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The influence of organic ligands on the adsorption of cadmium by suspended matter in natural waters studied by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry and electrochemical methods

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Natural water carrying a great amount of suspended particulate matter (SPM) was used as a model system for the study of the competition among organic ligands (dietilentetraamine pentaacetic acid, DTPA, nitrilotriacetic acid, NTA, and citrate, Cit) and natural complexants (SPM) for cadmium adsorption.

Speciation diagrams at the pH of the natural sample were obtained by electroanalytical techniques, processing the experimental data with the complexation constants and the mass balance of the system.

Results show that the adsorption equilibrium SPM-Cd is completely displaced by DTPA but not completely by NTA or Cit. Furthermore, larger Cit concentrations increase the amount of adsorbed Cd(II). The increment of the complexing capacity may be explained on the basis of SPM-Cit-Cd ternary complexes formation. This hypothesis was supported on the results obtained by applying for the first time the MALDI–TOF technique in a mixture of SPM, Cd(II), organic ligands and their complexes.

1. Introduction

Even though the adsorption of metal ions onto suspended particulate matter constituents (clays, oxides/hydroxides, humic acids) has been widely studied (Nagy et al., 1998; Wu et al., 2003; Lackovic et al., 2004), little research was focused on the effect of organic ligands on metal uptake in natural systems (Sillampää and Rämö, 2001; Yang et al., 2006). No studies related with the competence between anthropogenic organic ligands and SPM in natural water were reported. The presence of organic and inorganic ligands can enhance, suppress or cause no effect on the adsorption of metals onto SPM, depending on the characteristics of the ligand, the SPM constituents, and the metal species. Enhanced adsorption may be caused by the formation of surface complexes (surface sites-metal ion-ligand, surface site-ligand–metal ion) (Turner, 2007). Metal uptake may be reduced in the presence of ligands due to competition between the ligand and metal ions for surface sites, or through the formation of soluble complexes that do not adsorb onto the SPM surface (Malandrino et al., 2006).

Considering that natural waters, industrial waters and wastewaters generally contain organic substances in addition to heavy metals, it is very important to know how the heavy metals adsorb onto the SPM even in the presence of organic ligands (OL). For this reason the competition between OL and SPM for Cd(II) adsorption was evaluated.

In a previous work we study the complexing capacity of natural waters carrying a great amount of suspended matter (Rio de La Plata river). We found that in the case of Cd(II) the constitutive clays of the SPM were the most relevant complexing agents, while the contribution of organic ligands turned out to be negligible (Minaberry and Gordillo, 2007). For this reason we decided to use this natural water as a model system for studying SPM–OL competitive complexation. Results are relevant if we consider that many rivers around the world are characterized by high SPM concentration: Orinoco (132 mg dm^{-3}), Amazonas (162 mg dm^{-3}) (Depetris and Paolini, 1991) and Mississipi (200 mg dm^{-3}) (Manheim et al., 1972), as well as European rivers (Hakansona et al., 2005).

Three organic ligands were selected for this study: DTPA, NTA and citric acid. DTPA and NTA can be introduced into natural systems by anthropic activities, for example, using them as chelates for agricultural and industrial applications (Darban et al., 2000; Sillanpää et al., 2001; Wu et al., 2003). Citric acid was chosen because it can be effectively used in phytoremediation given its ability to increase metal bioavailability and hence the bioaccumulation of metals into plants (Evangelou et al., 2007). These three ligands have been used in soil remediation techniques, such as soil washing or phytoremediation, but cost, toxicity and degradability of DTPA may also restrict its application (Sillanpää et al., 2001; Evangelou et al., 2007).

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In addition, we studied the interaction of these three ligands with cadmium because the presence of this metal in natural waters is mostly due to anthropogenic activities and because its soluble compounds are highly toxic (Daher, 1995; Vink, 2009).

To determine the competitive speciation diagrams we applied an electrochemical technique (square wave anodic stripping voltammetry: SWASV) because it does not alter the nature of the sample and allows to determine the concentration of the labile (free or weakly complexed) electro active metals by direct electrodeposition from the sample (Gonçalves et al., 1985; Wang, 1996; Simoes Correia dos Santos et al., 2001; Lam et al., 2001).

To study the possibility of surface complexes formation we have used MALDI/TOF. It is worth mentioning that it was the first time that this method was applied to analyze a mixture of cations, organic acids and chelators of low molecular mass (LMM) on a natural SPM. To our knowledge, the MALDI/TOF technique for environmental analysis has been successfully used for the qualitative analysis of high-mass molecules, such as toxins, humic acid, and microorganisms, (Goheen et al., 1997; Hu et al., 2005) to study a mixture of LMM chelators. Results obtained by applying this technique together with those obtained by voltammetry are consistent with SPM-Cd(II)–OL ternary complex formation, fact that leads to an increase of the complexing capacity in natural waters.

