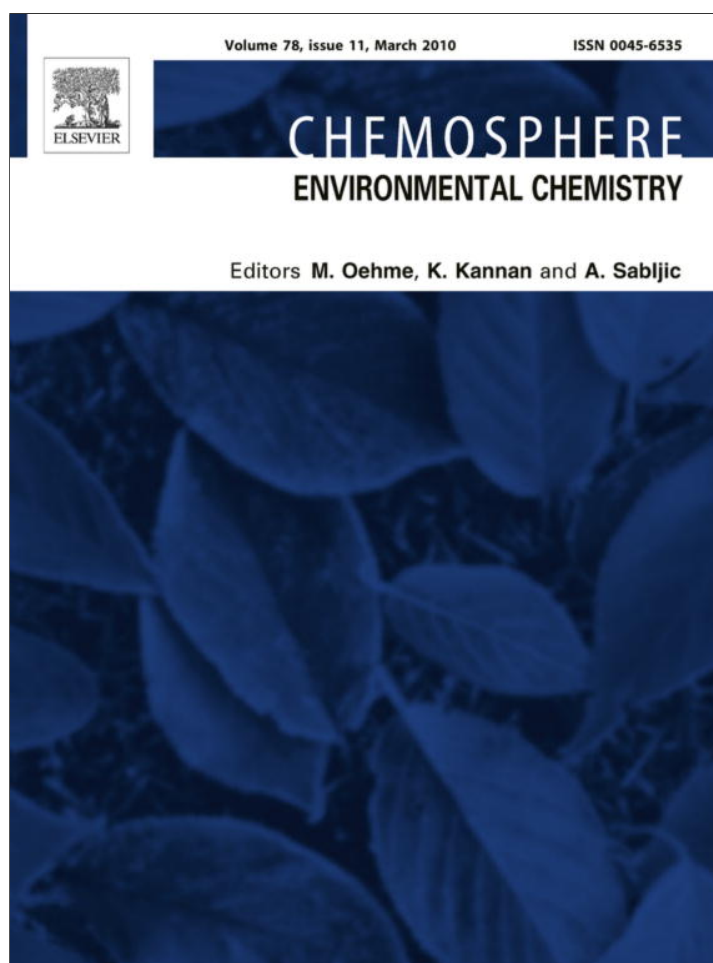


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The influence of organic ligands on the adsorption of cadmium by suspended matter in natural waters studied by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry and electrochemical methods

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ABSTRACT

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 (diethylenetriamine 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.

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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 (Sillanpää 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 Mississippi (200 mg dm^{-3}) (Manheim et al., 1972), as well as European rivers (Hakansson 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 Km² partially situated in the territories of Argentina, Brazil, Bolivia, Paraguay and Uruguay. Waters and sediments are brought together from 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 km² (Colombo et al., 1989), has a caudal ca. 22 000 m³ 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.

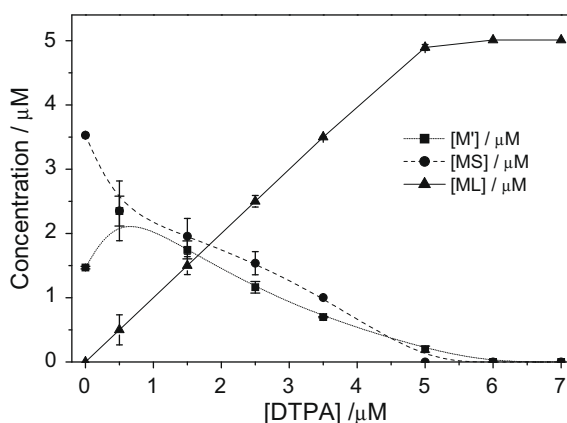


Fig. 1. Specie distribution diagram for Cd(II). [M], [ML] and [MS] are free Cd(II), Cd-DTPA complex and Cd-SPM surface complex concentrations respectively.

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 cm²), 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). Labile 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 (λ = 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

decanted, and freshly diluted buffer (Tris) was added. This procedure was repeated at least ten times.

Removal efficiency of dried residues from supernatant in the samples was evaluated based on a MALDI analysis of the supernatant of the washed samples. These mass spectra only showed matrix picks, confirming the effectiveness of the washed procedure (see Supporting information).

2.4.2. Sample preparation for MALDI-TOF

All samples were analyzed using 2,5-dihydroxybenzoic acid (2,5-DHB). DHB was chosen as a matrix because it was used in analysis with similar OL (Goheen et al., 1997; Mugo and Bottaro, 2004).

