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紫云英翻压条件下生物炭施用量 对水稻Cd迁移积累的影响

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摘要:【目的】稻田重金属污染已成为威胁我国粮食安全的主要问题之一。紫云英是我国南方种植水稻的主要绿肥作物,为研究翻压紫云英条件下,化肥配施生物炭对水稻产量及水稻镉(Cd)吸收、迁移和积累的影响。【方法】采用盆栽试验,在紫云英替代30%氮肥条件下,设置4个生物炭添加水平[CK(0 g/kg),C25(2.5 g/kg),C50(5 g/kg),C100(10 g/kg)],分析不同生物炭施用量对水稻生长及镉迁移积累的影响。【结果】生物炭表面具有多个不规则球状凸起,球状凸起表面有少量残屑附着且生物炭自身含有羟基、羰基和羧基等较多的含氧官能团;生物炭的施加可明显提高水稻各器官干物质量,C50处理水稻根干物质量显著($P<0.05$)高于C25和C100处理,分别提高了30.9%和44.4%;其水稻秸秆和籽粒干物质量显著($P<0.05$)高于CK和C100两个处理,秸秆干质量分别提高了14.3%和14.1%,籽粒干质量分别提高了52.5%和26.3%;与不添加生物炭相比,施用生物炭能明显提高水稻籽粒产量,在25 g/kg和50 g/kg的生物炭添加量时显著提高,分别提高了52.5%和33.7%;生物炭的施加可降低水稻籽粒中的Cd含量,C25、C50、C100 3个处理较对照分别降低了13.2%、14.1%和11.0%;生物炭能抑制Cd在水稻各器官中的转运,所有转运过程的转运系数(TF)均有降低,与对照相比,TF_{地上部位/根}的降低幅度为5%~11.6%,TF_{秸秆/根}的降低幅度为1.5%~10.4%,TF_{籽粒/秸秆}的降低幅度为6.1%~12.1%。【结论】生物炭具有较大的比表面积和多种含氧官能团,能有效钝化土壤重金属;翻压紫云英条件下添加生物炭不仅能提高水稻产量,还能降低水稻籽粒中的Cd含量,抑制Cd向水稻籽粒的转运,该施肥方案对Cd污染土壤的水稻安全生产具有一定参考价值。

关键词:水稻;紫云英;生物炭;Cd

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Effect of Biochar Application Rate on Cd Accumulation and Transportation in Rice under the Condition of Rolling *Astragalus sinicus* into the Soil

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Abstract: Heavy metal pollution in rice fields has become one of the main threats to China's food security. [Objective] *Astragalus sinicus* L. (Chinese milk vetch) is the main green manure crop for rice cultivation in southern China. This paper studies the effects of chemical fertilizer combined with biochar on rice yield and the absorption, migration and accumulation of cadmium (Cd) in rice under the condition of rolling Chinese milk vetch into the soil. [Method] In this study, a pot experiment was adopted. Four biochar addition levels were set under the condition of substituting Chinese milk vetch for 30% of nitrogen fertilizer [CK (0 control), C25 (2.5 g/kg), C50 (5 g/kg), C100 (10 g/kg)], to study and analyze the effects of different application amounts of biochar on rice growth and cadmium (Cd) migration and accumulation. [Results] The surface of biochar has a number of irregular spherical protrusions, and a small amount of debris is attached to the surface of these spherical protrusions. In addition, the biochar itself contains many oxygen-containing functional groups such as hydroxyl, carbonyl and carboxyl groups. The dry matter quality of rice organs was significantly improved under the conditions of applying biochar. In the treatments of C50, C25 and C100, there were significant differences in the dry matter quality of rice organs. The dry matter quality of rice roots treated with C50 was significantly higher ($P < 0.05$) than that treated with C25 and C100, increasing by 30.9% and 44.4%, respectively. At the same time, the dry matter quality of rice straw and grains was significantly higher ($P < 0.05$) than that in the two treatments of CK and C100, the dry matter quality of rice straw increased by 14.3% and 14.1%, respectively, and the dry matter quality of rice grains increased by 52.5% and 26.3%, respectively. Compared with no addition of biochar, the application of biochar increased the yield of rice grains significantly. Among them, the biochar addition amounts of 25 g/kg and 50 g/kg increased the yield of rice grain significantly, increasing by 52.5% and 33.7%, respectively. In addition, the application of biochar reduced the cadmium (Cd) content in rice grains, and the cadmium contents in the C25, C50, and C100 treatment groups decreased by 13.2%, 14.1% and 11.0% respectively compared with that in the control. It can be concluded that biochar can inhibit the transport of cadmium (Cd) in various organs of rice, and the transport coefficients of all transport processes reduced. Compared with the control group, the reduction range of TF aboveground part/root was 5%–11.6%, the reduction range of TF stalk/root was 1.5%–10.4%, and the reduction range of TF grain/stalk was 6.1%–12.1%. [Conclusion] In summary, since biochar has a large specific surface area and a variety of oxygen-containing functional groups, it can effectively passivate heavy metals in the soil. Besides, the addition of biochar under the condition of rolling Chinese milk vetch into the soil can not only increase rice yield, but also effectively reduce the cadmium (Cd) content in rice grains and inhibit the transport of cadmium (Cd) to rice grains. Therefore, this fertilization scheme has some reference value for the safe production of rice in cadmium (Cd) contaminated soil.

