

SPECIATION STUDIES OF CADMIUM-ORGANIC LIGAND COMPLEXES USING ULTRAFILTRATION AND DIFFERENT SOLID SORBENTS

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Astract

The speciation studies of Cd species in the presence of organic ligands such as humic acid (HA) were investigated based on a combination of physical characterization by size fractionation using ultrafiltration and chemical characterization by retention studies on different solid sorbents. The aim of this study is to distinguish the labilities of complexed Cd-HA among species with different chemical behaviors at different pH conditions. A set of three columns packed with different substrates, namely, a chelating ion exchange resin Chelex-100, an anion exchange resin Dowex 1-X8 and C-18 reversed phase was developed. The retention behavior of the complexes was compared according to their labilities onto the substrates as a function of pH. The applicability of the method to synthetic river water (SRW) sample spiked with Cd species in the presence of humic acid (HA) was demonstrated.

Keywords : Complexed Cd-HA, Speciation; Solid sorbents; Ultrafiltration

Introduction

In natural waters, trace metals are distributed in both dissolved and particulate phases. In the dissolved phase, trace metals exist in a variety of forms: free metal ions, hydrated ions, labile complexes with the respective anionic inorganic constituents of water and nonlabile complexes with components of dissolved organic carbon (DOC) [1]. Among the DOC components, humic substances are the predominant part. Humic acids are essentially mixture compounds of different molecular weights [2]. The ability of humic acid for trace metal complexation is significant in aquatic systems especially in fresh waters as this has an implication on metal transportation, the biological uptake and the toxicity of trace metals [3].

Recently, several speciation schemes for the discrimination of trace metal species in natural waters have been developed based on the retention behavior of metal species onto different solid sorbents such as Chelamine [4], AG MP-1 [5, 6] and C-18 reversed phase [4, 6] to evaluate cation, anion and neutral metal species, respectively. A procedure based on the combination of two or three sorbents in series was developed and applied to the speciation of trace metals.

The objective of this study was to develop a method for the classification of complexed Cd-HA labilities based on a combination of physical characterization by size fractionation using ultrafiltration and chemical characterization by retention studies on different solid sorbents, namely, Chelex-100, Dowex 1-X8 and silica C-18 sorbent. For this purpose, the distribution of Cd with various chemical forms in the presence of dissolved organic ligands of HA in SRW as a function of pH was compared in its retention behavior obtained onto different sorbents.

Materials and Methods

All experimental works, except metal determinations, were done in a clean room laboratory. High purity water (HPW) was produced with a Milli-Q system and used throughout. All chemicals used were of AR grade except that acids used to elute the analyte from column studies were of suprapure grade.

This work was carried out by using SRW spiked with 40 $\mu\text{g/L}$ Cd species with 20 $\mu\text{g/L}$ HA to complex at desired pH values, i.e., 5.5, 6.5 and 7.5. The sample was buffered with 0.2 M NH_4OAc . The buffered sample in each investigated pH value was fractionated into various size fractions by ultrafiltration under pressurized nitrogen gas. The speciation studies of the buffered sample was performed by using the ultrafiltrate in each size fraction to be loaded into a set of three columns packed with different solid sorbents, namely, a chelating cation exchanger Chelex-100, an anion exchanger Dowex 1-X8 and reversed phase silica C-18. The speciation scheme is illustrated in Fig. 1.

