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《环境科学》征订启事(70) 《环境科学》征稿简则(193) 信息(334,554,605)

生物质炭与铁钙材料对镉砷复合污染农田土壤的修复

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摘要: 选取了铁钙材料(FC)和山核桃蒲生物质炭(BC)制备得到复合材料(BF),用于修复农田土壤中镉砷复合污染,以降低水稻糙米中的镉和砷含量. 通过水稻盆栽试验,在植物生长期,采集了土壤孔隙水、根际土壤、非根际土壤、水稻植株和水稻根表铁膜,探究了铁钙材料、生物质炭及其复合材料对土壤中镉和砷生物有效性和植株中镉和砷含量的影响及机制. 结果表明,生物质炭材料能显著($P < 0.05$)提高非根际土壤(0.55~0.66个单位)和根际土壤(0.28~0.36个单位)pH,且提升土壤DOC含量;铁钙材料能显著($P < 0.05$)降低非根际土壤(0.14~0.27个单位)和根际土壤(0.38~0.41个单位)pH,同时降低土壤DOC含量. 铁钙材料和复合材料能够同时降低土壤孔隙水、根际土壤和非根际土壤有效态Cd和As含量,而生物质炭能降低Cd含量,却提高了As含量,其中复合材料1%添加处理的效果最佳,土壤有效态Cd和As分别降低了41.8%~48.2%和6.1%~10.1%. 生物质炭、铁钙材料和复合材料均能提高植株生物量(根、茎、叶和籽粒的干重),水稻籽粒干重较CK增加了48.5%~184.0%,根表铁膜含量增加7.5%~13.6%. 与空白对照组相比,生物质炭能够有效降低水稻糙米中Cd含量(21.0%~26.1%),铁钙材料和复合材料能够同时降低糙米中Cd和As含量,其中复合材料对糙米中Cd和As降低效果最佳,降幅高达36.9%~42.0%和40.4%~44.4%,使水稻糙米Cd和As含量均低于国家标准值(GB 2762-2017).

关键词: 生物质炭; 铁钙材料; 镉(Cd); 砷(As); 农田土壤

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Using Biochar and Iron-calcium Material to Remediate Paddy Soil Contaminated by Cadmium and Arsenic

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Abstract: In this study, iron-calcium material (FC) and hickory-cattail biochar (BC) were applied to prepare composite material (BF), which was used to repair the combined pollution of cadmium and arsenic in paddy soil to reduce the content of cadmium (Cd) and arsenic (As) in rice grain. Soil pore water, rhizosphere soil, bulk soil, rice plants, and root iron plaque samples were collected during the growth period of rice in a pot experiment to explore the effects and mechanism of FC, BC, and BF on the bioavailability of Cd and As in paddy soil and their contents in plants. The results showed that biochar could significantly ($P < 0.05$) increase the pH value of bulk soil (0.55-0.66 units) and rhizosphere soil (0.28-0.36 units) and elevate the soil dissolved organic carbon (DOC) content. FC material could significantly ($P < 0.05$) reduce the pH of bulk soil (0.14-0.27 units) and rhizosphere soil (0.38-0.41 units), as well as the soil DOC content. Iron-calcium materials and composite could simultaneously reduce the contents of available Cd and As in soil pore water, rhizosphere soil, and bulk soil, whereas biochar could reduce the content of Cd but increase the content of As. Among them, a 1% addition of composite had the best effect. The available Cd and As in soil decreased by 41.8%-48.2% and 6.1%-10.1%, respectively. Biochar, iron-calcium materials, and composites improved plant biomass (dry weight of root, stem, leaf, and grain). For example, the dry weights of rice grains under these treatments were higher (48.5%-184.0%) than that of CK, as was the root iron plaque content (7.5%-13.6%). Compared with that in the CK, biochar could effectively reduce the Cd content in rice grain by 21.0%-26.1%. Iron-calcium material and composite could simultaneously reduce the Cd and As contents in rice grain. Among them, the BF treatment had the best effect on the reduction of Cd and As in rice grain, with a decrease of 36.9%-42.0% and 40.4%-44.4%, respectively. The Cd and As contents in rice grain were lower than the national standard values (GB 2762-2017).

