Science of the Total Environment 569–570 (2016) 1–8

Contents lists available at ScienceDirect

Science of the Total Environment

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

# Catalytic degradation of the soil fumigant 1,3-dichloropropene in aqueous biochar slurry

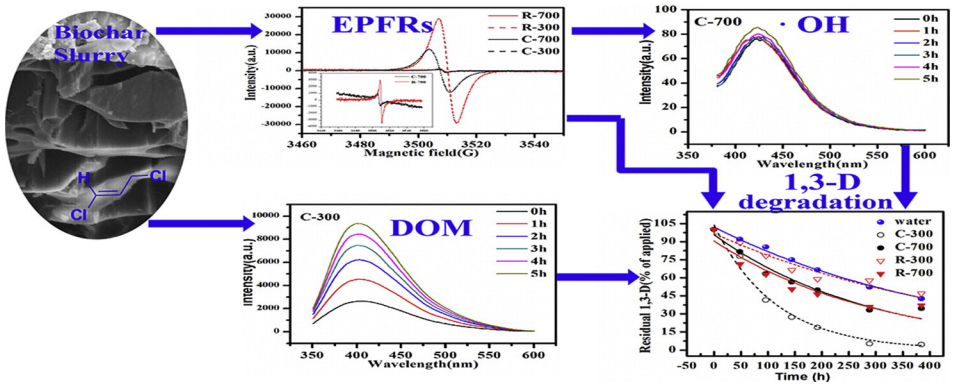
Jiaolong Qin [a], Yuxiao Cheng [b], Mingxing Sun [b], Lili Yan [a], Guoqing Shen [a,*]

[a] School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China
[b] Shanghai Entry–Exit Inspection and Quarantine Bureau, Shanghai 200135, PR China

## HIGHLIGHTS

- Hydrolysis of 1,3-D was accelerated in aqueous biochar slurry.
- 1,3-D adsorption kinetics on biochars fitted well with Langmuir model.
- Cow manure biochar showed higher catalytic degradation activity for 1,3-D than rice husk biochar did.
- EPFRs and DOM have potential roles in 1,3-D degradation on biochar.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 27 April 2016
Received in revised form 13 June 2016
Accepted 13 June 2016
Available online xxxx

Editor: J. Jay Gan

*Keywords:*
Biochar
Fumigant
Adsorption
Degradation
Environmentally persistent free radicals

## ABSTRACT

Biochar has been explored as a cost-effective sorbent of contaminants, such as soil fumigant. However, contaminant-loaded biochar probably becomes a source of secondary air pollution. In this study, biochars developed from cow manure and rice husk at 300 °C or 700 °C were used to investigate the catalytic degradation of the soil fumigant 1,3-dichloropropene (1,3-D) in aqueous biochar slurry. Results showed that the adsorption of 1,3-D on the biochars was influenced by Langmuir surface monolayer adsorption. The maximum adsorption capacity of cow manure was greater than that of rice husk at the same pyrolysis temperature. Batch experiments revealed that 1,3-D degradation was improved in aqueous biochar slurry. The most rapid 1,3-D degradation occurred on cow manure-derived biochar produced at 300 °C (C-300), with $t_{1/2}$ = 3.47 days. The degradation efficiency of 1,3-D on C-300 was 95.52%. Environmentally persistent free radicals (EPFRs) in biochars were detected via electron paramagnetic resonance (EPR) techniques. Dissolved organic matter (DOM) and hydroxyl radical (·OH) in biochars were detected by using a fluorescence spectrophotometer coupled with a terephthalic acid trapping method. The improvement of 1,3-D degradation efficiency may be attributed to EPFRs and DOM in aqueous biochar slurry. Our results may pose implications in the development of effective reduction strategies for soil fumigant emission with biochar.



