

Regular Article

Water-based fractionation of a commercial humic acid. Solid-state and colloidal characterization of the solubility fractions



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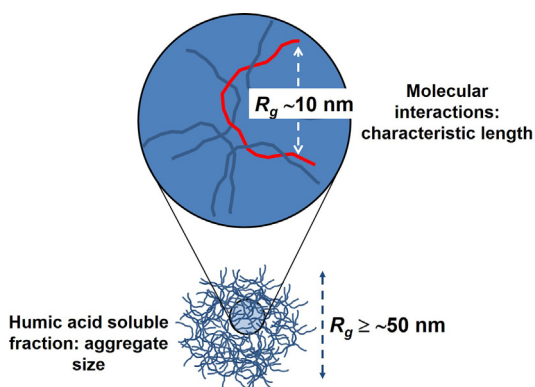
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GRAPHICAL ABSTRACT



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ABSTRACT

Background and hypothesis: Humic acid (HA) is of considerable environmental significance, being a major component of soil, as well as being considered for application in other technological areas. However, its structure and colloidal properties continue to be the subject of debate, largely owing to its molecular complexity and association with other humic substances and mineral matter. As a class, HA is considered to comprise supramolecular assemblies of heterogeneous species, and herein we consider a simple route for the separation of some HA sub-fractions.

Experiments: A commercial HA sample from Sigma-Aldrich has been fractionated into two soluble (**S1**, **S2**) and two insoluble (**I1**, **I2**) fractions by successive dissolution in deionized water at near-neutral pH. These sub-fractions have been characterized by solution and solid-state approaches.

Findings: Using this simple approach, the HA has been shown to contain non-covalently bonded species with different polarity and water solubility. The soluble and insoluble fractions have very different chemical structures, as revealed particularly by their solid-state properties (¹³C NMR and IR spectroscopy, and TGA); in particular, **S1** and **S2** are characterized by higher carbonyl and aromatic contents, compared with

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Zeta potential

11 and **12**. As shown by solution SAXS measurements and AFM, the soluble fractions behave as hydrophilic colloidal aggregates of at least 50 nm diameter.

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1. Introduction

The present paper considers the aqueous solubility and composition of a commercial sample of humic acid (HA). This has been chosen as an example of one of the classes of “humic substances” produced by the environmental decomposition of natural organic matter, and which are loosely defined in terms of the procedures used in their extraction. Humic substances are present in soils, rivers and other aquifers, and HAs have been shown to exist as aggregates of colloidal size at sufficiently high concentration [1,2]. Our original interest in these materials stems from their role in bitumen extraction from oil sand ores [3,4], where HA is mostly complexed with clays which, depending on the geological origin, can have different consequences for bitumen recovery [5,6]. However, the present work has a more general context.

On a molecular level, HAs are difficult to characterize. They are known to be (or contain) polyelectrolytes which interact strongly with certain cations to form insoluble complexes [7,8], and have been shown to be active in removing metal contaminants from water [9]. Other studies have demonstrated an improved ability of humic substances over conventional surfactants, such as Triton X-100 or sodium dodecyl sulfate, to aid soil bioremediation through the removal of pollutants such as polyaromatic hydrocarbons, thiophenes, sulfones or biphenyls [10].

As has recently been discussed [11], humic substances have been subdivided into three separate classes based on their respective solubility characteristics. Thus, humins are insoluble under alkaline conditions, fulvic acids are soluble throughout the pH range, and HAs are insoluble under acidic conditions. These materials have intrinsic surfactant-like tendencies, e.g. reducing the surface tension of aqueous solutions [2,12–14] and solubilizing organic molecules in colloidal aggregates [15].

The separation of humic substances has been the subject of a number of studies, as recently reviewed [16]. The analysis of different fractions taken from within individual classes has only served to highlight the molecular complexity of these substances, and detailed molecular structures still remain elusive. Indeed, this may not be surprising based on the arguments that humic substances are more likely to be a “continuum of progressively decomposing organic compounds” than “inherently stable and chemically unique compounds” [11].

