Radiolysis of HA in aqueous solutions using gamma rays (Postprint)

Authors: JIA Wenbao, WEI Yonghong, LIU Jianguo, LING Yongsheng, HEI Daqian, SHAN Qing, ZENG Jie

Date: 2023-06-18T00:00:00+00:00

Abstract

The present work investigated the radiolysis of HA (Humic acids) in aqueous solutions and under gamma radiation. Absorbances at the range of 200 800 nm and chemical oxygen demand (COD) were used to characterize the degree of degradation of HA. The results indicated that absorbances and the concentrations of COD were decreased with increasing of irradiation dose while with increasing of irradiation dose the pH of the solutions was decreased at first and then increase. In addition, the effects of initial pH and primary solution concentrations on HA degradation were also investigated. It is shown that the higher primary solution concentrations, the lower degradation efficiency under the same irradiation dose. And the degradation efficiency of HA under neutral conditions is better than in acidic or alkaline conditions.

Full Text

Preamble

Radiolysis of HA in Aqueous Solutions Using Gamma Rays

JIA Wenbao[1], WEI Yonghong[1],*, LIU Jianguo[2], LING Yongsheng[1], HEI Daqian[1], SHAN Qing[1], ZENG Jie[1]
[1]College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 211100, China
[2]Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China

Abstract
This work investigated the radiolysis of humic acids (HA) in aqueous solutions under gamma radiation. UV-Vis absorbance (200–800 nm) and chemical oxygen demand (COD) were used to characterize the degradation efficiency. Results

indicated that both absorbance and COD concentrations decreased with increasing irradiation dose, while the solution pH initially decreased and then increased with dose. Additionally, the effects of initial pH and HA concentration on degradation were examined. Higher initial concentrations led to lower degradation efficiency at the same irradiation dose, and HA degradation was more effective under neutral conditions than in acidic or alkaline environments.

Keywords
Radiolysis, Gamma rays, HA

Introduction

Humic acids (HA) are macromolecular organic substances present in natural water that contain various functional groups, including hydroxyl, carboxyl, benzoquinonyl, methoxy, and carbonyl groups [**?**]. During chlorination disinfection of drinking water, HA can react with Cl_2 to form chlorinated disinfection byproducts (DBPs) such as trihalomethanes (THMs) [**?**], affecting water color and taste. Since HA can complex trace metal elements [**?**], it can reduce water mineralization and even increase the toxicity of certain heavy metals. Therefore, removing or reducing HA concentration from water is critically important.

HA is a biorefractory material. In studies using activated sludge to degrade HA [**?**], X.Y. Xiong found its biodegradability to be very poor, with degradation proceeding extremely slowly. Traditional treatment methods include sedimentation [**?**], adsorption [**?**], ion exchange [**?**], and similar techniques. In recent years, advanced oxidation processes (AOPs) such as Fenton oxidation [**?**], photocatalytic oxidation [**?**], electrochemical oxidation [**?**], and ultrasound-assisted oxidation [**?**] have been applied to HA degradation. However, ionizing radiation technology represents an efficient, rapid advanced oxidation process that produces no secondary pollution and has been widely used for investigating organic pollutant degradation. Studies on HA degradation using ionizing radiation remain scarce. Hidehiko Arai et al. degraded HA using ionizing radiation combined with ozonation to investigate the chain reaction mechanism during HA oxidation [**?**]. H.B. Liang et al. used electron beam irradiation to degrade HA, examining changes in chemical structure and biological activity before and after irradiation [**?**].

This paper aims to investigate the degradation effect of gamma irradiation on HA in aqueous solutions. Degradation was evaluated by measuring changes in UV-Vis absorbance, COD, and pH before and after irradiation. Furthermore, the influence of factors such as pH and initial HA concentration on degradation efficiency was examined.

2.1 Materials

The humic acids (HA, BR grade) used in this study were purchased from Shanghai Fanke Biotech Company (Shanghai, China). Sodium hydroxide (AR grade) and sulfuric acid (AR grade) were obtained from Nanjing Reagent (Nanjing, China). All aqueous solutions were prepared with ultrapure water from an UP-10 ultrapure water system (NJQY, Nanjing, China) with resistivity >18.2 MΩ · cm.