Key words: biochar; iron-calcium material; cadmium(Cd); arsenic(As); paddy soil

随着中国工业化和现代化发展进程突飞猛进,我国土壤环境污染问题日渐严重,其中重金属污染较为突出,现状不容乐观. Mu等^[1]测定了我国南方水稻主产区的土壤重金属含量,发现 ω [镉(Cd)]和 ω [砷(As)]的平均值为 $0.45 \text{ mg}\cdot\text{kg}^{-1}$ 和 $11.80 \text{ mg}\cdot\text{kg}^{-1}$,已严重超过污染限制规定. 镉和砷通常存在于矿区周边的土壤及水体. 镉是一种具有致癌性的重金属元素^[2],会对人体的肾脏及骨骼部位产生不良影响^[3];砷则是一种具有强毒害作用的类金属元素,过量摄入砷会对人体的皮肤等组织造成损伤^[4]. 因现代工业快速发展,人类加剧对矿山的开采而产生大

量含重金属、类金属(Cd和As等)冶炼废水与矿渣,在污水的排放以及雨水的冲刷下,流入周边的水体,在周围的农田中沉积,最终富集在农作物中,威胁人类的粮食安全^[5]. 水稻作为我国主要粮食作物,对Cd和As具有强烈的富集能力^[6,7],具有较高的潜在污染

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风险. 可见, 镉和砷是污染面积较广、对人体危害较大的两种污染物.

由于镉和砷在土壤中赋存形式以及地球化学特性各异, 例如当 pH 上升会增强对 Cd 的吸附, 而对 As 的吸附由于静电排斥会降低, 在厌氧条件下 As 有效性增强, 而 Cd 的有效性会降低^[8]. 陈楸健等^[9]使用芦苇生物质炭修复土壤中 Cd-As 复合污染, 添加 5% 的芦苇生物质炭能够显著降低 (28.23%) 土壤中 TCLP 提取态 Cd 含量, 而对 TCLP 提取态 As 含量显著提升 37.42%. 水稻因长期处于淹水状态, 这使得根系处于还原条件, Cd 与 S²⁻ 易形成难溶性沉淀, 导致其有效性降低; As 被还原成难以被土壤吸收的可溶态, 反而会提高其有效性^[10]. Cd 以阳离子 Cd²⁺ 的形式存在于自然界中, 碱性材料如石灰、磷酸盐与生物质炭等都能促进其水解、沉淀与吸附^[11-13]; 而砷是以阴离子 H₂AsO₄⁻ 和 HAsO₄²⁻ 的形式存在于水体与土壤中^[14], 当使用碱性物质来治理土壤, 会造成对 As 阴离子的静电排斥而使得其移动性增强. 因此寻求一种能同时修复土壤镉和砷污染物的材料或方法显得尤为重要.

目前, 针对稻田镉污染问题, 现有研究采取原位钝化等技术^[15,16], 以提高土壤 pH 为切入点, 向镉污染农田土壤施入生物炭等碱性材料, 通过提高土壤 pH 值, 使其与 Cd 产生沉淀、吸附和络合反应等实现对 Cd 的修复; 但碱性材料会使 As 的移动性提高^[17-20]. 针对土壤复合重金属污染, 研究者通常将生物炭与其他修复材料进行改性, 以提高其对多种重金属的修复能力, 例如将生物炭作为基底的金属氧化物-生物炭和微生物-生物炭等复合材料^[21]. 其中金属氧化物-生物炭类是一种吸附效率高和环境影响小的吸附材料. 有研究表明, 生物炭因其比表面积大、孔隙结构丰富且表面官能团种类繁多, 对阳离子表现出较好的吸附效果, 但受表面负电荷影响, 生物炭类修复材料对亚砷酸根等重金属阴离子吸附效果不佳^[22-24]. 铁钙材料能有效吸附重金属阴离子是因为: 材料中的铁氧化物将 As(III) 氧化为 As(V) 从而降低了其毒害性, 且材料表面的羟基易与 As(III) 形成稳定的络合物^[25-27]; 铁钙材料在治理 As 污染废水时, 材料中的硫酸根会被砷酸根取代介入硫酸钙晶体, 表明硫酸钙对重金属污染溶液中的 As 具有较强的固定作用; 铁钙材料中的硫酸钙能够提高作物产量, 补充作物生长过程中的 Ca 元素^[28]. 袁峰等^[29]研

