Modeling surface charge and cation binding in humic substance extracted from the bottom sediments of Bayou Plaquemine Brule in Louisiana.

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INTRODUCTION

Humic substances in stream sediments is considered the key factor to control dissolved oxygen demand, pollutant binding, metal speciation, and nutrient availability in agricultural watershed. Humic substances are proposed to be irregular polymers with a number of chemically non-identical acidic functional groups with a variable electrical potential. The acidic functional groups of humic substances have been considered as the reactive groups for protons and metal ions in acid-base equilibrium reactions. The degree of acidity, or acid strength, of the colloid depends on the nature of the reactive group involved and of associated structures on the molecule, and the acidic character of humic substances which is usually attributed to ionization of COOH and phenolic OH groups (Jeong et al., 2007).

This study was conducted to compare the binding characteristics of proton and metal ion to humic acid extracted from sediment samples. Sediment samples from Bayou Plaquemine Brule watershed, main channel and tributaries were extracted by a modified IHSS procedure to isolate the humic substances as related to the different agricultural watersheds. In order to describe proton and metal binding with humic acid it is necessary to develop models in which various simplifications are made because of the complex heterogeneous nature of the humic material and the variable electrostatic interaction between functional groups. The simplified discrete binding group type of model (Model A) was applied to this binding study. Model A considered only a single carboxyl group type and a single phenolic hydroxyl group type with a variable electrostatic interaction factor that is expressed as a polynomial equation (Jeong et. al., 2007). Binding behaviors of proton and Cu binding with humic acid extracted from different sites were compared.

MATERIAL AND METHODS

Sampling sites

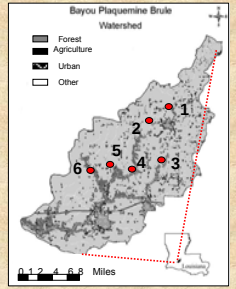

Figure 1. Sediment sampling sites in Bayou Plaquemine Brule Watershed.

Batch Titrations

The volume of titrant was increased by 0.05 mL at each step up to 2.00 mL in duplicate. Ten millimeter samples of the humic stock solution were added to each bottle. Each bottle was flushed and sealed with the N2 gas and stored at 20 °C for 7 days in the dark. The bottles were shaken manually once a day. After 7 days, the pH of the sample solution was measured under the N2 gas.

Metal binding

The batch experimental procedure was used to measure metal ion binding to the humic acid by the dialysis equilibrium. The dialysis membrane (molecular weight cut-off = 8,000) has small pores through which hydrated and free metal ions may migrate into the dialysis bag, while complexed metal ions are excluded. Thus, the concentration of free metal ions in the internal solution is the same as that in the external solution. Therefore, the concentration of free metal ions in the internal solution can be measured easily.

Surface Charge Calculation

The surface charge on humic acid is estimated using the ion charge balance which is derived from the titration data (pH, titrant volume). The distribution of ions between the double layer and the bulk solution are considered in the model calculations. As a result of this method, a more refined calculation may be applied to humic charge expressions. Tipping and Hurley (1992) expressed the volume of the DDL (liters per gram of humic substances) by the following equation:

$$V_D = \frac{10^3 N}{M}\frac{4\pi}{3}\left[(r+1/k)^3 - r^3\right] \qquad [1]$$

where k is the Debye-Huckel parameter (m^{-1}) and is approximately $3.29\times10^8\sqrt{I}$, N is Avogadro's number, r is the radius of humic molecule, and M is the humic molecular weight. The assumed value of the molecular weight was 15000, and the radius of the humic molecule was $1.72\times10^{-8}\,m$ (Tipping and Hurley, 1992).

The calculation of the concentration of NO_3^- in the bulk solution, $[NO_3^-]_B$, is calculated from the total concentration of $NaNO_3$ and HNO_3, assuming that the NO_3^- is confined to the volume outside the DDL.

$$[NO_3^-]_B = ([NaNO_3]+[HNO_3])\left(\frac{V_T}{V_B}\right) \qquad [2]$$

where V_T is the total solution volume and V_B is the bulk solution volume.

