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Characterization of pH-fractionated humic acids derived from Chinese weathered coal

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HIGHLIGHTS

- Humic acids from Chinese weathered coal were pH-fractionated successfully.
- The compositional and structural characteristics of HA fractions were investigated.
- The characteristics of HA fractions varied with the extraction solution pH.
- HA_{6-7} had the highest aromaticity and the most abundant COO/N-C=O groups.
- The nonprotonated carbon in HA fractions increased with the extraction solution pH.

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ABSTRACT

To reduce the compositional and structural heterogeneity of humic acids (HAs) and achieve better use of HA resources, in this study, we report a new sequential dissolution method for HAs derived from Chinese weathered coal. This method was used to separate HAs into seven fractions by adjusting the pH (3-10) of the extraction solution. The results showed that the HA fractions derived from Chinese weathered coal were concentrated up to 90.31% in the lower pH solutions (3-7). The compositional and structural characteristics of the HA fractions were determined by elemental analysis; ultraviolet–visible (UV-Vis), Fourier transform infrared (FTIR), and solid-state ^{13}C-nuclear magnetic resonance (NMR) spectroscopies; and other techniques. The results showed significant differences among the HA fractions. The concentrations of the total acidic groups and the carboxyl groups decreased with the increasing pH of the extraction solution. However, the HA fractions derived from extraction solutions with pH 3-4 had relatively lower aromaticity but a higher protonated carbon content. The HA fractions derived from extraction solutions with pH 6-7 had the highest aromaticity and the greatest abundance of COO/N-C=O. This study demonstrated that adjusting the pH of the extraction solution is one way to fractionate HAs from Chinese weathered coal and to obtain HA fractions with compositions and structures that could serve as useful material for study and utilization.

1. Introduction

Humic acids (HAs) are amorphous, colloidal and polydispersed organic compounds with complex compositions and structures resulting from chemical and biological degradation and the transformation of plant and animal residues and microbial cells (Hayes and Wilson, 1997; Dong et al., 2008). They are widely distributed in nature, and their composition, structure and usefulness for soil fertilization have been extensively investigated (Zheng, 1991; Stevenson, 1994). However, the high degree of heterogeneity in their compositions and origins have made their structures difficult to ascertain. Fractionation, especially by preparative high-performance size-exclusion chromatography, ultrafiltration, and precipitation, has been commonly employed to overcome this problem by reducing the heterogeneity of HAs to gain a better understanding of their composition and structure as well as their

Abbreviations: HAs, humic acids; UV-Vis, ultraviolet and visible; FTIR, Fourier transform infrared; NMR, nuclear magnetic resonance; CP/TOSS, cross polarization/total sideband suppression; DD, dipolar dephasing; PCA, principal component analysis.

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