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Effects of UV radiation on humic acid coagulation characteristics in drinking water treatment processes

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HIGHLIGHTS

- UV pretreatment could improve the removal of HA in coagulation at pH above 6.0.
- At pH < 5.5, the removal of HA would be inhibited after pretreatment.
- The molecular diameters and heights of HA increased notably after pretreatment.
- The E4/E6 ratio of HA solution decreased gradually as the radiation time increase.
- The enhanced removal of HA was mainly caused by the increase of zeta potential.

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ABSTRACT

Humic acid (HA) commonly exists in natural waters and drinking water treatment processes. The effects of UV light radiation on the coagulation of HA were investigated in this paper. It was determined that UV light radiation could effectively improve the removal of HA at pH above 6.0. The concentration of residual HA in the coagulated water was in the range of 1.5–3.0 mg/L, which was significantly lower compared to that without pretreatment. However, in waters tested with pH below 5.5, the UV light radiation showed an adverse effect on HA removal using coagulation, which might be connected to its high oxidation function under acidic conditions. The zeta potential of the HA solution with UV light radiation was approximately 10 mv higher compared to that without pretreatment at pH above 6.0; while its apparent diameters and heights increased from less than 130 nm and 0.5–3.5 nm to 100–240 nm and 1.0–4.5 nm respectively, after 2.0 h of UV light radiation as the aggregation of HA. The compressed double electric layer caused by the formation of positive charged sites after UV light radiation was considered to be the primary factor that led to the enhanced removal of HA in the following coagulation process.

1. Introduction

The presence of humic acid (HA) in drinking water treatment processes has received significant attention in recent years because of its adverse effects on the removal of pollutants in coagulation and the toxic disinfection by products (DBPs) formed in chlorination [1–5]. In addition to DBP formation, high concentrations of residual HA in the treated water can lead to an increase in color and odor as well as bacterial re-growth in the drinking water distribution system [6]. Currently, removal of HA from natural waters is primarily achieved using chemical coagulation/flocculation followed by sedimentation or flotation. However, the removal rate using coagulation is typically quite low, i.e., between 10% and 50% in traditional drinking water treatment processes [7]. The most accepted method for HA removal is enhanced coagulation which maximizes organic matter removal by providing an excess of coagulants. Numerous literature reports suggest that enhanced coagulation can effectively increase DBP precursor removal [8–10]; however, it is frequently observed that this process has limited removal of the low molecular weight fraction and uses a significantly larger coagulant dosage [11,12].

The application of advanced oxidation processes (AOPs) in HA removal, such as UV/H_2O_2 and UV/O_3, has deserved many studies these years [13,14]. These processes can effectively mineralize many organic contaminants because of their high oxidation effects

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of free radicals [14]. In contrast with other AOPs, such as O_3 and H_2O_2 oxidation, it is easier to remove DBP precursors during photocatalysis, especially UV light catalysis processes before disinfection [14]. Wang et al. determined that although H_2O_2 does not oxidize HA, when combined with UV light radiation, the rate of HA oxidation increased significantly [15]. Hydroxyl radicals generated from the direct photolysis of H_2O_2 have been proven to be the primary responsible species for HA elimination [13,15,16]. Furthermore, Haag et al. discovered that hydrated electrons, hydroxyl radicals, and other oxidant radicals could be produced when HA-containing water was irradiated under UV light, which might also contribute to the removal of HA in drinking water treatment processes [17]. Currently, disinfection and O_3, H_2O_2, and TiO_2 combined advanced oxidation are the primary applications of UV light radiation in water and wastewater treatment. However, no studies have reported the effects of UV light radiation, a common natural process, on the aggregation or coagulation characteristics of HA.

The photochemical degradation of HA plays an important role in carbon cycling in natural waters, either directly by the photochemical production of volatile carbon species or indirectly through the production of CO_2 using sequential photochemical and biological oxidation processes [18]. Li et al. determined that the HA solution lost nearly all of its yellowish-brown color in the process of UV light radiation; however, HA could not completely decompose because the oxidation capacity of the UV light was significantly weaker compared to that of the AOPs [19]. Meanwhile, aromatic compounds with low molecular weights, such as benzene and carboxylic acids, were produced in solution [19,20], which may affect the removal of the HA in coagulation. Bose and Reckhow believe that pre-ozonation would hinder the adsorption of HA on the flocs formed in the polyaluminum chloride (PACl) coagulation process [21]. Furthermore, Wang et al. determined the removal rate of the HA with ozone pre-oxidation was lower compared to that without pretreatment [12]. However, the removal capacity of the HA in coagulation was enhanced if the solution was pretreated with UV/ozone oxidation, which might attribute to UV light radiation. However, the characteristic transformation of the HA during UV light radiation and its subsequent effects on coagulation are still not well understood.