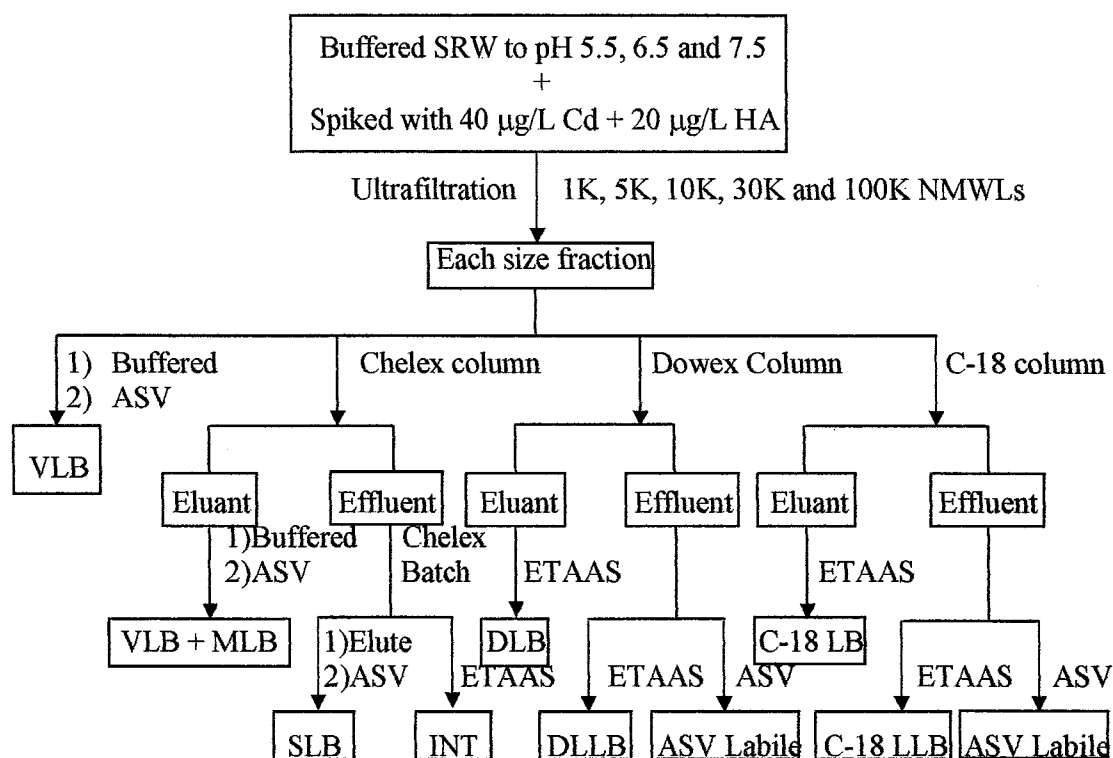


Figure 1. Speciation scheme for metal species using different solid sorbents, namely, Chelex-100, Dowex 1-X8 and silica C-18. VLB: Very Labile, MLB: Moderately Labile, SLB: Slowly Labile, INT: Inert, DLB: Dowex Labile, DLLB: Dowex Less Labile, C-18 LB: C-18 Labile, C-18 LLB: C-18 Less Labile, ASV: Anodic Stripping Voltammetry, ETAAS: Electrothermal Atomic Absorption Spectrometry.

Results and Discussion

The interaction of Cd species onto different solid sorbents was investigated separately. The retention of Cd-HA complexes was evaluated at three different pH values, i.e., 5.5, 6.5 and 7.5

found in the pH range of natural waters. The results obtained with the proposed method are given in Table 1.

Table 1. Uptake (%) of Cd in the presence of HA on different solid sorbents.

pH	Size fraction	Chelex-100				Dowex 1-X8			Silica C-18			
		Lability				Lability			Lability			
		VLB	MLB	SLB	INT	DLB	ASV	DLLB	C-18 LB	ASV	C-18 LLB	
5.5	<1K	-	48	3	4	7	45	2	8	40	-	-
	1K-5K	-	-	1	11	2	-	10	15	-	-	-
	5K-10K	-	-	-	33	1	-	33	37	-	-	-
	10K-30K	-	-	-	-	-	-	-	-	-	-	-
	30K-100K	-	-	-	-	-	-	-	-	-	-	-
6.5	<1K	-	62	5	3	7	56	4	10	58	-	-
	1K-5K	-	-	1	17	6	-	13	15	-	-	-
	5K-10K	-	-	-	12	1	-	13	17	-	-	-
	10K-30K	-	-	-	-	-	-	-	-	-	-	-
	30K-100K	-	-	-	-	-	-	-	-	-	-	-
7.5	<1K	-	84	2	4	10	75	2	5	77	-	-
	1K-5K	-	-	1	7	4	-	6	15	-	-	-
	5K-10K	-	-	-	3	-	-	3	3	-	-	-
	10K-30K	-	-	-	-	-	-	-	-	-	-	-
	30K-100K	-	-	-	-	-	-	-	-	-	-	-

In Table 1, the Cd species are categorized into three groups according to their interaction with different kinds of sorbent, i.e. Chelex-100 for positively-charged Cd species, Dowex 1-X8 for negatively-charged Cd complexes and reversed phase C-18 for neutral organic Cd complexes. It was observed that the percentage of Cd species found in the low molecular weight fraction (<1K) as MLB fraction by Chelex column or ASV-labile fractions by Dowex and reversed phase C-18 column methods increased with the increase in pH values. There was relatively close agreement among the three sets of percentage values.

For complexed Cd species, the uptake of Cd species onto different solid sorbents at different size fractions was evaluated as inorganic complexes with anion components of SRW in the low molecular weight fractions or strong organic complexes with HA ligands in the size range of 1000 to 10000 NMWLs at the three pH. The simple inorganic complexes were retained by Dowex 1-X8 column and given as DLB fraction whereas the strong organic complexes were desorbed and given as DLLB fraction. This should appear as the C-18 LB fraction when silica C-18 column was used. It is known that humic acids are essentially mixture compounds of different molecular weights (< 25K NMWLs in fresh waters [7]). Chelation by neighboring carboxyl (pKa of acetic acid = 4.8) and phenolic (pKa of phenol = 10) groups are the major modes of metal complexation [2]. Silica C-18 is able to adsorb hydrophobic or partially hydrophilic ones with a hydrophobic core of metal complexes. It is not specific for neutral complexes so that anionic aromatic complexes can also be retained by the ion exchanger. This

means that the C-18 LB fraction found not only consisted of neutral organic but also anionic Cd-HA complexes.

The effect of pH on the retention behavior of anionic complexed Cd species (DLB fraction) by Dowex 1-X8 was not conspicuous. In contrast, the effect of pH was shown clearly in the interaction of complexed Cd species onto silica C-18 as exhibited by a decrease in the uptake of complexed Cd-HA species from 60 to 23% when the pH value increased from 5.5 to 7.5.

Conclusions

The speciation studies of Cd species in the presence of organic ligand HA in SRW was conducted to classify soluble Cd species into various degrees of lability according to the affinity of their chemical forms onto different kinds of sorbents, i.e. Chelex-100 for cationic species, Dowex 1-X8 for anionic species and reversed phase silica C-18 for neutral organic species. The uptake of Cd species by different solid sorbents as a function of pH was studied. The Cd-HA complexes were found as the C-18 LB fraction on the silica C-18 column or essentially neutral species in the range of 23 to 60% depending on the pH whereas 10 to 14% of the Cd species was found in the anionic complex form. The change of pH did not seem to have a conspicuous effect on the uptake of anionic Cd complexes by Dowex column. In contrast, increasing pH seems to increase the uptake of cationic Cd species but decrease that of Cd-HA complexes.

References

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