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Article

Interaction of Mercury(II) with Humic Substances from the Rio Negro (Amazonas State, Brazil) by Means of an Ion Exchange Procedure

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Neste estudo investigou-se a complexação do íon mercúrio (II) por substâncias húmicas aquáticas extraídas (utilizando-se resina XAD 8) do Rio Negro - AM - Brasil. Frações lábeis/inertes de complexos de Hg(II)-SH foram caracterizadas por processo de troca iônica usando-se as técnicas em batelada e em coluna e resina Chelite S. Este coletor apresenta coeficientes de distribuição, K_d, em relação a Hg(II) da ordem de 10^4 diminuindo, contudo, em casos de pequenas razões Hg(II)/SH (< 0.1 μg Hg(II)/mg SH). A influência de diferentes parâmetros (razão de Hg(II)/SH, pH, tempo de contato, tempo de complexação) relevantes na complexação de Hg(II) em ambientes aquáticos foi avaliada. A labilidade de Hg(II) em SH dissolvida é influenciada, principalmente, pela razão de massa Hg(II)/SH e pelo tempo de complexação das espécies Hg(II)-SH formadas. Assim, no caso de baixa concentração de Hg(II) em relação à concentração de SH, lentos processos de transformação das espécies Hg(II)-SH recentemente formadas diminuem a labilidade causando recuperações abaixo da porcentagem total de Hg(II) ligado à SH.

The aquatic humic substances (HS) investigated in this study with respect to their binding capability towards mercury(II) were isolated from the river Rio Negro, Amazonas State - Brazil, by means of the adsorbent XAD 8. Labile/inert fractions of inorganic Hg(II) complexes formed with these HS were characterized using an ion-exchange batch and column technique, respectively, based on Chelite S. This collector exhibits high Hg(II) distribution coefficients, K_d, up to the order of 10^4 decreasing, however, in the case of small Hg(II)/HS ratios (< 0.1 μg Hg(II) / mg HS) . The influence of different complexation parameters (ratio of Hg(II)/HS, pH, contact time, complexing time) relevant for Hg(II) binding in aquatic environments was assessed. The Hg(II) lability in dissolved HS is mainly influenced by the mass ratio of Hg(II)/HS and the ageing of Hg(II)-HS species formed. This is particularly obvious in the case of low Hg(II) loading of HS where slow transformation processes of freshly formed Hg(II)-HS species significantly decrease their lability, leading to incomplete recoveries (< 20%) of the total Hg(II) bound to HS.

Keywords: *Mercury(II) speciation, ion exchange, aquatic humic substances, Rio Negro*

Introduction

The Rio Negro is one the two source rivers of the Amazonas. In accordance with data hitherto published[1], the main humic acid flux to the Amazon River system results from the Rio Negro which contributes 2.5 times the input of the Rio Solimões. The major mass of organic carbon dissolved in tropical aquatic environments, particularly in dark-colored rivers (“Rio Negro”) of the Amazon basin, is concentrated in humic substances (HS). Due to a broad spectrum of binding sites, HS are generally able to interact with heavy metal ions in aquatic systems[2], *e.g.* in surface waters, sediments and soil leakage waters. Therefore, deposition, hydrogeochemical cycles and bioavailability of environmentally problematic metals like mercury, are supposed to be strongly dependent on the nature and the thermodynamic stability of their macromolecular species formed with HS[3]. In aerobic natural waters, Hg(II) can complex with inorganic ligands (*e.g.* Cl-, OH-), interact with dissolved organic carbon (DOC), or adsorb to particulate matter[4].

In the Brazilian Amazon region goldmining has become a major activity, using mercury for amalgamation[5,6]. During this process, considerable amounts of mercury escape into the flowing river. The total loss of Hg has been estimated to be 1.32 kg Hg / kg Au, from which 45% are released into rivers and 55% into the atmosphere[7,8]. The pollution of the Amazon River afluents by mercury from gold mining is an important aspect to be considered for environmental protection measures[9]. Therefore studies of mercury species in aquatic HS, particularly on the lability/inertness of mercury(II) in humic-rich waters, are of increasing interest.