DHB was prepared at a concentration of 10 mg mL⁻¹ in Milli-Q water to produce a nearly saturated solution (Goheen et al., 1997). The resultant DHB solution was stored in a refrigerator at 4 °C and used when needed.

The Cd(II), NTA and Cit stocks solutions and the washed pellet were mixed with the matrix solution in a volume ratio of 1:10. Then 0.5 µL of the final solution was dispensed onto the stainless steel probe and left in the air for a few minutes to evaporate the solvent. This procedure was repeated twice, and then the sample plate was finally loaded into de ion source for analysis.

3. Results and discussion

3.1. Species of the analyzed system

The complexing capacity for cadmium of the natural waters used in this work has been previously determined by SWASV. It was found that, as a consequence of the great amount of SPM, the contribution of total organic ligands (O_T) may be neglected in the SPM concentration scale (µM). Thus, the complexing capacity of the studied waters is determined by the surface binding sites of the suspended particulate material which have also been characterized.

The analysis of samples collected over a 3 years period have shown practically the same conditional binding constants even though hydrodynamic conditions and temperatures were different.

Taking into account that cadmium only binds to SPM our system is adequate for studying the competitive effect of adding anthropogenic organic ligands. In this sense these waters may be considered as a model system for any natural waters that share the characteristic of carrying a great amount of SPM.

It has been shown that, at natural pH, the system is adequately described by considering a minimum of two kinds of binding sites (surface hydroxyl groups, ≡S–O–H, or permanent negatively charged sites, X⁻) characterized by their conditional binding constant, K_i, and volumetric concentrations, [≡S_i].

The results of the analyzed data from the titration curve of the system by multivariable regression have yielded values of log K₁ = 6.5, which correspond to inner sphere coordination complexes (≡S–O–Cd⁺ or ≡S₁), and log K₂ = 4.4 for outer sphere coordination complexes (S–O–H, Cd²⁺, or X₂²⁻–Cd²⁺ or ≡S₂). Also it has been found that the concentration of ≡S₂ sites is much greater than ≡S₁ sites one (25.3 µM and 0.49 µM respectively). These results are congruent with surface description that have been made for the constitutive clays, illite (Lackovic et al., 2003) and montmorillonite (Barbier et al., 2000).

To describe the competence between organic ligand and the SPM we have compared the stability constant of the three ligands with cadmium (DTPA: log β = 19, NTA: log β = 9.38 Cit: log β = 4.54) with the superficial ones. That comparison suggests that only the citrate could compete with the SPM for Cd(II).

To study the distribution of the species present in this complex system (Cd(II), OL, and SPM) the general mass balances and equilibrium constants have to be taken into account. In order to simplify the analysis we consider that metal ion interact with only one kind of surface active sites, ≡SM, which is congruent with the experimental observation that [≡S₂] ≫ [≡S₁]. Thus for the metal we have:

$$M_T = [M] + [ML] + [≡SM] \quad (1)$$

$$K_S = \frac{[≡SM]}{[≡S][M]} \quad (2)$$

$$K_L = \frac{[ML]}{[L][M]} \quad (3)$$

where M_T is the total metal concentration, S_T the total amount of binding sites per dm³ and L_T is the concentration of total organic ligands; ≡SM and ML represent a surface and soluble complex, respectively, while K_S and K_L are the complexing constants.

In order to simplify even more the analysis, we considered negligible the possibility of ligand adsorption onto SPM. This validity of this assumption was analyzed in details by MALDI-TOF studies.

Then the mass balance for sites and ligands are:

$$S_T = [≡S] + [≡SM] \quad (4)$$

$$L_T = [L] + [ML] \quad (5)$$

Voltammograms of DTPA cadmium complex (see Supporting information) show that for this ligand it is possible to determine the concentration of labile Cd(II), [M], by SWASV. In fact, in this potential range Cd-DTPA complex, ML, is not electroactive. Thus we determined [M] applying this electrochemical technique. It is not possible to obtain [ML] experimentally. However, taking into account the high value of β, it is considered that L_T = [≡SM] while L_T < M_T. Consequently, [≡SM] is obtained from Eq. (1). Fig. 1 shows the resulting speciation diagram.

The linear dependence (up to 5 µM) of Cd-DTPA complex concentration on the concentration of the DTPA added shows that the metal is totally displaced from the SPM binding sites.

