



The effect of UV and visible light radiation on natural humic acid EPR spectral and kinetic studies

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Abstract

The effect of polychromatic UV and visible light on the radical properties of humic acid (HA) extracted from composted shells of walnut tree *Juglans regia* was investigated. The exposure of HA solutions 2 mg/ml in 0.01 M Na₂CO₃ at pH=10.8 to the light from a 150-W xenon lamp increases the signal amplitude of electron paramagnetic resonance (EPR). Using the set of cut-off filters at 390, 340, 280 and 200 nm, the efficiency of free radical formation was determined. It shows the maximum efficiency of radicals generation in the range 280–340 nm, which corresponds to the maximum in absorption spectra of quinones and naphthoquinones in the UV range. Generation of the free radicals during visible light irradiation is connected with photosensitized properties of HA. The single exponential decay of the EPR signal observed after irradiation, calculated *g*-value and spectral and kinetic studies of photoinduced EPR amplitude changes in aerated and deaerated solutions indicate that the reactive oxygen species (ROS) and excited molecules in the triplet state are very probably the factors leading to the formation of stable quinoid type of free radical in HA. Observed linear increase of free radicals generated during irradiation indicates on the great capacity of HA to efficiently stabilize free radicals inside its structure.

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1. Introduction

The knowledge of chemical and physical properties of humic substances (HS) is essential in under-

standing their interactions with environmental factors, particularly with the UV and visible light and oxygen. These interactions are photophysico-chemical in nature and depend on the chemical composition and structure of HS. The behavior of bulk humic substances (HS) or humic acid (HA) in reactions with light, oxygen and prooxidants present in soil and aquatic environment (Sławińska et al., 1975a,b; Sławińska and Michalska, 1978; Hoigne et al.,

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1989; Senesi, 1990; Senesi and Miano, 1994; Drozd et al., 1997; Chen et al., 2003) may differ significantly from those of individual HA component. In this respect, a high content of unpaired spins is an important factor as the organic matter of geoderma is far from thermal equilibrium with atmospheric oxygen. The main factor which slows down an unavoidable oxidation reaction of organic matter is the different multiplicity of the reactions substrates, i.e. the singlet of organic matter and triplet of molecular oxygen.

The absorption of light by chromophores existing in humic acid (HA) may lead to alterations of HA structure and composition which is reflected by the changes in absorption, fluorescence, chemiluminescence, NMR, IR and EPR spectra (Senesi and Miano, 1994; Sławiński et al., 1998; Jezierski et al., 2000; Kalbitz et al., 2000; Piana and Zahir, 2000; Tratnyek et al., 2001; Imai et al., 2002; Chen et al., 2003). When quinone moieties in HS undergo one-electron reduction, free radicals of semiquinones and charge-transfer complexes are formed. They are efficient absorbers of light in a broad spectral range. It was shown that quinone moieties in HA are relevant not only to radical content but also to HA's antioxidant activity (Polewski et al., 2002), regulation of redox reactions in metabolic plant and microbial processes (Kalyanaraman, 1990; Jurcsic, 1994; Scott et al., 1998) and metal-ion pollutants (Jezierski et al., 2000, 2002).

Recently, a HA fraction from composted green shells of walnut tree (*Juglans regia* L.), containing a large amount of naphthoquinones, was obtained (Sławińska et al., 2002, 2004). Naphthoquinones, especially 5-hydroxy 1:4 naphthoquinone (juglone) were found in *J. regia* L and *Juglans nigra* (Blumenthal, 1998). Juglone and its derivatives occur in the roots, fruits, leaves and wood of *J. regia* L and exhibit a wide spectrum of pharmacodynamic activity, especially cytotoxicity and genotoxicity (Thompson, 1987; Babich and Stern, 1993). There is a large number of plants, soil microorganisms and animals sensitive to allelopathic polyphenolic and quinoid compounds like juglone that can be incorporated into HA during the humification process. However, no systematic studies have been done on these aspects of HA originating from humified litter of *Juglans* species.

For all these reasons, it is interesting to examine the photophysico-chemical and paramagnetic properties of HA obtained from composted plant residue abundant in hydroxynaphthoquinones.

The aim of this work is to investigate the influence of UV and visible light on the natural humic acid from walnut shells which was isolated and characterized for the first time (Sławińska et al., 2002). The effect of the UV and visible radiation is investigated using EPR spectroscopy method. The applied cut-off filter limits, at 280 and 340 nm, correspond to the upper limits of UV-C and UV-A solar radiation which increasingly penetrates the Earth biosphere.

2. Materials and methods

The HA was isolated from the composted hulls of walnut *J. regia* rich in naphthoquinones. Details of the preparation procedure and physico-chemical properties of the HA are given elsewhere (Sławińska et al., 2002). EPR spectra of solid HA were measured in a 2-mm quartz tube. EPR measurements of aqueous samples in 0.01 M Na₂CO₃ at pH=10.8 of 2 mg/ml HA were carried out at room temperature using quartz flat cell and in situ irradiation of the samples (Rożanowska et al., 1995).

Electron paramagnetic resonance (EPR) measurements of solid and aqueous samples of HA were carried out using a Bruker ESP 300 E spectrometer operating at X-band at 9.5-GHz frequency and equipped with 100-kHz field modulation, modulation amplitude 0.946 G, sweep width 110 G, conversion time 82 ms, time constant 327 ms.

The spectrometer type SE/X 2544 (Radiopan, Poznań, Poland) equipped with a resonance chamber RCX 660 was used to obtain spectra of solid HA sample and a standard. EPR signals were recorded at room temperature with the following settings: microwave power 3 mW, time constant 1 s, scan rate of 20 mT/2 min, modulation frequency of 100 kHz/0.2 mT and a microwave frequency of 9.45 GHz. The signals were used to calculate the peak-to-peak amplitude (a.u.). The 2,2-diphenyl-1-picrylhydrazyl (DPPH) was employed as the standard to determine the g coefficient ($g=2.005$) and concentration of spins. Care was taken to ensure constant conditions

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