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Lability of Cd, Cr, Cu, Mn and Pb complexed by aquatic humic substances

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Abstract: The lability of Cd(II), Cr(III), Cu(II), Mn(II) and Pb(II) complexed by humic substances (HSs) was investigated by means of ion exchange on cellulose modified with p-aminobenzoic groups (Cell-PAB), using a batch procedure. The HSs were extracted from water samples using adsorption in a column packed with XAD 8 resin. The metal-HS complexes were prepared by adding solutions containing all the aforementioned metal ions (Cd(II), Cr(III), Cu(II), Mn(II) and Pb(II)). The results indicated that the distribution coefficients (Kd) of Cell-PAB decreased with the presence of HSs, and that the lability of metal fractions complexed by HSs decreases in pH values > 4.0, complexation time > 10 h and HS concentration > 500 mg L^{-1}. The metal exchange between HSs and Cell-PAB exhibited the following order of metal ion lability: Cd < Pb < Mn ≅ Cr < Cu.

Keywords: aquatic humic substances; cellulose modified with p-aminobenzoic groups; lability of metal species.

Introduction

The main mass of organic carbon distributed in aquatic systems and soils consists of humic substances (HSs). These compounds are the final product of chemical and biological degradation processes of animal and plant residues in soil and waters, and they consist of a mixture of organic macromolecules of varying molecular-weight distributions, substructures and functionalities. HSs can be transported into natural waters by leaching or formed directly in aquatic environments.[1]

The concentrations of dissolved metal ions and HSs and their ratio may vary considerably and may influence not only the formation of metal-HSs species but also their distribution between liquid and solid phase (e.g., suspended matter, sediment) [2]. Accordingly, transport processes, hydrogeochemical cycles and bioavailability of trace metals in waters often depend on the thermodynamic stability and formation kinetics of metal-HSs complexes. Therefore, investigations into the exchange/complexation processes between HSs and metal ions are of great interest when studying the hydrogeochemical turnover of metal ions in natural waters. [3]

The complexation properties of HSs towards dissolved metal ions, their complexing capacity and the resulting equilibrium of formation and/or dissociation reactions of metal-HSs species can be

investigated by a variety of methods [4]. Electrochemical methods [5], molecular spectroscopy and physicochemical separation procedures [2] are preferentially utilized in the investigation of metal binding in HSs. Modified solid supports (e.g., cellulose) in particular have proved efficient multi-element collectors for the differentiation of labile and inert metal species in HSs [6-8]. In the cited study, both the kinetics and degree of metal ion exchange were used to operationally characterize metal ion labilities in aquatic HSs.

The present paper reports on a simple batch procedure for evaluating labile metal fractions (e.g., Cd, Cr, Cu, Mn and Pb) in aquatic HSs based on separations by cellulose modified with p-aminobenzoic groups ion-exchanger (Cell-PAB) and subsequent determinations by flame-AAS. The Cell-PAB ion-exchanger has proved to be a highly efficient collector with fast kinetics for traces of metal ions dissolved in aqueous saline solutions [9,10]. Applying an optimized batch procedure based on the use of the Cell-PAB, a number of important parameters (such as pH, HSs concentration, complexation time), which influence the lability of metal ions in HSs, were evaluated.

Experimental

Chemicals and reagents

The multi-element solution of the metal ions and all the acids and bases for the preparation of solutions and HSs isolation were of analytical grade (e.g., Merck Suprapur, Riedel-de Haen p.a. plus). Water deionized by a Milipore MiliQ system was used.

Preparation of Modified Cellulose

Microcrystalline cellulose (Merck, Germany) with specific surface area of 22 $m^2.g^{-1}$ was activated at 353 K under vacuum (10^{-3} Torr). About 16 g of this cellulose was immersed in 100 mL of purified dimethylformamide (Mallinckrodt, Germany) and 30 mL of phosphorus oxychloride (Merck, Germany) was added. The mixture was refluxed under glycerine bath for 16 h at 383-423 K, filtered, washed with, ethanol (Merck, Germany) and dried on a filter paper under vacuum. The resulting solid was immersed in 200 mL of purified dimethylformamide and 14 g of sodium p-aminobenzoate (Merck, Germany) was added. The mixture was stirred for 35 h at 423 K. The resulting modified cellulose named Cell-PAB, was filtered off, washed with dimethylformamide, ethanol and then it was dried.[10]

HSs extraction by XAD 8 resin

The analytical grade XAD 8 resin (Serva Feinbiochemica) required to isolate aquatic HSs was pre-purified by successive soaking with 0.50 mol L^{-1} HCl, 0.50 mol L^{-1} NaOH and analytical grade ethanol (24 h each).

