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Darkening mechanism and kinetics of humification process in catechol-Maillard system

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HIGHLIGHTS

• Effect of varied catechol content on catechol-Maillard reaction was studied.

- Contribution of N-containing groups to darkening effect was revealed.
- Kinetic constants of two-step humification reaction were determined.
- Increasing catechol promoted yields of Fulvic-like acids and Humic-like acids.
- · Catechol content affected degree of unsaturation of Humic-like acids.

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ABSTRACT

Humic acids, products of humification process, are capable of interacting with contaminants and can be applied to environmental remediation. Browning mechanisms of humification is critical to understand and further control the process. This study aimed to investigate the mechanism of abiotic humification by tracking the fate of the precursors in systems containing glucose, glycine, and various CT concentrations, which were promoted by MnO₂. Results show that the N-containing organic molecules significantly contributed in controlling the darkening effect. Increasing CT promoted the formation of Fulvic-like acids (FLAs) and Humic-like acids (HLAs). The entire reaction could be divided into two steps following pseudo-second-order kinetics equation and pseudo-zero-order kinetics equation. Moreover, increasing CT contributed to the increase of the degree of unsaturation in HLAs.

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1. Introduction

Humic substances are ubiquitous in the environment. Humification of organics occurs spontaneously during landfilling and composing, (Binner et al., 2011; Qi et al., 2012a), which is always used as an important evaluation indicator of the stability and safety of organics. Numerous studies have shown humic acids, degradation products of dead organic matter, portend great promise as inexpensive amendments to mitigate the environmental risks of ecotoxicant, such as heavy metals, herbicides, and polycyclic aromatic hydrocarbons (Christl et al., 2005; Porras et al., 2014). The application of humic-based remediation technologies has acquired tremendous achievements. The humic acids, obtained from humification of olive oil mill wastewater enhanced by MnO_2 , can served as organic amendment to improve soil quality and immobilize heavy metals. (Clemente and Bernal, 2006; Brunetti et al., 2007; Masciandaro et al., 2010). Being as environmentallyfriendly resource, humic-like acids (HLAs) have been produced with biomass waste (Fukushima et al., 2009b; Wei et al., 2014) and organics from leachate by extensive attempts (Xu et al., 2006). Therefore, the mechanism of humification has become a hot issue. Identification of key substances affecting organic humification process is of great significance in environmental restoration. Biotic humification by microorganisms is usually time-consuming and environmentally sensitive, whereas abiotic humification can provide a new perspective to produce high quality HLAs. Sugars, amino acids, and phenols, which are the major ingredients of biomass wastes, are often used as model humic precursors of abiotic humification to form HLAs (Hardie et al., 2009;







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Fukuchi et al., 2010). Abiotic humification can be achieved via several approaches, and oxidative polymerization of phenols is regarded as one of the main processes. Phenol humification is attracting increasing research attention, and studies on this area have made remarkable progress (Huang, 2004).

Naturally, inorganic mineral materials often coexists with biomass waste, which can be used as Lewis acids by accepting electrons originating from humic precursors to enhance the humification process (Jokic et al., 2004a; Fukuchi et al., 2010; Qi et al., 2012a). Mineral materials enhance humification by initiating the formation of semiquinone radicals from ring cleavage of phenol oxidation. Semiquinone radicals and other small molecules of organic matter undergo a series of oxidation coupling reactions for polymerization (Liu and Huang, 2002; Nishimoto et al., 2013). Mn (IV) oxide is considered as a most effective oxidant with respect to the abiotic humification among mineral materials (Shindo and Huang, 1982). The Maillard reaction involving polycondensation reactions between amino acids and reducing sugars is known as an important humification pathway in nature. Considerable progress has been achieved (Jokic et al., 2001a,b). However, adding catechol (CT) to a Maillard system can promote the formation of darkening substances, which is better than the Maillard system alone (Jokic et al., 2004b). The positions of the OH groups on the benzene ring and molar ratio of various polyphenols can cause ring cleavage with varying degrees, and further affect humification and the amount of released carbon dioxide in the integrated polyphenol-Maillard reaction system (Hardie et al., 2007; Chien et al., 2009).

