

Copper-binding efficacy of water-soluble chitosans: characterization by aqueous binding isotherms

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Abstract

The major objective of the study is to measure directly the isotherms of copper binding onto soluble chitosan preparations, using ion-selective electrode technique. Copper uptake is found to decrease strongly when chitosan acetylation degree or chitosan concentration increased. When relating the bound copper concentrations to content of non-acetylated amine groups in a chitosan, differences between copper uptake on different chitosan preparations become reduced but not disappear. Other effects, in addition to the contents of non-acetylated amine groups, can involve differences in the copper binding by different chitosans. Due to isotherm non-linearity, the distribution coefficient K_d of copper between a water-soluble chitosan and an aqueous solution may vary by two orders of magnitude as the free copper concentration C_{free} varied. Linear relation between $\log K_d$ normalized by free amine group content of chitosans and $\log C_{\text{free}}$ may help in preliminary estimating of the copper binding by water-soluble chitosans at a certain pH.

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1. Introduction

Chitosans, poly-(1 → 4)-β-D-glucosamine derivatives, produced by deacetylation of chitin are well known to sorb effectively metals from aqueous solutions

(Muzzarelli et al., 1989; Roberts, 1992; Bailey et al., 1999; Kumar, 2000; No and Meyers, 2000). In the light of their high metal sorption efficacy, wide availability and environmental safety, it has been suggested that chitosans may be useful in various applications such as waste water treatment, metal recovery from effluents, prevention (or reduction) of heavy metal pollution in industrial and urban areas, remediation of metal-polluted soils, etc. (see e.g. Bailey et al., 1999; Bassi et al., 1999; Kumar, 2000; El-Sawy et al., 2001; Rhazi et al., 2002a; Seo et al., 2002; Steenkamp et al., 2002).

Many studies have aimed to characterize the metal-binding capability of various non-soluble chitosan-based

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sorbents in terms of the sorption isotherms and the sorption thermodynamics. Such factors as the nature of the heavy metal, the solution pH and the degree of chitosan acetylation were examined, and numerous sorption data for many metals on various chitosans have been reported in the literature (e.g. Jansson-Charrier et al., 1996; Piron and Domard, 1997; Monteiro and Airoldi, 1999; Bassi et al., 2000; No and Meyers, 2000; Erosa et al., 2001; Chu, 2002; Juang and Shao, 2002; Ngah et al., 2002).

Less work was done to quantify the interactions between heavy metals and soluble chitosans by means of binding thermodynamics. Soluble chitosans (i.e. not in precipitated form) may be expected to have a well-hydrated and (relatively) open structure with minimal complications resulting from intermolecular chitosan aggregation (as compared with non-soluble chitosans). Hence, determination of isotherms for metal–chitosan complex formation in solution may provide more insight and assist in elucidating the strength of interactions between metal ions and macromolecules of chitosans.

Specifically, such a characterization based on potentiometry and spectrophotometry has been published (Rhazi et al., 2002a,b). On the assumption that proton release took place as metals were bound by chitosan monomeric units (amine groups), the stability of the copper–chitosan complex was examined, and stability constants were calculated (Rhazi et al., 2002b). It was demonstrated, for example, that a certain chitosan polymerization degree is needed for the effective copper binding (Rhazi et al., 2002b). Interactions between chitosan-derivatives and heavy metals in solution were also examined, by means of equilibrium dialysis, cyclic voltametric measurements, electron paramagnetic resonance and Mossbauer spectra (Chiessi et al., 1993). It was suggested that the functional groups in each monomeric chitosan residue provide an effective site for binding one metal ion.

More research is needed to directly measure the heavy metal binding isotherms on water-soluble chitosans, without explicit assumptions of H^+ /metal competition or of any other scheme for metal–chitosan interactions. Such a measured (i.e. model-free) binding curve would include information on the potential of different chitosan moieties to interact with heavy metals in solutions. Coefficients for the distribution of heavy metals between the aqueous solution and the dissolved chitosan macromolecules, as derived from experimentally measured binding isotherms, would be helpful in evaluating the metal-extracting potential of water-soluble chitosans. Determination of the heavy metal binding curves on water-soluble chitosans may be carried out by means of the ion-selective electrode technique.

Therefore, the feature of this work is the direct determination of binding interactions of water-soluble chito-

sans with copper, selected as a model heavy metal. It is considered that better understanding of metal–chitosan interactions will be helpful in developing environmental applications of chitosan preparations. Hence, the major objective of the present study was to determine the isotherms for the copper binding onto several soluble chitosan preparations, using ion-selective electrode measurements. Specific objectives included: (1) examination of the effects of chitosan acetylation and chitosan concentration on the copper binding; (2) comparison of the efficacy of several water-soluble chitosan preparations in terms of copper binding at various copper concentrations.

2. Experimental section

2.1. Materials

Six chitosan preparations designated as (I), (Ia), (Ib) and (II)–(IV) were used in the copper-binding experiments. Chitosans (I) (Koyo Chemicals Co, Japan; $500\,000\text{ g mol}^{-1}$, the acetylation degree 5%), (II) (Koyo Chemicals Co, Japan; $1\,000\,000\text{ g mol}^{-1}$, acetylation degree 5%), (III) (C-3646, Sigma Chemical Co. St. Louis, MO; $1\,000\,000\text{ g mol}^{-1}$, acetylation degree 15%) and (IV) (Vanson, WA; $500\,000\text{ g mol}^{-1}$, acetylation degree 17%) were purchased and used without further purification. Chitosans (Ia) (acetylation degree 25%) and (Ib) (acetylation degree 35%) were prepared by partial reacylation of the commercial chitosan (I) according to the method described by Aiba (1994). The moisture content of the chitosan preparations was 10% w/w. Ash contents of studied chitosan preparations were around 0.5–0.6% w/w. The acetylation degree of chitosans indicated above was determined according to described technique (Muzzarelli and Rocchetti, 1985). Molecular weight determination of chitosan preparations was carried out using high performance gel permeation chromatography according to recommendations (Terbojevich and Cosani, 1997). Copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, Sigma, Analytical Grade) was used for preparation of the aqueous (Millipore) copper solutions.

2.2. Copper–chitosan binding experiment

Three experimental series were performed: (1) determination of the copper-binding isotherms on different chitosan preparations; (2) examination of the effect of the acetylation degree of chitosan on the interactions with copper; (3) examination of the effect of chitosan concentration on the copper binding. All three series of experiments were carried out at pH 6.2, which is close to the optimal pH for the copper sorption by non-soluble chitosans (Bassi et al., 2000; El-Sawy et al., 2001;

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