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Key role of common anions on the photocatalytic degradation profiles of the molecular size fractions of humic acids

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Humic acids are the most abundant components of the colloidal and dissolved fraction of natural organic matter (NOM) and widely known to be representatives of NOM behavior in the aquatic environment.

The objective of this study was to investigate the influence of common anions on the photocatalytic degradation of humic acid and its different molecular size fractions. A representative range of anions were added to humic acid to simulate diverse characteristics of surface water. Induced effects on the removal of the target organic compound were studied. With the aim of assessing the photochemical processes under irradiation conditions, the photocatalytic removal efficiency of humic acid was determined taking into account the major background factors. The results revealed that some specific UV–vis parameters agreed well with the information provided by fluorescence spectroscopy. Despite the complex nature of humic acids in the presence of a solution matrix, the spectroscopic parameters could be regarded as indicators for the photocatalytic removal of humic acid and its molecular size fractions. Depending on the presence of low and high anion matrix, different kinetic model parameters were attained for the photocatalytic removal of the molecular size fractions of humic acid. The photocatalytic degradation rates could be expressed by the half-life values ranging from 20 min to 133 min.

1. Introduction

Natural organic matter (NOM) is a collective term assigned to a mixture of chemicals that are present ubiquitously in the aquatic environment with different molecular sizes ranging from a few hundred to 100,000 daltons (Da). NOM affects water quality by providing precursor material for disinfection by-products (DBPs), substrate for biogrowth, and complexation sites for heavy metals. To understand these processes better and to control their effects on drinking water quality, it is necessary to study the chemistry of NOM in detail. Although the components of NOM can be classified as humic acids, fulvic acids, polysaccharides, hydrophilic acids, proteins, lipids, amino acids and hydrocarbons, no single “molecule” of NOM exists. To a certain extent, different NOM samples can be considered as having a set of average properties, which depend on the source material, the degree of subsequent degradation reactions, and transport related fractionation processes. Differences in these average properties can have a marked effect on processes involved in water treatment. Therefore, characterization of the molecular size of humic acid is a valuable tool when assessing its geochemical origin as well as its effect on the performance of water treatment systems.

Ultrafiltration has been frequently used for the physical fractionation of humic substances [1,2]. An overview of the fractionation techniques can be found in the recent review of Matilainen et al. [2] and Sulzberger and Durisch-Kaiser [3]. It has generally been reported that structural and spectral properties varied among molecular size fractions, regardless of the fractionation technique employed. Humic acid fractions that were obtained using ultrafiltration were characterized for their chemical, structural, and molecular properties [1,4,5].

The chemical analyses showed that the alkyl hydrophobic components were mainly distributed in the largest molecular-size fractions, while phenolic and oxygen-containing groups were predominant in the low nominal molecular weight fractions. Humic substances mainly humic acids constitute the major fraction of natural organic matter in water supplies, therefore, their photocatalytic degradation has been studied in detail [6–8]. Considering the impact of the solution matrix on the photocatalytic degradation process, recently the photocatalytic removal efficiency of humic acids under different conditions simulating surface and groundwater was investigated [9,10]. Since humic acid is a noncharacterized complex mixture of organic macromolecules, the molecular weight of which varies over a wide range, the work presented herein

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is a continuation of the efforts to understand the photocatalytic degradation of its molecular size fractions. Considering the real case of natural water samples, this work was carried out in an attempt to mimic natural water conditions and account for the effect of anions which would have an influential role on the humic-TiO_2 binary system by exerting ionic interactions, diverse conformational and compositional changes in the structure. Specific UV–vis and fluorescence parameters were also employed for the assessment of the photocatalytic degradation efficiencies in the presence of selected anions commonly found in natural waters, namely fluoride, chloride, bromide, nitrite, nitrate, sulfate and phosphate.

2. Materials and methods

Raw humic acid (humic acid sodium salt, Aldrich) solution ($50\,mg\,L^{-1}$) was prepared to account for natural organic matter containing surface waters. Initially, humic acid solutions were filtered through $0.45\,\mu m$ (M1) cellulose acetate membrane filter (Millipore). Subsequently, humic acid was fractionated by ultrafiltration (Amicon 8050) into three nominal molecular size fractions of 100 kDa (M2), 30 kDa (M3) and 3 kDa (M4).

Standard mix solution containing seven of the anions as nitrate, nitrite, phosphate, sulfate, fluoride, chloride and bromide anions were obtained from Dionex (Product number: 0575909). To avoid excessive phosphate concentration and keep an effective load of anions, difference by one order of magnitude was selected for the studied range of anion concentrations. Anions of low concentration (LC) were: $[F^-]$, $[Br^-] = 2 \times 10^{-6}\,mol\,L^{-1}$, $[Cl^-]$, $[NO_2{}^-]$, $[NO_3{}^-] = 1 \times 10^{-5}\,mol\,L^{-1}$; $[SO_4{}^{2-}]$, $[PO_4{}^{3-}] = 3 \times 10^{-6}\,mol\,L^{-1}$ whereas anions of high concentration (HC) were as follows: $[F^-]$, $[Br^-] = 2 \times 10^{-5}\,mol\,L^{-1}$; $[Cl^-]$, $[NO_2{}^-]$,$[NO_3{}^-] = 1 \times 10^{-4}\,mol\,L^{-1}$; $[SO_4{}^{2-}]$, $[PO_4{}^{3-}] = 3 \times 10^{-5}\,mol\,L^{-1}$. The quantification of anions was carried out using Dionex ICS-3000 Ion Chromatography. To prepare working solutions, each molecular size fraction of humic acid (M1–M4) was added anions of low and high concentrations to simulate surface water conditions. Experiments were conducted at natural pH of the samples ($pH \sim 6$) without any adjustment. All of the experiments were performed in duplicate and the variability between replicate experiments was <5%.

