A Simple Model for Vapor-Moisture Equilibrium in Biomass Subtrates

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Equilibrium moisture content (EMC) plays a fundamental role on the properties of bioderived solids such as food, waste biomass, seeds, and many others. For foods, the moisture content affects flavor, texture, and the way the food is stored. In other applications, moisture affects drying conditions and energy requirements for biomass processing. Adequate modeling of EMC in biomass as a function of the water activity is very important in many engineering applications. Most models used to correlate EMC with water activity are based on traditional adsorption models which take into account the adsorption energy of water with the substrate only and do not consider other nonadsorption interactions of water within the substrate such as mixing and swelling effects. Many other models are empirical, which are commonly used for interpolation. Although a detailed description of this type of substrate is very complex, we present a simple model based on standard molecular-thermodynamic models and standard statistical mechanics formulations to correlate the EMC with water activity that attempts to consider both adsorption and nonadsorption interactions of the water with the substrate. Although the model is basic, it captures the behavior of water in this type of systems fairly well and it can be used to fit experimental data with parameters that provide better physical insight on the nature of system. We suggest how to improve the model fundamentally if better knowledge of the water interactions in the substrate are available. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1595–1603, 2009

Keywords: equilibrium moisture content, waste sludge, biosolids, municipal waste, thermodynamics, moisture equilibrium, adsorption, water sorption isotherms

Introduction

Moisture plays a fundamental role on the properties and behavior of any biologically derived material, in general. Understanding the moisture interaction and equilibrium properties is of great interest for a variety of industrial processes. In the food industry, moisture affects flavor, handling, shelving, and stability of the products to pathogens. By controlling the moisture in the product, many quality characteristics are maintained and the life of the product is preserved. For example, many legumes are soaked in water to prepare them for market distribution and in cases such as chickpeas to gelatinize the starch in the grain.[1] Other examples in which moisture control is of significance include the production of skimmed milk powder, whey powder, and yoghurt powder. Other applications, besides foods, include municipal waste sludge conditioning, wood drying, and biomass conversion to energy among many others. In these, understanding equilibrium moisture content helps determining energy demands for conditioning and design of drying systems as well as defining the lower and upper limits of moisture for handling and processing in general.

There have been extensive efforts, both experimental and theoretical, to more clearly understand moisture effects. Understanding the moisture contents is important to design and control the operations and final quality of the products. From the modeling standpoint, the efforts have focused on using traditional adsorption models (and their modifications),

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which are based on one or more adsorption layers, where the adsorbate and adsorbent interact only through one or more adsorption energies. Other types of interactions such as van der Waals type or swelling phenomena are usually not taken into account. Most models are versions of the Brunauer-Emmett-Teller (BET) equation[2] and the Guggenheim-Anderson-de Boer (GAB) equation.[3–5] Both of the these are derived using both kinetics and statistical mechanics arguments. The main difference between these two models is that in the BET model, the adsorbed molecules in the first layer are characterized by a specific potential energy and the molecules in the subsequent layers are characterized by the potential energy of the pure adsorbate. On the other hand, the GAB equation allows for a number of layers between the first and the bulk to have a different potential energy (see Theoretical Background section for more details). Biomass such as food and municipal waste sludge consist of complex and highly heterogeneous biopolymer networks with a high water content. The water energetic interactions in these materials vary substantially with the nature of the biomass, but include many other effects besides adsorption, including hydrogen bonding, intracellular water, and attractive–repulsive interactions product of mixing among others.

In this work, we present a simple model to describe EMC with water activity in biomass that takes into account both adsorption and nonadsorption phenomena. For nonadsorption interactions, the model incorporates the basic effects of polymer mixing and swelling; and for adsorption interactions, the models distinguishes between bonded and nonbonded water. The model is a first attempt to incorporate other effects besides adsorption on the equilibrium behavior of water in these biomass materials. We suggest ways to incorporate more details in the model based on the knowledge available of the biopolymer network. The model captures well the behavior of water adsorption isotherms type II and III typically found in this type of biomass experimentally. For fitting purposes, the model does using two adjustable parameters to describe adsorption and two additonal paramters to describe mixing and swelling interactions. The model is a good start to incorporate additional water–biomass interactions besides adsorption. The model behaves well with appropriate parameters with substantial possibilities for improving the model fundamentally.

Theoretical Background

The literature on adsorption phenomena is vast and by no means this is an account of the work performed in this area. Here, we briefly describe some common models used to model and fit equilibrium moisture content data as a function of relative humidity or water sorption isotherms data, in general. One of the most common early models used for this purpose (with many modified versions available) is the Brunauer, Emmett, and Teller equation (BET equation).[2] In this model, the water is adsorbed with two characteristic molecular potential energies, namely, ε_a for bonded water and ε_f for nonbonded water. In the original version of model is also assumed that there is no limit on the number of layers that molecules can build upon. Letting ω be the water adsorbed and σ the adsorbing capacity available, the BET equation is given by:

$$\frac{\omega}{\sigma} = \frac{c a_{\mathrm{w}}}{(1 - a_{\mathrm{w}})(1 - a_{\mathrm{w}} + c a_{\mathrm{w}})}, \tag{1}$$

where a_{w} is the water activity and c is a constant defined as

$$c = \frac{a_1 b_2}{a_2 b_1} \exp\left[(\varepsilon_f - \varepsilon_a)/RT\right].$$