2. Materials and methods

2.1. Description of the study area

The Río de la Plata estuary (Fig. 1) is the output of a huge drainage basin embracing an area of 3.1 millions Km^2 partially situated in the territories of Argentina, Brazil, Bolivia, Paraguay and Uruguay. Waters and sediments are bring together form the Andes, the Mato Grosso Rain Forest and the South-east Brazilian mountains near the Atlantic Ocean. This estuary, of a total length of 317 km and a surface of 30 212 km^2 (Colombo et al., 1989), has caudal ca. 22 000 $m^3 s^{-1}$, and carries about 80 million t/y of particulate matter from temperate and tropical regions of South America (Colombo et al., 1989; Depetris and Paolini, 1991). The samples analyzed in this work were collected in the superior part of the estuary where the low salinity of the waters (0.03%) and low depth from bottom (2 or 5 m) characterize this sector. Tides due to the oceanic influence have amplitude that does not exceed a metre but sporadic meteorological phenomena characterized by strong South-east wind (known as "Sudestada") can increment the level in more than 1 m and produce strong surf.

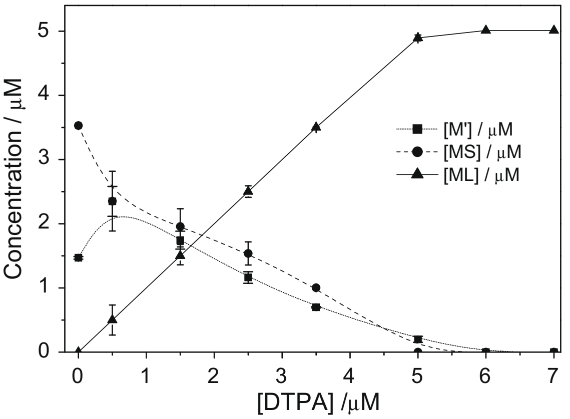

Fig. 1. Specie distribution diagram for Cd(II). [M], [ML] and [MS] are free Cd(II), Cd-DTPA complex and Cd-SPM surface complex concentrations respectively.

2.2. Reagents, solutions and water sample

All solutions were made with Milli-Q water and Merck reagents. Cadmium stock solutions 10^{-4} M were prepared from a standard of Cd(II) (concentration 1000 ± 2 mg L^{-1}) provided by Merck (Merck Certipure). DTPA, NTA, and (Cit) stock solutions were made by dissolving each reagent in Tris (hydroxymethyl) aminomethane buffer (Tris/HCl pH 8) to reach a final chelator concentration of 0.05 μM and 0.1 mM. A buffer Tris (pH 8) was used to keep the stock solutions at natural pH of the sample.

The water sample used in this study was collected in the 2008 summer during the phenomena called "sudestada" (VS08).

Details about collection and characterization were found in previous work (Minaberry and Gordillo, 2007). Aliquots for chemical speciation studies were stored deep-frozen at their natural pH with no addition of any reagent; this procedure has proved not to alter the speciation of metals in the samples during storage.

2.3. Competitive complexation between OL and SPM

2.3.1. Voltammetric equipment

The voltammetric measurement system includes Princeton Applied Research (PAR) 203A and a PAR303A mercury drop electrode (area of 0.024 ± 0.0004 cm^2), an Ag/AgCl reference electrode (3.5 M KCl) and a platinum wire counter electrode. Samples contained in a 10 ml PAR voltammetric cell cups were deoxygenated with oxygen free nitrogen.

2.3.2. Experimental procedure

Each natural water sample was sonicated for 10 min before divided into nine aliquots. The Cd(II) stock solution was added to each aliquots to reach a final concentration of 5 μM.

The suspensions were equilibrated for 24 h at room temperature. Preliminary studies showed that equilibrium was reached in 24 h. (Minaberry and Gordillo, 2007). Labil Cd(II) measured in those conditions was taken as zero added OL. After that, aliquots of DTPA, NTA and Cit stocks solutions were added to the eight waters samples–Cd(II) mixtures to reach OL concentrations of 0–7 μM, 0–25 μM and 0–100 μM respectively. The mixtures were equilibrated for 24 h and then they were analyzed by SWASV. The applied potential in the deposition step was different depending on the ligand used (DTPA: −0.9 V; NTA and Cit: −1.1 V). These potentials were chosen on the basis of previous electrochemical studies of these metal–ligand complex (see Supporting information).

2.4. MALDI–TOF experiments

The MALDI–TOF mass spectra were obtained from Miniflex (bruker Daltonics, Germany). The instrument was equipped with a nitrogen laser ($\lambda = 337$ nm) to desorb and ionize the samples. The accelerated voltage used was 19 kV. A stainless steel target with 49 spots was used as MALDI substrate on which the samples are deposited. The instrument is equipped with a video camera, displaying the sample image on the monitor and allowing us to aim the laser at a specific spot within the area of target. The measurements were performed in positive and negative linear mode. The spectra were externally calibrated using the Cd(II), NTA, Cit in buffer Tris stocks solutions as standards. In general 60 laser shots were averaged to generate a spectrum.

2.4.1. Adsorption experiments

To analyze the adsorption of Cd(II), NTA and Cit, aliquots of their stocks solutions were added to natural waters samples (previously sonicated during 10 min). After equilibrated for 24 h the mixtures were centrifuged at 5000 rpm for 60 min, the supernatant was