Voltammograms of NTA and Citrate cadmium complexes show a quasi-reversible electrochemical behavior at the deposition potential. Thus both, Cd(II) and Cd-complex concentrations are determined simultaneously in each case. As a consequence of this the first and the second terms of Eq. (1), [M] + [ML] = Y, are determined simultaneously.

Using Eqs. (1), (3) and (5), labile metal concentration is obtained from the following quadratic expression:

$$[M]^2 + [M] \left(L_T - Y + \frac{1}{K_L} \right) - \frac{Y}{K_L} = 0 \quad (6)$$

Once obtained [M], [ML] is easily calculated from Eq. (5).

Fig. 2 shows the resulting speciation diagram for Cd-NTA system.

In this case the limit of 5 µM for Cd-NTA complex is never reached even though the organic ligand concentration becomes higher than the SPM binding sites one. Thus ca. 20% of the metal still remains bound to SPM for [NTA]_T = 25 µM. It is clear that NTA cannot displace all the metal from the SPM binding sites.

Fig. 3 shows the resulting speciation diagram for Cd-Citrate system.

In this case it is striking that, after a little decay, Cd-SPM concentration seems to increase when citrate is added to the system. This unexpected result brings doubts about the assumption of no ligand adsorption onto SPM used for speciation calculation. Then, a more reliable explanation for the observed results is based on the existence of ternary complexes formed between surface bind-

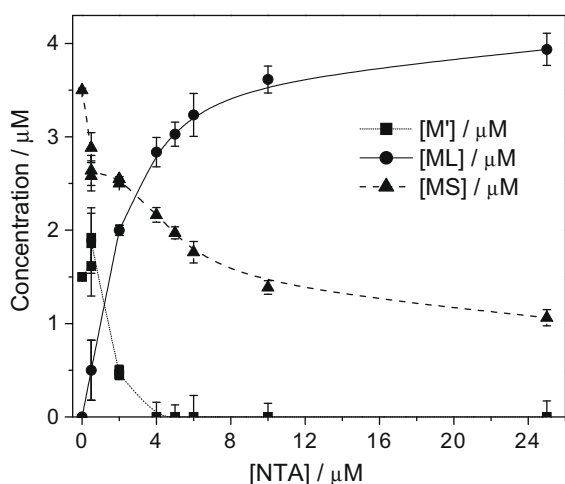


Fig. 2. Specie distribution diagram for Cd(II). [M], [ML] and [MS] are free Cd(II), Cd-NTA complex and Cd-SPM surface complex concentrations respectively.

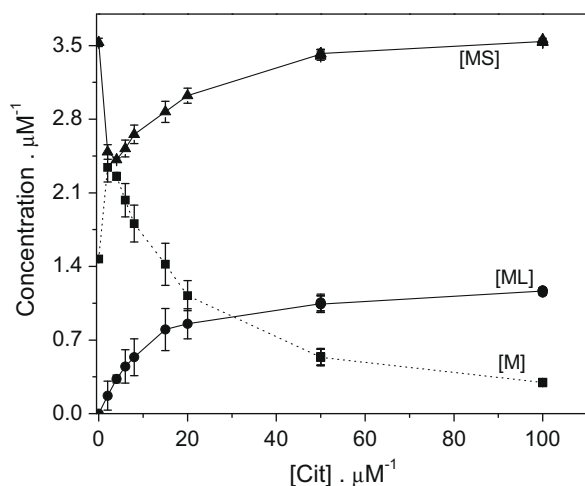


Fig. 3. Specie distribution diagram for Cd(II). [M], [ML] and [MS] are free Cd(II), Cd-Citrate complex and Cd-SPM surface complex concentrations respectively.

ing sites of SPM, anthropogenic organic ligands and cadmium (Benjamin and Leckie, 1981; Bradl, 2004).

3.2. MALDI-TOF studies

In order to support this assumption we have applied MALDI-TOF to analyze the adsorption of Cd(II), organic anthropogenic ligands (NTA and Citrate) and their complexes. Concentrations of 5 μM , 20 μM and 5 μM for Cd(II), NTA, and Citrate respectively were chosen in accordance with the previous electrochemical studies.

It is important to notice, in all cases, that the SPM acts as an inert support (see Supporting information). The matrix, 2,5 DHB, and SPM mixture's spectrum only shows the signals attributable to first one; $[\text{DHB} + \text{H}]^+$ and $[\text{DHB} + \text{Na}]^+$ at m/z 155 and 177 respectively, in the positive mode and $[\text{DHB} - \text{H}]^-$ and others respectively at m/z 153 and $m/z > 300$ in the negative mode (Goheen et al., 1997). Besides, the spectrum of Tris buffer, used to keep in all the mixture at pH 8, shows picks at m/z 120, $[\text{TRIS} - \text{H}]^-$, and m/z 122, $[\text{TRIS} + \text{H}]^+$. The m/z values and assignments of the ions observed in positive and negative mode for standard solution mixtures, matrix, and buffer of Cd(II), NTA and Citric acid are shown in Table 1.