Keywords: rice; *Astragalus sinicus*; biochar; Cd

【研究意义】水稻是我国主要粮食作物之一,近年来随着城市工业化的快速发展,土壤重金属污染问题日益加重,导致优质耕地面积大幅缩减^[1-2]。在稻田土壤中有效态镉超标时,不仅会降低水稻产量,还会污染稻米,直接危害到人类的身体健康^[3-5]。因此,稻田土壤镉污染的治理是保证水稻安全生产的关键,也是农业绿色发展过程中亟待解决的关键难题之一。**【前人研究进展】**生物炭是农业、林业废弃物在限氧条件下热裂解、炭化而成的一种固体材料,是具有丰富稳定态的有机碳,可明显提高土

壤肥力,同时增加农作物产量^[6]。不仅如此,生物炭还具有大量的活性含氧官能团、高 pH、丰富的孔隙度及较大的比表面积等特性,使其在施入重金属污染土壤中时能起到较好的修复作用,因此近年来生物炭受到国内外环境领域科技工作者的极大关注^[7-9]。Zheng 等^[10]发现豆桔生物炭和稻草生物炭的施用均可显著降低水稻中的镉浓度。陈乐等^[11]研究发现,在不同酸化水平土壤中施加谷壳生物炭,土壤中有效态 Cu 含量均随生物炭施用量的增加而减少。李芸芸等^[12]研究也发现随着水稻秸秆生物炭施用量的增加,土壤中 Cd、Pb 的有效态含量显著降低,且水稻糙米中重金属含量也随之降低。而张丽等^[13]采用根际箱培养的方式研究不同生物炭施用量对水稻 Cd 含量的影响,结果表明 50 g/kg 的生物炭施用量处理较 25 g/kg 和 100 g/kg 的生物炭施用量处理更能降低水稻糙米和稻壳中的 Cd 含量。因此,生物炭施用一定程度上可降低土壤重金属风险,且不同生物炭量的施用对水稻生长发育和籽粒重金属含量的影响不同,但目前不同生物炭量的施用对其影响规律的研究报道较少。【本研究切入点】紫云英是我国主要的绿肥作物之一,也是江西水稻生产主要的有机肥源^[14]。谢杰等^[15]研究表明,紫云英长期还田条件下会提高稻田土壤中具有生物活性 Cd 形态的比例。喻成龙等^[16]也发现在 Cu 污染土壤中,化肥和紫云英配施处理下水稻糙米存在一定的重金属污染风险。该研究还发现将生物炭与紫云英联合施用可在减少化肥施用的同时,降低稻田重金属污染风险,提高作物产量,但目前关于紫云英还田条件下不同生物炭施用量对重金属污染稻田产量及水稻重金属含量影响的研究鲜见报道。【拟解决的关键问题】因此,本文通过盆栽种植水稻,在翻压紫云英的条件下,研究不同生物炭施用量对水稻产量、Cd 含量及 Cd 在水稻中的迁移转运的影响。旨在为南方重金属污染稻田安全高效生产提供一定的基础数据和理论指导。

1 材料与方法

1.1 试验材料

供试早稻品种为荣优华占,紫云英品种为余江大叶(鲜质量 0.08 kg/盆);供试土壤采自江西农业大学化工厂周边 Cd 污染水稻田。土壤基本化学性质 pH 5.46,有机质 15.09 g/kg,碱解氮 66.74 mg/kg,有效磷 22.59 mg/kg,速效钾 197.80 mg/kg,Cd 2.41 mg/kg。供试的化学肥料分别为尿素、钙镁磷肥和氯化钾。试验中所用生物炭购自南京勤丰秸秆科技有限公司(以水稻稻壳为原料采用 450 ℃无氧充氮裂解法制成,生物炭中 Cd 含量未检出)。