The present study concentrates on interactions between HS (isolated by the collector XAD 8)[10] from Rio Negro (RN) water, and inorganic Hg(II), the predominant species besides CH_3-Hg^+ in natural waters[11]. For the discrimination between labile and inert Hg(II) bound to HS the chelating ion exchanger Chelite S (SERVA Company) containing immobilized thiophenol as functional groups was chosen[12]. Both, the degree and the kinetics of separation were assumed to be useful parameters for the operational characterization of the lability of traces of Hg(II) bound to HS-RN under defined conditions (*e.g.* pH, HS concentration, ratio of Hg(II)/HS-RN, complexing time), in analogy to previous ion-exchange studies with other heavy metal ions[13-15].

Experimental

Chemicals and reagents

All reagents used were of high-purity grade unless otherwise stated. Diluted acids and bases necessary for HS isolation were prepared from 30% hydrochloric acid (suprapur, Merck AG) and sodium hydroxide-monohydrate (suprapur Merck AG), respectively, employing high-purity water (Milli-Q system, Millipore), The adsorbent XAD 8 p.a. (Serva Feinbiochemica) required for the isolation of aquatic HS was purified by successive soaking with 0.5 mol/L HCl, 0.5 mol/L NaOH and methanol p.a. (24 h, each) prior to use. The chelating ion exchanger Chelite S used for the distinction of labile/inert Hg(II) species was precleaned by successive soaking with 10 mol/L HCl p.a.

HS isolation by XAD 8

The HS investigated in this study were isolated from the Rio Negro at Tarumanzinho, Amazonas State, Brazil. For this purpose, a mixed water sample (50 L, continuously collected within 1 h) was filtrated through 0.45 μm cellulose-based membranes and acidified by concentrated HCl to pH 2.0. Then, HS from the acidified sample were isolated on the collector XAD 8. After elution with 0.1 mol/L NaOH, the obtained HS concentrate (containing 2.5 mg/ml DOC equivalent to about 5 mg/mL HS) was neutralized and stored in a refrigerator at ± 4 °C.

Determination of dissolved organic carbon (DOC)

The DOC in water samples and HS concentrates was evaluated by its oxidation to carbon dioxide subsequently measured with an IR-analyzer (Shimadzu TOC 2000).

Hg(II) selective ion exchangers

The separation of reactive Hg(II) fractions from dissolved HS was carried out by employing the thiophenol-containing ion exchanger Chelite S. Both, batch and flow procedure were used for this purpose[13]. Hg(II) retained on Chelite S could be eluted quantitatively with 10 mol/L HCl.

Batch procedure

The HS containing samples (50 mL, each) were pretreated up to 24 h with traces of Hg(II) keeping constant the chosen pH value. Then, 0.1 g of Chelite S was added under mechanical stirring. After the reaction time chosen, the collector was isolated on a filter paper pre-cleaned with 2 mol/L HCl. Then Hg(II) bound to the collector was eluted with 2.5 mL of 10 mol/L HCl.

Flow procedure

Small glass columns (5 mm i.d.) filled with Chelite S (0.25-0.5 g) were inserted into a small flow system consisting of a peristaltic pump (Gilson 2) and a three-way valve for sample introduction, cleaned with 10 mol/L HCl and washed with high-purity water. The contact time between the exchanger phase and the flowing sample was changed by varying the flow rate from 0.1 to 20 mL/min.

"Ageing" process

Several HS solutions (25 mL, each) were spiked with 10 μg of Hg(II) and conditioned at pH 5.0 and 25 $^{\circ}$C in the dark for different periods of time (0.25 to 240 h). Afterwards, labile Hg(II) fractions of these samples were removed and collected according to the described flow procedure.