The darkening phenomenon is an important indicator of nonenzymatic humification and enzymatic humification in nature. Key substances induce the darkening phenomenon in humification via chemical redox polymerization reaction, which occurs in biomass in a natural environment, such as small molecules stemming from degradation of proteins, sugars, lipids, polyphenols, and biological metabolites (Rouet-Mayer et al., 1990; Hidalgo and Zamora, 2000; Zamora and Hidalgo, 2005; Mecozzi et al., 2014). Moreover, key factors affecting the formation of colored polymers are induced by carbonyl-amine reactions (Hidalgo and Zamora, 2000) and hydrogen bonds between carbohydrates and proteins (Mecozzi et al., 2014). In addition, the pH of the humification system can influence the color of solutions, and oxidative polymerization at high pH in the presence of MnO₂ has been confirmed to be the preferable reaction conditions (Shindo and Huang, 1982). The relative abundance of functional groups in colored substances can be characterized by UV-Vis absorption. Absorbance at 400 nm is introduced as an indicator to monitor the formation of browning substances via organics polymerization, which is considered a key process of humification, indicating the generation of organic chromophoric group, which is closely related to the darkening effect of humification (Shindo and Huang, 1982; Fukushima et al., 2009a; Nadi et al., 2012; Qi et al., 2012b; Nishimoto et al., 2013). Relevant colored functional groups include chromophores, such as aromatic C=C, ketonic C=O, diazo N=N and azomethine CH=N groups. Additionally, auxochromes, such as C-OH and C-NH₂. Auxochromes do not confer color but increase the color of chromophores in a conjugated system (Leenheer et al., 1987).

The effect of increasing contents of sugars and phenols on the Maillard system enhanced by inorganic mineral materials has been well documented (Jokic et al., 2001a, 2004b; Hardie et al., 2007, 2009). However, the function of increasing phenol concentrations in influencing the darkening effect of the integrated polyphenol-Maillard humification pathway as catalyzed by MnO₂ remains obscure, and very little investigation has been conducted on this topic. Moreover, the kinetics of humification remains unclear because of a complex series of reactions associated with

complicated products. The present work aimed to investigate the function of varied CT concentrations in abiotic humification and related products, including the color controlling mechanism and kinetics law of generating HLAs in the catechol-Maillard system.

2. Methods

2.1. Reagents

CT (>99% purity) was purchased from Tokyo Chemical Industry. Glycine (>99% purity) and glucose (>99% purity) were obtained from Nacalai Tesque. MnO_2 and thimerosal were obtained from Xilong Chemical Company, Guangdong, China. All the reagents mentioned above were used without further purification. Thimerosal has been proved to produce no significant effects in the abiotic humification reaction as a sterilant (Wang et al., 1983). DAX-8 resin was purchased from Sigma–Aldrich. Solutions for humification experiments contained 0.2 M (M) phosphate buffer (NaH₂PO₄ and Na₂HPO₄, pH 8.00) in which 0.02% thimerosal was added as a preservative, thereby providing significant effects on abiotic humification. All solutions were prepared with ultrapure water (resistivity = 18.2 M Ω cm).

2.2. Humification systems

Humification systems do not require the involvement of microorganisms in the reactions. All glassware and ultrapure water were autoclaved (120 °C for 20 min) prior to use. Powdered glycine and glucose were added to 300 mL Erlenmeyer flasks containing 170 mL of phosphate buffer (pH 8.00), 0.02% (w/v) thimerosal, and 2 g of MnO₂ to obtain solutions with glycine and glucose concentrations of 0.06 M. CT was added into flasks to obtain concentrations of 0, 0.03, 0.06, 0.12, and 0.24 M. All reaction systems were performed in duplicates. One flask with buffer solution only was used as control 1, and another flask with buffer solution and MnO₂ was designated as control 2. All mixtures were shaken at 35 °C in a rotatory shaker at 150 rpm for 360 h.

2.3. UV-Vis absorption for the darkening reaction

Samples of 1 mL were withdrawn from each reaction system at 0, 3, 6, 18, 28, 48, 76, 124, 172, 240, and 360 h during incubation, and centrifuged at 10000 rpm for 5 min. A 500 μ L aliquot of the supernatant of each sample was diluted to 20 mL with ultrapure water to determine the concentration of dissolved organic carbon (DOC). Another 100 μ L aliquot of the supernatant was diluted to 10 mL with ultrapure water to analyze the absorbance at 400 nm (A_{400}), which was employed to indicate changes of organic chromophores and formation of browing substances in humificaton (Shindo and Huang, 1982; Andersen et al., 2000; Hardie et al., 2009).

2.4. Separation and purification of humic-like substances

The extraction and purification of HLAs was according to the method recommended by the International Humic Substances Society. Samples of 5 mL were extracted from the reactors at 0, 18, 48, 76, 124, 172, 240, and 360 h. The samples were then centrifuged at 10000 rpm for 10 min using a Kubota 3740 centrifuge, and filtered with a 0.45 μ m micropore filter membrane. The filtrate was acidified to pH 1.0 with concentrated HCl, and allowed to subside for 24 h. After centrifugation, the precipitate containing HLAs was re-dissolved in 0.1 M NaOH. The supernatant containing Fulvic-like acids (FLAs) was allowed to flow through 1 mL of DAX-8 resin to absorb FLAs.

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