1.2 试验设计

盆栽试验于 2019 年在江西农业大学生态科技园进行。设 4 个处理:紫云英+化肥(CK,对照)、紫云英+化肥+2.5 g/kg 生物炭(C25)、紫云英+化肥+5 g/kg 生物炭(C50)、紫云英+化肥+10 g/kg 生物炭(C100)。各处理肥料用量相等,所有肥料以基肥、分蘖肥和穗肥按照 4:3:3 的比例施入。在直径 30 cm、高 40 cm 的橡胶桶内装入 10 kg 风干土,人工移栽秧苗,每桶 2 株,每个处理 3 个重复。水稻生育期保持约 3 cm 的淹水状态。

1.3 样品采集及测定方法

水稻成熟期采集植株样品,将植株根、秸秆、籽粒分开,105 ℃杀青 1 h、80 ℃烘干、称量并粉碎过 100 目筛备用。土壤 pH 使用 pH 计(雷磁 pHS-3C)进行测定。土壤有机质、碱解氮、有效磷和速效钾分别采用重铬酸钾容量法-外加热法、碱解扩散法、Olsen 法和火焰光度法进行测定^[17]。土壤采用三酸消解法进行消解备用^[16],植株采用硝酸-微波消解法进行消解备用^[18]。土壤和植株中的重金属含量分别使用原子吸收分光光度计(上海光谱仪器有限公司 SP-3530 和 SP-3500GA)进行测定。

转运系数(TF)计算:TF_{a/b}=C_b/C_a。TF 表示 Cd 从 a 到 b 的转运系数,C_a、C_b 代表水稻各器官中 Cd 含量。

1.4 统计分析

采用 Excel 2010 进行数据处理和相关分析,采用 SPSS 25.0 进行显著性分析($P<0.05$),利用 Origin 2020 软件进行作图。

2 结果与分析

2.1 生物炭施用量对水稻各部位干物质量的影响

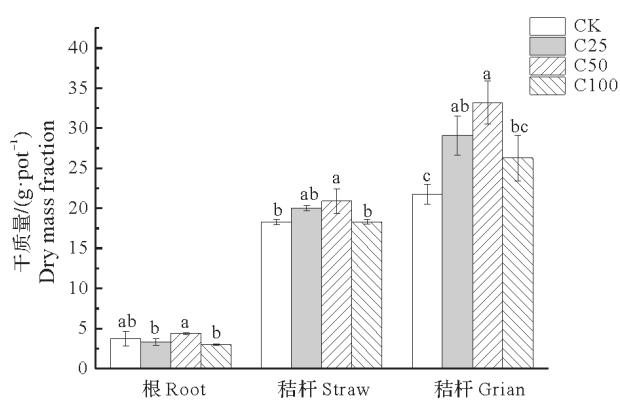
由图1可知,在30%紫云英翻压条件下,施加不同量生物炭对水稻不同器官干物质量影响不同。添加生物炭后,水稻各部位生物量由大到小依次为C50、C25和C100。C50处理的水稻各器官干物质量都明显高于其他处理,C25与C100处理水稻各器官生物量均无显著差异。对于水稻根来说,C50处理最高,且显著($P<0.05$)高于C25和C100处理,分别提高了30.9%和44.4%;对于水稻秸秆来说,C50处理显著($P<0.05$)高于CK和C100两个处理,分别提高了14.3%和14.1%;对于水稻籽粒来说,规律基本与秸秆干物质量一致,C50处理最高,且显著($P<0.05$)高于CK和C100,分别提高了52.5%和26.3%。表明在30%紫云英翻压条件下,施加生物炭能提高水稻产量,且在5 g/kg施用量时产量最高。

