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Application of the NICA–Donnan approach to calculate equilibrium between proton and metal ions with lignocellulosic materials

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Abstract

The NICA (nonideal competitive adsorption)–Donnan model is employed to describe the interactions between Cu^{2+}, Pb^{2+}, Cd^{2+}, Mn^{2+}, and Fe^{3+} ions and the lignins extracted from wheat bran (lignocellulosic substrate, LS) and from kraft pulp (residual kraft lignin, RKL), and between Cu^{2+}, Mn^{2+}, and Fe^{3+} ions and wood fibers from kraft pulps. The charge of the LS and the fiber charge need to be obtained from potentiometric titration data for the LS, and by use of Donnan equilibrium, mass balance, and electroneutrality equations for the kraft fiber. The proton binding parameters for the LS and the kraft fiber, the total site densities ($Q_{\max,1}$ and $Q_{\max,2}$), the median protonation constants (K_1 and K_2), and nonideality–generic heterogeneity parameters (m_1 and m_2) (subscripts 1 and 2 refer to the carboxyl and phenolic functional groups) are obtained by fitting these charge data. With the above proton parameters, the interactions between metal ions and the lignins (LS and RKL)/kraft fibers are calculated, and the metal binding parameters are obtained. These parameters are the binding constants of metal i ($K_{i,1}$ and $K_{i,2}$), ion-specific nonideality parameters ($n_{i,1}$ and $n_{i,2}$), and intrinsic heterogeneity parameters (p_1 and p_2). p_1 and p_2 are the same for all metal ions binding to a specific sorbent. Here, p_1 and p_2 values obtained by fitting the binding data of a specific metal ion are used directly in binding calculations for other metal ions, and do not need to be fitted. By use of the above parameters for single metal ion binding, the binding relationship between a mixed metal ion and lignocellulosic substrate/kraft fiber can be predicted.

Keywords: NICA–Donnan model; Ion binding; Sorption; Lignin; Wood fiber; Metals

1. Introduction

A number of models describing the interaction between metal ions and wood fibers have been presented in the literature. Towers and Scallan [1] have shown that the distribution of mono- and divalent metal ions between a cellulose fiber and the surrounding solution can be modeled by using an ion-exchange model based on the Donnan theory. In the Donnan equilibrium framework, the fiber–water suspension is described as a two-phase system consisting of the fiber phase and the external solution (liquor) phase [1]. It is assumed that the fiber wall is permeable to metal ions and water. Bygrave and Englezos [2] introduced activity coefficients to the Donnan equilibrium model and used it to predict the distribution of calcium and sodium ions between kraft pulp fibers and the surrounding liquor. Athley and Ulmgren [3] combined Donnan theory and complex formation to describe the interaction of calcium and manganese ions with oxygen-delignified hardwood and softwood pulp fibers. Rasanen and Stenius [4] combined Donnan theory with complexation models to determine the acid/base properties and metal ion (Na^+, K^+, Ca^{2+}, Mg^{2+}, and Mn^{2+}) sorption on hardwood kraft fibers.

Donnan-type models account for nonspecific interaction. A Donnan-type model for nonspecific binding of ions combined with the nonideal competitive adsorption (NICA) equation for specific binding, known as the NICA–Donnan model, is available. This approach, which combines a continuous distribution of affinity constants and a Donnan phase, has been successfully applied to calculate interactions of protons and metal ions (Cu^{2+}, Pb^{2+}, Cd^{2+}, etc.) on various

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kinds of fulvic and humic acids [5–10]. Recently, Bouanada et al. [11] employed the NICA–Donnan model to satisfactorily predict acid/base properties of the lignocellulosic substrate. Dupont et al. [12] studied the sorption properties of a lignocellulosic substrate toward lead, copper, and cadmium. However, it is noted that there are no applications of the NICA–Donnan model to describe the interaction between metal ions with residual kraft lignin and with wood fibers. These are systems of considerable industrial interest and there is evidence from ESR spectra that metal ions in wood fibers do not have the same chemical environment as in solution, which is evidence for specific metal–fiber interactions [13].

Thus, the objective of the present study was to apply the NICA–Donnan model to describe interactions between metal ions and lignocellulosic materials.

2. NICA–Donnan equation

The partitioning of proton or metal ions between the lignocellulosic material (lignin or wood fiber) and the external solution (or liquor) is described by considering the equilibrium, electroneutrality, mass balance relationships, and binding of proton or metals with the various functional groups on the lignins/fibers. This approach combines chemical heterogeneity and electrostatic effects. The proton or metal binding to lignin/fiber is assumed to occur with specific interactions between the cation and the surface functional groups with negative charge and by nonspecific electrostatic binding to any residual negative charge. Specific binding is described by the NICA equation, and nonspecific binding is expressed by the Donnan equation.