The constants a_i and b_i are related to rate constants for adsorption and desorption in the first and second layers.[4] For the case of restricting the number of adsorption layers n, the BET equation becomes:

$$\frac{\omega}{\sigma} = \frac{c a_{\mathrm{w}}}{1 - a_{\mathrm{w}}} \left[\frac{(1 - (n+1) a_{\mathrm{w}}^n + n a_{\mathrm{w}}^{n+1}}{1 - a_{\mathrm{w}} + c a_{\mathrm{w}} - c a_{\mathrm{w}}^{n+1}}\right]. \tag{2}$$

Brunauer et al.[6] proposed a generalized version of the equation to include the different types of isotherms which is of the form:

$$\frac{\omega}{\sigma} = \frac{c a_{\mathrm{w}}}{1 - a_{\mathrm{w}}} \times \left[\frac{(1 - (ng/2 - n) a_{\mathrm{w}}^{n-1} - (ng - n + 1) a_{\mathrm{w}}^n + n g a_{\mathrm{w}}^{n+1}/2}{1 + (c-1) a_{\mathrm{w}} + (cg/2 - c) a_{\mathrm{w}}^n - c a_{\mathrm{w}}^{n+1}/2}\right], \tag{3}$$

where $g = \exp[(\varepsilon_f - \varepsilon_n)/RT]$ and ε_n is the average molecular potential energy of the n-th and final layer.

A popular modification to the BET model is the Guggenheim-Anderson-deBoer (GAB) equation.[3–5] In this approach, an extra adsorption potential energy parameter is used to characterize the molecules adsorbed in the second to about the nineth layer. In the original formulation, this new energy parameter is defined as $\varepsilon_{2\text{ to }9} = \varepsilon_f + d$, where d is added to ε_a as well. The consequence of this modification for the BET equation can be summarized as a modification of the activity of the solvent or sorbate by a factor $f = \exp(d/RT)$; therefore, a_{w} in the BET formulation is replaced by $a_{\mathrm{w}}^{\mathrm{GAB}} = f a_{\mathrm{w}}^{\mathrm{BET}}$ to obtain the GAB equation. This modification has shown to be very successful in overcoming many of the limitations of the original BET model in fitting and modeling adsorption isotherms.

There are many other models reported in the literature for fitting equilibrium moisture data, but most tend to be semi- and empirical modifications of the BET and GAB models. Table 1 shows some typical equations used to fit equilibrium moisture content data as a function water activity. In general, most of these are modifications of models developed to study the adsorption of gases on hard surfaces without taking into account other potential significant phenomena such as polymer swelling and mixing characteristic of softer materials. Many of the applications in which EMC data are used deals with handling and characterization of softer substrates such as food and similar (biomass) in which the water activity can affect significantly the swelling and mixing of the biomass and therefore it should be taking into account when modeling the water equilibrium characteristics.

Table 1. Typical Models Used to Fit Equilibrium Moisture Data as Function of Water Activity in Substrates Such as Waste-Water Activated Sludge and Food Products

Source	Model
Chung Pfost[7]	$\omega = \frac{-1}{c_1}\ln\left[-\ln(a_w)\frac{T+c_2}{c_3}\right]$
Modified Halsey[8]	$\omega = \left[\frac{-\exp(c_1+c_2T)}{\ln(a_w)}\right]^{1/c_3}$
Oswin[7]	$\omega = (c_1+c_2T)\left[\frac{a_w}{1-a_w}\right]^{c_3+c_4T}$
Thompson[9]	$\omega = \left[\frac{-\ln(1-a_w)}{c_1(T+c_2)}\right]^{1/c_3}$

There are significantly more models available in the literature, but most of them are some type of modification of the BET and GAB equations (to best of knowledge). The vectors c_i are constants regressed using experimental data.

Model Description

The biomass systems of interest can be described as being composed of an air–water gas phase interacting with a water-biomass phase mixture (i.e., solid-liquid mixture). Our interest is to determine and model the water in thermodynamic equilibrium between these two main phases. The water in equilibrium in the biomass phase for a given set of conditions of relative humidity, temperature, and pressure is defined as the equilibrium moisture content (EMC). The main challenge consists of determining how the water activity in the biomass phase (i.e., the solid–liquid mixture) gets affected by the biomass nature. For complex biomass mixtures such as municipal sludge and foods, the water activity gets dependant on many factors including ionic conditions, pH, surface tension, and adsorption energies among others. In this work, we propose a simple model for the biomass phase as a first attempt to include other effects in addition to adsorption phenomena. We model the biomass as being composed of two phases with water in thermodynamic equilibrium with each other and in equilibrium with the air-water phase. The first biomass phase consists of water adsorbed in the biopolymer network characterized by an average molecular potential energy ε_a (bonded water or water adsorbed phase, also denoted in this work as the *a*-phase). The water in this phase bonds strongly to the network through adsorption mechanisms, intracellular water, and similar. The biomass second phase consists of water still in the biomass phase, but it is absorbed in a more freely manner (relatively *free water* compared with the adsorbed phase or *a*-phase). This water is characterized by an average molecular potential energy ε_f and it could described as *free* water (also denoted as the *f*-phase in this work). In the later phase, the water activity is mostly affected by surface tension effects, swelling and mixing of the biomass network, and interactions with the water in the adsorbed phase. The proposed model consists of defining appropriate expressions for the Helmholtz free energy and chemical potential of the water in the different phases aforementioned and then using thermodynamic equilibrium conditions to determine the EMC in the biomass phase as function of the relative humidity (water activity).