In this study, the authors evaluated the effects of UV light radiation on the physical and chemical characteristics of HA and related the changes in physical and chemical properties of HA with its coagulation removal efficiency. Different from the AOPs which would inhibit the removal of HA because of the formation of large amounts of small molecular organic matters and an increase in the hydrophilicity of HA [14,21], our results suggested that UV light radiation could effectively improve the removal rate of HA in the following coagulation process at pH 6.0–9.0, and possible reaction mechanisms were provided. Considering the contribution of this work to the enhanced removal of HA and understanding the carbon cycling process in natural waters, the experimental results obtained in this paper is useful for the water industry.

2. Experimental materials and methods

The HA (Jufeng Chemical Technology, Shanghai, China) is extracted from peat coal and contains 56.2% of C, 3.91% of H, 36.1% of O, and 1.07% of N. A stock solution was prepared as follows: 5.00 g of HA was dissolved under an alkaline condition, filtered through a 0.45 mm glass fiber membrane filter and stored at a 4 °C condition. Synthetic water was prepared by adding a measured amount of HA stock solution into deionized water (Table 1). The pH of the test water was adjusted using 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. Except for the experiment investigating the effects of pH on HA removal, the pH of the HA solution was controlled at 7.5.

The UV light radiation was conducted using a 20 W UV light lamp which was inserted into a hollow quartz pipe located at the center of the reactor. A tap water cooling loop was used to prevent the lamp from overheating and maintain the water at room temperature [12]. The light intensity was approximately 0.05 W/cm^2 with a major emission at 254 nm. The treated water was withdrawn from the reactor at different time intervals. The mineralization of the HA was determined by subtracting the remaining total organic carbon (TOC) from the initial TOC. To observe the effects of UV radiation on the molecular distribution of the HA, the HA sample was fractionated into eight fractions using a stirred ultrafiltration cell device (Model 8200, Merck Millipore, Germany) with nominal molecular weight cutoffs of 0.5, 1, 3, 5, 10, 30, 50, and 100 kDa regenerated 63.5 mm cellulose membranes (Ultracel PL, Merck Millipore, Germany). The experimental details follow the procedure performed by Kitis et al. [22].

The stock solution or the UV pretreated solution of the HA was diluted with ionized water to reach the designed concentration for the coagulation experiment (Table 1). The pH of the bulk solution was adjusted to the desired value using NaOH and HNO_3. The raw water was coagulated in a program-controlled jar tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) with an addition of 5.0 mg/L PACl (calculated as Al). The coagulation procedure involved a rapid mixing at 200 rpm for 1.0 min, followed by a 15 min flocculation period at 50 rpm and a 30 min settling period. The final solution turbidity in each experiment was recorded. Samples were taken from 2.0 cm below the water surface and filtered through a 0.45 μm filter before further analysis was conducted.

The concentration of HA was analyzed using a total organic carbon analyzer (SHIMADZU, TOC-VCPH, Japan) calibrated with 5, 10, and 20 mg/L (as carbon) potassium hydrogen phthalate standard solutions before each run. The pH was measured using a pH meter (Model 828, Thermo Electron Corporation, USA). The electrode was calibrated using buffers with a pH of 4.0 and 7.0, and a slope of above 98.5% was consistently attained. The turbidity was determined using a turbidity meter (HI93703-11, Hanna, Italian). Elemental analysis of the HA was conducted using an auto elemental analyzer (Carlo Erba EA 1108, Rodano, Italy). The average particle size and zeta potential of the HA colloids were determined using a zeta meter (Nano-Z, Malvern, UK). To observe the HA

Table 1
Factors and their levels selected in coagulation.

Factors	UV pretreatment	TOC (mg/L)	pH	Alkalinity (mg/L)	Selected level							
					(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
pH	With	12.0	Var.[**]	5.0	4.0	4.5	5.0	5.5	6.0	7.0	8.0	9.0
	Without	12.0	Var.	5.0	4.0	4.5	5.0	5.5	6.0	7.0	8.0	9.0
MW[*] (K Dalton)	With	12.0	7.0	5.0	<1	1–3	3–5	5–10	10–30	30–50	50–100	>100
	Without	12.0	7.0	5.0	<1	1–3	3–5	5–10	10–30	30–50	50–100	>100

[*] Stand for the apparent molecular weight.

[**] The variable parameter.