Oxidative polymerization and chemical characterization of 1,8-dihydroxynaphthalene using Ultraviolet (UV)-Visible spectroscopy, Fluorescence spectroscopy and mass spectrometry analysis

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Abstract

Dissolved organic matter (DOM) is a complex mixture of organic molecules, some with relatively low molecular weight and others that are biomolecules such as proteins with larger molecular weight. DOM can originate from several marine and terrestrial sources which are subject to continuous biological and chemical processes. Understanding the chemical composition of DOM on a molecular level helps interpret the optical properties and molecular signatures of DOM that greatly depend on its origins. Photochemical reactions are one of the processes that produce and modify DOM in aquatic environments. In this study, we oxidize and initiate the polymerization of 1,8-dihydroxy naphthalene (DHN) by addition of hydrogen peroxide and/or with Ultraviolet (UV) irradiation. The results of UV-visible spectroscopy indicate significant loss of DHN absorption due to photo-oxidation and an extreme shift of absorbance spectra from 1,8-dihydroxy naphthalene to humic-like spectra. Fluorescence spectroscopy of original and oxidized samples showed that there are initially three signature peaks with excitation wavelengths at 302, 318 and 332 nm in the emission spectrum of 1,8-dihydroxynaphthalene. For the oxidized samples with humic-like absorbance spectrum, the emission spectrum indicates a different pattern with a new broad peak at 425 nm. These results indicate the formation of dimers and oligomers from oxidative polymerization of 1,8-dihydroxy naphthalene. Mass spectrometry analysis of untreated and oxidized samples was done by negative-mode electrospray ionization (ESI) in the Orbitrap Elite mass spectrometer. The results of mass spectrometry analyses showed new mass patterns for the oxidized samples, which demonstrated evidence of oligomers being formed from 1,8-dihydroxy naphthalene. Overall, the results of optical measurements and mass spectrometry analyses strongly support the idea that simple molecular structures such as dihydroxy naphthalene can produce humic-like optical properties through simple oxidative steps.