究发现, 铁钙材料在二水石膏与氧化铁的添加质量比为 7:3, 对 As 污染农田土壤的修复效果最佳. 基于生物质炭和铁钙材料的特性, 本文研制生物质炭-铁钙材料 (BF), 以同时修复水稻土壤 Cd 和 As 复合污染. 前期水溶液试验结果表明, 当生物质炭 (BC) 和铁钙材料 (FC) 的添加质量比为 3:7 时, 复合材料 (BF) 对镉和砷同时具有较高的去除率, 分别为 67.7% 和 52.5%, 水溶液试验中复合材料的添加量是 5 000 mg·L⁻¹ (未发表). 因此本文在此基础上开展水稻盆栽试验研究.

本研究选取镉砷复合污染农田土壤, 通过水稻盆栽试验, 分析测定土壤孔隙水、根际和非根际土壤、水稻植株样品中的 Cd 和 As 含量, 探究生物质炭、铁钙材料及其复合材料对土壤中 Cd 和 As 污染的修复效果, 以及对水稻安全生产的影响, 旨在为生物质炭-铁钙材料在 Cd-As 复合污染土壤中的修复应用提供理论依据.

1 材料与方 法

1.1 供试材料制备

生物质炭材料制备: 以杭州临安区山核桃蒲废弃物为原材料, 将收集后的山核桃蒲放入烘箱 50℃ 烘干 3 d, 再进行粉碎后置于马弗炉 (JZ2-4-10, 九州空间, 中国) 内 500℃ 无氧热解 2 h, 待冷却至室温将其研磨过 100 目筛后储存于塑封袋中备用. 测得山核桃蒲生物质炭 pH 为 9.85.

铁钙材料的制备: 将过 100 目筛的二水石膏 (CaSO₄·2H₂O) 和氧化铁 (Fe₂O₃), 以质量比为 7:3 称取 (精确至 0.000 1) 后, 置于离心管中混合, 在 (25±1)℃、250 r·min⁻¹ 的条件下恒温均匀振荡 1 h, 所得产物即所需铁钙材料, 各试剂均由国药集团化学试剂公司提供.

复合材料的制备: 将生物炭和铁钙材料, 以质量比 3:7 称取 (精确至 0.000 1) 后, 置于离心管中混合, 在 (25±1)℃、250 r·min⁻¹ 的条件下恒温均匀振荡 1 h, 所得产物即为复合材料.

1.2 土壤采集与分析

2022 年 3 月在浙江省绍兴市上虞矿区周边受镉砷复合污染农田, 采集 0~20 cm 深度的耕作表层土壤, 将采集的土壤自然风干后, 研磨过 10 目筛保存备用. 供试土壤的基本理化性质和镉砷含量见表 1.

表 1 土壤的全量 Cd 和 As 及基本理化性质

Table 1 Total amount of Cd and As and the basic physical and chemical properties of the tested soil

指标	pH 值	ω(全 Cd) /mg·kg ⁻¹	ω(全 As) /mg·kg ⁻¹	ω(SOM) /mg·kg ⁻¹	ω(砂粒) /%	ω(粉粒) /%	ω(黏粒) /%
数值	5.72	0.98	71.72	19.71	30.77	58.37	10.85