Helmholtz free energy

The dimensionless Helmholtz free energy of a given phase is defined as

$$\tilde{A} = -\ln Q, \tag{4}$$

where Q is the canonical partition function of the phase (the Helmholtz free energy and similar become dimensionless by dividing by k_BT on a molecular basis or by RT on a mol basis, where k_B is the Boltzmann constant, R the ideal gas constant, and T the absolute temperature). We consider the water between the phases within the biomass (bonded water and nonbonded water) to be in thermodynamic equilibrium with each other and in equilibrium with the air–water gas mixture. To derive the partition function of the adsorbed phase (i.e., *a*-phase), we follow the approach by Hill[10] for multimolecular adsorption on a surface. Defining θ as the water adsorbed in the biomass phase with molecular potential energy ε_a and α the water adsorbed also in the biomass phase with average molecular potential energy ε_f such that $\omega = \alpha + \theta$, then the partition function Q_a for the water adsorbed phase is then defined as

$$Q_a = \binom{\sigma}{\theta}(q_a)^\theta = \frac{\sigma!}{\theta!(\sigma-\theta)!}(q_a)^\theta, \tag{5}$$

where q_a is the partition function for an adsorbed water molecule and $\binom{\sigma}{\theta}$ is the binomial coefficient (notice that $\theta \le \sigma$) representing the number of ways that θ identical molecules can be distributed among the adsorbing sites characterized by σ. The partition function for a water molecule in this adsorbed phase is defined as the product of partition functions, namely, (a) a harmonic oscillator and (b) the rest of the internal degrees of freedom such that (assuming the Hamiltonians are additive)

$$q_a = \left(\frac{k_BT}{hv_a}\right)^3 \exp(\beta\varepsilon_a) \times q_{\text{int}}, \tag{6}$$

where h is the Planck's constant, v_a the characteristic vibration frequency, and q_{int} corresponds the partition function all the internal degrees of freedom of the molecule.

For the nonbonded water adsorbed phase (i.e., *f*-phase), the partition function Q_f is defined as

$$Q_f = \binom{\omega-1}{\theta}(q_f)^\alpha = \frac{(\omega-1)!}{\theta!(\alpha-1)!}(q_f)^\alpha, \tag{7}$$

where $\binom{\omega-1}{\theta}$ is the binomial coefficient representing the number of ways the remainder water α can be distributed with repetition on the upper layers of the adsorbed-phase. Similarly, the individual partition function q_f is defined as

$$q_f = \left(\frac{k_BT}{hv_f}\right)^3 \exp(\beta\varepsilon_f) \times q_{\text{int}}, \tag{8}$$

where v_f the characteristic vibration frequency and ε_f is the molecular potential energy characterizing the water in the *f*-phase.

Applying the definition of the Helmholtz free energy given by Eq. 4 and using the Stirling's approximation[11] to estimate the logarithms of large numbers, the following expressions for the Helmholtz free energies of the *a* and *f* phases are obtained (also notice that $\alpha \gg 1$ and $\theta \gg 1$):

$$\tilde{A}^{(a)} = (\sigma - \theta)\ln(\sigma - \theta) + \theta \ln \theta - \sigma \ln \sigma - \theta \ln q_a \quad (9)$$

and

$$\tilde{A}^{(f)} = \theta \ln \theta + \alpha \ln \alpha - (\alpha + \theta)\ln(\alpha + \theta) - \alpha \ln q_f. \quad (10)$$

The free energy of the water in the biomass phase can also be defined as the free energy of the pure water plus the excess contributions with respect to pure water due to mixing of the nonbonded water with the biomass, swelling of the biomass networks, and the excess due to the adsorption of the bonded water. There are additional effects that can be taken into account such as surface tension, pH, and ionic strength among others, but in this formulation, these are not taking into account explicitly. We expect that the adjustable parameters in the model will capture some of these contributions although this will affect the actual physical interpretation of the adjustable parameters. Within this framework, the free energy of the water in the *f*-phase is defined as

$$\tilde{A}^{(f)} = \tilde{A}^{o}_{\mathrm{w}} + \Delta\tilde{A}_{\mathrm{mix}} + \Delta\tilde{A}_{\mathrm{swl}} + \Delta\tilde{A}_{\mathrm{ads}}, \quad (11)$$

where $\tilde{A}^{o}_{\mathrm{w}}$ is the free energy of the pure water, $\Delta\tilde{A}_{\mathrm{mix}}$ is the excess due to mixing, $\Delta\tilde{A}_{\mathrm{swl}}$ the excess due to swelling of the biomass network, and $\Delta\tilde{A}_{\mathrm{ads}}$ the excess due to adsorption of water in the *a*-phase (energy parameter ε_a).

