



Research Paper

Compost-derived humic acids as regulators for reductive degradation of nitrobenzene



Ying Yuan^{a,b,c}, Beidou Xi^{a,b,c}, Xiaosong He^{b,c,*}, Wenbing Tan^{b,c}, Rutai Gao^{b,c}, Hui Zhang^{b,c}, Chao Yang^{b,c}, Xinyu Zhao^{a,b,c}, Caihong Huang^{b,c}, Dan Li^{b,c}

^a College of Water Sciences, Beijing Normal University, Beijing 100875, China

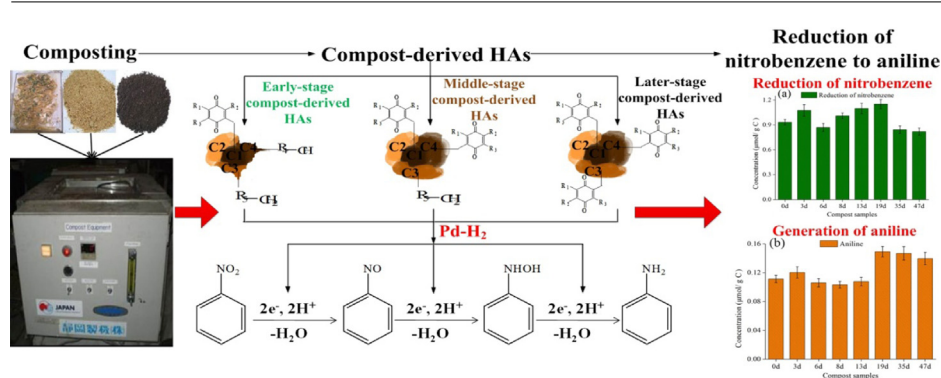
^b State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

^c State Environmental Protection Key laboratory of Simulation and Control of Groundwater Pollution, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

HIGHLIGHTS

- Compost-derived HAs were able to reduce nitrobenzene (NB) to aniline (AN).
- Middle and late-stage compost-derived HAs had better reduction of NB to AN.
- Redox functional groups within compost-derived HAs influenced NB reduction.
- Compost-derived HAs had a broad application prospect for NB remediation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 May 2016

Received in revised form 18 June 2017

Accepted 20 June 2017

Available online 23 June 2017

Keywords:

Composting

Humic acid

Nitrobenzene reduction

ABSTRACT

Nitrobenzene (NB) is a major class of contaminants in soil and groundwater. The current methods involved in the reductive degradation of NB suffer either cost-ineffective or slow conversion rate. Here, we investigated the mechanisms regarding compost-derived humic acids (HAs) as cost-effective regulators to enhance the reduction of NB to aniline (AN). Our results show that the compost-derived HAs, which have been reduced by a Pd-H₂ catalytic system, were able to reduce NB to AN, and their redox properties were the main factors governing the reduction of NB to AN. The decreasing reduction of NB was mainly caused by the decreasing phenol content of compost-derived HAs during composting. In addition, the results reveal that the increase in the generation content of AN was mainly attributed to the increase in the quinones, aromaticity and humic-like components of compost-derived HAs. The findings demonstrate that the HAs derived from compost are effective regulators to enhance the reduction of NB to AN, and that they exert a bright application prospect for the remediation of the NB-contaminated soil.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Nitrobenzene (NB) is widely used during chemical processes producing dyes, pesticides, aniline (AN), pharmaceuticals, solvents and organic synthesis intermediates [1–3]. Due to improper handling, disposal practices and accidental spills, NB becomes a major

* Corresponding author at: No. 8 Dayangfang, Beiyuan Road, Chaoyang district, Beijing 100012, China.

E-mail address: hexs@cares.org.cn (X. He).

class of contaminants in soil and groundwater [1,4]. Many governments list it as a priority pollutant owing to its mutagenicity, recalcitrance, and tendency to accumulate in environments [1,5]. To date, a numerous of chemical and biological methods involved in the reduction of NB to AN have been developed, such as biological anaerobic process [6], electrochemical reduction [7], and micro electrolysis [8]. Compared to the biological process, the chemical methods exhibit higher NB conversion rates. However, the chemical process is often cost-ineffective and may cause secondary pollution [1]. Therefore, it is significantly important to explore cost-effective and efficient methods for the remediation of NB-contaminated soil and groundwater.

Composting is a biological transformation process of organic solid substrates, and humic acids (HAs) were synthesized during the process, which can be used to increase soil nutrient content, improve soil structure, and enhance microbial activity [11,12]. Furthermore, given that natural HAs have been confirmed to reduce NB to AN in aqueous solution [14], we speculate that the HAs derived from compost, which are similar to the natural HAs [9,10], have the potential for facilitating the reduction of NB as well.

In this study, the Pd-H₂ catalytic system, which has been widely used to assess the capacities of HAs to reduce redox-active contaminants [15–19], was employed to investigate the capacities of compost-derived HAs to reduce NB. Meanwhile, the composition and structures of compost-derived HAs were analyzed to reveal the factors affecting compost-derived HAs to reduce NB. The objectives of this research were to test whether compost-derived HAs were able to reduce NB, and to identify the factors governing the reduction of NB to AN in compost-derived HAs.