In this paper, we are particularly interested in the composition and colloidal properties of HA component species. In the majority of previous studies, chemical and molecular size differences have been exploited in order to effect fractionation. For example, the recent procedure used by Chilom et al. [13] involved alkali- and solvent-based extractions, enabling the isolation of one lipid-like and two humic-like fractions. Powell and Town solubilized HAs using a combination of pH and different ionic media which were then fractionated based on molecular size using gel permeation chromatography combined with equilibrium dialysis [17]. Conte et al. used preparative size exclusion chromatography to produce seven fractions from a lignite HA which were shown by different spectroscopic analyses to vary in aromatic-aliphatic character and oxidized state [18]. Using ultrafiltration, Carlsen et al. produced six molecular size fractions ranging from <1 kDa to <100,000 kDa from Aldrich HA and examined their respective interactions with Eu^{3+} ions [19]. Similarly, Francioso et al. produced six fractions from Na humate solution ranging from 5–

10 kDa to >300 kDa using tangential ultrafiltration, which were characterized by vibrational and NMR spectroscopic techniques [20].

However, Pitois et al. [21] used a different approach to produce “chemical adsorptive” fractions from commercial HA by adsorption on quartz sand. They found that adsorption of HA was a two-stage process, one occurring faster (~ 3 h) than the other (~ 45 h). The HA solutions remaining after each adsorption period were analyzed using asymmetric flow-field flow fractionation coupled with UV/visible absorption spectrophotometry, which showed that adsorption of lower molecular weight components (<4800 Da) occurs initially, followed by higher molecular weight components (1400–9200) [21]. Fractions produced by this method are clearly towards the lower molecular weight end of the ultrafiltration fraction ranges.

A contemporary model for the structure of HAs proposes supramolecular assemblies of smaller heterogeneous molecules held together by hydrophobic interactions and hydrogen bonding [22,23]. The composition of humic substances, including HA, are naturally heterogeneous and source-dependent, since they originate from the breakdown of plant and animal matter by microbiological and abiotic transformation.

Herein, we present results from an experimental study on a commercial HA sample from Sigma-Aldrich which has been the subject of several reports in the literature over the years [1,7,9,12,21]. We report that it is possible to isolate “solubility fractions” based on differential solubility in deionized water under near-neutral pH conditions. Klučáková and Pekař [24,25] have previously noted different dissolution/solubility characteristics of solid HAs, including a commercial sample from Fluka, which on the basis of its pH-concentration behavior is considered similar to the product used herein (see later). These workers proposed a multi-step dissolution mechanism upon interaction with water, involving dissolution, with or without acid dissociation [24,25]. We were therefore interested to investigate further the water solubility of the commercial HA and the nature of the solubility fractions produced.

2. Experimental

2.1. Materials and HA fractionation in water

All reagents, including neutral HA, the corresponding sodium salt (NaHA), the inorganic salts NaCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, and cetyltrimethylammonium bromide (CTAB) were the highest purity grades available from Sigma-Aldrich, UK and were used as received. Aqueous solutions were prepared using deionized water (resistivity 18.2 $\text{M}\Omega \cdot \text{cm}$) from a Millipore Direct-Q system.

Inorganic matter is known to be an impurity in HA and this is confirmed by the lower elemental compositions in the present sample of HA compared with the literature values of a similar product produced from NaHA: found (lit. [26]) (%): C, 36.9 (49.7); H, 3.10 (4.49); C/H ratio 0.99 (0.92). On the other hand, the similar C/H ratio found for the present unpurified product is consistent with an impurity devoid of carbon and hydrogen. Thermal analysis data are reported later in this paper. Since the compositions of HA and NaHA could potentially vary from sample to sample, experiments were conducted as much as possible using a single commercial batch (identified by lot number).

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