We use the Flory-Huggins lattice theory[12–14] to formulate the free energy of mixing of the water in the biomass network. We realize that this is a substantial simplification given the biomass nature typical of municipal sludge or food is highly nonideal and heterogeneous, but as mentioned in the introduction, we want first to propose a simple model that captures some elements of the nature of the network and elements of the adsorption phenomena with few adjustable but meaningful parameters. Modifications to the Flory-Huggins theory such as the extended Flory-Huggins[14] and the use of other frameworks that take into the account the random nature of the network could be consider to improve the model. Within the traditional Flory-Huggins framework, the Helmholtz energy of mixing is giving by

$$\Delta\tilde{A}_{\mathrm{mix}} = n_{\mathrm{w}} \ln(1 - \phi_{\mathrm{p}}) + n_{\mathrm{p}} \ln \phi_{\mathrm{p}} + n_{\mathrm{w}}\phi_{\mathrm{p}}\chi, \quad (12)$$

where n_{w} is the number of molecules of water, n_{p} the number of polymer molecules, ϕ_{p} is the volume fraction of polymer, and χ is the Flory-Huggins segmental interaction parameter. Within our framework, n_{p} represents the amount of dried biomass and the biomass volume fraction is given by

$$\phi_{\mathrm{p}} = \frac{n_{\mathrm{p}} v_{\mathrm{pw}}}{\omega + n_{\mathrm{p}} v_{\mathrm{pw}}}, \quad (13)$$

where v_{pw} is the ratio of an average specific volume of the biomass with respect to the specific volume of water. In the Flory-Huggins framework, the polymer volume fraction is defined in terms of the fraction of lattice points ocuppied by the polymer.

For the swelling excess Helmholtz free energy, there is more than one option to consider. A classical approach would be to use the Flory-Rehner theory[14–18] such that

$$\Delta\tilde{A}_{\mathrm{swl}} = n_{\mathrm{p}}\left[\frac{3}{2}(\delta^2 - 1) - \ln \delta^3\right] + \xi \ln \delta^3, \quad (14)$$

where δ is the expansion factor, n_{p} is the total number of chains, and ξ is the cycle rank. For a perfect network,[18] ξ can be defined in terms of the functionality of the network as

$$\frac{\xi}{n_{\mathrm{p}}} = 1 - \frac{2}{\Psi}, \quad (15)$$

where Ψ is the functionality of the network. In Eq. (14), the squared bracket term represents the energy change due to the affine deformation of polymer network in a lattice, and the second term the free energy change of the joining points in the network. For biomass type of substrates this model is not realistic, but we use it as a generic form. It is possible to consider different types of deformation within this framework by redefining the expansion factor δ.[17] For a affine deformation, the expansion factor is a function of the volume fraction of the polymer and it is defined as:

$$\delta = \left(\frac{\phi_0}{\phi_{\mathrm{p}}}\right)^{1/3}, \quad (16)$$

where ϕ_0 is the volume fraction of polymer in the reference state.

Equation 14, as a generic form to model swelling excess free energy, has the disadvantage that the model is only applicable to networks that expand only and it is defined within the context of a lattice. In other words, $\delta > 1$ and therefore such model will not be able to capture any potential volume-change transitions or volume contractions, which requires δ to be smaller than unity. For biomass it might be useful to consider a model capable of capturing volume-change effects. In the spirit of the Flory-Rehner theory, we take into account two contributions to the swelling contribution, namely, network deformation (volumetric expansion and contraction) and joining junction points. We assume that these two contributions are additive in a polynomial form that is a function of a volumetric parameter characteristic of the biomass (the choice of the polynomial form is arbitrary). We choose v_{pw} as such parameter and we keep it adjustable due to the difficulty of characterizing it accurately in a complex media such as biomass. Therefore, the swelling contribution is of the form

$$\Delta\tilde{A}_{\mathrm{swl}} = \Gamma v_{\mathrm{pw}}^2 + \zeta v_{\mathrm{pw}}, \quad (17)$$

where Γ is a function characterizing the network deformation and ζ a function characterizing the junction points. For Γ, we use an expression proposed by Grosberg and Kuznetsov[19] for elastic free energy change in polymers of the from $k[\delta^{-2} + \delta^2]$, where k is a constant. This expression does not have the limitations of the first term in Eq. (14) on the values of the expansion factor (i.e., δ can be <1). For ζ, we use the same function provided by the Flory-Rehner theory [see Eq. (14)]. Therefore, the expression for the swelling contribution becomes

$$\Delta\tilde{A}_{\mathrm{swl}} = \frac{3}{2} v_{\mathrm{pw}}^{2} \left[\delta^{2} + \delta^{-2} - 2\right] + v_{\mathrm{pw}} \ln \delta^{3}. \tag{18}$$