The HSs under study were isolated from a water sample collected from a tributary stream of the Itapanhaú River in Bertioga, state of São Paulo, Brazil, according to the XAD 8 procedure proposed [11]. After filtration through 0.45 mm membrane filters, the water sample was acidified (pH = 2.0) with 10.0 mol L^{-1} HCl and 40 L of each sample was run through XAD 8 columns at a flow rate of 5.0 mL min^{-1}. The HSs was then eluted from the XAD 8 columns with 100 mL of 1 mol L^{-1} NaOH. The HS solution obtained was neutralized with 6.0 mol L^{-1} HCl and stored in a polyethylene bottle under refrigeration at +4ºC.

Dissolved organic carbon – DOC

The DOC value of the HSs sample was determined by oxidation to CO_2 and measurement with an IR-analyzer (Shimadzu TOC 2000). The HSs concentration was evaluated at 10 mg mL^{-1}, due to a DOC[12] concentration of 5 mg mL^{-1}.

Complexing capacity of HSs

The HSs sample displayed a complexing capacity of 4.3 mmol Cu(II) g^{-1} DOC, which was determined by a Cu(II)-selective electrode. [2]

Preparation of standardized HSs solutions

The HSs standards were prepared from their concentrates by dilution to 0.1 mg mL^{-1} DOC. To remove the metals occurring naturally in HSs, 1 g (dry weight) of highly pure ion exchange Cellulose-Hyphan (Riedel-deHaen) was added and the mixture kept under agitation for 72 h at pH = 5.0[13]. After filtration, the pH was adjusted to 4.5, and the HSs standards were stored in polyethylene bottles under refrigeration at +4ºC.

Preparation of HS-metal ion solutions

The species formed between metal ions and HSs (metal-HSs) were prepared by adding aliquots of multi-element solutions of metal ions. The pH was adjusted [7,13] to a range of 1.0 - 5.0 by adding 0.1 mol L^{-1} NaOH or HCl. The volumes were topped to 50 mL with deionized water and the solutions stirred for 24 h. The metal concentrations in the HS solutions were 0.50 mg L^{-1} Cd, 2 mg L^{-1} Cr, 2 mg L^{-1} Cu, 1.0 mg L^{-1} Mn and 5.0 mg L^{-1} Pb .

Ion-exchange procedure for labile metals in HSs-Metal – Batch Procedure

100 mg of Cell-PAB resin was added to the HS-metal ion solution and stirred for 60 min under mechanical agitation. After this period, the ion-exchanger was separated by centrifugation, transferred to small flasks and extracted for 60 min with 5 mL of 1.0 mol L^{-1} HCl. After centrifugation, the metal ions contained in the extracts were determined by flame atomic absorption spectrometry (FAAS).

Metal determination by FAAS

The concentration of metal ions gathered from the Cell-PAB column was determined by FAAS according to the standard guidelines of the manufacturer (Spectrometer: VARIAN-INTRALAB AA-1475). For the calibration curves, synthetic metal standard solutions were used, based on 1.0 mol L^{-1} HCl comparable to the samples.

Results and discussion

Influence of pH

The discrimination of lability/inertness metal fraction complexed with HSs by ion-exchange requires a high performance collector forming immobilized metal complexes even at relatively high HS concentrations and slightly acid pH values [13,14]. Multi-element preconcentrations by ion exchangers require collectors offering high distribution coefficients, Kd, preferably > 104, as calculated by the following equation:

$$K_d = C_{col.}/C_{sol.} \quad (1)$$

where $C_{col.}$ = concentration of metal ions in the ion-exchanger (mg g^{-1}), and $C_{sol.}$ = concentration of metal ions in the solution (mg mL^{-1}).