2.1. Specific binding interaction

The NICA equation is employed for the specific binding relationship between a proton or metal ion and a functional group on the lignin/fiber. The NICA equation assumes a continuous distribution of site affinities. It allows that the affinity distributions for a proton and the various metal ions not only have different median affinities for each ion, but also have ion-specific nonideality or heterogeneity.

The proton or metal ion binding to each site of type S at the sorbent is described by the reaction

$$S^- + M^{z+} = SM^{(z-1)+}, \tag{1}$$

where M^{z+} is a cation of charge $z+$, and S^- and $SH^{(z-1)+}$ are surface species.

The total fractional surface coverage of component i is expressed by the integral equation

$$\theta_{i,\mathrm{T}} = \int_{\Delta \log K_i} \theta_{i,\mathrm{L}} f(\log K_i)\, d(\log K_i), \tag{2}$$

where $f(\log K_i)$ is the distribution function of the affinity constant, K_i; $\theta_{i,\mathrm{L}}$ is the local adsorption isotherm, i.e., the isotherm for binding of ion i to a group of identical sites [14]; and $\Delta \log K_i$ is the range of $\log K_i$ considered. Koopal et al. [15] derived the monomodal form of the NICA equation. Usually there are two major types of sites in the affinity distribution for the binding of protons or metal ions to lignin/fiber, considered to be due to carboxylic-type groups and phenolic-type groups, respectively. The NICA equation in its thermodynamically consistent version is

$$\begin{aligned} Q_i = {} & Q_{\max,1} \frac{n_{i,1}}{n_{\mathrm{H},1}} \frac{(K_{i,1} c_{\mathrm{D},i})^{n_{i,1}}}{\sum_j (K_{j,1} c_{\mathrm{D},j})^{n_{j,1}}} \\ & \times \frac{\left[\sum_j (K_{j,1} c_{\mathrm{D},j})^{n_{j,1}}\right]^{p_1}}{\left[1 + \sum_j (K_{j,1} c_{\mathrm{D},j})^{n_{j,1}}\right]^{p_1}} \\ & + Q_{\max,2} \frac{n_{i,2}}{n_{\mathrm{H},2}} \frac{(K_{i,2} c_{\mathrm{D},i})^{n_{i,2}}}{\sum_j (K_{j,2} c_{\mathrm{D},j})^{n_{j,2}}} \\ & \times \frac{\left[\sum_j (K_{j,2} c_{\mathrm{D},j})^{n_{j,2}}\right]^{p_2}}{\left[1 + \sum_j (K_{j,2} c_{\mathrm{D},j})^{n_{j,2}}\right]^{p_2}}, \end{aligned} \tag{3}$$

where subscripts 1 and 2 refer to the carboxylic- and phenolic-type parts of the distribution, respectively; subscript H refers to the proton; Q_i is the total amount of component i bound to the surface species of the lignin/fiber (in mol kg^{-1}); $Q_{\max}$ is the number of sites (in mol kg^{-1}); K_j is the median affinity constant for component j; and $c_{\mathrm{D},j}$ is the local concentration of component j near the binding sites (in mol L^{-1}). The various summations are over all j components. This includes the proton and all metal ions present. The relationship between $c_{\mathrm{D},j}$ and the concentration of component j in aqueous phase (c_j) is determined by a Boltzmann factor, which depends on the local electrostatic potential in the lignin phase. The Donnan model is used to calculate $c_{\mathrm{D},j}$ as shown in Section 2.2. The parameter n_i accounts for the "nonideal" behavior ($n \neq 1$, nonideal; $n = 1$, ideal) of component i. For ion adsorption, n_i takes values of $0 < n \leqslant 1$. The value of p ($0 < p \leqslant 1$) determines the width of the distribution due to the intrinsic chemical heterogeneity of the sorbent and is the same for all components.

The total number of sites, $Q_{\max,1}$ and $Q_{\max,2}$, are expressed by the sum of the concentration of all the surface species:

$$Q_{\max,1} = Q_{\mathrm{S}1} + Q_{\mathrm{H}1} + \sum Q_{\mathrm{M}_j 1}, \tag{4}$$

$$Q_{\max,2} = Q_{\mathrm{S}2} + Q_{\mathrm{H}2} + \sum Q_{\mathrm{M}_j 2}. \tag{5}$$

Here subscripts 1 and 2 refer to the two-component distribution; Q_{S} is the number of sites in the free state, S^- (free of bound ions); Q_{H} is the number of protonated sites; and $\sum Q_{\mathrm{M}_j}$ is the number of sites occupied by cations, M^{z+}. Thus, the net charge of the lignin/fiber, q (in Eq kg^{-1}) is given by the charge contributions from the various surface species of the two distributions, with

$$q_1 = -Q_{\max,1} + Q_{\mathrm{H}1} + z \sum Q_{\mathrm{M}_j 1}, \tag{6}$$

$$q_2 = -Q_{\max,2} + Q_{\mathrm{H}2} + z \sum Q_{\mathrm{M}_j 2}, \tag{7}$$