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SUPPLEMENTARY INFORMATION

Humic-like Substances from Urban Waste as Auxiliaries for Photo-Fenton Treatment: a Fluorescence EEM-PARAFAC Study

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Table S1. Fluorescence characteristics of EEMs spectroscopy components from PARAFAC model.

Component	pH 3 (Ex /Em)	pH 5 (Ex /Em)	pH7 (Ex /Em)	Description
C1	315 / 405	310 / 410	320 / 430	humic-like fraction of organic matter from microbial production
C2	340 / 480	355 / 495	365 / 505	humic-like substances from terrestrial organic matter
C3	285 / 345	285 / 350	285 / 385	Amino acid (tryptophan-like)

Complexation Modeling

The binding parameters between fluorescent components derived from PARAFAC and Fe(III) were determined using a modification of the complexation model reported by Ryan and Weber.[3] This model has been extensively used for describing metal ion binding to humic substances. [4, 5] PARAFAC decomposes the complex mixture of HLS fluorophores into independent fluorescent components; hence the application of a binding model to the individual PARAFAC components is more descriptive than the application of the Ryan and Weber equation to a single condition of excitation/emission wavelength. PARAFAC analysis of EEMs obtained for HLS in the presence of different Fe(III) concentrations shows that, within the experimental domain analyzed, the relative emission profiles of the most significant components can be described by assuming two contributions to the fluorescence

$$\frac{I}{I_0} = \frac{I_q}{I_0}\left(1 - f\right) + \frac{I_{nq}}{I_0} \tag{1}$$

where ***I₀*** is the intensity of HLS solutions without added Fe(III), ***I*** is the intensity recorded at a given metal concentration, ***I_q*** is the fluorescence intensity quenchable by ferric ions, ***f*** is the fraction of ***I_q*** quenched at a given metal concentration, and ***I_{nq}*** is the fluorescence intensity that is unaffected by the presence of iron.

In order to obtain the dependence of ***f*** with iron concentration, we assumed that the quenchable fluorescence is due to the formation of 1:1 complexes between ferric ions and fluorescent-active binding sites on HLS.

$$K = \frac{[MH]}{[M][H]} \tag{2}$$

where ***K*** denotes the conditional stability constant at a given pH and ionic strength, ***[MH]*** is the molar concentration of complexed active sites, ***[M]*** is the concentration of ferric cations not bounded to HLS fluorescent-active sites, and ***[H]*** is the concentration of quencheable fluorescent-active sites on HLS not bounded to ferric cations. Thus ***f*** can be written as:

$$f = \frac{[MH]}{[H]_0} \tag{3}$$

where H_0 is the total concentration of fluorescence-active sites of HLS. Taking into account the mass balance equations for both the metal and the fluorescent-active sites on HLS that are accessible to iron cations, it can be easily shown that the value of ***f*** is given by

$$f = \frac{\left(K\left(H_0 + M_0\right) + 1\right) - \sqrt{\left(K\left(H_0 + M_0\right) + 1\right)^2 - 4K^2 H_0 M_0}}{2KH_0} \tag{4}$$

where M_0 is the metal concentration. Combining eq. 1 and eq. 4 is possible to derive the following equation:

$$\frac{I}{I_0} = 1 + \left(\frac{I_{nq}}{I_0} - 1\right)\frac{(KH_0 + KM_0 + 1) - \sqrt{(KH_0 + KM_0 + 1)^2 - 4K^2H_0M_0}}{2KH_0} \quad (5)$$

Nonlinear fitting was applied on the fluorescence data recorded at different Fe(III) concentration to estimate K, H_0 and I_{nq} values.

References:

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