**Supplementary materials**

Table S1 Abiotic humification reaction conditions for 12 SHLAs.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| HA  Samples | Catechol  /mol/L | Glycine  /mol/L | Glucose  /mol/L | Temperature  /℃ | pH | MnO2 addition amount/g | Reaction time |
| SHLA1 | 1 | 1 | - | 45 | 7 | 13.33 | 24 h |
| SHLA 2 | 1 | 1 | 1 | 45 | 7 | 13.33 |
| SHLA 3 | 0.5 | 0.5 | - | 45 | 7 | 13.33 |
| SHLA 4 | 0.25 | 025 | - | 45 | 7 | 13.33 |
| SHLA 5 | 0.5 | 1 | - | 45 | 7 | 13.33 |
| SHLA 6 | 0.25 | 1 | - | 45 | 7 | 13.33 |
| SHLA 7 | 1 | 1 | - | 25 | 7 | 13.33 |
| SHLA 8 | 1 | 1 | - | 35 | 7 | 13.33 |
| SHLA 9 | 1 | 1 | - | 45 | 6 | 13.33 |
| SHLA 10 | 1 | 1 | - | 45 | 8 | 13.33 |
| SHLA 11 | 1 | 1 | - | 45 | 7 | 25 |
| SHLA 12\* | 0.25 | 0.25 | - | 25 | 8 | 25 |  |

(\*The condition used to synthesize SHLA 12 were determined on the basis of the initial 11 SHLAs’ COOH contents.)

**The method for extracting and purifying SHLA**

The reaction mixture was centrifuged at 10,000 rpm for 10 minutes, and the supernatant filtered through a 0.45 μm polyethersulfone membrane by vacuum filtration. The filtrate was acidified to pH 1 with concentrated HCl and stirred for 24 h. The SHLA fraction precipitated. The slurry was centrifuged at 10,000 rpm for 15 minutes. The precipitate was transferred to a beaker, re-dissolved in 0.1 M NaOH and filtered through a 0.2 μm polyethersulfone membrane twice by vacuum filtration. The filtrate was acidified to pH 1 with concentrated HCl, stirred for 24 h and centrifuged at 10,000 rpm for 15 minutes. The resulting precipitate (SHLA) was dialyzed by a Spectra/Por 6 dialysis membrane (Spectrum Labs, USA, molecular weight cut-off (MWCO) 1000 Da) and freeze-dried.



Figure S1 Desorption efficiency for different eluents (SHLA dose 35 mg/35 mL, Cu2+ concentration of 50 mg/L, ionic strength of 0.1M NaNO3, pH of 5, and T=25 ℃ resulting in a Cu2+ loading of 36.59±0.15 mg/kg on the SHLA; mean values, n=3 ± standard deviation).

Table S2 Acidic functional group contents of 12 SHLAs.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | COOH (mmol/g) | Phenolic-OH (mmol/g) | Total acidity (mmol/g) |
| SHLA1 | 4.10 | 8.61 | 12.72 |
| SHLA 2 | 3.64 | 12.26 | 15.90 |
| SHLA 3 | 4.61 | 6.72 | 11.32 |
| SHLA 4 | 4.83 | 7.41 | 12.24 |
| SHLA 5 | 4.57 | 9.53 | 14.10 |
| SHLA 6 | 4.62 | 8.92 | 13.54 |
| SHLA 7 | 4.81 | 7.86 | 12.67 |
| SHLA 8 | 4.31 | 8.54 | 12.85 |
| SHLA 9 | 4.33 | 9.29 | 13.62 |
| SHLA 10 | 4.66 | 11.55 | 16.21 |
| SHLA 11 | 4.59 | 14.61 | 19.19 |
| SHLA 12 | 5.03 | 6.55 | 11.58 |

Table S3. Assignments of FTIR absorption bands present in the spectra for SHLA 12 (Stevenson, 1994; Jokic et al., 2004; Fukushima et al., 2009; Hardie et al., 2009; Shiotsuka et al., 2015; Stuart, 2004).