1.3 盆栽试验

在恒温温室中开展水稻盆栽试验,以生物质炭、铁钙材料及其复合材料为修复材料,共设置7组处理.参考已有研究中生物质炭钝化重金属的水稻盆栽试验,并考虑到过量含铁物质对土壤以及水稻植株产生毒害作用,本研究修复材料的添加量设置为0.5%和1%(质量分数)^[30-32],具体处理设置为CK(未添加钝化剂)、BC1%(添加1%的生物炭)、BC0.5%(添加0.5%的生物炭)、BF1%(添加1%的复合材料)、BF0.5%(添加0.5%的复合材料)、FC1%(添加1%的铁钙材料)和FC0.5%(添加0.5%的铁钙材料),每个处理设置4个重复.试验选取的水稻品种为南方地区常见的中浙优1号,其生长周期适中,且对重金属元素积累能力强.

将风干土壤(3 kg)、修复材料和肥料(每kg风干土壤施入0.2 g尿素,0.1 g磷酸二氢钾)混合均匀后,置于盆底无透气孔的塑料盆(直径22 cm,高度18 cm)中,加水至60%的田间持水量,并保持2周.将培养3周的水稻幼苗以每盆4株的密度移栽至盆中,幼苗期保持淹水状态,在为期100 d的培养过程中保持干湿交替,使土层表面灌水至2~3 cm,待自然落干后再次灌水,在收获前10 d停止灌水.在水稻移栽10 d后,将孔隙水采集器插入水稻盆中靠近水稻根系部分,每隔7 d采集一次土壤孔隙水,用于测定土壤孔隙水中的镉砷含量.水稻成熟后采集水稻植株样品、根际土壤以及非根际土壤样品.

1.4 样品测试方法

水稻Cd和As测定:称取0.1 g干植物样品于试管中,加入10 mL优级纯浓HNO₃,瓶口放弯颈漏斗静置过夜,150 °C消煮2 h后揭去小漏斗,在消煮至溶液澄清或者淡绿色只有少量(1 mL)为止,用5% HNO₃(优级纯)定容至50 mL. Cd使用石墨炉原子吸收分光光度计(AA-7000, SHIMADZU, Japan)测定; As用双道原子荧光光度计(AFS-2202E, 北京海光仪器, 中国)测定. 本试验中Cd和As测定过程均利用标准物质进行质量监控,两者加标回收率控制在90%~110%.

根表铁膜分析:采用DCB(连二亚硫酸盐-柠檬酸盐-重碳酸盐, dithionite-citrate-bicarbonate)提取法浸提根表铁膜.称取0.6 g水稻根系,置于烧杯中,加入40 mL DCB溶液(0.03 mol·L⁻¹ Na₂C₆H₅O₇·2H₂O、0.06 mol·L⁻¹ Na₂S₂O₄和0.125 mol·L⁻¹ NaHCO₃的混合溶液),室温下浸泡0.5 h,其后提取剩余白根(无铁膜),去离子水洗净后60 °C烘干至恒重(m_1),铁膜含量为(0.6- m_1)×1 000/0.6 mg·kg⁻¹.

土壤有效态Cd和As测定:使用0.01 mol·L⁻¹

CaCl₂(土水质量比1:15,2 h)提取有效态Cd,石墨炉原子吸收分光光度计(AA-7000, SHIMADZU, Japan)测定Cd含量.使用0.5 mol·L⁻¹ NaH₂PO₄(土水质量比1:15,16 h)提取有效态As,双道原子荧光光度计(AFS-2202E,北京海光仪器,中国)测定As含量.本试验中Cd和As测定过程均利用标准物质进行质量监控,两者加标回收率控制在90%~110%.

土壤理化性质分析:土壤DOC在土水质量比1:5下进行浸提,使用TOC分析仪(TOC-L CPN, Shimadzu, Japan)测定.土壤pH值测定参考农业标准(NY/T 1377-2007),采用1:2.5土水质量比进行浸提,采用pH计(Seven Excellence Cond meter S700, Mettler Toledo, Switzerland)测定.