Chemical potential and equilibrium expressions

The chemical potential for water in each of the phases is obtained by differentiating the Helmholtz free energy expressions with respect to the number of water molecules at constant n_{p}, T, and V. For the a-phase, we take the partial derivative with respect to θ to obtain:

$$\tilde{\mu}^{(a)} = -\ln(\sigma/\theta - 1) - \ln q_{a}, \tag{19}$$

and for the f-phase, we take the partial derivative with respect to α producing:

$$\tilde{\mu}^{(f)} = -\ln(1 + \theta/\alpha) - \ln q_{f}. \tag{20}$$

Notice that q_f includes the molecular potential energy parameter ε_f of water molecules in equilibrium in the f-phase. The value of this parameter is affected by the adsorption of water in the a-phase, the mixing of water in the biomass network, and the swelling of the biomass structure. One can obtain a similar expression for the case of not having the mixing and swelling contributions in the chemical potential and assuming that the molecular potential energy parameter in the f-phase is that of pure water denoted by ε_f^o. For this case, the chemical potential becomes

$$\tilde{\mu}_{o}^{(f)} = -\ln(1 + \theta/\alpha) - \ln q_{f}^{o}, \tag{21}$$

where q_f^o is characterized by the molecular potential energy parameter ε_f^o. The first term in Eqs. (20) and (21) represents the contribution to the chemical potential of the water in the f-phase due to adsorption of water in the a-phase and the second term in Eq. (21) represents the chemical of the pure water defined by

$$\tilde{\mu}_{\mathrm{w}}^{\mathrm{o}} = -\ln q_{f}^{\mathrm{o}} = \tilde{\mu}_{\mathrm{w}}^{\mathrm{ig}} + \ln[P_{\mathrm{sat}}(T)] - \ln P, \tag{22}$$

where $\tilde{\mu}_{\mathrm{w}}^{\mathrm{ig}}$ is the dimensionless chemical potential of water in the ideal gas state, $P_{\mathrm{sat}}(T)$ is the vapor pressure of pure water, and P the pressure of the system.

The chemical potential of water in the f-phase can be also obtained by replacing $-\ln q_f$ in Eq. (20) by the mixing and swelling contributions to the chemical potential. We use Eq. (18) to obtain the swelling contribution and Eq. (12) to obtain the mixing contribution producing the expressions

$$\Delta\tilde{\mu}_{\mathrm{swl}} = \frac{v_{\mathrm{pw}}}{n_{\mathrm{p}}} \phi_{0} \left[\left(\frac{\phi_{\mathrm{p}}}{\phi_{0}}\right)^{1/3} - \left(\frac{\phi_{\mathrm{p}}}{\phi_{0}}\right)^{5/3} \right] + \frac{\phi_{\mathrm{p}}}{n_{\mathrm{p}}} \tag{23}$$

and

$$\Delta\tilde{\mu}_{\mathrm{mix}} = \ln(1 - \phi_{\mathrm{p}}) + \phi_{\mathrm{p}} + \chi\phi_{\mathrm{p}}^{2}, \tag{24}$$

respectively.

The biomass volumetric fraction is less than unity and assuming that the term $\phi_{\mathrm{p}}/n_{\mathrm{p}}$ is small such that $(1 + 1/n_{\mathrm{p}})\phi_{\mathrm{p}} \approx \phi_{\mathrm{p}}$ [notice that this term shows up by adding Eqs. (23) and (24)], then Eq. (23) can be simplified further to

$$\Delta\tilde{\mu}_{\mathrm{swl}} = v_{\mathrm{pw}} \phi_{0} \left[\left(\frac{\phi_{\mathrm{p}}}{\phi_{0}}\right)^{1/3} - \left(\frac{\phi_{\mathrm{p}}}{\phi_{0}}\right)^{5/3} \right]. \tag{25}$$

For fitting purposes, if the term $\phi_{\mathrm{p}}/n_{\mathrm{p}}$ is not small, we expect that the adjustable parameter v_{pw} will take into account its contribution. The expression for the biomass volumetric fraction can be rearranged as

$$\phi_{\mathrm{p}} = \frac{v_{\mathrm{pw}}}{\omega/n_{\mathrm{p}} + v_{\mathrm{pw}}}, \tag{26}$$

and for practical purposes, we take a basis of n_{p} when regressing the adjustable parameters of the model using experimental data. By inspection of Eq. (20), the contribution to the chemical potential of the water in the f-phase due to water adsorption is given by

$$\Delta\tilde{\mu}_{\mathrm{ads}} = -\ln(1 + \theta/\alpha). \tag{27}$$

The complete expression for $\tilde{\mu}^{(f)}$ becomes

$$\tilde{\mu}^{(f)} = \tilde{\mu}_{\mathrm{w}}^{\mathrm{o}} - \ln(1 + \theta/\alpha) + \Delta\mathcal{F}(\circ), \tag{28}$$

where

$$\Delta\mathcal{F}(\circ) = \Delta\tilde{\mu}_{\mathrm{mix}} + \Delta\tilde{\mu}_{\mathrm{swl}}, \tag{29}$$

with $\Delta\tilde{\mu}_{\mathrm{mix}}$ and $\Delta\tilde{\mu}_{\mathrm{swl}}$ given by Eq. (24) and Eq. (25), respectively.