Determination of Hg(II)

Hg(II) determinations in solutions were carried out by means of conventional cold-vapor atomic absorption spectrometry (CVAAS), using the sodium borohydrite method[16]. Manufacturer recommendations where taken into account for the Varian-Intralab AA 1475 spectrometer used. The detection limit (3 s) was 0.1 ng/mL Hg(II) and the relative standard deviation 5% (2 ng/mL Hg(II), n = 10).

Results and Discussions

HS in the Rio Negro River

The aquatic humic matter transported in huge amounts from the Rio Negro into the Amazon River has already been the subject of various studies[1,17,18]. Accordingly, the Rio Negro exhibits DOC values in the range of 10-12 mg/L of C which are mainly to be attributed to dissolved HS, thus representing a flux of approximately 320-350 kg HS / s in this river[1]. The Rio Negro HS, “HS-RN”, used in this study for interaction experiments with Hg(II), was isolated from a mixed water sample (50 L) by means of the “standardized” XAD 8 procedure[10]. Relevant parameters of this water sample with its HS-RN are summarized in Table 1 showing that about 65% of the measured DOC (12 mg/L) was collected by the adsorbent XAD 8, assuming a 50% C-content of HS. The complexation capacity of HS-RN towards Cu(II) ions as determined with a Cu(II)-selective electrode yielded the relatively high value of 2.8 mmol Cu(II)/g C.

The concentrations of trace metals were characterized in the Rio Negro water and the HS-RN isolated. They range from the analytical detection limits [*e.g.* Cd (< 0.1μ/L and < 4μ/g), Co (< 0.1 μ/L, and < 8 μ/g) Cr (< 0.1 and < 8 μ/g,) to considerable contents at the mg/L level [Al (150 μ/L and 260μ/g), Fe (1850 μ/L and 450 μ/g)]. As expected, the HS isolation from the acidified sample solution (pH 2.0) causes an extensive remobilization of the metal ions naturally bound to HS, except for a considerable fraction of acid-inert Al and Fe.

Hg(II) separation from HS with Chelite S: Influence of Hg(II) loading and pH-value

The discrimination between exchange-labile and -inert metal fractions in HS by chelate-forming ion-exchanger requires collectors of high selectivity forming strongly immobilized metal complexes[19,20]. Under this condition the separation capability of the chosen collector Chelite S were studied in slightly acidic and neutral solutions of mercury(II)-loaded HS-RN (pH 5 and 7) and characterized by means of the Hg(II) distribution coefficients, K_d, (mL/g), as a function of an increasing mercury(II) loading of HS-RN, μg Hg(II)/mg HS-RN (see Fig. 1). Accordingly, the Hg(II) distribution coefficients K_d on Chelite S exhibit a strong dependance on the Hg(II) loading of the studied HS. In the case of very small Hg(II) loadings (< 0.1 μg Hg(II)/mg HS-RN) Chelite S merely exhibits K_d values of 10^2 (mL/g), requiring a multistage column procedure for quantitative remobilisation of Hg(II) ions from their binding sites in HS-RN. In the case of increased Hg(II) loadings (> 1 g Hg(II)/mg HS-RN) K_d values of about 10^4 (mL/g) are available enabling the separation of labile Hg(II) even by means of a single-stage batch procedure.