2. Methods

2.1. Composting process and sample collection

Composting was conducted in an indoor composting reactor with a volume of 34 L and height × diameter of 400 mm × 330 mm. The ventilation was controlled at 0.5 L min⁻¹ kg⁻¹. Composting materials consisted of kitchen wastes (10.5 kg), soil (9 kg), sawdust (0.23 kg) and a composite microbial system (1.6 kg). Composting lasted for 47 days (d), and the changes of temperature and pH are shown in Fig. S1. The compost samples, which mixed from three sub-samples collected at the 5-, 15- and 25- cm depth of the composting reactor, were obtained after 0, 3, 6, 8, 13, 19, 35 and 47 d of composting, respectively. The samples were then freeze-dried and stored at -20 °C until analysis.

2.2. HAs extraction

The isolation of compost-derived HAs was performed according to the IHSS standard assay [20]. The detailed process was as follows. 30 g sample was placed in a 500 ml triangular flask containing 200 ml solution of 0.1 M Na₄P₂O₄ and 0.1 M NaOH (1:1), and then shaken for 24 h at room temperature. The residue (humic and other insoluble compounds) was separated from the supernatant by centrifugation (15 min, 7000 rpm). Then, the supernatant was acidified by diluted hydrochloric acid (6 M HCl, pH 2.0), the compost-derived HAs were then purified and precipitated [21] and finally stored in phosphate buffer (pH = 7) at 4 °C.

2.3. Analytical technique

All samples were filtered by filter membranes with an aperture of 0.22 μm, and their dissolved organic carbon (DOC) content was measured by a TOC automatic analyzer (MultinN/C2100TOC/TN). The filtrates were freeze-dried, and then Fourier transform infrared absorption spectra (FTIR) were recorded on a Hitachi EPI Infrared

Spectrophotometer using the KBr disk method. Solid-state CP/MAS ¹³C NMR spectra were measured by using a Bruker model AV-300 spectrometer at 12 kHz with a standard 4 mm double-bearing probe head. The recycle delay time, contact time and pulse width time were set to 1 s, 2000 μs, and 2.4 μs, respectively. The percentages of area regions of 14–39, 50–60, 65–80, 110–140 and 164–185 ppm in the NMR spectra were calculated.

Three dimensional excitation-emission matrixes (3DEEM) were recorded with a Hitachi model F-7000 luminescence spectrophotometer equipped with a 150 W xenon arc lamp as the excitation source. The slit widths of the excitation and emission monochromators were set at 5 nm, the voltage of the photomultiplier tube was adjusted to 700 V, and the emission (Em) wavelength was scanned from 280 to 550 nm by increasing the excitation (Ex) wavelength in 5 nm increments from 200 to 450 nm with a scan speed of 12,000 nm min⁻¹. The EEM spectra of distilled water were obtained and subtracted from the EEM spectra of the compost-derived HAs [19]. Parallel factor (PARAFAC) analysis was applied to the three-dimensional data array on MATLAB 7.0 (Mathworks, Natick, MA) with the DOM Fluor toolbox [22,23]. The F_{max} value, which labeled as the scores in the score matrix, was obtained through EEM-PARAFAC analysis and used to evaluate the relative concentration of the fluorescence components [23].

UV-vis spectroscopy was performed on a UNICO model UV-4802 double beam spectrophotometer. Specific UV absorbance values SUVA₂₅₄ (=UV₂₅₄ × 100/DOC) [24,25], SUVA₂₆₈ (=UV₂₆₈ × 100/DOC), SUVA₂₉₀ (UV₂₉₀ × 100/DOC) [17], SUVA₃₃₀ (=UV₃₃₀ × 100/DOC) [26,27] and SUVA₄₇₅ (=UV₄₇₅ × 100/DOC) [28] were calculated by dividing the absorbance at 254, 268, 290, 330 and 475 nm by the corresponding DOC concentration, respectively. These parameters were used to characterize the aromaticity and quinone contents of compost-derived HAs.

2.4. EAC and EDC measurements

The EAC and EDC of compost-derived HAs were determined using the modified mediated electrochemical reduction (MER) and oxidation (MEO) methods described by Aeschbacher [29]. Briefly, the measurement process were conducted in 4–5 ml solutions (0.1 M KCl, 0.1 M phosphate, pH 7) using a 3 mm diameter glassy carbon disk working electrode (WE), a platinum wire counter electrode, and an Ag/AgCl reference electrode (All electrochemical materials were purchased from Chenhua, China). Diquat dibromide monohydrate (99.5%, Supelco) (DQ, 3 mg) and 2,2'-azino-bis (3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt (>99%) (ABTS, 6 mg) were used as mediators for MER and MEO, respectively. The electrode was equilibrated to the desired potentials (E_h = +0.61 V in MEO and E_h = -0.49 V in MER, respectively) before the reaction. Subsequently the mediators DQ for MER and ABTS for MEO were spiked. After the reaction reached equilibrium, compost-derived HAs (20 mg CL⁻¹) were injected into the solution. After re-equilibrium of constant background currents, the transferred amount of electrons was measured by chronocoulometry. All electrochemical measurements were conducted in an anoxic glovebox (N₂ atmosphere at 25 °C, O₂ < 0.1 ppm). Aqueous solutions were made under anoxic condition by purging with N₂ for 45 min. All solutions used for electrochemical experiments contained 0.1 M KCl as electrolyte. Potentials were measured vs Ag/AgCl but are reported vs SHE.

2.5. Reduction of nitrobenzene

Compost-derived HAs were reduced by the Pd-H₂ catalytic system (palladium-coated carbon powder, 10% Pd, Urchem) [17]. In detail, 0.2 M phosphate buffer with pH 7.0 was prepared in

Download English Version:

<https://daneshyari.com/en/article/4979358>

Download Persian Version:

<https://daneshyari.com/article/4979358>

[Daneshyari.com](https://daneshyari.com)