2.2 Analysis Methods

Solution pH was measured using a PHS-3C pH meter. Chemical oxygen demand (COD) was analyzed using a COD meter (ET99718, Italy). UV-Vis absorbance was determined with a UV-1800 spectrophotometer (Shimadzu, Japan).

2.3 Experimental Procedure

HA solutions of desired concentrations (0.02–0.12 g/L) were prepared using ultrapure water. Solution pH was adjusted using H_2SO_4 (1 mol/L) or NaOH (1 mol/L). Each 50 mL sample was sealed in a 100 mL brown glass bottle with a plastic cap. Two samples were prepared for each HA concentration: one was irradiated under gamma radiation (^{60}Co, 1 kGy/h, NUAA) at doses ranging from 0 to 40 kGy (determined by silver dichromate dosimetry), while the other was stored in the dark as a blank control. All samples were analyzed after irradiation, and all operations were performed at room temperature.

3.1 Effect of Irradiation Dose on UV-Vis Absorption Spectrum

To clarify the degradation characteristics of HA under gamma irradiation, spectroscopic data for irradiated and unirradiated samples were compared. Figure 1 shows the UV-Vis absorption spectrum of HA at 0.12 g/L concentration, with absorbance measured from 190 to 800 nm and a maximum absorption peak at 310 nm. Strong absorbance was observed at 250–400 nm, likely due to HA' s complex composition containing numerous benzene rings and large conjugated systems within the HA molecule [**?**]. The absorbance at 200–500 nm decreased with increasing irradiation dose, confirming effective HA decomposition under gamma irradiation. However, absorbance at 500–800 nm initially increased slightly at low doses before decreasing with further irradiation, suggesting that some intermediates formed during the initial decomposition stage were subsequently degraded at higher doses.

[Figure 1: see original paper]

3.2 Effect of Irradiation Dose on COD Removal

COD removal was used to quantify the degree of HA degradation by gamma radiation, calculated as follows:

$$\text{COD removal } (\%) = \frac{\text{COD}_0 - \text{COD}_D}{\text{COD}_0} \times 100$$

where COD_0 and COD_D represent COD concentrations before and after gamma irradiation, respectively.

Figure 2 [Figure 2: see original paper] shows the effect of irradiation dose on COD removal for an initial HA concentration of 0.12 g/L. COD removal increased with irradiation dose, reaching 52% at 40 kGy, demonstrating that gamma irradiation effectively degrades HA solutions.

3.3 Change of pH

The effect of irradiation dose on pH was investigated at an initial HA concentration of 0.12 g/L. As shown in Figure 3, the initial pH of the HA solution was 7.05. After irradiation, the pH decreased with increasing dose due to formation of small-molecule organic acids such as oxalic acid and formic acid during HA decomposition [**?**]. However, at 40 kGy, the solution pH showed a slight increase, possibly because these small-molecule acids were completely mineralized to CO_2 and H_2O under high-dose conditions.

[Figure 3: see original paper]

3.4 Effect of Initial Concentration on COD Removal

Figure 4 [Figure 4: see original paper] shows COD removal for different HA concentrations (0.02, 0.04, 0.08, and 0.12 g/L) after gamma irradiation at various doses. The initial pH of all solutions was 7.05. Initial concentration played an important role in HA decomposition, with COD removal decreasing as initial concentration increased under the same irradiation dose. For example, at 15 kGy, COD removal was 95% for 0.02 g/L HA but only 31% for 0.12 g/L HA. This occurs because the amount of organic carbon is greater at higher HA concentrations, while the amount of OH radicals formed depends on irradiation dose, resulting in lower degradation efficiency at high concentrations [**?**].

3.5 Kinetic Analysis of COD Removal

As shown in Figure 4, COD removal increased approximately exponentially with irradiation dose, suggesting that HA degradation follows pseudo-first-order kinetics. Assuming the gamma irradiation process obeys pseudo-first-order kinetics, the relationship between COD removal and irradiation time can be expressed by Eq. (2):

$$\ln \frac{C_t}{C_0} = -kt$$

where C_0 and C are COD values before and after irradiation, t is irradiation time (h), and k is the reaction rate constant.