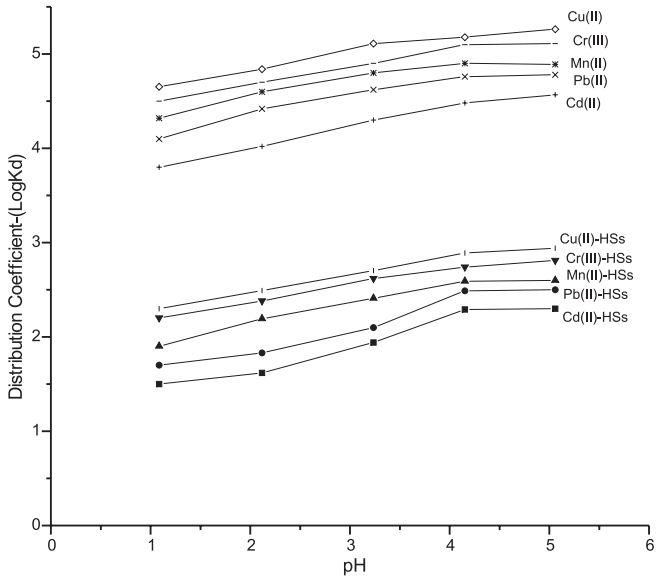

Figure 1. Metal distribution coefficient, Kd, on Cell-PAB in the absence and presence of HS as a function of pH (0.1 mg mL^{-1} HS, 24 h equilibrium, 50 mL sample, 100 mg Cell-PAB).

Figure 1 illustrates the characteristic separation using the Cell-PAB ion-exchanger as the collector of the reactive metal fractions by means of the distribution coefficient, Kd, as a function of the pH. Using the batch procedure, these studies were performed in the presence of 0.1 mg mL^{-1} HSs (HSs-metal, stirred for 24 h) and without HSs. In the absence of HSs, the Cell-PAB collector exhibited K_d values as high as (10^4 – 10^5) for metal ions at a pH exceeding 5.0. In the presence of HSs, the enrichment of metal ions in the collector phase decreased, and the Kd values were also lower, in the order of a factor of 100 to 300 in the pH range of 1 to 5. As shown in figure 1, all the metal ions displayed curves whose maximum lay in slightly acidic solutions (pH = 4 - 5) and a reduction in solutions with pH < 4. Thus, in slightly acidic solutions, the metal ions were increasingly remobilized from both HS molecules and carboxylate groups of the Cell-PAB collector.

Kinetic studies - Determination of lability order

Cellulose ion-exchangers often display high distribution coefficients in the order of 10^4 for some metal ions in saline solutions without HSs [10]. According to previous studies [7,8], cellulose-based ion-exchangers can be used as effective collectors of labile trace metal remaining in water samples. Applying an optimized batch procedure, both the kinetics and degree of metal ions removed from HSs can be useful for characterizing the lability/inertness of metals bound to HSs. In principle, the exchange of metal ions between resins and labile macromolecular metal complexes such as HSs-M can be described by the following equilibrium:

$$\underset{\text{Solution}}{\text{HSs–M} \overset{K_{HS}}{\rightleftharpoons} \text{HSs} + \text{M}} + \underset{\text{Exchange}}{\text{Ex} \overset{K_{Ex}}{\rightleftharpoons} \text{M–Ex}} \quad (2)$$

where **HSs-M** indicates the species formed between metal and **HSs**, **EX** is the solid phase ion exchanger, and **M-Ex** represents the species formed between the metal and the collector. Thus, the, HSs-M and M-Ex concentrations governed by the equilibrium constants K_{HS} and K_{EX} are shifted, depending on parameters such as pH, concentration of humic substances, complexation time, and the metal ions to HSs ratio.

Table 1 shows the gradual separation of all the metal ions complexed by HSs. A contact time of more than 60 min is generally required to reach the exchange equilibrium given by equation 2 and to achieve a final recovery of 65-75% of metal ions by Cell-PAB, depending on the element. The effectiveness of the separation does not change thereafter. The separation of metal ions from HSs solutions pre-conditioned for 24 h shows the typical lability order of Cd < Pb < Mn < Cr < Cu.

Table 1. Recovery of metal ions pre-complexed by HS as a function of contact time with the Cell-PAB ion exchanger. Conditions: 0.1 mg mL^{-1} HSs, pH 5, 24 h complexation time, 100 mg Cell-PAB.