The amount of sodium in the DDL ($\langle Na^+\rangle_D$) is calculated by the difference between the total amount of sodium and the amount of sodium in the bulk solution.

$$\langle Na^+\rangle_D = ([NaOH]+[NaNO_3])V_T - \langle Na^+\rangle_B \qquad [3]$$

where the amount of sodium in bulk solution, $\langle Na^+\rangle_B$, may be calculated from:

$$\langle Na^+\rangle_B = [Na^+]_B(V_T - V_D) \qquad [4]$$

The concentration of sodium in the bulk solution is calculated from a charge balance:

$$[Na^+]_B = [NO_3^-]_B + [OH^-]_B - [H^+]_B \qquad [5]$$

The concentration of sodium in the DDL can be expressed:

$$[Na^+]_D = \frac{\langle Na^+\rangle_D}{V_D} \qquad [6]$$

The concentration of hydrogen ions in the DDL, $[H^+]_D$, can be derived from a Donnan equation:

$$\frac{[H^+]_D}{[H^+]_B} = \left(\frac{[M^{z+}]_D}{[M^{z+}]_B}\right)^{\frac{1}{z}} \qquad [7]$$

Thus,

$$[H^+]_D = \frac{[Na^+]_D[H^+]_B}{[Na^+]_B} \qquad [8]$$

and so absolute value of the humic surface charge (cmolc Kg^{-1}) can be calculated from:

$$|Z| = \frac{([H^+]_D + [Na^+]_D)V_D}{[HA]V_T} \qquad [9]$$

Equation 9 assumes that and are only counterions.

Model A: Proton binding

The total acid group concentration (T_A) was measured from the humic acid. The total phenolic hydroxyl group concentration was calculated by the difference between the total acid group concentration (T_A) and the total carboxyl group concentration (T_C). Thus, the equation for net humic surface charge ($|Z|$, cmolc Kg^{-1} HA) is as follows:

$$|Z| = \frac{K_{int}^{C}\exp(2\omega Z)(H^+)^{-1}T_C}{1+K_{int}^{C}\exp(2\omega Z)(H^+)^{-1}} + \frac{K_{int}^{\phi}\exp(2\omega Z)(H^+)^{-1}(T_A - T_C)}{1+K_{int}^{\phi}\exp(2\omega Z)(H^+)^{-1}} \qquad [10]$$

where K_{int}^{C} and K_{int}^{ϕ} are the intrinsic constant of the carboxyl group and the phenolic hydroxyl group, respectively, and ω is the electrostatic interaction factor.

The two intrinsic acidity constants, carboxylic group and phenolic hydroxyl group (K_{int}^{C} and K_{int}^{ϕ}) were described as a third-order polynomial function of the square root of ionic strength ($\sqrt{I}$) and the electrostatic interaction factor,, was calculated as a linear function of .

Model A: Metal binding

Metal ion binding to humic acid is considered as a metal ⇔ proton exchange reaction. The electrostatic interaction factor in Model A is considered specific to the binding ion. A mechanistic explanation for this may be that different ions specifically adsorb in slightly different 'planes' relative to the humic acid surface. Therefore, a given surface charge may correspond to a range of 'ion-specific' potentials in several adsorption planes. We therefore denote the electrostatic interaction factor as *WH* or *WM* for protons or specific metal ions. These are related by a proportionality factor *FW*, such that:

$$W_M = F_W W_H \qquad [11]$$

Model A can describe 4 different types of metal binding sites: 1 carboxyl group; 1 phenolic hydroxyl group; 2 carboxyl groups; and 1 carboxyl group & 1 phenolic hydroxyl group. The concentration (mol$_c$ g^{-1}) of bound metal complexes is denoted as [*M*] with the subscripts *C* or ϕ to signify a combination with one or more carboxyl or phenolic hydroxyl groups, respectively.

