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Biochar preparation from *Solidago canadensis* and its alleviation of the inhibition of tomato seed germination by allelochemicals

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Solidago canadensis is a malignant invasive plant widely distributed in China. In this study, it was used as a biomass source to prepare biochar *via* an oxygen-limited pyrolysis method. The effect of temperature, heating rate and pyrolysis time on the yield and surface characteristics of the biochar was identified. The adsorption properties for dimethyl phthalate (DMP), a typical allelochemical of *Solidago canadensis*, of the biochar were explored. In addition, a pot experiment was conducted to reveal the effect of the biochar on tomato seed germination in the presence of allelochemicals. The maximum yield of the biochar was observed when *Solidago canadensis* was pyrolyzed at 300 °C for 2 h, with a heating rate of 8 °C min^{-1}. Variation of pyrolysis conditions had little influence on the surface characteristics of the biochar. The adsorption of DMP on the biochar could be well described by the Langmuir model, with a maximum adsorption capacity of 59.37 mg kg^{-1}. The addition of biochar to the soil could promote tomato seed germination in the presence of allelochemicals. Therefore, the biochar prepared from *Solidago canadensis* can be used for soil amendment for invaded sites.

1. Introduction

Solidago canadensis is one of the most destructive and widespread invasive species, which is now widely distributed throughout most provinces in China, particularly in eastern China.[1,2] Many researchers have revealed that this invasive species has led to serious threats to the native environment and to the security of human life, in particular, by changing the structure and functions of the ecosystems.[3,4] Thus, it has been listed as one of the 16 alien invasive harmful plants by the Customs Inspection and Quarantine Department of China.[5,6] Several departments have tried to eradicate it from the invaded sites. To control the alien invasion, specific strategies have been proposed, such as an *in situ* burning treatment, the seeding of native species, limiting grazing before and after treatment and harvesting over a protective winter snowpack.[7] Among these strategies, the burning treatment is still the most used method. However, *Solidago canadensis* contains abundant biomass resources, such as cellulose and lignin. If it is simply burned, the biomass resources are wasted. Moreover, it may result in secondary ecological problems, such as air pollution.[8]

Preparation of biochar from biomass resources is now a hot topic of research. Different biological materials, including corncob, rice straw, pistachio hull and *Parthenium hysterophorus*, have been used to produce biochar.[9–12] However, there are few reports concerning the preparation of biochar from *Solidago canadensis*. Due to the extensive distribution of *Solidago canadensis* and the urgent need to deal with the biomass, the production of biochar from *Solidago canadensis* may provide a feasible and economic way to manage this invasive plant. During the conversion of biomass to biochar, the unstable carbon is transformed into an aromatic carbon skeleton and stored in certain carriers. The prepared biochar has a highly porous structure, large specific surface area, ion exchange abilities and pH buffering abilities, and can be used for soil amendment, as a sorbent for heavy metal and organic matter, *etc.*[13–16] Several aspects can influence the yield and quality of the biochar, such as the pyrolysis temperature, residence time and heating rate.[14,17,18] To promote the biomass utilization efficiency, the pyrolysis conditions need to be optimized.

Invasive species can exhibit allelopathic effects on native species, such as disrupting the mycorrhizal colonization of native species and inhibiting seed germination and crop growth.[19–21] Studies have shown that *Solidago canadensis* restricted the germination and growth of other plants by releasing allelochemicals, such as dimethyl phthalate (DMP).[2,22] The allelochemicals will remain in the soil even though the *Solidago canadensis* is eradicated from the invaded sites. Therefore, the invaded sites are still not suitable for agricultural use.[23] The biochar prepared from *Solidago canadensis* can be used as a competent sorbent for allelochemicals, which could alleviate the allelopathic effects of the soil and amend the

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invaded sites. Therefore, we propose a strategy to amend the soil of *Solidago canadensis* invaded sites with biochar. At the invaded sites, the *Solidago canadensis* is harvested, transformed into biochar and used for soil amendment. This makes the amendment of invaded sites a relatively self-sustaining system, which could reduce the material and energy input. To our knowledge, few studies have been done on this theme to date.

In this study, biochar was prepared from *Solidago canadensis.* The effect of pyrolysis temperature, residence time and heating rate on the yield and surface characteristics of the biochar was investigated to optimize the preparation conditions. In addition, the adsorption of DMP on the biochar was characterized by carrying out batch experiments. A pot experiment was conducted to reveal the effect of the biochar on tomato seed germination in the presence of allelochemicals. The results could provide a feasible way of amending the soil of *Solidago canadensis* invaded sites with biochar prepared from *Solidago canadensis*.

2. Materials and methods

2.1. Solidago canadensis

A sample of *Solidago canadensis* was collected from an extensively invaded site in the Luqiao District, Taizhou City, Zhejiang Province, China. After sampling, the stems and leaves were removed from the collected sample. Then, the sample was cleaned, dried and cut into 0.5–1.0 cm long segments. The segments were further crushed, screened and homogenized. The obtained powder was used for the preparation of the biochar.