## 1. Introduction

Soil fumigation is an important agronomic practice in the production of numerous high-value vegetable and fruit crops, but the use of chemical fumigants can lead to excessive atmospheric emissions (Qin et al.,

* Corresponding author.
*E-mail address:* gqsh@sjtu.edu.cn (G. Shen).

http://dx.doi.org/10.1016/j.scitotenv.2016.06.092
0048-9697/

2016). For instance, 1,3-dichloropropene (1,3-D) is a major chemical soil fumigant replacing the banned methyl bromide (MeBr), which is a broad-spectrum fumigant. However, 1,3-D is considered as a possible carcinogen and listed as a hazardous air pollutant under the Clean Air Act (Gan et al., 1998). Covering the treated field with plastic films following fumigation is a widely used strategy to reduce fumigant emission loss (Luo et al., 2013). Nevertheless, holes can easily be formed on plastic films and thus may cause fumigants to escape into the atmosphere (Xuan et al., 2012).

Biochar, which is a carbon-rich solid produced mainly through the thermal decomposition of biomass under $O_2$-limited conditions (Mohan et al., 2014), has been extensively investigated because of its potential agricultural and environmental applications (Lehmann, 2007; Manyà, 2012). Biochar has been recognized as a highly efficient and cost-effective sorbent to remove contaminants (Cui et al., 2016; Srinivasan and Sarmah, 2015). This substance has also been widely explored as a sorbent of soil fumigants. Graber et al. (2011) demonstrated that biochar derived from corn straw mixed with soil yields substantial 1,3-D sorption capacity. Wang et al. (2014) showed that the amendment of soil surface with ≥0.5% biochar reduces the total 1,3-D emission loss by >92%. These remarkable reductions in emissions have been attributed to the adsorption of 1,3-D onto biochar. However, adsorption is a non-destructive process that transfers contaminants from one phase to another (Fang et al., 2015). Absorbed 1,3-D may be released through desorption. Therefore, designing strategies to degrade biochar-absorbed 1,3-D is critical to address the increasingly stringent air quality regulations. Our previous work revealed that the amendment of soil surfaces with aqueous biochar slurry is an effective strategy to decrease fumigant emission (Shen et al., 2016). We assumed that the mechanism of this reduction is related to the enhancement of the physical absorption and catalytic degradation of soil fumigant in aqueous biochar slurry. Gan et al. (2001) showed that MeBr and MeI decompose rapidly on activated carbon. Zhang et al. (2013) demonstrated that pig manure-derived biochar promotes the hydrolysis of carbaryl and atrazine. Xu et al. (2014) revealed that biochar derived from pig manure and sewage sludge can completely oxidize $H_2S$ into $SO_4^{2-}$. Wang et al. (2016) reported that soil amendment with biochar can be an effective strategy to reduce fumigant emissions through strong adsorption and chemical degradation. However, the catalytic degradation of 1,3-D on biochar has yet to be fully elucidated.

1.3-D is mainly eradicated from the environment through dehalogenation (Batzer et al., 1997). Hydrolysis is an important mechanism of 1,3-D degradation (Guo et al., 2004). The hydrolysis of 1,3-D can be simply described as follows:

$$\begin{aligned} &ClCH_2-CH=CHCl+H_2O\rightarrow HOCH_2-CH=CHCl+Cl^-+H^+\\ &ClCH_2-CH=CHCl+OH^-\rightarrow HOCH_2-CH=CHCl+Cl^- \end{aligned} \quad (1)$$

Carbonaceous materials are non-inert adsorbents and may be directly involved in the abiotic transformation of adsorbed organic molecules. Mackenzie et al. (2005a, 2005b) reported that the hydrolysis reactions of activated carbon-adsorbed lindane and 1,1,2,2-tetrachloroethane are faster than those of the dissolved compounds at neutral or slightly alkaline pH; however, the mechanism controlling the catalytic effects was unclear. In addition, organic contaminants may react directly or indirectly with environmentally persistent free radicals (EPFRs) by activating other small molecular free radicals, such as hydroxyl radical (•OH), or even oxygen (Yang et al., 2016; Fang et al., 2014, 2015). Klüpfel et al. (2014) confirmed that biochar can act as an electron shuttle to mediate electron transfer reactions. Fang et al. (2015) reported that EPFRs in maize straw and pine needle char suspensions can induce hydroxyl radical generation and degrade diethyl phthalate. Tuazon et al. (1984) noted that reactions with •OH is one of the main routes for 1.3-D atmospheric degradation. Cole et al. (2007) also reported that free radicals, such as hydroxyl radical and hydrated electron, can induce the degradation of the fumigant chloropicrin.