Table 1 presents the kinetic parameters. The high correlation coefficient (R^2) values indicate that HA degradation by gamma radiation follows pseudo-first-order kinetics. The rate constant k decreased with increasing initial HA concentration, confirming that at lower concentrations, HA has a higher probability of reacting with OH radicals under the same irradiation conditions and pH.

Table 1 Degradation kinetics for HA solutions at different initial concentrations

Concentration (g/L)	Kinetics Equation	Correlation Coefficient (R^2)
0.02	ln(C /C_0) = -0.0194t + 9.2607$×10^{-4}$	
0.04	ln(C /C_0) = -0.3683t + 0.0149	
0.08	ln(C /C_0) = -0.0863t -0.0658	
0.12	ln(C /C_0) = -0.2387t + 0.1257	

3.6 Effect of Initial pH on COD Removal

To investigate pH effects on degradation efficiency, experiments were performed at an initial HA concentration of 0.1 g/L, an irradiation dose of 25 kGy, and pH values ranging from 3 to 12. As shown in Figure 5, COD removal varied with initial pH, with optimal removal occurring at pH 3. The pH may affect HA molecular structure, resulting in different degradation efficiencies. Additionally, the oxidation potential of OH radicals is higher at low pH than at high pH, favoring HA degradation under acidic conditions.

[Figure 5: see original paper]

Conclusions

The results demonstrate that gamma irradiation is an effective method for HA degradation in aqueous solution. After irradiation, HA solutions showed significant declines in UV-Vis absorbance and COD concentration. For example, with an initial concentration of 0.12 g/L and initial pH of 7, 40 kGy irradiation reduced UV-Vis absorbance at 310 nm by 90% and COD concentration by 52%. The COD concentration changes followed first-order kinetics, with higher initial concentrations yielding lower reaction rate coefficients.

Both initial concentration and pH significantly affect irradiation degradation efficiency. Under the same irradiation conditions, degradation efficiency decreases as initial concentration increases. The highest irradiation degradation efficiency occurs at initial pH values between 6 and 8, while extremely low or high pH values are unfavorable for HA degradation.

References

1. Jarek W, Didier R, Joanna S G, et al. J Photochem Photobio A: Chem, 2002, 152: 267-273.
2. Tan X W, Zhou X L, Hua R, et al. Bioinformatics and Biomedical Engineering (iCBBE), 2010 4th International Conference. Chengdu, 2010, 1-5.
3. Ali S K, Yalcin S Y, Bulent K, et al. Sep Purif Technol, 2008, 59: 175-182.
4. Xiong X Y, Yu J T. Environ Eng, 1998, 6: 7-10.
5. Santosa S J, Kunarti E S, Karmanto. Appl Surf Sci, 2008, 254: 7612-7617.
6. Ngah W S W, Hanafiah M, Yong S S. Colloid Surface B, 2008, 65: 18-24.
7. Kati R, Vaisanen P, Metasa M S, et al. Desalination, 1998, 118: 273-283.
8. Wu Y Y, Zhou S Q, Ye X Y, et al. Colloid Surface A, 2011, 379: 151-156.
9. Ankesh B, Madhavi S, Timothy T, et al. Catal Today, 2008, 131: 250-254.
10. Mahvi A H, Maleki A, Rezaee R, et al. Iran J Environ Health, 2009, 6: 233-240.
11. Artur J, Motheo, Laerte P. Sci Total Environ, 2000, 256: 61-65.
12. Jiang S J, Liu Z Y. J Chongqing Jianzhu Univ, 2002, 2: 67-76.
13. Hidehiko A, Michimasa A, Akihisa S. Water Res, 1986, 20: 885-891.
14. Liang H B, Ma Z J, Guo C J. The radiation declines the Process, 2004, 22: 8-12.

Note: Figure translations are in progress. See original paper for figures.