At equilibrium, the chemical potential of water in the gas mixture, the a-phase, and the f-phase has to be equal. From these equilibrium conditions, by equating Eq. (28) with Eq. (19), the following equilibrium relationship is obtained

$$\theta(\alpha + \theta)\exp[\Delta\tilde{\varepsilon}] = \alpha(\sigma - \theta)\exp\left[\Delta\mathcal{F}(\circ)\right]. \tag{30}$$

where $\Delta\tilde{\varepsilon} = \beta(\varepsilon_f^o - \varepsilon_a)$, which is an adjustable parameter in this model.

The chemical potential of the water in the gas phase is estimated as

$$\tilde{\mu}_{\mathrm{w}}^{(g)} = \tilde{\mu}_{\mathrm{w}}^{ig} + \ln(\hat{\varphi}_{\mathrm{w}}^{v}) + \ln(y_{\mathrm{w}}), \tag{31}$$

where $\hat{\varphi}_{\mathrm{w}}^{v}$ is the fugacity coefficient for the water in the gas phase, which for low pressures can be assumed to have the value of unity and y_{w} is the water mole fraction in the gas mixture. Equating Eq. (28) with Eq. (31) produces

$$(\alpha + \theta)\mathcal{H}_{\mathrm{r}} = \alpha\exp\left[\Delta\mathcal{F}(\circ)\right], \tag{32}$$

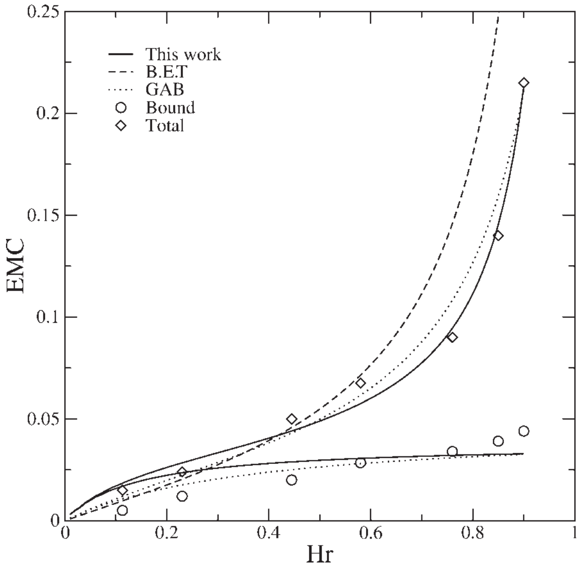

Figure 1. Water sorption isotherm for methyl cellulose films at 25°C.

Experimental data reported by Herrera-Gómez et al.[21] (circles and diamonds).

where $\mathcal{H}_r$ is the relative humidity defined as

$$\mathcal{H}_r = \frac{y_w P}{P_{sat}(T)}. \tag{33}$$

Equations (30) and (32) determine, for a given temperature, the equilibrium moisture content (i.e., $\alpha + \theta = \omega$) as a function of the water activity in the gas phase defined here as the relative humidity (design variable in laboratory setups). Notice that, these equations have to be solved simultaneously with a given set of parameters to obtain α and θ, which added equals to the EMC. To obtain the parameters from experimental data, an appropriate objective function has to optimized. A typical one would be to minimize the least-squares sum of the residuals between experimental measurements and predicted values of the EMC. There are many optimization methods that can be used, but the Marquardt–Levenger algorithm[20] seems to be reasonable for the examples presented in this work.

Results and Discussion

We apply the model to water sorption in two systems: (a) methyl cellulose and (b) municipal waste biosolids (sludge). For the first case, there is experimental data available including measurements of bonded and nonbonded water (sometimes called free water). Also, the system has been modeled using both the BET and GAB equations. The second system is quite different in nature in the sense that is highly heterogeneous and complex. Other systems such as natural and processed foods also present similar characteristics to waste biosolids in terms of the behavior of EMC as a function of the water activity. Therefore, we expect that this model will work well in food engineering applications as well. In general, water sorption isotherms in biomass type of materials tend to be type II typical of adsorption on macroporous adsorbents with strong interactions between the water and the biopolymer network. The bound water isotherm tend to be Langmuir type typical of microporous adsorbents or stronger adsorption energies.

Table 2. Parameters Obtained for the Equilibrium Model Described by Eqs. 30 and 32

Case Study	σ	$\Delta\tilde{\varepsilon}$	χ	v_{pw}
Methyl cellulose	0.038	−1.962	1.633	0.049
Municipal Sludge	0.044	−3.362	1.690	0.104

For the methyl cellulose case, the experimental data used to obtain the parameters are from Herrera-Gómez et al.[21] and, for the case of municipal activated sludge, the experimental data used are from Vaxelaire.[7]

Water-methyl cellulose

Herrera-Gómez et al.[21] provide experimental data and fitting parameters for both the BET and GAB models. Figure 1 shows a sorption isotherm for this system at 25°C, including both the total water adsorbed and bound water. We observe that the BET equation does poorly above relative humidities of 0.6 (which is expected) and the GAB model performs well modeling both the total and bound water for the full range. Our model (solid lines) also performs well. It seems that the fit of the total water by our model is better than GABs and the prediction for the bound water seems reasonable, although better with the GAB equation. Notice though that the bound water for our model is predictive; in other words, the experimental data reported for bound water was not used to regress the parameters of the model. Table 2 shows the parameter values regressed using the data reported by Herrera-Gómez et al.[21] Notice that the excess exchange parameter for adsorption ($\Delta\tilde{\varepsilon}$) has a reasonable value and it is close to the heat of solidification of water in magnitude. For the Flory-Huggins χ parameter, it is also reasonable and typical of a polymer structure in poor solvent conditions,

