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Influence of chemical compositions and molecular weights of humic acids on Cr(VI) photo-reduction

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ABSTRACT

Humic acids (HA) strongly affect the fate of trace metals in soils and aquatic environments. One of the remarkable properties of HA is its ability to reduce Cr(VI), an extremely toxic anion. However, it is unclear which HA components are involved in Cr(VI) reduction and possess the photo-induced properties. In this study, an ultrafiltration technique was used to fractionate HAs into four fractions of different nominal molecular weights (M_w): >100, 50–100, 10–50 and <10 kDa. Each HA fraction was characterized by spectroscopic analyses followed by examining Cr(VI) removal on each fraction of HA at pH 1–5. Spectroscopic results indicated that low-M_w HA was enriched with polar and aromatic domains. These polar, including polar C in aliphatic region, and aromatic groups were the major sites for Cr(VI) reduction because they disappeared rapidly upon interaction with Cr(VI). As a result, low M_w of HA exhibited greater efficiency of Cr(VI) reduction. Light induced the rapid transfer of electrons between chromate-phenol/carboxyl ester, or the formation of peroxide radicals or H_2O_2 through the ready decay of peroxy radicals associated with polar substituents, explained the rapid scavenging of Cr(VI) on polar and aromatic groups of HAs under illumination.

1. Introduction

Soil organic matter (SOM) consists of two major components, unaltered debris and humus, which are defined as a recognizable skeleton and an invisible feature of its original organism, respectively. Humus is an amorphous brown-colored polymer, which can be subdivided according to solubility in strong acid and base: humic acid (HA, insoluble in acid), fulvic acid (FA, soluble in both acid and base) and humin (insoluble in both acid and base). These humic substances (HS) strongly affect the fate of trace metals and organic contaminants in terrestrial and aquatic environments through various binding and degrading processes, including photo-chemical reactions [1–4]. Because HS have complex chemical compositions with molecular weight (M_w) ranges of hundreds to several hundred thousand Daltons, fractionation of HS is an effective method for better insight into the characters of HS and their interactions with pollutants [5].

It has been observed that the chemical composition and total acidity of HAs differed greatly between high and low M_w fractions [6]. With the fractionation of an Andisol HA by coupling size exclusion chromatography (SEC) and polyacrylamide gel electrophoresis (PAGE), Richard et al. [7] found that carboxylic groups could be concentrated in low M_w fractions, while polysaccharides and peptides were in high M_w fractions, and the UV–vis absorbance and A_{465}/A_{665} ratio increased as M_w of HA decreased. Christl and Kretzschmar [8] used a hollow fiber ultrafiltration (UF) technique to fractionate HA into four M_w: 10–30, 30–100, 100–300 and >300 kDa. They observed that the negative charge of HA decreased steadily with increasing M_w fractions over a pH range of 3–10 in a 0.1 M background electrolyte, and the decrease was consistent with the decrease of phenolic and carboxylic C in HA. Moreover, high M_w fractions exhibited generally lower photo-inductive activities and weaker fluorescence emission compared to low M_w fractions and bulk HAs [5,9]. These studies clearly demonstrated that the major functional groups and the properties of chromophores depended greatly on the M_w of HAs.

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Therefore, the HAs of various M_w should exhibit different chemical reactivities, including photo-induced abilities, when in contact with environmental pollutants. The activated sites on HAs may be identified upon their enrichment through a fractionation of HAs into various M_w prior to interactions of pollutants.

HS serve as electron donors in many redox reactions. In particular, the elimination of environment pollutants such as Cr(VI) by HA have received much scientific attention [10–13]. Cr(VI) is toxic to both plants and animals [14,15] and is carcinogenic to human beings [16]. Therefore, the conversion of Cr(VI) to less toxic Cr(III) by HS can eliminate its hazard to organisms, and the redox reaction is considered a self-cleaning function in Cr(VI)-loaded environments. The interactions of Cr(VI) with HA have been investigated in many previous studies [11,17]; however, which functional groups of HAs participate in Cr(VI) reduction remains unknown. The utilization of bulk HA, bearing extremely complex structures, as a reactant may inhibit the detailed observations of the activated groups of HA involved in Cr(VI) reduction. Thus, fractionating HAs into different M_w with dominant chemical compositions may facilitate mechanistic studies of Cr(VI) reduction on HAs. Photo-induced Cr(VI) reduction by HA may occur in an environment receiving sunlight and thus, the investigation of photo-detoxification of Cr(VI) by HA can help delineate the overall Cr(VI) behavior in ecosystems. In this study, HA was obtained from a mountain peat soil of Taiwan, and fractionated into four M_w (i.e. <10, 10–50, 50–100 and >100 kDa) using UF technique. The adsorption and photo-reduction of Cr(VI) by different M_w of HAs were investigated and the specific groups of HAs involved in Cr(VI) removal were also evaluated. The experiments were conducted at pH 1–5; nonetheless, Cr(VI) reduction by HA proceeded slowly at a higher pH, and thus, we mainly presented a representative result obtained at pH 1. In addition, an extremely acidic effluent with Cr(VI) derived from electroplating industries had been detected in an open irrigation ditch or a river closed to the discharging points [18]. Therefore, the current experimental results can demonstrate the interactions of HA with Cr(VI) in a natural system.