The proportion of free carboxyl groups present in the protonated form, is given by:

$$P_{CH} = \frac{1}{1+K_{int}^{C}\exp(2wZ)(H^+)^{-1}} = \frac{[CH]}{[C^-]+[CH]} \qquad [12]$$

When 1 carboxyl and 1 phenolic hydroxyl group binding is considered, the concentration of metal bound to monodentate sites may be calculated from:

$$[M]_C = \frac{\beta_{int}^{M,C}\exp((2wZ)(1-F_W z))P_{CH}[M^{z+}](H^+)^{-1}(1-P_{\phi C})(T_C(1-P_{CC}))}{1+\beta_{int}^{M,C}\exp((2wZ)(1-F_W z))P_{CH}[M^{z+}](H^+)^{-1}} \qquad [13]$$

The concentration of metal bound to bidentate sites consisting of 1 carboxyl and 1 phenolic hydroxyl group may be calculated from:

$$[M]_{C\phi} = \frac{\beta_{int}^{M,C}\beta_{int}^{M,\phi}\exp((2wZ)(2-F_W z))P_{CH}P_{\phi H}[M^{z+}](H^+)^{-2}P_{\phi C}T_C(1-P_{CC})}{1+\beta_{int}^{M,C}\beta_{int}^{M,\phi}\exp((2wZ)(2-F_W z))P_{CH}P_{\phi H}[M^{z+}](H^+)^{-2}} \qquad [14]$$

Similarly, the concentration of metal hydroxide ions considered only in monodentate binding sites is calculated as the above equations for metal bivalent ions.

The concentration of metal counter-ions in the DDL was included in Model A:

$$[M]_{ID} = \frac{([M^{z+}]_D + [MOH^{+}]_D)([HA]V_T - [HA]_{bound}V_{bulk})}{[HA]V_T} \qquad [15]$$

The total concentration of bound metal may be calculated from the sum of all occupied binding sites and the DDL metal counter-ions:

$$[M]_{bound} = [M]_C + [M]_\phi + [M]_{CC} + [M]_{C\phi} + [MOH]_C + [MOH]_\phi + [M]_D \qquad [16]$$

The optimization of model parameters was achieved using the Marquardt procedure (Press et al., 1990) to minimize the residual standard deviations (RSD);

$$RSD = \sqrt{\frac{\sum(observedvalue - predictedvalue)^2}{N - numberof\ parameters}} \qquad [17]$$

where, *N* is number of data points.

RESULTS AND DISCUSSION

The analysis of proton binding affinity on the humic surfaces is a first step to understand the behavior of the specifically adsorbing ions on humic surfaces because the proton is the primary adsorbing species for humic substances under environmental condition. The results displayed in table 1 showed the model A resolved equations for the intrinsic acidity constants and electrostatic interaction factor. The value of total acidity (TA) was relatively higher at site 5, and the model resolved value of total carboxylic acid (TCOOH) was relatively higher at site 6. However, humic sample from site 1, the upstream of Bayou Plaquemine Brule, showed relatively lower TCOOH contents.

Table 1. Resolved polynomial expressions for the variation in the intrinsic acidity constants and linear equation for electrostatic factor as a function of ionic strength (*I*).

	TA (mol$_c$ Kg^{-1})	TCOOH (mol$_c$ Kg^{-1})	pK_{int}^{C}	pK_{int}^{ϕ}	W	RSD
Site 1	4.81	1.99	1.50 - 0.10 $I^{1/2}$ + 0.10 I - 0.31 $I^{3/2}$	5.68 – 0.10 $I^{1/2}$ + 1.69 I - 1.01 $I^{3/2}$	818 – 10 log_{10} I	0.179
Site 2	4.82	2.45	4.46 - 0.11 $I^{1/2}$ + 0.44 I – 1.03 $I^{3/2}$	7.65 – 1.27 $I^{1/2}$ + 1.33 I – 0.13 $I^{3/2}$	1269 – 10 log_{10} I	0.123
Site 3	4.69	2.37	4.61 - 0.86 $I^{1/2}$ + 0.71 I – 0.68 $I^{3/2}$	5.74 – 1.50 $I^{1/2}$ + 6.22 I – 1.01 $I^{3/2}$	1229 – 10 log_{10} I	0.178
Site 4	4.41	2.36	1.28 – 1.02 $I^{1/2}$ + 1.01 I – 1.08 $I^{3/2}$	5.18 – 0.48 $I^{1/2}$ + 0.14 I – 0.18 $I^{3/2}$	912 – 51 log_{10} I	0.172
Site 5	4.91	2.61	3.83 – 0.19 $I^{1/2}$ + 0.35 I – 0.86 $I^{3/2}$	5.47 – 1.02 $I^{1/2}$ + 5.95 I – 1.02 $I^{3/2}$	1476 – 11 log_{10} I	0.139
Site 6	4.89	2.79	2.82 – 0.11 $I^{1/2}$ + 0.24 I – 1.01 $I^{3/2}$	3.47 – 0.11 $I^{1/2}$ + 4.53 I – 1.01 $I^{3/2}$	1778 – 12 log_{10} I	0.176

