



Copper complexing properties of melanoidins and marine humic material

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Abstract

Melanoidins, condensation products of sugars and amino acids, represent a key link in the transformation of polysaccharides to humic material in the marine environment. We investigated the complexing capacity of melanoidins that were prepared in deionized water and seawater and separated into different molecular mass fractions. The copper complexing properties of humic material isolated from marine lagoon sediments were determined for comparison. Melanoidins prepared using condensation times longer than two days exhibit complexation properties towards copper ions that appear to depend on the basicity of the amino acid precursor and the molecular mass of the product. Pseudomelanoidins, prepared from glucose only, do not complex copper ions at all, regardless of the molecular mass. The highest copper complexing capacity value among melanoidins was measured for a glucose–lysine melanoidin with molecular mass fraction >10 kD ($L_T = 2.1 \times 10^{-7}$ molCu²⁺/L). Melanoidin prepared from glucose and glutamic acid >10 kD was similar in complexing capacity to fulvic acid (1–20 kD molecular mass) isolated from lagoon sediments. The presence of calcium and magnesium ions and other macro and microconstituents in the seawater used to prepare melanoidins influences its complexing properties towards metal ions.

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1. Introduction

Melanoidins, natural condensation products of sugars and amino acids, have gained attention from geochemists due to their chemical similarities to nat-

ural humic substances. Some 90 years ago, Maillard investigated these dark brown condensation products (Maillard, 1913). Since then melanoidins have been shown to have commercial, nutritional and toxicological significance. They play a role in colour and flavour of food, have antioxidative properties, and improve protein function (Painter, 1998; Rivero-Perez et al., 2002; Miwa et al., 2002). The possible origin of humic substances in soil, lakes, and seawater, especially the role of melanoidins in humification, have

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been discussed in several reviews (Dawson and Duursma, 1981; Gagosian and Lee, 1981; Benner, 2002). The macromolecular nature and complexation properties of humic substances toward microconstituents present in natural waters have also been widely investigated (Buffle, 1988). The interaction of humic matter with different metal ions changes the biogeochemical cycle of these trace metals, and also influences their bioavailability.

Lignin polymers have been suggested as the major source of terrestrial humic substances, but carbohydrates are more abundant in marine environments and are thus more likely precursors of marine humic acids (Hedges, 1978). Synthetic melanoidins are commonly prepared in laboratories by prolonged heating (Hedges, 1978; Larter and Douglas, 1980; Ikan et al., 1990, 1992), but they also may be formed under natural environmental conditions in soil as well as in sea water. For example, melanoidins have been identified in archeological plant remains from excavations in Egypt and thus must have been produced by reactions that occurred in buried organic matter (Evershed et al., 1997). Microbially formed melanoidins have also been found in stone monuments (Saiz-Jimenez, 1995; Polikreti and Maniatis, 2003). Duursma (1965) and later Keil and Kirchman (1994) suggested that abiotic reactions, e.g., of amines and aldehydes, might be partially responsible for the loss of labile amino acids and proteins from seawater.

Here we determine how conditions of melanoidin preparation can influence their complexation properties towards metal ions, particularly copper ions. The conditions we varied include length of reaction time, reactants used, and reaction medium used, whether distilled water or seawater. We also separated the products into different molecular mass fractions. We applied the technique of anodic stripping voltammetry (ASV) to determine copper complexing capacity (CCu). This method of determining complexing capacity has been widely applied to the study of metal-organic interactions in natural waters especially with regard to monitoring and regulating copper toxicity (e.g., Kogut and Voelker, 2001, 2003). A similar electrochemical technique for CCu determination, cathodic stripping voltammetry (CSV), which uses competitive ligand equilibration, is also widely and concurrently applied (e.g., Shank et al., 2004a,b). Advantages and disadvantages of

these techniques have been thoroughly reviewed by Donat and Bruland (1990). In both ASV and CSV the detection window determines the lability of the complex of interest. In ASV, how labile the complex is depends on the diffusion layer thickness at the electrode surface, which depends directly on the stirring rate during metal ion deposition (Davison, 1978; Ellwood, 2004), while in CSV the lability depends on the competing ligand and its concentration (e.g., Van den Berg, 2000; Buck and Bruland, 2005). We examined and correlated copper complexing capacity values of 24 differently prepared melanoidins and two humic acids (HA). One of these HA was fulvic in nature and was isolated from natural lagoon sediments.

2. Experimental

2.1. Sample preparation

Fulvic acid (FA) was isolated from Cannel lagoon sediments (France) at the University of Perpignan (Fauget, 1982) by extracting sediments with alkaline solution (0.01 M NaOH + 1% Na₄P₂O₇). After centrifugation and flocculation of mineral colloids with NaCl (20 g/L), the solution was acidified to pH 2.0 with 2N HCl. The humic acid fraction precipitated and was removed from the fulvic fraction in solution. The fulvic acids were purified by dialysis and on cation exchange resin DOWEX 50W-X8, and then lyophilized (Kononova and Belchikova, 1960). The molecular weight distribution of this fulvic acid was measured at EAWAG (Swiss Federal Institute for Environmental Science and Technology) by exclusion chromatography with carbon detection. We used a commercially available humic acid (Aldrich) that originates from peat. Ochs et al. (1994) measured the molecular weight distribution of Aldrich humic acid by separation on Sephadex columns and the sulfur content (3.26%). The molecular weight distribution of the FA and HA used here are in the range of humic material in natural environments (Ochs et al., 1994). In Table 1, we compare elemental composition, acidity and molecular mass of these preparations as well as data from Hedges (1978) for three melanoidins prepared in the same way as ours but with a reaction time of seven days.

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