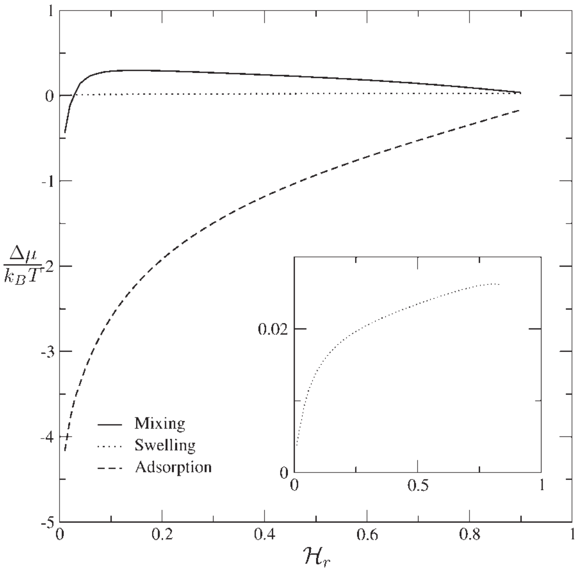

Figure 2. Contributions to the water chemical potential in the *f*-phase for the methyl cellulose case study [see Eq. 28 and Eq. 27 for details].

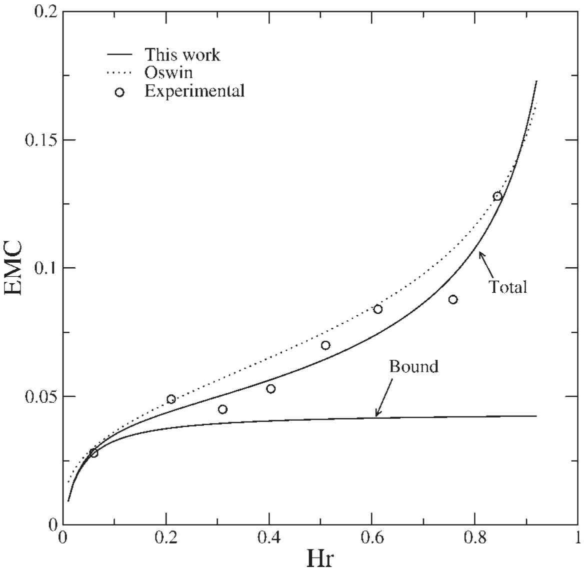

Figure 3. Desorption isotherm for activated municipal sludge at 39°C.

Experimental data reported by Vaxelaire[7] (circles). The parameters used for the Oswin model are also reported by Vaxelaire.[7]

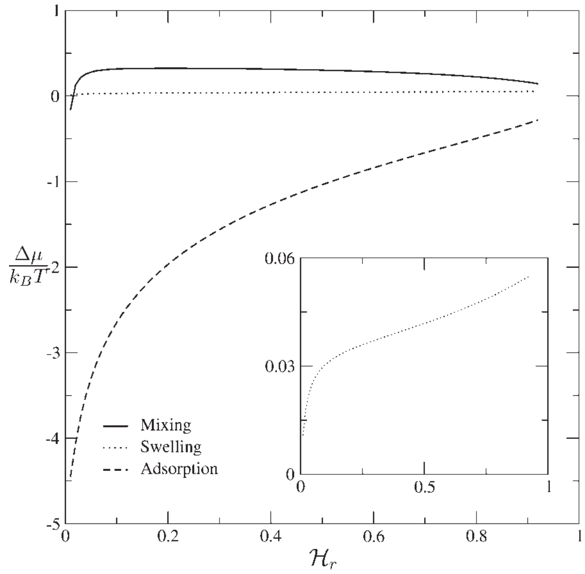

Figure 4. Contributions to the water chemical potential in the *f*-phase for the municipal sludge case study [see Eq. 28 and Eq. 27 for details].

which seems adequate in this case. Figure 2 shows the excess contributions to the chemical potential of water in the *f*-phase. The swelling contribution is small with respect to the other two, in particular, at low values of relative humidity. This suggests that it is possible to simplify the model even further by eliminating the swelling contribution, although does not reduce the number of adjustable parameters. The inset in Figure 2 shows the behavior of the swelling contribution as a function of the relative humidity, which seems to follow a logical qualitative behavior.

Activated municipal sludge

Vaxelaire[7] provides experimental data and parameters for different fitting models. For illustration purposes, we used the water sorption isotherm at 39°C only (any of the other isotherms can be used as well). Figure 3 shows the experimental data together with Vaxelaire's best fitting results using the Oswin model (see dotted line). The solid lines show the results of our model for both total and bound water. The results provided by Eq. (30) and Eq. (32) are excellent with more meaningful parameters from a physical standpoint (i.e., the parameters σ, v_{pw}, $\Delta\tilde{\varepsilon}$, and χ have a direct physical interpretation in the proposed model). Table 2 shows the parameters regressed using the experimental data reported by Vaxelaire.[7] The physical interpretation of the parameters in the Oswin model is not clear and it seems that the fit is not optimal for this particular isotherm.