2.2 生物炭施用量对水稻各部位Cd含量的影响

由图2可知,对于水稻根部而言,翻压紫云英条件下配施生物炭能提高水稻根部重金属Cd的含量,在2.5 g/kg生物炭配施时根部Cd含量最高,C25、C50和C100处理较对照CK处理分别提高了8.4%、2.8%和2.8%。不同生物炭用量影响了水稻秸秆Cd含量,在2.5 g/kg和10 g/kg的生物炭施用量处理时,水稻秸秆的Cd含量没有明显变化,而在5 g/kg的生物炭施用量处理时,秸秆Cd含量有明显的降低,较之对照组降低了7.8%。对于水稻籽粒,在施用生物炭后,所有处理的籽粒中Cd含量均有较为明显的下降,C25、C50和C100处理较对照分别降低了13.2%、14.1%和11.0%,说明生物炭能有效降低水稻籽粒中重金属Cd的含量。

2.3 生物炭施用量对水稻重金属转运系数(TF)的影响

从表1可以看出,紫云英翻压条件下生物炭施用量影响了水稻重金属Cd从根部向地上部位转运量。在添加生物炭后,Cd由根到地上部位的转运系数 $TF_{\text{地上部位}/\text{根}}$ 均有降低,且不同生物炭施用量的降低效果有所不同,C25、C50和C100处理较对照分别降低了10.6%、11.6%和5.0%,说明翻压紫云英条件下添加生物炭能抑制Cd从水稻根部向地上部位的迁移。对于秸秆到根的转运系数 $TF_{\text{秸秆}/\text{根}}$,添加生物炭后的处理较对照组降低,其中在5 g/kg的生物炭施用量处理时 $TF_{\text{秸秆}/\text{根}}$ 最低,较对照降低了10.4%,C25和C100处理较对照组分别降低了6.4%和1.5%。从重金属Cd由秸秆到籽粒的转运系数 $TF_{\text{籽粒}/\text{秸秆}}$ 来看,紫云英翻压条件下添加生物炭能减少Cd从秸秆到籽粒的转运,C25、C50和C100处理较对照分别降低了7.3%、6.1%和12.1%。

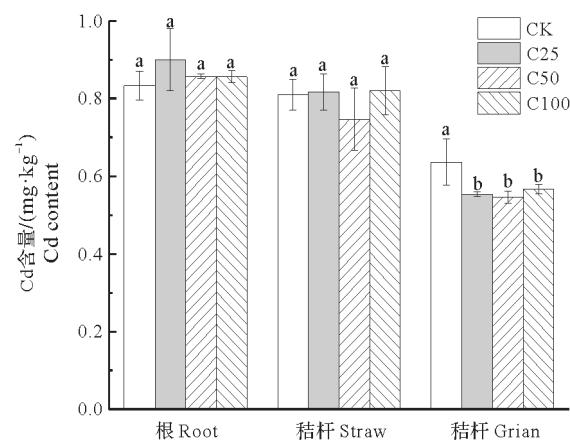


同一水稻部位不同字母表示各处理间在5%水平差异显著。

Different letters in the same rice organs mean significant difference at 0.05 level using Duncan's test.

图1 紫云英翻压条件下生物炭对水稻干物质量的影响

Fig.1 Effect of biochar on dry matter quality of different parts in rice under incorporation of *Astragalus sinicus*



同一水稻部位不同字母表示各处理间在5%水平差异显著。

Different letters in the same rice organs mean significant difference at 0.05 level using Duncan's test.

图2 紫云英翻压条件下生物炭对水稻各器官Cd含量的影响

Fig.2 Effect of biochar on Cd content in different parts of rice under incorporation of *Astragalus sinicus*

表1 紫云英翻压条件下生物炭对水稻中Cd转运系数(TF)的影响

Tab.1 Effect of biochar on Cd transport factors in rice under incorporation of *Astragalus sinicus*

处理 Treatment	地上部/根 The aboveground part/Root	秸秆/根 Straw/Root	籽粒/秸秆 Grain/Straw
CK	1.737±0.108	0.972±0.029	0.784±0.076
C25	1.571±0.145	0.910±0.047	0.727±0.116
C50	1.556±0.121	0.871±0.089	0.736±0.090
C100	1.654±0.043	0.957±0.056	0.689±0.053

2.4 生物炭的物理化学特性

图3为生物炭的场发射扫描电镜图,其中a、b为生物炭放大500、2 000倍的SEM图的电镜表征图。由图3(a,b)可知,生物炭表面具有多个不规则球状凸起,并呈紧密排列状,其内有部分孔隙结构,球状凸起表面有少量残屑附着,且凸起表面较为光滑。