1.5 数据处理分析

本研究利用Microsoft Excel 2013、OriginLab Origin 2018和IBM SPSS Statistics 22软件进行数据统计分析和制图.

2 结果与分析

2.1 修复材料对土壤性质以及重金属有效性的影响

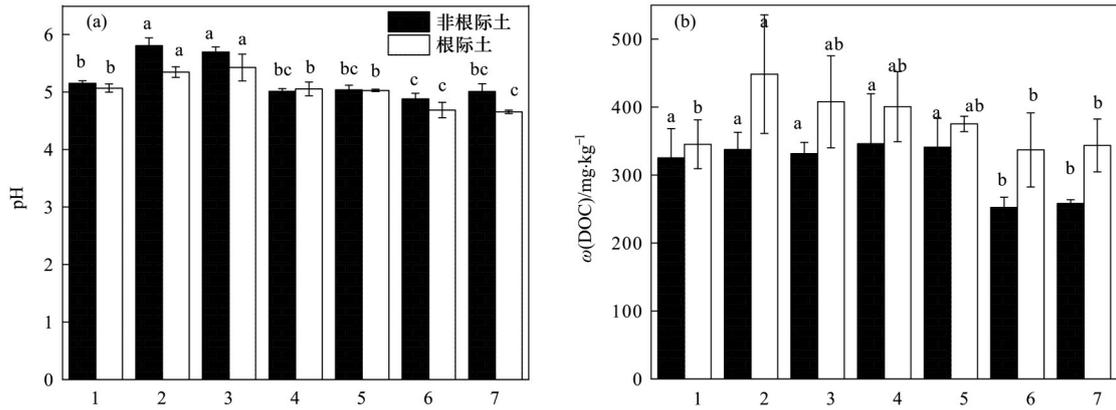
2.1.1 修复材料对土壤pH以及DOC的影响

由图1(a)可知,生物质炭的添加能够显著($P < 0.05$)提高土壤pH,非根际土壤和根际土壤pH分别提高了0.55~0.66和0.28~0.36个单位.而铁钙材料的添加则能降低土壤pH,非根际土壤和根际土壤pH分别下降了0.14~0.27和0.38~0.41个单位.复合材料的添加对非根际土壤和根际土壤pH没有显著性影响($P < 0.05$).总体上来看,在水稻成熟期非根际土壤pH高于根际土壤.

在水稻成熟期的土壤中,非根际土壤DOC含量低于根际土壤.生物质炭和复合材料添加,均提升了根际土壤和非根际土壤DOC含量.而铁钙材料的添加能降低非根际土壤的DOC含量,在FC1%和FC0.5%处理中分别下降了22.4%和20.6%;铁钙材料的添加对根际土壤DOC含量未有显著性($P < 0.05$)影响.

2.1.2 修复材料对土壤孔隙水镉砷浓度的影响

在水稻整个生长期,不同修复材料处理下的土壤孔隙水Cd浓度先上升后呈下降趋势,总体而言,各修复材料处理下土壤孔隙水Cd浓度都处于较低范围[图2(a)].除BC1%和BC0.5%处理外[图2(b)],其余不同处理的土壤孔隙水As浓度变化较为相似.从第20 d开始,土壤孔隙水As浓度逐渐升高,直至第30 d达到第一个峰值,随后迅速下降,在第50 d左右到达最低点.在第75 d左右又出现第二个峰值,之后