2. Materials and methods

2.1. The source of HAs

A peat soil sample was collected from the Yangmingshan Mountain area located in Taipei County, northern Taiwan (25°090N, 121°320E, Fig. 1). The Yangmingshan soil contains 156 g/kg organic carbon (OC), and is classified as medial, amorphic, thermic, Typic Melanudand. Other physical/chemical properties of the peat soil can be found in our previous work [19].

2.2. Extraction and fractionation of HAs

HAs were extracted from the peat soil, following the standard procedure recommended by the International Humic Substances Society (IHSS) [19]. The HA samples were transferred to a solution with 0.1 M NaOH and 0.01 M NaCl at pH 7, and were passed through membranes with nominal molecular weight cut-offs (MWCO) of 100, 50 and 10 kDa using a Molecular Stirred Cell (Molecular/Porÿ Stirred Cells, S-76–400). The separation was carried out stepwise under a pressure of 16 psi, beginning with the highest MWCO, and the filtrate passing through the membrane was collected and transferred to the next membranes with a lower MWCO for separation. Each HA size-fraction obtained was stored in a dark glass bottle as a stock solution and placed in a refrigerator for further use.

2.3. Characterization of HA fractions

The elemental contents (C, H, N and O) of the HA fractions were investigated by a Heraeus CHNOS Rapid F002 Elemental Analyzer. The optical densities ratios of dilute HA solutions at 465 and 665 nm (E_4/E_6) were evaluated according to the method of Chen et al. [20]. ^{13}C CP-MAS NMR spectra and infrared spectra of HA fractions were obtained using a Bruker DSX400WB NMR spectrometer and Fourier Transform Infrared (FTIR) Spectrometer (Thermo Nicolet NEXUS), respectively. ^{13}C CP-MAS NMR spectra of the samples were collected on a Bruker DSX400WB NMR spectrometer [19]. Spectroscopic analyses of the specific functional groups of HA involved in Cr(VI) reduction was obtained by comparing the changes in the spectra of Cr(VI)-loaded HA with the untreated HA samples. A control experiment was also conducted by mixing Cr(III) [i.e. $CrCl_3$] up to 9.62 mM with untreated HA samples to evaluate the possible complexation of the redox products, i.e., Cr(III), on spectroscopic analyses.

2.4. Cr(VI) reduction by various M_w of HA

Appropriate amounts of the stock solution of each HA fraction was diluted with 0.001 M $CaCl_2$ to obtain a C concentration of ≈52 mg L^{-1}, measured by TOC analyzer. A small aliquot of Cr(VI) stock solution (1.923 mM) was diluted with 0.001 M $CaCl_2$ and then transferred to a water-jacketed reaction vessel containing HA. Consequently, the final concentration of Cr(VI) was 0.1923 mM, and the final HA concentration was 26 ± 2 mg C L^{-1}. Cr(VI) reduction by HA was conducted in 1 L reaction vessel at pH 1–5, and a circulating water bath connected to the vessel to maintain the reaction temperature at $25 \pm 1\,^{\circ}$C. A 100 W medium-pressure mercury UV lamp (ACE Glass Incorporated) was inserted into a borosilicate well to exclude the irradiation from UVB and placed in the center of the reaction vessel. The schematic setup of the reaction system can be referred to our previous works [4]. The lamp emits mostly in the range 310–1000 nm, with the most intense lines at 303, 313, 366, 405, 436, 546, and 578 nm. The average light intensity of $2.15 \times 10^{-4} \pm 5.74 \times 10^{-5}$ einstein s^{-1} L^{-1} ($n = 18$) was measured by an actinometric technique [17]. Light control experiment was also performed to evaluate Cr(VI) reduction in the absence of HA. HA suspensions were periodically extracted and passed through a 0.2 μm pore-size membrane filter to collect the filtrates. Cr(VI) concentration in the filtrate was determined using a UV/VIS spectrophotometer (Varian Cary 50) at 540 nm after reaction with an 1,5-diphenylcarbazide indicator (DPC) [21]. The dark control was conducted when the light was turned off. Total chromium was determined using atomic absorption spectroscopy (AAS; Hitachi Z-2000) at $\ddot{y} = 359.3$ nm. The differences between total Cr and Cr(VI) concentrations obtained by AAS and DPC methods, respectively, were attributed to Cr(III).

3. Results and discussion

3.1. Mass distribution of each HA fraction

The HA fraction with the greatest molecular cutoff (i.e. $M_w > 100$ kDa) consists of 85.9% of the total HA mass recovered from the UF process. There was a dramatic decrease in the mass distribution of HA for 50–100 kDa, and 10–50 kDa had the lowest mass distribution (Table 1). The smallest molecular cutoff (i.e. $M_w < 10$ kDa) constituted 17.3% of the total HAs mass. The results indicate that the major mass distributions of HAs were within a narrow range of M_w, consistent with several previous studies using UF to fractionate HAs derived from different sources [22–24].

3.2. Characterizations of HA

3.2.1. Elemental analysis

The bulk HA sample derived from Yangmingshan peat soil had C, H, N and O contents of 51.3, 5.3, 2.5 and 38.5%, respectively (Table 1).