TA : Total Acidity, TCOOH : Total carboxylic acid content, pK_{int}^{C} : negative log of the intrinsic dissociation of carboxylic groups, pK_{int}^{ϕ} : negative log of the intrinsic dissociation of carboxylic groups, W : electrostatic factor.

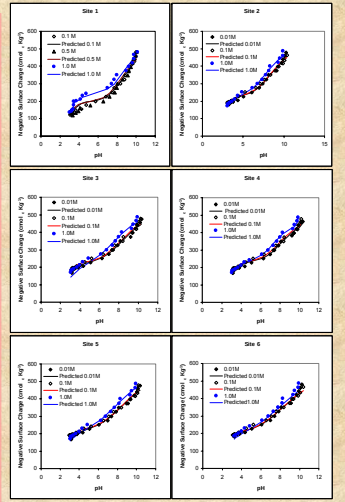

Figure 1. Plots of humic surface charge against pH as a function of ionic strength ($NaNO_3$).

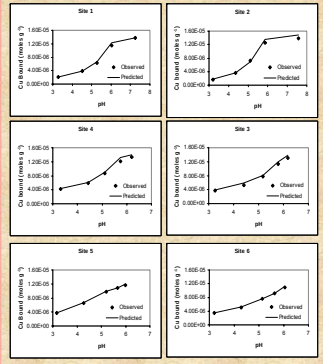

Figure 2. Model A applied to Cu binding to humic acid. Data is presented in Cu bound as a function of pH. One fixed Cu concentration (1.57 X 10^{-4} M) was used and pH was varied.

The surface charge (cmol$_c$ Kg^{-1}) on the humic acids became more negative as the ionic strength increased (Figure 1). The solid lines present the fit of model A using all three titrations analyzed as a single combined data set for 6 different humic acids. Model provided a good representation of batch titrations (Table 1).

Figure 2 shows Cu bound as a function of pH using Model A applied to different humic acid samples. At low pH, relatively lower Cu binding showed in site 1 and 2, the upstream of Bayou Plaquemine Brule.

Combined Cu binding data (site 1 to 6) was applied to model, and resolved overall metal – proton exchange constants for sediment humic acid from the Bayou Plaquemine Brule (Figure 3).

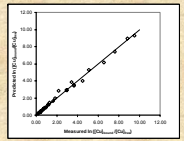

Figure 3. Model A applied to unified Cu binding data (site 1 to 6). Cu was the only metal present. The bound species considered included: CuC, CuCC, and CuCΦ. The background electrolyte was 0.1 M $NaNO_3$. Data are presented as ln ([Cu]$_{bound}$/[Cu]$_{free}$), measured vs. predicted. The concentration of Cu$_{bound}$ includes all Cu-HA complex forms and Cu held as a counter ion; Cu$_{free}$ includes all free inorganic species. The values of optimized model A parameters were: $pK_{int}^{M,C}$ = 1.02, $pK_{int}^{M,\phi}$ = 4.54, P_{CC} = 0.098, $P_{\phi C}$ = 0.485 and F_W = 0.197. The solid line indicates a 1:1 relationship; RSD = 0.219, n=30.

CONCLUSIONS

The elucidation of the proton affinity on humic acids extracted from the different location of bottom sediments showed unique trends of humic surface charge. There was a good agreement between experimental data and model fit, and the resolved value of TCOOH was relatively higher at site 6.

The results of Cu binding to humic acid with varied pH showed the different trends of Cu binding from Bayou Plaquemine Brule watershed. Humic samples from the down stream and tributaries showed more strong Cu binding on the surface at lower pH condition.

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