

SUPPORTING INFORMATION

Characterization of Adsorption of Humic Acid onto Alumina using Quartz

Crystal Microbalance with Dissipation

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The humic acid (HA) used in the experiment was a commercial HA extracted from Yellow River sediment. It was further fractionated by ultrafiltration and resin adsorption (1). Additionally, the HA had previously been characterized well by Yanmei Zhou and Hongxiao Tang. The results of elemental analyses, CPMAS ^{13}C NMR Spectroscopy, and ^1H NMR Spectrometry were previously published in a Ph.D. dissertation by Zhou in Chinese (2). The data is presented in the Supporting Information, as well.

Ultrafiltration. Hollow-fiber modules and ultrafiltration membranes (A/G Technology) with nominal molecular weight cut-offs of 30, 3 and 1 kilo-Dalton (kDa) were used to sequentially fractionate dissolved organic matter (DOM). The membranes were made of cellulose derivatives with a total surface area of 24 cm^2 . The applied pressure through the membranes ranged from 250 to 350 kPa. The total organic carbon (TOC) of the effluent from each membrane and of the raw water were measured to determine the content of each cumulative fraction. The HA could be divided into three types, $< 30\text{ kDa}$, $< 3\text{ kDa}$, and $< 1\text{ kDa}$. The results are shown in Figure S1.



FIGURE S1. Molecular weight distribution of HA characterized by ultrafiltration.

Resin adsorption. Amberlite XAD-8 resin was used to fractionate DOM following the procedures of Thurman and Malcolm (3) and Malcolm and MacCarthy (4). Water samples were directed to an XAD-8 packed column. The HA in the effluent was hydrophilic in nature, and the fractions where absorption by the resin occurred were hydrophobic in nature. The latter was recovered by backwashing the column with 0.1 M H_3PO_4 and NaOH. The columns were 3-cm-diameter and 30-cm-height glass chromatographic columns with PTFE caps. A constant flow rate of 100 mL min^{-1} through each column was maintained using peristaltic pumps. The results are shown in Figure S2.

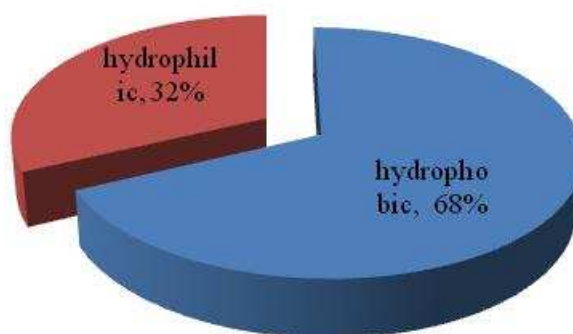


FIGURE S2. Polarity distribution of HA characterized by resin adsorption.

Elemental analyses. Elemental analyses of HAs were determined in triplicate with a total organic carbon analyzer (Apollo 9000, Tekman-Dohrmann Co., USA) and Vario EL Elemental Analyzer (Elementar Co., Germany), respectively. The DOC, carbon,

hydrogen, nitrogen, and oxygen contents along with the O/C and H/C ratios are listed in Table S1.

TABLE S1. DOC, Carbon, Hydrogen and Oxygen Contents and O/C and H/C Ratios of HA.

DOC (%)	C (%)	H (%)	O (%)	O/C ^a	H/C ^a
0.87	62.53	4.80	32.34	0.39	0.92
^a Atomic ratio					

CPMAS ¹³C NMR Spectroscopy. CPMAS ¹³C NMR spectra of solid HA were measured on a Bruker Advance 300 MHz NMR-spectrometer (Breker Analytic GmbH, Germany) equipped with a 4 mm rotor. The experimental parameters were as follows: ¹H frequency of 300 MHz and 75 MHz for ¹³C; spinning rate of 13 KHz; contraction time of 2 ms; recycle delay time of 1 s; sweep width of 27 KHz (368 ppm); and line broadening of 100 Hz. The spectra were divided into the following chemical shift regions: 0-40 ppm, alkyl carbon (C); 40-100 ppm, alkyl-O or C-O, C-N bonds as in alcohols, ethers, carbohydrates and amines; 100-140 ppm, aromatic C; 140-165 ppm, phenolic C; 165-185 ppm, carboxyl and amide C; and 185-220 ppm, aldehyde and ketone C. The region 0-40 ppm pulsing 100-140 ppm was considered as nonpolar C, and the combined fraction of 40-100 ppm and 140-185 ppm presented the polar C. The region from 0-100 ppm presented aliphatic C while 100-165 ppm consisted of aromatic C. The hydrophobic index was the ratio of nonpolar C content to polar C content, and total aromaticity and aliphaticity were calculated by dividing the fraction

of aromatic C and aliphatic C by the sum of the fraction of all components of C, respectively. The CPMAS ^{13}C NMR spectra of HA are shown in Figure S3, and the analyzed results are presented in Table S2

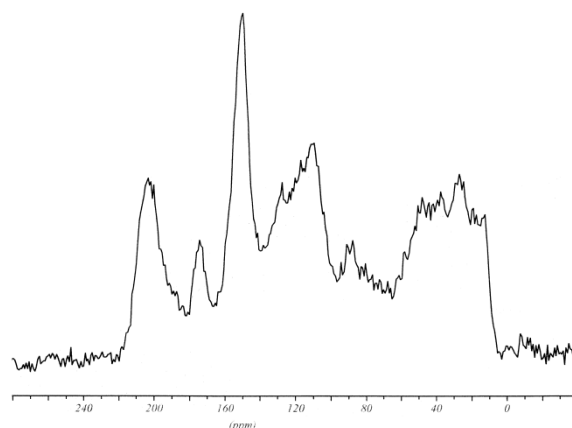


FIGURE S3. CPMAS ^{13}C NMR spectra of HA.