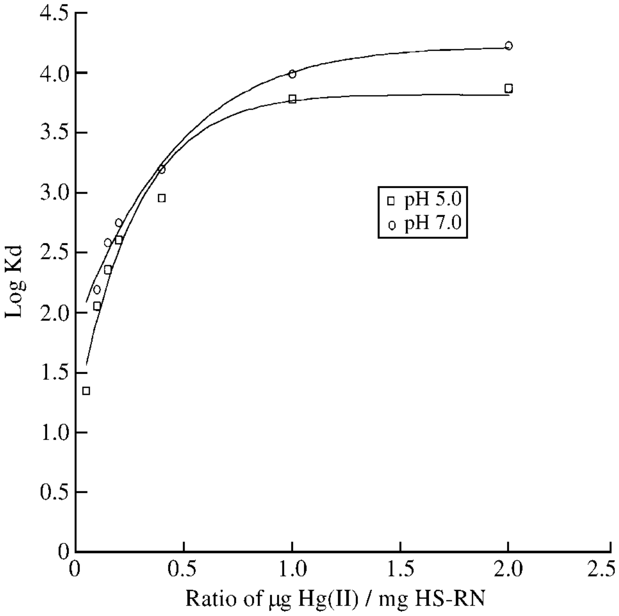

Figure 1. Hg(II) distribution coefficients, K_d, on Chelite S as a function of the ratio μg g(II) / mg HS-RN at different pH values. Spiking of HS-RN: 50 mL sample, 0.05 - 1.0 mg/ml HS-RN, 5 μg Hg(II); equilibration for 24 h, then 24 h in contact with 0.1 g Chelite S; batch procedure.

Table 1. Characterization of HS from Rio Negro (HS-RN) waters of Tarumanzinho colleccted in February95.

pH	6.5
Conductivity	58 μS cm^{-1}
Temperature	27 °C
Dissolved organic carbon	12 mg/L of C
HS-RN (isolated by XAD 8)	8,25 mg/L
Complexation capacity of HS-RN	2.8 mmol Cu(II)/g C
Hg	< 0.01 μ/L (water) and < 0.4μ/g (in HS-RN)

Considerable mercury losses (> 5%) by partial reduction of Hg(II) to Hg(0) in the presence of dissolved HS as previously reported[21] could not be observed in the case of HS-RN.

Hg(II) separation with Chelite S: Influence of the contact time

The influence of the contact time and HS concentration on the Hg(II) separation from solutions of HS-RN by means of the Chelite S batch procedure was studied in detail as shown in Fig. 2. As can be seen, nearly quantitative Hg(II) recovery is obtained within 15 min in the case of a high ratio of Hg(II)/HS, whereas a decrease of this ratio reduces the recovery rate and delays considerably the time period necessary for equilibration.

Influence of the ratio Hg(II)/HS on the Hg(II)-lability

In accordance with[22] both the thermodynamic and the kinetic stability, the HS/metal complexes are highly dependent on the ratio of metal loading to the complexation capacity of HS. At low metal loading, metal ions are preferentially bound to functional groups which provide formation of complexes of maximum thermodynamic stability[23]. The opposite behaviour can be expected in the case of increasing metal loading, leading to successively increased lability and metal recovery. The results of a respective experiment with Hg(II) and HS-RN are shown in Fig. 3. Accordingly, Hg(II) can be quantitatively recovered at > 0.5 µg Hg(II)/mg HS-RN showing evidence for only labile species. In contrast, a recovery of < 10% is observed at < 0.05 µg Hg(II)/mg HS-RN. Such an ion-exchange procedure, however, is not able to distinguish between thermodynamic and kinetic inertness of the metal species studied.