|  |  |
| --- | --- |
| Wavenumber/cm-1 | Assignment |
| 2918 | C-H stretching of aliphatic structures |
| 2121 | C≡C stretching and the presence of cyano group |
| 1717 | C=O stretching of carbonyl groups |
| 1579 &1488 | C=C ring stretching, symmetric C–O stretch of COO- and N-H deformation and C=N stretching (amide II band) |
| 1382 | O-H deformation of phenols, C-H deformation, symmetric and asymmetric stretching of CH3 and C-O stretch of COO- |
| 1179 | C–O stretching and C–O–H deformation of alcohols, phenols and ethers |

The adsorption process of Cu2+ onto SHLA was divided into both 2 stages and 3 stages at first (Figure S1). Then the intra-particle diffusion rate constant *kid* and the intercept *C* calculated from the second portion of plot of qt versus t0.5 were calculated and shown in Table S4. Although there is a slight decrease in p value between the two- and three- stage model, the higher R2 values of the three stage model lead us to adopt that model for our data.



(a)



(b)

Figure S2 Intraparticle diffusion models for 2 stages (a) and 3 stages (b) with different HA doses.

Table S4 Intraparticle diffusion rate constant (kid) and C values for the adsorption of Cu2+ onto SHLA at SHLA doses (estimated values ± standard deviation).

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Two stage model | | | | |  | Three stage model | | |
| SHLA dose (g/L) | | kid | C | R2 | p | kid | C | R2 | p |
| 0.5 | | 0.375±0.092 | 21.4±0.9 | 0.7691 | <0.01 | 0.773±0.144 | 18.8±1.0 | 0.9349 | <0.05 |
| 1 | | 0.653±0.109 | 27.0±1.2 | 0.8774 | <0.01 | 1.134±0.127 | 23.9±0.9 | 0.9755 | <0.05 |
| 2 | | 0.651±0.115 | 35.56±1.2 | 0.8649 | <0.01 | 1.155±0.150 | 32.3±1.1 | 0.9676 | <0.05 |

Table S5 Fitted isotherms of Cu2+ onto SHLA by bi-Langmuir model.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Temperature  /℃ | qm,1  (mg/g) | KL,1  (L/mg) | qm,2  (mg/g) | KL,2  (L/mg) | R2 | p |
| 25 | 20.77±1.58 | 4.338±0.719 | 27.92±1.44 | 0.0892±0.014 | 0.9995 | <0.0001 |
| 35 | 24.21±2.69 | 3.807±0.930 | 37.38±2.23 | 0.0501±0.012 | 0.9990 | <0.0001 |
| 45 | 26.41±4.66 | 3.969±1.591 | 39.98±3.74 | 0.0442±0.019 | 0.9971 | <0.0001 |



Figure S3 Metals removal efficiency of SHLA in multi-metal systems at different initial metal mole concentrations

**References**

Fukushima, M., Miura, A., Sasaki, M., Izumo, K., 2009. Effect of an allophanic soil on humification reactions between catechol and glycine: Spectroscopic investigations of reaction products. JOURNAL OF MOLECULAR STRUCTURE 917, 142-147.

Hardie, A.G., Dynes, J.J., Kozak, L.M., Huang, P.M., 2009. The role of glucose in abiotic humification pathways as catalyzed by birnessite. Journal of Molecular Catalysis A: Chemical 308, 114-126.

Jokic, A., Wang, M.C., Liu, C., Frenkel, A.I., Huang, P.M., 2004. Integration of the polyphenol and Maillard reactions into a unified abiotic pathway for humification in nature: the role of δ-MnO2. ORGANIC GEOCHEMISTRY 35, 747-762.

Shiotsuka, M., Ueno, Y., Asano, D., Matsuoka, T., Sako, K., 2015. Synthesis and photophysical characterization of ruthenium(II) and platinum(II) complexes with bis-pyridylethynyl-phenanthroline ligands as a metalloligand. TRANSITION METAL CHEMISTRY 40, 673-679.

Stevenson, F.J., 1994. Humus chemistry: genesis, composition, reactions. John Wiley & Sons.

Stuart, B., 2004. Infrared spectroscopy: Fundamental and applications. Wiley, Canada.