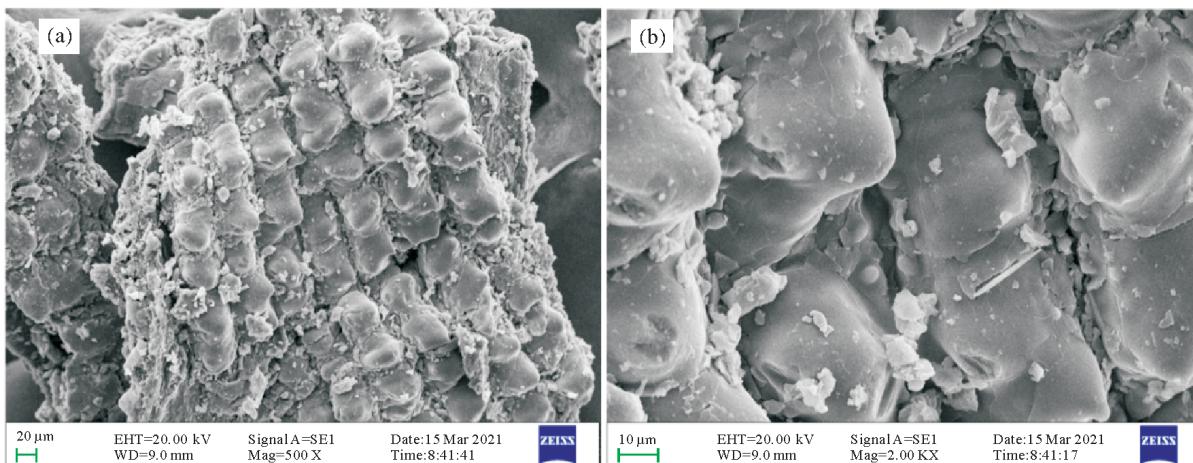


图3 生物炭的FESEM图

Fig.3 FESEM diagram of biochar

由图4可知,图中生物炭的特征峰位于 3448 cm^{-1} 、 1642 cm^{-1} 及 1089 cm^{-1} 。在 3448 cm^{-1} 峰值附近有伸缩振动的羟基(-OH)官能团,但峰强较弱;在 1642 cm^{-1} 峰附近存在羧基(-COOH)的伸缩振动吸收峰;在 1089 cm^{-1} 峰归属于芳香环中的羰基和酚羟基的振动而产生的吸收峰^[19]。这表明生物炭自身含有较多的含氧官能团,可与重金属离子形成配位结构,从而达到钝化土壤重金属的作用。表2为部分重金属污染土壤改良剂中的主要官能团,其中溶解性有机质(DOM)中主要官能团有羟基、羧基和酚羟基等^[20];凹凸棒与重金属离子络合的官能团主要有羟基、羧基和C-C键官能团^[21];而羟基磷灰石中主要

表2 重金属污染土壤修复改良剂的主要官能团

Tab.2 Main functional groups of soil remediation improvers contaminated by heavy metals

改良剂 Amendment	官能团 Functional group	化合物 Compound	参考文献 Reference
生物炭 Biochar	OH、C=O 伸缩	酸、醛等	[19]
水溶性有机物 DOM	OH、C=O、C-C 伸缩	酸、芳香环、酚等	[20]
凹凸棒 Attapulgite	OH、C=O、C-H 伸缩	酸、醛、杂环等	[21]
羟基磷灰石 Hydroxyapatite	OH、C=O 伸缩	酸、醛等	[22]

有羟基、羧基等官能团^[22]。本研究中生物炭的主要官能团与这些改良剂类似,表明生物炭可通过表面大量的官能团与土壤中的重金属离子发生反应,起到钝化土壤重金属的效果。

3 讨论与结论

据报道^[23~25]土壤中添加生物炭能提高土壤肥力,为作物提供良好的生长环境,有效促进作物生长,增加作物产量。本文研究表明,翻压紫云英条件下施用不同量生物炭对水稻生物量的影响不同,随着生物炭添加量的增加,水稻生物量呈现先升高后降低的趋势,这与阿力木等^[26]研究结果类似。可能是生物炭含碳量过高而其他养分含量过低,施入土壤后水稻可吸收利用的养分有限,且土壤C/N比提高而降低了土壤中氮素的有效性^[27];也可能是生物炭对土壤中氮元素有缓释作用,导致水稻在生育后期仍持续吸收氮素,使水稻贪青且影响籽粒灌浆^[28]。Khan等^[29]研究发现,在部分土壤上单独施用生物炭甚至会导致作物减产。