The catalytic degradation of soil fumigants on biochar have yet to be reported. Considering the influence of biochar feedstock and pyrolysis temperature, we produced two types of biochars from cow manure and rice husk at 300 °C and 700 °C to elucidate the mechanism of 1,3-D catalytic degradation on biochars. This study aimed (1) to investigate 1,3-D adsorption and degradation on cow manure- and rice husk-derived biochar produced at 300 °C and 700 °C pyrolysis temperatures and to (2) explore the potential adsorption mechanism and catalytic degradation dynamics of 1,3-D in biochar. EPFRs and dissolved organic matter (DOM) in biochars were also detected. Our findings could help elucidate the catalytic degradation behavior of 1,3-D on biochar slurry.

## 2. Materials and methods

### 2.1. Chemicals

1,3-D (≥96%, including 50:50 *cis*- and *trans*-isomers) was obtained from J&K Scientific Ltd. (Shanghai, China). Chromatography-grade acetone was obtained from Merck KGaA Darmstadf, Germany. Anhydrous sodium sulfate (AR, 99.0%) and terephthalic acid (THA, AR, 99%) were purchased from China National Medicines Corporation Ltd. (Beijing, China). 2.2-Diphenyl-1-picrylhydrazyl (DPPH, 97%) was obtained from CNW Technologies GmbH (Düsseldorf, Germany). Dried cow manure and rice husk were purchased from commercial markets.

### 2.2. Preparation and characterization of biochar

Cow manure and rice husk were used in this study. After being dried at 70 °C for 48 h, the biomass were grounded and sifted through a 100-mesh sieve. Biomass powder was placed in porcelain crucibles. The filled porcelain crucibles were covered and pyrolyzed in a muffle furnace under $O_2$-limited conditions. The biochar samples pyrolyzed at 300 °C and 700 °C were denoted as follows: C-300 and C-700 for cow manure chars; R-300 and R-700 for rice husk chars.

The specific surface area (SSA) and pore size distribution of the biochars were evaluated using Brunauer–Emmett–Teller (BET) nitrogen adsorption technique at 77 K (ASAP 2010 M + C, Micrometitics Inc., USA). Scanning electron microscopy (SEM; S-2150, Hitachi High-Technologies Corp., Japan) images were obtained. Fourier transform infrared (FTIR) spectra were obtained on powdered chars mixed with KBr at a ratio of 10:1 and then placed in a diffuse-reflectance cell of a Nicolet 6700 (Thermo Fisher Scientific). The extractable metal ions of the biochar samples were determined using inductively coupled plasma optical emission spectroscopy (ICP-PS3500DD, Hitachi) based on the acid digestion method (Wang et al., 2013).

The extractions of dissolved organic matter (DOM) from cow manure-derived and rice husk-derived biochar were performed by soaking 0.5 g of biochar in 40 mL of deionized water. The biochar–water mixture was placed on a shaker platform operating at 200 rpm at 25 °C for 48 h. The suspension was then passed through a 0.2 μm membrane filter. An aliquot of the filtrate (1.5 mL) was used for 1,3-D degradation. DOMs extracted from C-300, C-700, R-300, and R-700 were denoted by $DOM_{C-300}$, $DOM_{C-700}$, $DOM_{R-300}$, and $DOM_{R-700}$.

### 2.3. Adsorption experiments

The adsorption of 1,3-D on biochars was determined in batch adsorption experiments. Biochar (0.5 g) was placed in 21 mL glass headspace vials. Liquid 1,3-D (1–20 μL) was injected into the bottom of the vials by using gas-tight syringes. The vials were immediately capped with Teflon-faced butyl rubber septa and aluminum crimp seals. Afterwards, the vials were stored in the dark at 25 °C for 24 h. Preliminary experiments revealed that 24 h equilibration under these conditions was adequate to achieve equilibrium. After equilibrium was reached, an aliquot of the headspace (200 μL) was withdrawn by using a gas-tight syringe (Agilent) and transferred to the bottom of a 21 mL headspace vial