Figure 4 shows the excess contributions to the chemical potential of water in the *f*-phase. As in the previous case study, the swelling contribution small (dotted line) compared with the other two. The inset shows the behavior of the swelling contribution as a function of the relative humidity. The qualitative trend of this contribution seems logical in the sense that it increases with water activity, in particular, in the lower range of the relative humidities and it slows down at higher values.

The solution of Eqs. (30) and (32) also provides the equilibrium biomass volume fraction (i.e., ϕ_{e} is the value of ϕ_{p} at equilibrium). Figure 5 shows the behavior of ϕ_{e} for both case studies. The trends seem reasonable qualitatively with appropriate asymptotic behavior.

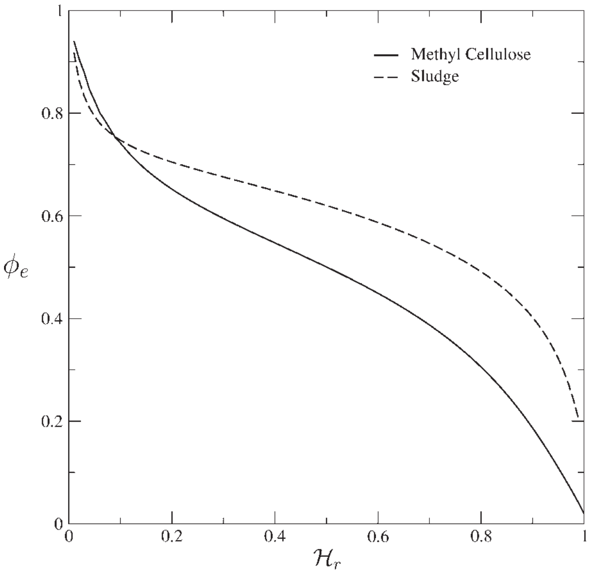

Figure 5. Estimated methyl cellulose and municipal sludge equilibrium volume fractions.

Concluding Remarks and Future Work

We have proposed a simple model based on combining standard molecular thermodynamic approaches and statistical mechanics to model equilibrium moisture content as a function of water activity in biomass materials such as municipal sludge and foods. The model attempts to consider both bonded and nonbonded interactions of the water with the substrate. Although the model is basic, it captures the behavior of water in this type of systems and it can be used to fit experimental data with parameters that provide more physical insight of the water activity in these type of systems. In general, the model works well when compared with traditional models used for the same purpose, it has relatively few parameters and it has significant potential for improvements by adding components describing in more detail the water interactions with this type of substrates.

Fundamentally, the model can be improved in several ways. For instance, one could use the GAB approach by adding more characteristic molecular energy parameters to describe the different water interactions in the biomass network or one could specify in more detail the contributions to the Helmholtz free energy in the *f*-phase [see Eq. (11) for details]. Among additional contributions to take into account include pH, ionic conditions, and surface tension (γ) to obtain an expression of the form

$$A^{(f)} = A_{\mathrm{w}}^{\mathrm{o}} + \Delta A_{\mathrm{mix}} + \Delta A_{\mathrm{swl}} + \Delta A_{\mathrm{ads}} + \Delta A_{\mathrm{pH}} + \Delta A_{\mathrm{ion}} + \Delta A_{\gamma}. \tag{34}$$

This type of improvement can be very useful for practical applications because it can provide more insight on how to manipulate the EMC more efficiently in this type of substrates. Additionally, the model can be improved by using a better model to describe the biomass structure. At present, we use an ideal lattice model to describe the biomass mixing with water, which can be replaced with a more realistic model for this type of materials. A possibility is to use random polymer network models such as a Gaussian network. From a practical perspective, it seems that modifications to Eq. (11) might provide more immediate benefits in terms of applications. We are in process of exploring some of these ideas and also we are studying the use of our model in food engineering applications.

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Notation

List of symbols

A = Helmholtz free energy
R = ideal gas law constant
T = temperature
P = pressure
Q = partition function
a = activity
h = Max Planck constant
q = partition function
y = gas phase mole fraction
kJ = kilo-Joules
k_{B} = Boltzmann constant
$\mathcal{H}_r$ = relative humidity

Greek letters

α = water adsorbed–nonbonded
θ = water adsorbed–bonded
ω = total water adsorbed
σ = number of adsorbing sites
δ = expansion factor
ϕ = polymer fraction
χ = Flory-Huggins parameter
ε = molecular potential energy parameter
β = inverse of Boltzmann constant
v = characteristic vibration frequency
ξ = network cycle rank
Ψ = functionality of the network
γ = constant, surface tension

Subscripts and superscripts

mix = mixing
swl = swelling
ads = adsorption
sat = saturated
f = indicates phase
o = indicates pure state
p = polymer
ig = ideal gas
a = indicates phase
w = water

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