TABLE S2. Distribution of Carbon Intensity in Different Regions of CPMAS ^{13}C NMR Spectra of HA as a Present of Total C.

alkyl	alkyl-O	aromatic	phenolic	carboxyl	carbonyl	hydrophob	Aroma	Alipha
(0-40	(40-100	(100-140	(140-165	(165-185	(185-220	ic index ^a	ticity ^b	bicity ^c
ppm)	ppm)	ppn)	ppm)	ppm)	ppm)			
17.8	23.1	23.9	17.0	5.3	12.4	0.92	41.1	41.1
^a [(0-40)+(100-140)]/[(40-100)+(140-185)]; ^b (100-165)/(0-240); ^c (0-100)/(0-240)								

^1H NMR Spectrometry. 0.01 g humic acid sample and 1 ml 99.9 % D_2O were continuously mixed on a shaker for 60 h, and afterwards the mixture was centrifuged for 30 min at 2000 rpm. ^1H NMR spectra of the supernatants were obtained (Avance

DPX 500MHz NMR-spectrometer, Bruker Analytic GmbH, Germany) under the following experimental conditions: probe diameter of 5 mm; recycle delay time of 1 s; sweep width of 8012 Hz (16 ppm); line broadening of 3.00 Hz; scan number of 1000; and a detection temperature of 295 K. A water gate sequence was used to depress the resonance of water (4.704-4.706 ppm). The spectra were integrated according to the following regions: alkyl (0-1.6 ppm), nonpolar substituted alkyl and acetylene (1.6-3.0 ppm), polar substituted alkyl (3.0-4.0 ppm), polar aromatic and olefinic (4.0-6.5 ppm), nonpolar aromatic (6.5-8.5 ppm), and carboxyl and aldehydes (8.5-10 ppm). The absolute contents of H-containing function groups equaled the product of relative contents and DOC contents. The regions consisting of 0-0.3 ppm combined with that of 6.5-8.5 ppm were considered as nonpolar groups, and the region of 3.0-6.5 ppm was considered as polar groups. 0-4.0 ppm presented the aliphatic groups contents while 4.0-8.5 ppm contained the aromatic contents. The ^1H NMR spectra of HA are shown in Figure S4, and the analyzed results are presented in Table S3.

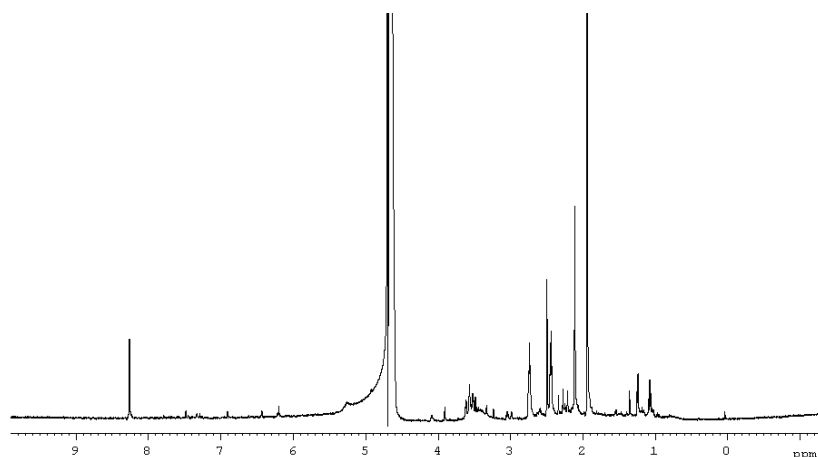


FIGURE S4. ^1H NMR spectra of dissolved fraction contained in HA.

TABLE S3. ^1H NMR Integration Results of Dissolved Fraction Contained in HA.

nonpolar aliphatic (0-3.0 ppm)	polar aliphatic (3.0-4.0 ppm)	phenolic (4.0-6.5 ppn)	aromatic (6.5-8.5 ppm)	Carboxyl/ aldehyde (8.5-10.0 ppm)	hydrop hobic index ^a	Aroma ticity ^b	Aliphatic icity ^c
15.4	2.1	82.0	0.5	NA ^d	0.19	82.5	17.5

^a [(0-3.0)+(6.5-8.5)]/[(3.0-6.5)+(8.5-10.0)]. ^b (4.0-8.5)/(0-10.0). ^c (0-4.0)/(0-10.0). ^d Not analyzed.

Literature Cited

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