Humic acid working solutions were subjected to photocatalytic degradation in a completely mixed reactor utilizing UV-A light (125 W BLF lamp, $I_o = 2.85 \times 10^{16}$ quanta s^{-1}) and TiO_2 Degussa P-25 in powder form ($0.25\,mg\,mL^{-1}$). More details about the experimental procedure have been reported [11]. Prior to analysis, TiO_2 was removed from the solution by filtration ($0.45\,\mu m$, cellulose acetate membrane filter). The extend of mineralization of organic content was determined by dissolved organic carbon (DOC, $mg\,L^{-1}$) measurements using the Total Organic Carbon Analyzer (Shimadzu TOC-VWP). Humic acid was identified by spectroscopic parameters (m^{-1}) such as $Color_{436}$ (absorbance at 436 nm), UV_{365} (absorbance at 365 nm), and UV_{254} (absorbance at 254 nm) by UV–vis spectrophotometry (Perkin Elmer lambda 35). Synchronous scan fluorescence spectra were acquired in the excitation wavelength range of 300–650 nm using the bandwidth of $\Delta\lambda = 18$ nm between the excitation and emission monochromators (FI_{syn},) using Perkin Elmer LS 55 Luminescence Spectrometer. In addition to UV–vis absorbance and fluorescence intensity measurements, their DOC normalized values defined as specific UV absorbance ($SUVA_\lambda$, DOC normalized UV_λ at $\lambda = 254$ nm and 365 nm $(mg\,C\,L^{-1})^{-1}\,m^{-1}$), specific color absorbance (SCOA, DOC normalized $Color_{436}$ $(mg\,C\,L^{-1})^{-1}\,m^{-1}$) and specific fluorescence intensity (SFI_{syn}, specific synchronous fluorescence intensity at λ_{max}: 470 nm) were also presented [12].

3. Results and discussion

3.1. UV–vis and fluorescence spectral features of humic acid and its molecular size fractions under non treatment and post treatment conditions

It is known that the molecular size distribution profiles of the humic substances exhibit a general decreasing trend from high molecular size fractions to lower molecular size fractions irrespective of the origin and source of the organic matter [5]. Spectroscopic characterization of the molecular size fractions were presented with respect to specific absorbance ratios of each fraction derived from humic acid and the natural water sample [5,13]. For simplicity purposes, E term was used to designate either UV or Color when presenting the absorbance ratios. 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 was not required. Under conditions of total decolorization, the use of E_{250}/E_{365} was also recommended relevant to the spectroscopic changes acquired during oxidative treatment [5,14]. For comparison purposes selected spectroscopic parameters of humic acid size fractions in relation to photocatalytic treatment efficiencies were presented in Figs. 1–3.

Although the UV–vis spectral features of humic acid and its size fractions appeared to be broad and featureless, showing no maxima or minima, specific absorbance intensities at 254, 365, and 436 nm as SUVA and SCOA displayed variations among the fractions [5]. The polydisperse nature of humic acid unifying components of dissimilar molecular weights was clearly observed from the presented absorbance ratios of each size fraction (Fig. 1). When ultrafiltration was applied, it did not involve explicit size or functional group separation however, it produced fractions of a certain molecular size distribution that showed spectroscopic evidence of structural discrepancies. The spectroscopic ratios calculated for the different molecular size fractions of humic acid showed slight differences depending on the presence of anions. The ratios for M4 were significantly higher than the other fractions studied. It was reported by several researchers that the quotient E_{250}/E_{365} (absorbance at 250 nm and 365 nm), which is a property of aquatic humic substances, increased as the aromaticity and molecular size decreased [15]. High molecular weight fractions and unfractionated humic acid contained a relatively higher amount of aromatic or polyphenolic structures compared to low molecular weight fractions. As a general trend, the absorbance ratios of the fractionated humic acids increased with decreasing molecular size.

E_{254}/E_{436} and E_{250}/E_{365} ratios for raw M1 and M2 fractions of humic acid showed constant tendency irrespective of the presence of anions. After treatment for 60 min increase of ratios became

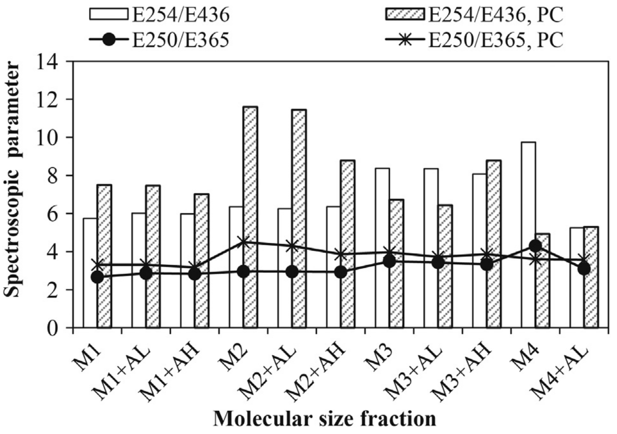

Fig. 1. Spectroscopic parameters of the molecular size fractions of humic acids with respect to treatment conditions (PC: photocatalytic oxidation for 60 min).