Radiation Physics and Chemistry 97 (2014) 12–15

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Short Communication

The effect of electron irradiation on aqueous dispersions of humic acids and lignin

I.E. Makarov *, P.K. Metreveli, A.K. Metreveli, A.V. Ponomarev

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Leninsky Prospect, Moscow 119071, Russia

HIGHLIGHTS

- Electron irradiation promotes coagulation in aqueous dispersions of lignin and humic acids.
- Maximal effect of coagulation is achieved at absorbed dose 5–15 kGy.
- Negative charge accumulating by absorption of incident electrons results in stabilizing negatively charged micelles.

ARTICLE INFO

Article history:
Received 25 September 2013
Accepted 21 October 2013
Available online 29 October 2013

Keywords:
Lignin
Humic acids
Irradiation
water treatment
Coagulation
Uncompensated charge

ABSTRACT

The effect of irradiation by accelerated electrons on optical absorption of diluted aqueous solutions of lignin and humic acids was studied under two different irradiation conditions: when thickness of irradiated solution layer was less than the electrons range in the solution (mode **I**) and vice versa (mode **II**). Dominating agglomeration and sedimentation of the compounds has been demonstrated to take place under irradiation in mode **I**, maximal effect being achieved at absorbed dose 5–15 kGy. Under irradiation in mode **II**, *i.e.* when all the incident electrons were being absorbed, the radiation-induced coagulation was depressed. The dependence of radiation effect on irradiation conditions may be caused by stabilizing action of accumulating excess charge of absorbed electrons on negatively charged micelles of lignin and humic acids.

1. Introduction

Under the action of ionizing radiation changes in stability of colloid and coarsely dispersed systems take place. The phenomenon is of interest, in particular, of radiation technologies for purification of natural water and industrial wastewater contaminated by ultra-dispersed organic compounds (Woods and Pikaev, 1994; Sampa et al., 2007). In many cases superficial water has increased color and turbidity due to humic compounds and lignin, which is rather characteristic of river and lake water of northern regions of Russia (Pikaev et al., 1996; Lobbes et al., 2000), as well as of other surface waters (Perdue, 2009). The compounds often come with water from environing bogs or are dispersed from wood bottom sediment formed as a result of timber rafting, additional contamination results from activity of paper mills and other industrial enterprises. Conventional water treatment based on continuous-flow filtering and chlorination does not often remove the color caused by ultra-dispersed phytogenous matter, one of results of which is deposit formation on inner surface of water pipeline systems.

Since electron accelerators are proposed to be the most actual sources of ionizing radiation in water treatment technologies, in the present work an attempt has been made to estimate specific action of electron irradiation on stability of aqueous dispersions of humic acids (HA) and lignin. Special attention was paid to influence of irradiation conditions on the process of natural organic matter coagulation, namely, to the effect of relationship between effective penetration of incident electrons and thickness of irradiated matter layer.

2. Materials and methods

2.1. Solutions

There were studied aqueous solutions of pine lignin (commercial preparation “Polyphepan” by “Scientech” company) and of humic acids mixture (by “ACROS” company). The solutions were prepared by adding appropriate amount of powdered substance to distilled water and mixing. Colloid solutions (or dispersions) of HA (10–50 mg/L) and lignin (50–325 mg/L), prepared in such a way,

* Corresponding author. Tel.: +74992346244.
E-mail address: makarov@ipc.rssi.ru (I.E. Makarov).

0969-806X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.radphyschem.2013.10.010

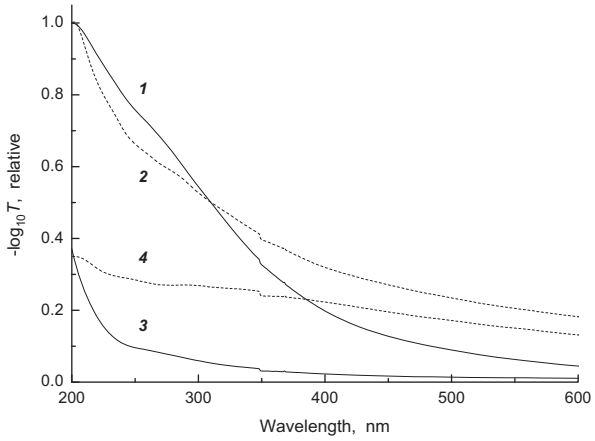

Fig. 1. Optical spectra of solutions 11 mg/L HA (1, 3) and 63 mg/L lignin (2, 4): 1, 2 – initial solutions; 3, 4 – solutions irradiated at 30 kGy in mode I.

were kinetically stable during more than 2 days. For that time optical spectra of the solutions, representing broad unstructured bands in the region of 200–900 nm (Fig. 1), remained unchangeable.

2.2. Irradiation

Two types of accelerated electrons sources were used in the experiments. Linear accelerator UELV-10-10T, used for irradiation in mode **I**, generated horizontal beam of 8 MeV electrons. Range of such electrons in water is about 40 mm (Woods and Pikaev, 1994). The samples were exposed to irradiation in open vials with irradiation width 15 mm. Under those irradiation conditions the samples were irradiated uniformly, and incident electrons left the samples. In irradiation mode **II** the transformer type pulsed accelerator URT-1 was used which generated vertical beam of electrons with continuous energy spectrum in the region of 0.2–0.7 MeV, ~90% of the electrons' energy being concentrated at 0.5–0.7 MeV. Range of electrons of such energies in water does not exceed 3 mm. Used in the experiments 3 mm layer of aqueous solution completely absorbed all the incident electrons. All the solutions were irradiated in the presence of air.