Metals	Contact Time (min)											
	5	10	15	20	30	40	60	80	100	120	140	160
	Recovery (%)											
Cd	12	18	24	28	38	46	55	54	53	55	55	54
Cu	23	28	31	37	44	62	75	74	75	73	74	75
Cr	19	24	30	34	41	57	70	69	68	71	69	70
Mn	16	20	26	32	48	53	67	66	65	67	66	67
Pb	13	19	25	30	38	51	63	62	62	63	61	63

The kinetics and reaction order of this ion-exchange process is illustrated in figure 2, which shows the separation of the exchanged labile Cd, Cu, Cr, Mn and Pb (concentration ratio - C_L) plotted as a function of the contact time. At the onset of separation (contact time < 30 min), the fraction of labile metal ions complexed by aquatic HSs is separated relatively quickly. In this case, an exchange of metal ions occurs between the HSs solutions and the solid ion-exchanger, following a second order kinetics (2nd order). Thus, the metal ions complexed with HSs react directly with the carboxylate groups of Cell-PAB. After 30 min, the separation of HS-bound metal ions proceeds with uniform $t_{1/2}$ values of about 40 - 50 min, revealing rather slow first order (1st order) kinetics compared with the metal exchange by Cell-PAB from aqueous saline solutions ($t_{1/2}$ in the range 50 – 60 s) [9, 10, 15]. These first-order (1st order) kinetics indicate either that slow dissociation of the macromolecular HSs-metal complexes occurs or that delayed transport of macromolecular HSs-metal complexes in the narrow pore system of the cellulose collector takes place.

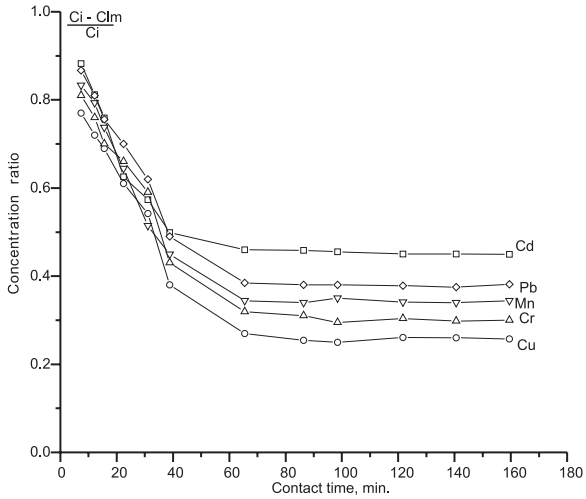

Figure 2. Separation of exchange-labile fractions from HS as a function of contact time. Conditions: (0.1 mg mL^{-1} HS, 24 h equilibrium, 50 mL sample, pH= 5.0; 100 mg Cell-PAB).

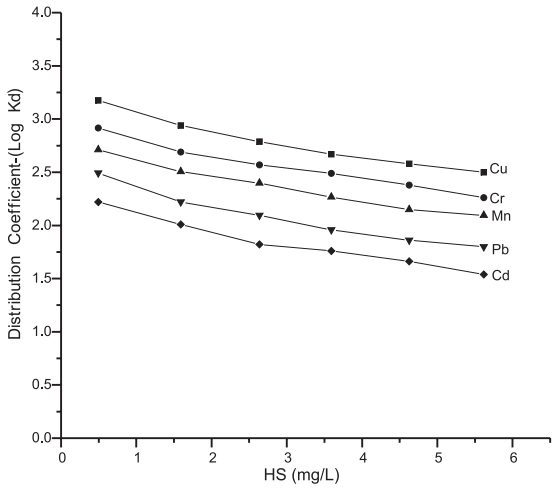

Figure 3. Metal distribution coefficients as a function of HS concentration. Conditions: pH 5, 24 h complexation time, 100 mg Cell-PAB.

Effect of HS concentration and time complexation on the lability of HSs-metal ions

Figure 3 shows the influence of the increase in the metal distributed on the Cell-PAB collector. According to figure 3, all the metal ions were better recovered in solutions with lower HS concentrations. The complexing capacity increased with high HS concentrations because more binding sites were available for metal ion complexation, and the equilibrium shifted towards the HSs-M species. Thus, humic-rich waters are important natural "buffers" for heavy metals in the environment [7,12].