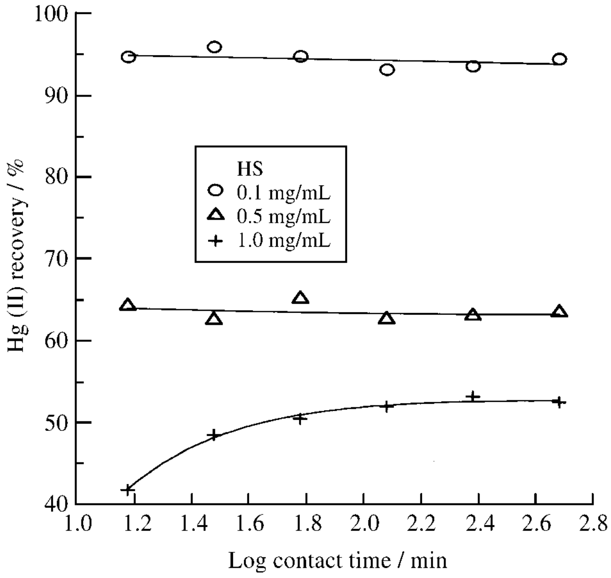

Figure 2. Influence of contact time and HS concentration on the recovery of Hg(II) from HS. Spiking of HS-RN: 50 mL sample, 5 µg Hg(II), pH 5.0, equilibration for 24 h with 0.1 g Chelite S; batch procedure.

The influence of loading and contact time on the Hg(II) separation from HS-RN by using the Chelite S flow procedure is shown in Fig. 4. The separation curves, exhibited there, also demonstrate that high Hg(II) loadings of HS result in highest lability and recovery.

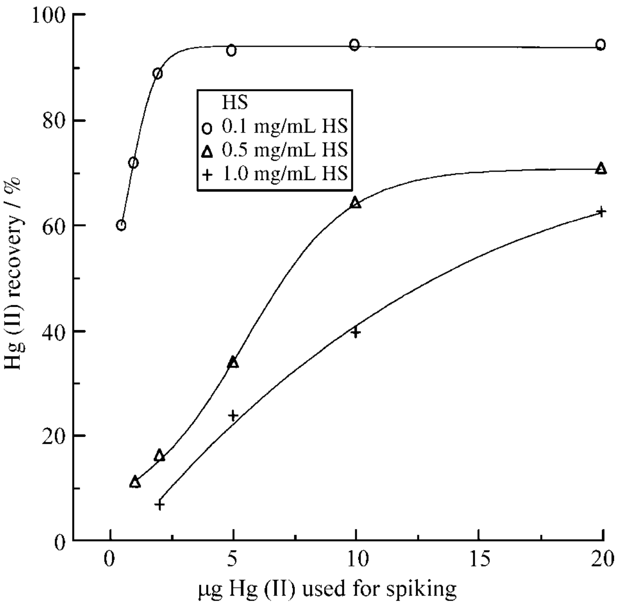

Figure 3. Influence of the loading degree on the lability of Hg(II) bound to HS. Spiking of HS: 50 mL sample, 0.1-1.0 mg/mL HS-RN, 1-20 µg Hg(II), pH 5.0, equilibration for 24 h with 0.1 g Chelite S; batch procedure.

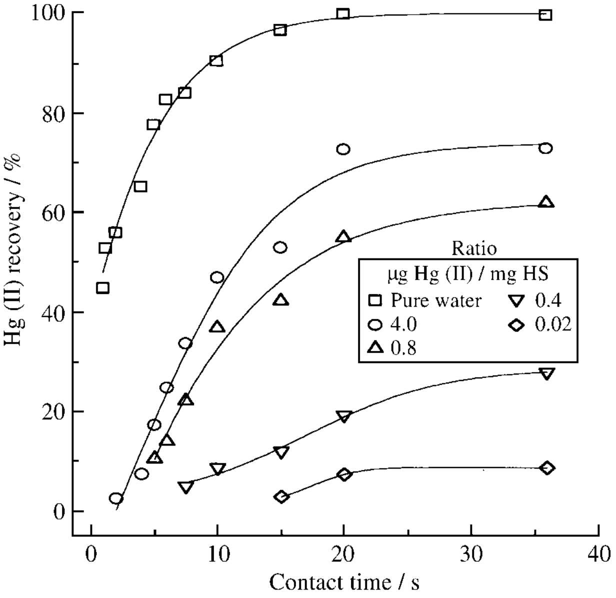

Figure 4. Separation of Hg(II) from HS as a function of the contact time at different Hg(II) loadings. Flow procedure: column filled with 0.2 g Chelite S; 0.1-1.0 mg/mL HS-RN, 0.02-0.4 g/mL Hg(II), 25 mL sample, pH 5.0, complexing time 24 h. Without HS: 25 mL sample,0.4 µg/mL Hg(II), pH 5.0, 0.5 mol/L NaCl.