2.2. Preparation of biochar

Biochar was prepared *via* an oxygen-limited pyrolysis method. In detail, a 50 g *Solidago canadensis* plant sample was weighed and put in a furnace (Nabertherm L40/11) under a nitrogen atmosphere. The effect of pyrolysis temperature, residence time and heating rate on the preparation of the biochar was explored. The effect of pyrolysis temperature on biochar preparation was investigated over a temperature range from 300 to 500 °C, with a residence time of 4 h and heating rate of 6 °C min^{-1}. The effect of residence time on biochar preparation was investigated over a residence time range from 2 to 6 h, with a pyrolysis temperature of 300 °C and heating rate of 8 °C min^{-1}. The effect of heating rate on biochar preparation was investigated over a heating rate range from 4 to 8 °C min^{-1}, with a pyrolysis temperature of 300 °C and residence time of 4 h. The pyrolyzed sample was then cleaned with 1.0 mol L^{-1} hydrochloric acid and hydrofluoric acid, and dried to form biochar. The product yield of biochar was determined according to eqn (1):

$$\eta = \frac{m_1}{m_2} \times 100\% \quad (1)$$

where η is the yield of biochar (w w^{-1}, %), and m_1 and m_2 are the mass of biochar and dry weight of *Solidago canadensis* (mg), respectively.

2.3. Characterization of biochar

The morphology of the biochar was observed using a scanning electron microscope (SEM) (Hitachi S-4800, Japan) with a mode Quanta 200 FEG ESEM l. An energy dispersive spectrometer (EDS) (Horiba 7593H, England) was used to characterize the elemental composition. The surface functional groups of biochar were analyzed by Fourier transform infrared spectroscopy (FTIR) (Shimadzu Iraffinity-1, Japan).

2.4. Batch adsorption experiments

Batch adsorption experiments were conducted and equilibrated using a model KYC-1102 air-temperature-controlled shaker (Ningbo Jiangnan Instrument Factory, China) at 100 rpm. A variety of solutions of 0.1 g biochar and 50 mL DMP, with initial concentrations varying from 0–50 mg L^{-1}, were added separately into a conical flask (250 mL). The mixtures were equilibrated at 25 °C for 24 h. After reaching equilibrium, the mixtures were centrifuged for 20 min at 4000 rpm. The concentration of DMP was analyzed by gas chromatography (Shimadzu 2010plus). Batch experiments were conducted in triplicate to ensure the accuracy of the obtained data.

The amount of DMP adsorbed on the biochar was calculated according to eqn (2):

$$q_e = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 and C_t are the initial and instantaneous concentrations of DMP (mg L^{-1}); V is the volume of the solutions (L); m is the mass of biochar (g).

2.5. Plant germination experiment

The *Solidago canadensis* sample was mixed with distilled water with a solid to liquid ratio of 1 : 3. The mixture was stirred in a water bath at 30 °C for 24 hours and filtered to obtain the *Solidago canadensis* aqueous extract. Then, three different artificial soils, namely artificial soil A, artificial soil B and artificial soil C, were prepared according to Table 1.

Uniformly sized full ripe tomato seeds were selected for the germination experiments. The beakers with artificial soil A, artificial soil B and artificial soil C were placed in a constant temperature light incubator at a temperature of 20 °C (12 h) during the day and 15 °C (12 h) at night. The relative humidity was kept at around 75.0%. Twenty-five seeds were placed in each beaker, with the seeds buried at a depth of about 0.8 cm. During the experiment, distilled water was added regularly to maintain the stability of the culture solution. The state of germination was observed and the number of germinated seeds

Table 1 Components of the artificial soils

	Distilled water (mL)	Quartz (g)	Biochar (g)	Extract (mL)
Artificial soil A	50	100	—	—
Artificial soil B	—	100	—	50
Artificial soil C	—	100	2.0	50

was recorded. All of the plant germination experiments were carried out in triplicate.

The accumulated germination rate ϕ was calculated according to eqn (3):

$$\phi = \frac{n}{N} \tag{3}$$

where n is the number of seeds that germinated and N is the total number of seeds, which is 25 in this study.