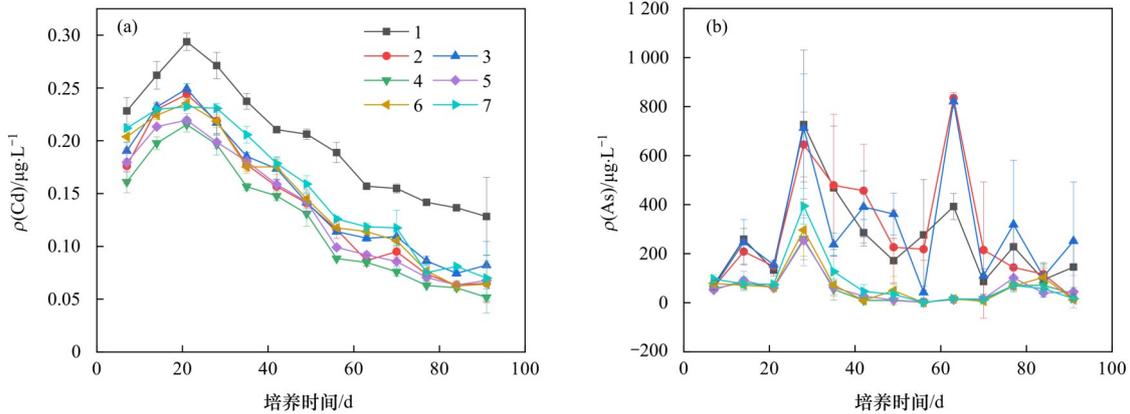
1. CK, 2. BC1%, 3. BC0.5%, 4. BF1%, 5. BF0.5%, 6. FC1%, 7. FC0.5%; 误差线表示±标准误; 不同小写字母表示处理间的显著性差异 ($P < 0.05$)

图1 根际和非根际土壤 pH 和 DOC 含量

Fig. 1 The pH and DOC concentrations in rhizosphere and bulk soil

迅速下降,直至第 90 d 达到稳定. 与空白对照相比,添加生物质炭在水稻全生育期内可以提升土壤孔隙水 As 浓度,而复合材料和铁钙材料在水稻全生育期内能够降低土壤孔隙水 As 浓度,添加修复材料均降低了土壤孔隙水 Cd 浓度. 土壤孔隙水 As 的两个峰值

分别出现在第 30 d 和 75 d,对应为水稻的分蘖期和抽穗期,在这两阶段水稻根系对水分以及土壤养分有着强烈吸收作用,土壤孔隙水中具有高浓度营养物质,会导致 As 从土壤表面释放到溶液中,因此出现两个 As 峰值.



1. CK, 2. BC1%, 3. BC0.5%, 4. BF1%, 5. BF0.5%, 6. FC1%, 7. FC0.5%; 误差线表示±标准误

图2 土壤孔隙水中 Cd 和 As 浓度随时间的变化

Fig. 2 Changes over time in Cd and As concentration in soil pore water

2.1.3 修复材料对土壤有效态镉砷含量的影响

由图 3(a)可见,修复材料添加均降低了根际土壤和非根际土壤有效态 Cd 含量,其中,生物质炭和复合材料添加对土壤有效态 Cd 降低达到了显著性水平 ($P < 0.05$),以 BF1% 处理降幅最大,使根际和非根际土壤分别显著降低了 48.1% 和 41.8%. 不同材料对土壤 Cd 有效态含量的下降效果,大小依次为:复合材料>生物质炭>铁钙材料.

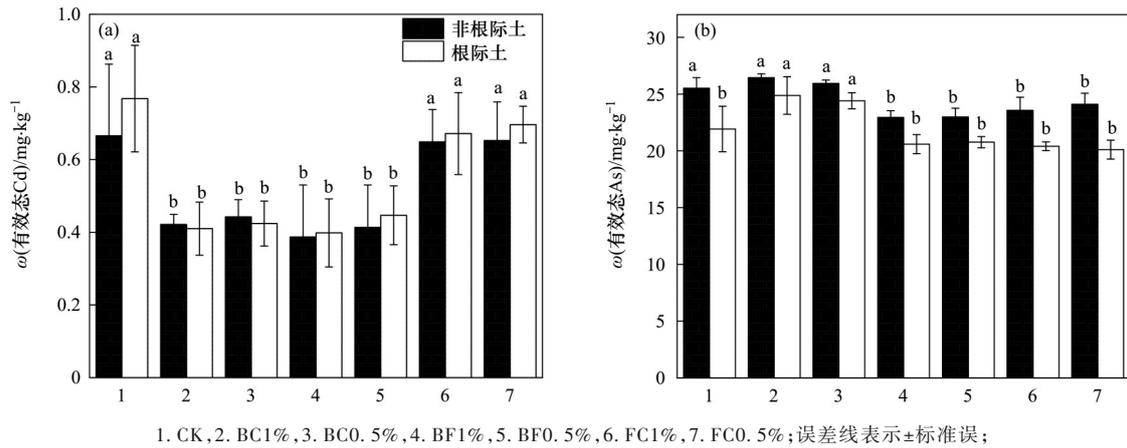
由图 3(b)可知,所有处理中非根际土壤 As 的有效态含量高于根际土壤. 铁钙材料和复合材料的添加降低了非根际土和根际土壤有效态 As 含量,其中 BF1% 处理降低效果最明显,使非根际土和根际土壤有效态 As 分别降低 10.1% 和 6.1%,添加铁钙材料也