As it has been shown by Goheen et al. (1997), amine-based ligands compounds yield better signals in the positive mode whereas the small organic acid, like citric acid, yield better signals in the negative mode.

To investigate the cadmium adsorption onto the SPM, a pellet obtained from the incubation of this mixture was analyzed by MALDI-TOF in the positive mode.

Fig. 4a displays a strong protonated $[\text{Cd} - \text{OH}]^+$ peak, followed by two weak peaks at m/z 154 and 60, assigned to matrix and $[\text{Cd}]^{2+}$ respectively. These results confirm that cadmium remains adsorbed onto SPM in accordance with our electrochemical results.

The NTA and NTA-Cd(II) adsorption was evaluated with the incubation of these species with SPM. Fig. 4b (NTA-Cd) shows similar peaks to those observed in the NTA standard spectrum (see Table 1). This result is in agreement with the possibility of ligand adsorption in SPM. Besides, some peaks are assignable to $[\text{NTA} + 2\text{Cd}]^{2+}$ m/z 211 and $[\text{NTA} + \text{Cd}]^+$ m/z 309 in the mixture NTA-Cd(II)-SPM confirming the formation of this ternary complex. Both results match up with the specie distribution diagram of NTA-Cd(II)-SPM mixture, where the NTA cannot totally displace the Cd (II) adsorbed on the SPM surface.

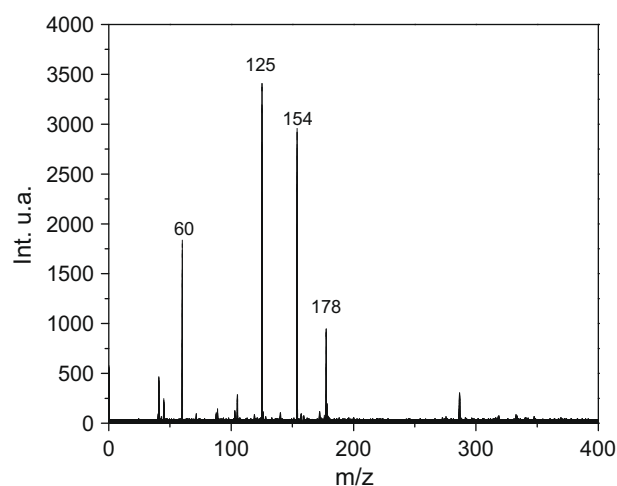


Fig. 4a. Mass spectrum for a mixture of cadmium standard solution and clay detected in positive linear mode.

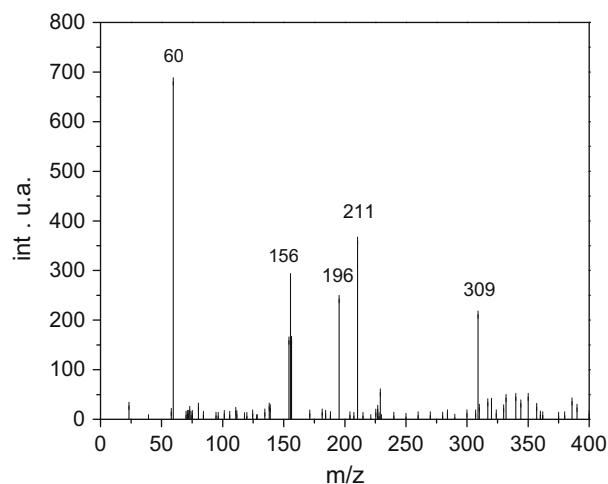


Fig. 4b. Mass spectrum for a mixture of cadmium, NTA and clay, detected in positive linear mode.

Table 1
Most relevant positive and negative ions observed by MALDI-TOF MS.