2.3. Measurements

Dosimetric measurements were carried out with the help of film dosimeter based on copolymer with phenazine dye. UV-Vis spectrophotometer "Cary-100" was used for optical measurements. Transmittance of the samples $T=I/I_0$ (I and I_0 being intensities of passed and incident light), expressed in figured as $-\log_{10}T$, reflected both real light absorption and scattering. Quantitative determination of color of the solutions (in color degrees) was carried out by colorimetric analysis in a similar manner as described elsewhere (Standard Methods, 2012).

3. Results

3.1. Irradiation in mode *I*

Irradiation of the solutions results in notable changes in their spectra. Maximal increase in optical transmittance of HA solutions under irradiation in mode **I** takes place at rather low absorbed doses (D). Thus, the most noticeable transmittance change for the solutions with concentration ≤ 50 mg/L (initial color 383 degrees) is observed at $D \approx 5$–15 kGy. The highest discoloration quotient was estimated to be equal to 25 degree/kGy. Optical transmission upon irradiation increases in the entire region from 200 to 900 nm (see Fig. 1), being, mainly, the result of coagulation. Thereby, settling takes place.

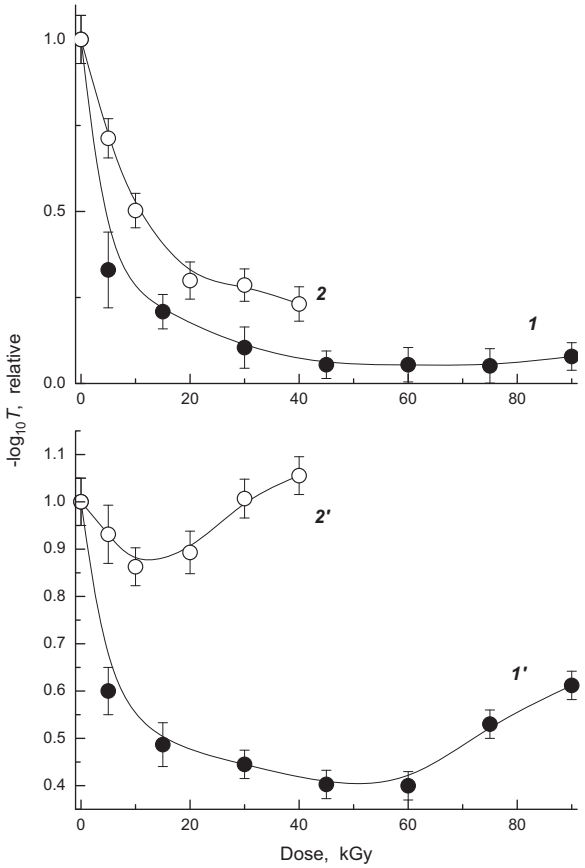

Fig. 2. Effect of absorbed dose on transmittance T of 11 mg/L HA solution at 380 nm (1, 2) and 205 nm (1′, 2′) under irradiation in mode I (1, 1′) and in mode II (2, 2′).

Effect of absorbed dose on discoloration depends on initial HA concentration. *E.g.*, for solution 11 mg/L (initial color 85 degree) slow increase in optical transmission is observed up to $D \approx 60$ kGy (Fig. 2, curves 1, 1′). In the dose region $60 \leq D \leq 90$ kGy changes in visible part of optical spectrum are comparatively small. However, increase in absorbed dose is accompanied by the rise of optical absorption at $\lambda \leq 240$ nm which is due to appearance of soluble products of HA fragmentation (curve 1′). For HA solution with concentration 50 mg/L, color rising begins at absorbed dose $D \geq 30$ kGy.

Similar coagulation processes are observed also in lignin solutions. However, these solutions appeared to be more stable to irradiation. For 63 mg/L lignin solution (initial color ~50 degrees) in the region of absorbed dose from 15 up to 90 kGy optical transmission at 380 nm remains practically unchanged (Fig. 3). Transmission in the UV region at doses higher than 45 kGy decreases with increasing the dose. Increase in transmission in the entire studied spectral region takes place also upon irradiation of lignin solutions with as high concentration as 325 mg/L (initial color ~265 degrees). At rather low absorbed dose (~10 kGy) near twofold reduction of the color is observed, initial discoloration quotient being about 13 degree/kGy. Irradiation at higher dose does not produce any appreciable spectral changes.

Irradiation of combined samples containing both lignin (65 mg/L) and HA (11 mg/L) results in spectral changes which are close to those for individual solutions. However, initial optical transmission of combined solution in the region of 200–900 nm is some higher than the sum of individual solutions transmissions (Fig. 4) which may be mainly due to formation of complex micelles of lignin and HA. At $D \leq 30$ kGy a monotone rise of transmission in visible and UV region is observed. At higher doses (≥ 60 kGy) smoothed decrease in transmission takes place, like in individual HA solution. Initial