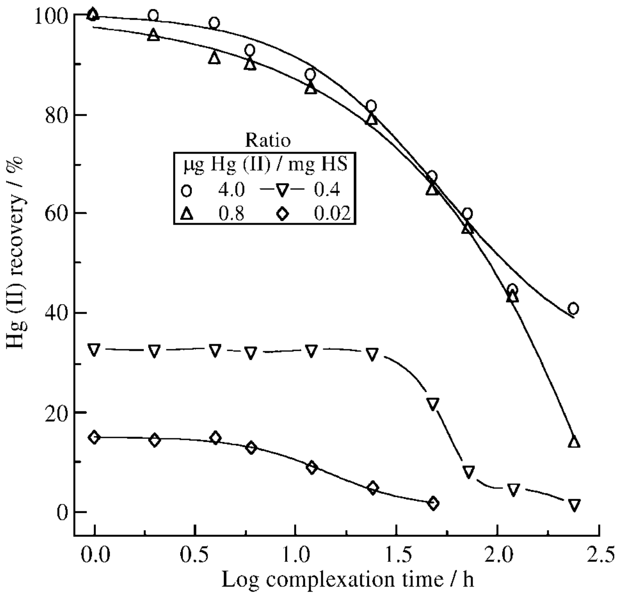

Figure 5. Influence of "ageing" on the lability of Hg(II)-HS species at different Hg(II) loadings. Flow procedure: column filled with 0.2 g Chelite S; 0.1-1.0 mg/mL HS-RN, 0.02-0.4 µg/mL Hg(II), 25 mL sample, pH 5.0, contact time: 35 s.

Another environmentally important parameter influencing the reactivity of metals in HS may be potential transformation processes ("ageing") of the formed macromolecular metal species[15]. It can be supposed that metal ions freshly bound to HS are preferably complexed by functional groups easily accessible in such macromolecules, whereas "aged" metal loadings increasingly occupy inner-sphere binding sites. The influence of such "ageing" processes on the lability of Hg(II) ions bound to HS-RN is demonstrated in Fig. 5. The separation curves for Hg(II) recovery show that the increase of the complexation time retards the Hg(II) exchange with Chelite S to a larger and larger extent, even when the Hg(II) loading is relatively high (> 1 µg Hg(II)/mg HS-RN). After 10 days of "ageing", the resin Chelite S collects only 40% of the bound Hg(II) in the case of 4 µg Hg(II)/mg HS-RN. Low Hg(II) loadings of the studied HS (0.02 µg Hg(II)/ mg HS-RN) appear to be practically inert.

Conclusions

HS are suggested to strongly bind mercury in aquatic and terrestrial systems forming predominantly inert macromolecular species, presumably due to thio-containing functional groups[24,25].

Therefore, the thiophenol group containing ion exchanger Chelite S was chosen as a competitor for HS-RN and proved to be a very efficient collector for Hg(II) providing both, fast separation kinetics and high distribution coefficients K_d for traces of dissolved Hg(II), even in the presence of relatively high HS concentrations. Thus, under standardized conditions, the suggested procedure can be utilized for a reproduceable operational characterization of labile Hg(II) in HS.

It was shown that the Hg(II) lability in HS isolated from the Rio Negro is strongly influenced by the ratio of Hg(II)/HS-RN and by "ageing" of the Hg(II)-HS-RN species formed. Obviously, in the case of a small Hg(II) loading continuous transformation processes occur, strongly decreasing the Hg(II) "availability" in HS-RN. These results are comparable to those previously obtained with HS from other aquatic environments[12] and suggest that Hg(II) in concentrations as found in Rio Negro water (see Table 2) and even at greater concentration is efficiently made "unavailable" in HS-rich environments.

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