3. Results and discussion

3.1. The effect of pyrolysis conditions on the yield of biochar

Fig. 1 shows the effect of pyrolysis conditions on the yield of biochar. The biochar yield decreased with an increase in pyrolysis temperature (Fig. 1(a)), which is generally in line with the previous reports.[24,25] The thermal degradation of cellulose was reported to experience two types of reaction, including gradual degradation, decomposition and charring at lower temperatures and rapid volatilization at higher temperatures.[26] At low temperatures, the cellulose degraded into a more stable anhydrocellulose, which resulted in a higher biochar yield. At high temperatures, the cellulose was transformed into volatile compounds, which decreased the biochar yield. It should be noted that the biochar yield at 250 °C was not given in this study, as pyrolysis at 250 °C was not able to completely carbonize the *Solidage canadensis.* An increase in residence time resulted in a decrease in the biochar yield (Fig. 1(b)), which was expected as the increase in residence time extended the time of degradation. This effect was extremely evident when the pyrolysis temperature was relatively low. As the study of the effect of residence time was carried out with a pyrolysis temperature of 300 °C and a heating rate of 8 °C min^{-1}, the biochar yield declined significantly from 13.7% to 6.4% when the residence time was increased from 2 h to 6 h. A long residence time could enhance the degradation and volatilization of the organic matter, resulting in a low biochar yield. This result was in agreement with the results of Zhao *et al.*[27] and Weber and Quicker.[28] An increase in heating rate was beneficial to the biochar yield (Fig. 1(c)). The high heating rate provides less time for gradual degradation. In addition, the rapid heating of the biomass favors the polymerization of cellulose, which could increase the yield of biochar.[29]

3.2. Characterisation of biochar

According to the above results, the highest biochar production was reached when the pyrolysis temperature was 300 °C, the heating rate was 8 °C min^{-1} and the residence time was 2 h. In contrast, the lowest biochar production could be observed with a pyrolysis temperature of 500 °C, heating rate of 4 °C min^{-1} and residence time of 6 h.to238.8(p8.7(epar-243.8(i3(und(at)-602.3(loTJ-6.8

correlation coefficients (R^2) of the Freundlich, Langmuir
Langmuir–Freundlich models are 0.975, 0.983 and 0.429,
pectively. This indicated that the Langmuir model was more
able to describe the adsorption than the Freundlich and
gmuir–Freundlich models. The adsorption capacity of DMP
biochar was 59.37 mg g^{-1} according to the fitted parameter
he Langmuir equ908.96691-1.3341-1.3341TD(The)5480.8(Langmuie)53
(feof)0-26.4(of)0-27(8(the)0292.4(adsorbent)1423.1(and20443.5(ttms)TJ

the Langmuir parameter (R_L) could be calculated with eqn (7), which could be used to predict the favorability of the adsorption process.

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where C_0 is the initial concentration (mg L^{-1}).

The isotherm is considered to be unfavorable ($R_L > 1.0$), linear ($R_L = 1.0$), favorable ($1 > R_L > 0$) or irreversible ($R_L = 0$) depending on the value of R_L.[32–34] The R_L values ranged from 0.11 to 1.0 in this study, which indicated that the adsorption of DMP on biochar was a favorable process.

3.4. The effect of biochar on tomato seed germination

A pot experiment was carried out to verify the impact of biochar on plant germination. The result is shown in Fig. 5. The tomato seeds cultured in artificial soil A showed a germination rate of 46.7% at day 3, while the tomato seeds cultured in artificial soil B and C began to germinate at day 5. The germination rate of tomato seeds cultured in artificial soil A reached 76.0% by day 5. However, the germination rate of tomato seeds cultured in artificial soil B and C did not reach that value by the end of the study. This suggested that the extract of *Solidago canadensis*, which contained allelochemicals, inhibited the germination of tomato seeds.

At day 5, the germination rate was 14.4% for tomato seeds cultured in artificial soil C, which was significantly higher than that in artificial soil B (8.0%, $P < 0.05$). From day 5, the germination rate of tomato seeds cultured in artificial soil C was consistently higher than that in artificial soil B ($P < 0.05$). This suggested that the addition of biochar to soil promoted the germination rate of tomato seeds. The results of this study have shown that the biochar had considerable adsorption capacity for DMP, which is identified as the typical allelochemical of *Solidago canadensis*.[2,22] The added biochar could act as a sorbent for the allelochemicals. Therefore, the inhibitory effect of allelochemicals on the tomato seeds was alleviated. For *Solidago canadensis* invaded sites, the soil contains a considerable amount of allelochemicals even if *Solidago canadensis* is removed. The residual allelochemicals may inhibit the growth of other plants, which hampers the agricultural use of the invaded sites. The biochar prepared from *Solidago canadensis* may be used for soil amendment for *Solidago canadensis* invaded sites, which could alleviate the inhibitory effect of allelochemicals. This strategy makes the amendment of invaded sites a relatively self-sustaining system, which could reduce external material and energy input.

4. Conclusion

The invasive plant *Solidago canadensis* was used to prepare biochar. The highest biochar yield was observed with a pyrolysis temperature of 300 °C, heating rate of 8 °C min^{-1} and residence time of 2 h. Variation of pyrolysis temperature, heating rate and residence time had little effect on the surface characteristics of the biochar. The prepared biochar had considerable absorption capacity for DMP, a typical allelochemical of *Solidago canadensis*. The adsorption of DMP on biochar could be well described by the Langmuir model, with a maximum capacity of 59.37 mg kg^{-1}

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