In the environment, interactions between HSs and metals occur over a relatively long period of complexation (ageing). This is therefore an important factor which may affect the lability of metal fractions complexed by HSs, as has recently been shown in a paper dealing with the exchange process between HSs-metal species and exchanger collectors [13]. Figure 4 shows that the lability of metal fractions bound in aquatic HSs decrease as the complexation time increases. Not all metals behave in similar fashion. Cu(II), for instance, shows a remarkable decrease in lability after a complexation period of 6 days, during which time this recovery drops from 60% to 10%. The metal ions complexed with the most external groups of HS macromolecules usually react preferentially with the functional groups of the resin (Cell-PAB). Therefore, metal that remains complexed for a long time may do so as a result of transformation processes and inner rearrangements. As the complexation time increases (ageing), less accessible HSs binding sites may be occupied, causing the metal ions to shift from weaker to stronger binding sites. [6,7,12]

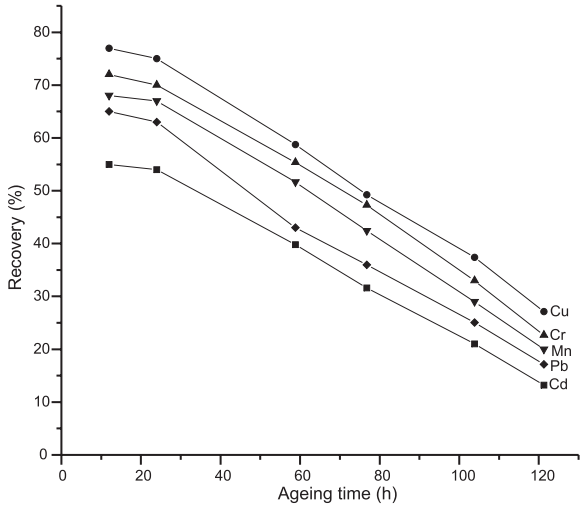

Figure 4. Influence of complexing time (ageing) on the lability of metals. Conditions: 0.1 mg mL^{-1} HS, pH 5, 100 mg Cell-PAB.

Conclusions

The thermodynamic and kinetic stabilities of HSs-metal species depend on a variety of environmental factors, particularly on the pH values, the metal and HSs concentrations and their ratio. The present study using the Cell-PAB collector to characterize labile fractions in aquatic HSs confirms the usefulness of the ion-exchanger method. The influence of the contact time between the ion-exchanger (Cell-PAB) and the HSs-metal species solution is characterized at $t_{1/2}$ values of about 40-50 min. Another factor that strongly influences the lability of metal fractions bound to aquatic HSs is the ageing process. This transformation process showed a gradual decrease of the overall lability of metal ions in dissolved HSs, probably due to slow metal exchange processes caused by an inner

rearrangement in the binding sites within the HSs molecules. Thus, it can be concluded that the accumulation, transportation, hydrogeochemical cycles and bioavailability of trace metals in natural waters depend not only on their thermodynamic stability but also on typical transformation processes. Our studies using the Cell-PAB collector in ion-exchange procedures, however, allowed only for the description of a relative order of metal labilities in dissolved HSs under standardized conditions.

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G. R. de Castro, C. C. F. Padilha, J. C. Rocha, J. P. S. Valente, A. O Florentino, P. M. Padilha. Labilidade de Cd, Cr, Cu, Mn e Pb complexados por substâncias húmicas aquáticas.

Resumo: A labilidade de Cd, Cr, Cu, Mn e Pb complexados por substâncias húmicas aquáticas (HSs) foi investigada por estudos de troca iônica em batelada, utilizando-se celulose modificada com grupos p-aminobenzóico (Cell-PAB). As SHs foram extraídas de amostras de água por adsorção sobre coluna empacotada com resina XAD 8. Os complexos metal-HS foram preparados misturando-se soluções contendo SHs com soluções padrões mista dos íons metálicos (Cd, Cr, Cu, Mn e Pb). Os resultados obtidos indicaram que houve um decréscimo nos valores dos coeficientes de distribuição (Kd) da Cell-PAB com a adição das SHs nas soluções dos íons metálicos, e que a labilidade das frações metálicas complexadas pelas SHs é menor em valores de pH < 4,0, tempo de complexação > 10 h e concentração de SHs > 500 mg L^{-1} . A troca iônica entre a Cell-PAB e os complexos metal-SHs obedecem as seguintes ordens de labilidade: Cd < Pb < Mn ≅ Cr < Cu.

Palavras-chave: substâncias húmicas aquáticas; celulose modificada com grupos p-aminibenzóico; labilidade de espécies metálicas.

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