本研究发现,在盆栽试验中翻压紫云英条件下添加生物炭会增加水稻根部Cd含量,这与刘冲^[30]在油麦菜生长过程中施加0.8%的钙镁磷肥和桉树炭发现其根部重金属Cd含量升高的研究结果一致。生物炭在施入土壤后,能改善土壤理化性质如pH、CEC等,同时生物炭本身具有的多孔径结构和巨大的比表面积,使其具有强大的吸附能力,且生物炭中丰富的官能团也能与重金属离子发生络合反应和共沉淀反应,降低土壤中镉的生物有效性,影响水稻对Cd的吸收,进而降低糙米中Cd的含量^[31~34]。本文在翻压紫云英条件下添加不同量生物炭后,也发现水稻籽粒中重金属Cd含量均有明显减少,但并非生物炭的添加量越多修复效果越佳。张丽等^[13]发现水稻糙米中的Cd含量随生物炭用量的增加呈先降低后升高的趋势,本研究结果与其一致,汪玉瑛等^[35]也发现在1%、2%、5%的羊栖菜炭添加量处理下,2%的炭添加量处理对土壤交换态Cd含量的降低效果最好。其原因可能是生物炭对土壤重金属污染的修复作用除了与生物炭本身的多种性质有关,还会受到生物炭的原材料、土壤性质及作物生长环境等多种因素影响,其内在的修复机制仍需进一步研究。

翻压紫云英条件下添加生物炭后发现水稻中Cd从根部向地上部位及秸秆的转运系数和秸秆向籽粒的转运系数均有降低,说明生物炭的施用能抑制Cd在水稻中的转运,这可能是由于生物炭添加后降低了土壤中酸溶态Cd含量及土壤地上部位Cd的积累量^[36],导致Cd在水稻中从下到上的转运能力降低,最终减少了籽粒中重金属Cd的含量。本研究是在盆栽试验条件下进行的,研究结果对田间水稻安全生产具有一定的指导与借鉴意义。

通过一系列表征对生物炭的物理化学特性进行了分析,研究发现生物炭具有明显的多孔结构,生物炭表面较为粗糙,这可为生物炭基肥提供更多的官能团和更大的比表面积。而傅里叶红外光谱分析表明生物炭具有大量的含氧官能团。Jiang等^[37]通过对生物炭的傅里叶红外分析发现,生物炭中的羟基、羧酸根等官能团可与土壤中的Cd发生络合反应,提升其对重金属污染土壤中Cd的吸附能力。Uchimiya等^[38]通过自制生物炭研究其对土壤中重金属的固定效果,研究表明生物炭主要通过表面官能团与Cu进行反应,从而达到钝化土壤重金属的效果。表面多孔径的结构、大量含氧官能团等特性,均可能是生物炭对重金属污染土壤修复的潜在原因。

翻压紫云英条件下,不同量生物炭配施均能提高水稻籽粒产量,5 g/kg生物炭施用量时籽粒产量最高,较对照提高了52.5%。翻压紫云英条件下施加生物炭能有效降低水稻籽粒中重金属Cd含量,5 g/kg

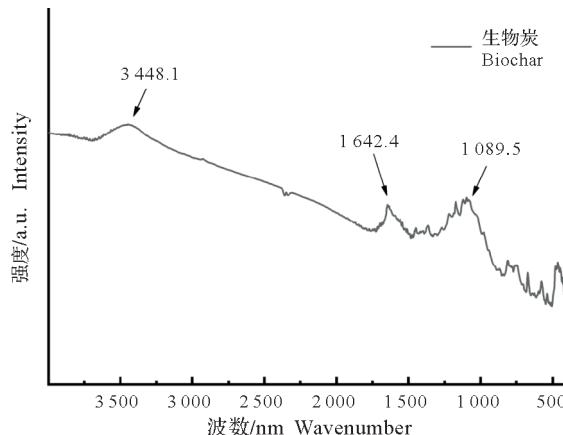


图4 生物炭的FT-IR图

Fig.4 FT-IR spectrum of biochar

生物炭配施处理时效果最好,较对照降低了 14.1%;且添加生物炭后,水稻各器官中 Cd 的转运系数均有降低。与紫云英配施化肥处理相比,“紫云英+化肥+生物炭”的施肥方案既可提高水稻产量,也更能降低水稻籽粒中 Cd 的含量,对 Cd 污染土壤水稻安全生产具有参考意义。

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