1–3]. This organic matter can be transported to natural waters by the leaching process or it can be formed directly in aquatic environments by the decomposition of plants and aquatic organisms [4]. Besides their considerable variety and heterogeneity, HS mostly exhibit comparable functional groups of the phenolic and carboxylic types that are characterized by their exceptional complexation capabilities towards metal ions in comparison with other natural complexing groups, which have been studied exhaustively over the last decade [5,6]. The physicochemical properties of HS depend on their origin and vary as a function of their solubility [7,8].

Owing to their complexation properties, HS are important natural buffers in the environment, strongly binding both inor-

---

∗ Corresponding author. Tel.: +55 15 32282466; fax: +55 15 32282466.
E-mail address: ahrosa@sorocaba.unesp.br (A.H. Rosa).

0003-2670/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2006.03.046

ganic and organic pollutants. The thermodynamic and kinetic stability of HS/pollutant species directly influences their transportation, accumulation and bioavailability in the biosphere [9,10]. In aquatic systems, the concentration and ratio of dissolved metal ions and HS can vary considerably and may therefore exert a considerable influence on the formation of HS/metal species, as well as their distribution between liquid and solid phase (e.g., suspended matter, sediment). Therefore, investigations into exchange processes between HS and metal ions are of great interest when studying potential hydrogeochemical turnover of metals in soil and natural waters [9,10], particularly under the influence of acid rain caused by increasing atmospheric pollution by man-made nitrogen and sulfur oxides [11].

From this standpoint, analytical information on the lability of HS/metal species and their possible transformation into species of either higher or lower stability is of increasing relevance. A variety of methods have been proposed, such as electrochemical and chromatographic techniques, in order to study the complexing capacity of HS, HS/metal equilibrium and the dynamics of complexes [5,6,10]. The advantageous application of immobilized chelators to differentiate labile and inert metal species in HS by ligand exchange has been described in other reports [12–14]. Both the kinetics and the degree of metal exchange have been used as parameters for the operational characterization of metal labilities in aquatic HS. However, these studies were carried out in the laboratory after sampling, storage and treatment of water samples. Also, most of the models of interpretation of complexation reactions have been developed in the laboratory, based on simplistic systems using reactions with “pure solutions” that often contain only one ligand and one or a few metals. These models have undoubtedly contributed to further our understanding of metal complexation reactions by simple ligands, but the use of these models to understand environmental phenomena in aquatic systems containing a large variety of hydrocolloidal, polyelectrolytic and polyfunctional ligands is inadequate [15].

This paper discusses the development of a new analytical procedure that can be applied in situ for the differentiation of labile and inert metal species in aquatic systems using cellulose membranes and ligand exchangers. This procedure is based on a system (MD–Chelator) that consists of a cellulose bag containing tetraethylenepentamine hexaacetate (TEPHA), which can be placed directly into a body of water (river, lake, etc.), enabling one, as a function of time and quantity of exchanger, to characterize the relative lability of the metal species present in the aquatic system in question. The parameters that affect the performance of the MD–TEPHA system, such as pH, complexation time, and characteristics and concentration of metals and organic matter, were evaluated to check the system’s performance/applicability in in situ experiments in different bodies of water.

2. Experimental

2.1. Chemicals and reagents

All the reagents were of high-purity grade unless otherwise stated. Diluted acid and alkaline solutions necessary for aquatic HS isolation were prepared by diluting 30% hydrochloric acid (suprapure, Merck AG, Germany) or sodium hydroxide-monohydrate (suprapure, Merck AG, Germany) in high-purity water (Milli-Q system, Millipore, USA). The XAD 8 adsorbent (Serva Feinbiochemica, Germany) required for the isolation of aquatic HS was pre-purified by successive soaking with 0.5 mol L^{-1} HCl, 0.5 mol L^{-1} NaOH and methanol (24 h, each). The working solutions of the metals (Cu, Cd, Fe, Mn and Ni) were prepared daily by dilution in the stock solutions (1000 mg L^{-1}; Normex®, Carlo Erba). The ion exchanger TEPHA has the anchor group tetraethylenepentamine hexaacetate and was obtained by Fluka, Switzerland (Metalfix Chelosolve No. 63981).

2.2. Study area

Water samples were collected in October 2004 from a tributary of the Itapanhaú river located in the Serra do Mar State Park (S23°50′23″, W46°08′21″) in an area of environmental protection located in the 7th Hydric Resources Management Unit (UGRHIs) in the Baixada Santista region, municipality of Bertioga, SP, Brazil.

2.3. Water sample characterization

The pH, temperature, conductivity and dissolved oxygen were determined in situ. In the laboratory, the water samples were digested with concentrated HNO_3 heated to 120 °C and the metal concentrations of Cu, Cd, Mn and Ni were determined by FAAS (Varian 240FS) and/or GFAAS (Varian 240Z). Table 1 lists the results of the preliminary characterization of the water samples.

2.4. Isolation of aquatic humic substances by XAD 8 resin

The aquatic HS were isolated from a mixed water sample collected from the study area. For this purpose, 100 L of surface water (about 25 cm below the water’s surface) were filtered on site through 0.45 μm cellulose-based membranes and acidified

Table 1
Preliminary characterization of water samples collected from a tributary of the Itapanhaú river in October 2004

Parameters	
pH	5.2
Temperature (°C)	22.2
Conductivity (μS cm^{-1})	73.2
Dissolved oxigen (mg L^{-1})	3.7
Total organic carbon (mg L^{-1})	12.3
Absorbance at 436 nm (A)	0.069
Molar absortivity (A L/cm mol C)	67.0
Total metal	
Fe (μg L^{-1})	880.0
Mn (μg L^{-1})	428.0
Cu (μg L^{-1})	3.5
Cd (μg L^{-1})	2.67
Ni (μg L^{-1})	7.67