Analyte	Molecular mass	Ion observed and m/z (-)	Ion observed and m/z (+)
Cadmium	112	-	$[\text{Cd}]^{2+}$ 59 $[\text{Cd} + \text{OH}]^+$ 125
NTA	191	$[\text{NTA} - \text{H}]^-$ 190 $[\text{NTA} - 2\text{H}]^{2-}$ 95	$[\text{NTA} + \text{Na}]^+$ 120–123 $[\text{NTA} + 2\text{H}]^+$ 194–195
Citric acid	192	$[\text{Cit} - \text{H}]^-$ 191	$[\text{Cit} + \text{H}]^+$ 193

We have examined the possibility of Citrate and Citrate-Cd(II) adsorptions incubated mixtures of citrate and citate-Cd(II). Fig. 4c, obtained in negative mode, shows the same peak observed for the citrate standard spectrum, $[\text{Cit} - \text{H}]^-$ m/z 191 and others peaks assignable to the matrix, m/z 153 and 306.

On the other hand, the mass spectrum of the mixture SPM-citrate-Cd(II), Fig. 4d, shows that there are two mass peaks, m/z 193 $[\text{Cit} + \text{Cd}]^+$ and m/z 302, attributable to $[\text{Cit} + \text{H}]^+$. The later result supports the hypothesis that Cd(II) adsorption on SPM is enhanced because of the ternary complex formation (SPM-Cit-Cd(II)).

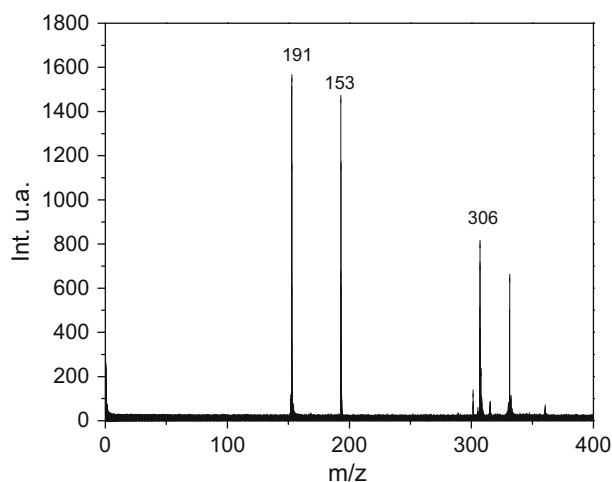


Fig. 4c. Mass spectrum for a mixture of citrate standard solution and clay detected in negative linear mode.

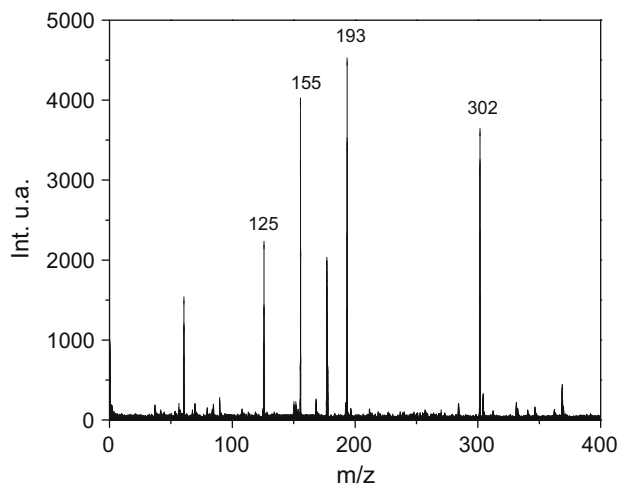


Fig. 4d. Mass spectrum for a mixture of cadmium standard solution, citrate and clay detected in positive linear mode.

4. Conclusions

The presence of organic ligands in natural waters with great SPM has important implications for trace metal speciation. The results reveal different behaviors for the three OL in the study for the mixture OL-Cd(II)-SPM by electroanalytical methods. While the DTPA totally removes the cadmium adsorbed onto SPM, the NTA cannot displace all the metal from the SPM binding sites. Finally, the presence of Citrate leads to an increment of Cd(II) adsorption onto SPM even though its concentration exceeds the inorganic binding sites concentration.

These data suggest that the last two cases would be explained by ternary complexes formation. The confirmation of this hypothesis is based, for the first time, on the use of the MALDI-TOF technique for this kind of environmental mixtures. Results obtained by applying this technique confirm not only the adsorption of cadmium and OL at SPM but also the formation of their ternary complex. The present study is, therefore, significant because it combine two techniques that give the advantages of rapidness and simplicity for studying the speciation in a complex environmental system like SPM-OL and heavy metal in natural waters.

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Appendix A. Supplementary material

Section S1: electrochemical information, Figures S11–S13. Section S2: MALDI-TOF information, Figures S14–S114. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2010.01.004](https://doi.org/10.1016/j.chemosphere.2010.01.004).

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