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Implementation of spectroscopic parameters for practical monitoring of natural organic matter

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Abstract

Humic acids have been widely studied in the literature as a representative to natural organic matter (NOM) in drinking water supplies due to their composite heterogeneous nature comprising a variety of different molecular weight compounds. However, humic acids are difficult to isolate from water primarily due to their low concentration, resulting in time-consuming and laborious processes for their isolation and purification. In this study the applicability of surrogate parameters such as E_{250}/E_{365}, E_{254}/E_{436}, E_{365}/E_{465} and E_{465}/E_{665}, which are widely used in the literature for NOM characterization, were investigated in relation to aquatic and terrestrial model humic acids and a natural water sample. Molecular size fractionation of the samples was employed in an approach to understand the UV-vis properties of each size fraction. The specified ratios for both aquatic and terrestrial humic acids do not exhibit any significant differences up to 30 kDa. Lower molecular size fractions are differentiated in comparison to the natural water sample. E_{254}/E_{436} and E_{250}/E_{365} ratios exhibit a molecular size specific distribution with respect to the type of humic acids. The ratio of E_{254}/E_{436} was proposed to assess the composition of altered NOM provided that the total removal of color-forming moieties is not required. Under conditions of total decolorization, the use of E_{250}/E_{365} is also recommended relevant to the spectroscopic changes acquired during treatment.

Keywords: Humic acids; Natural organic matter; UV-vis spectroscopy; Molecular size fraction

1. Introduction

A major fraction of natural organic matter (NOM) present in surface or ground waters is composed of humic substances, which are complex macromolecular products of the chemical and biological degradation of plant and animal residues including lignin, carbohydrates and proteins. The term “humic substances” is used as a generic name to describe colored material or its fractions obtained on the basis of solubility char-

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acteristics. The fraction called humic acid (HA), which is insoluble in water under acidic conditions (pH <2) and soluble at higher pH values, constitutes a major fraction of humic substances.

Humic substances can affect water quality adversely in several ways by contributing undesirable color, complexing with metals and yielding metal concentrations exceeding normal solubility. Furthermore, humic substances are important from a water treatment perspective due to their role as precursors to the formation of chlorination by-products such as trihalomethanes as well as their role in the transport of organic and inorganic pollutants. Hence, it is desirable to minimize the concentration of humic matter in drinking water supplies or process water. Korshin et al. [1] reported UV spectrum of NOM as a representative to a composite of three distinct bands, the intensities and widths of which might be related to the concentration and type of aromatic chromophores, and suggested the use of differential UV spectroscopy to monitor disinfection by-products formed after chlorination. However, quantitative prediction and mechanistic description of reactivity in both natural and engineered environmental systems require detailed delineation of chemical, structural and molecular characteristics for HA.

The organic carbon content in water is used as a surrogate parameter to represent NOM concentration. Additionally, UV absorbance at 254 nm (UV_{254}) is interchangeably measured with total organic carbon (TOC) to represent the NOM content in natural waters [2]. Recently, the specific UV absorption defined as UV_{254} per milligram of organic carbon ($SUVA_{254}$) has also been used as another surrogate of the DBP precursors. The UV absorptivity at 280 nm was also introduced to represent total aromaticity because π–π^* electron transition occurs in this UV region (ca. 270–280 nm) for phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons with two or more rings [3,4].

Numerous studies have been performed using HA as model compounds to minimize the abovementioned effects. Their composite, heterogeneous nature resembles that of natural waters. Aiming at focusing on a comparative basis, the molecular size, or parameters indirectly linked to molecular size, of four different types of (aquatic and terrestrial source) HA samples and a natural water sample from the Omerli water reservoir were measured by UV-vis spectroscopy after molecular size fractionation. The molecular size distribution data were used in conjunction with spectroscopic parameters of the samples to tailor process options for the treatment of natural waters.

2. Experimental

2.1. Materials

HA of different origin (terrestrial and aquatic) were used in bench-scale experiments. Suwannee River HA (IHSS HA) standard material, isolated from the Suwannee River, Georgia, as well as soil HA (Lot No: 1S102H) (IHSS Soil HA) as a terrestrial source were purchased from the International Humic Substance Society. Commercial HA samples were supplied from Aldrich (HA salt) (AHA) and Roth (HA). The original natural water samples were collected from the Omerli water storage reservoir.

2.2. Methodology

Molecular size fractionation of commercial HA (50 mg/L) was carried out after adjusting the pH to 6.5±0.5 with standard NaOH (0.1 N) and HCl (0.1 N). The pH of the raw water sample from the Omerli reservoir was 6.9. It was used as received without any pH adjustment. The samples were fractioned into different nominal molecular size ranges using ultrafiltration (UF). Initially, the samples were filtered through 0.45 μm Millipore