使非根际土和根际土壤有效态 As 含量分别下降 5.5% ~ 7.5% 和 6.9% ~ 8.3%. 而生物质炭的添加则提升了土壤有效态 As 含量,其中 BC1% 和 BC0.5% 处理使根际土壤有效态 As 含量分别显著 ($P < 0.05$) 提高了 13.5% 和 11.4%.

2.2 修复材料对水稻生长和镉砷累积的影响

2.2.1 修复材料对根表铁膜的影响

水稻长期处于淹水状态,因此水稻根系泌氧使得根际环境中的还原性物质附着于水稻根系表面,形成根表铁膜^[33,34]. 水稻根表铁膜具有吸附、拦截重金属的作用. 不同修复材料处理下的铁膜含量见表 2,所有修复材料均能增加水稻根表铁膜含量,其中 BF1% 效果最佳,与空白对照相比,水稻根表铁膜含量增加了 13.6%.



1. CK, 2. BC1%, 3. BC0.5%, 4. BF1%, 5. BF0.5%, 6. FC1%, 7. FC0.5%; 误差线表示±标准误;

不同小写字母表示处理间的显著性差异($P < 0.05$), 下同

图3 根际和非根际土壤中Cd和As生物有效态含量

Fig. 3 Concentrations of bioavailable Cd and bioavailable As in rhizosphere and bulk soil

表2 水稻生物量、株高和根表铁膜含量¹⁾

Table 2 Plant height, dry weight, and iron plaque content on root surface

处理	根重/g·株 ⁻¹	茎重/g·株 ⁻¹	叶重/g·株 ⁻¹	籽粒重/g·株 ⁻¹	株高/cm·株 ⁻¹	根表铁膜/mg·g ⁻¹ ·株 ⁻¹
CK	3.95±0.20c	10.56±0.73c	3.31±0.30c	3.32±0.37d	63.08±1.30e	625±57.30a
BC1%	5.39±0.43bc	14.08±1.98bc	5.50±0.38a	5.42±0.83c	77.38±2.30ab	671.79±13.45a
BC0.5%	4.34±0.18bc	12.80±1.68c	3.79±1.09bc	4.93±0.88cd	73.63±2.52bc	691.25±96.7a
BF1%	8.98±1.61a	21.60±2.57a	5.67±0.35a	8.05±0.86ab	78.4±2.27a	710.29±77.10a
BF0.5%	7.89±0.78a	20.17±4.79ab	5.66±0.88a	9.43±1.35a	71.75±3.61c	678.12±36.82a
FC1%	8.04±2.24b	15.62±2.31ab	5.17±1.33ab	7.28±1.40b	69.58±2.41cd	710.25±125.76a
FC0.5%	6.36±2.56bc	13.95±1.74abc	4.94±0.70ab	5.56±0.86c	66.18±2.43de	679.21±28.13a

1) 数据为平均值±标准误差; 同一列不同小写字母表示处理间显著性差异($P < 0.05$)

2.2.2 修复材料对水稻植株生长的影响

修复材料对水稻植株生长影响见表2. 与空白对照相比, 所有修复材料均促进了水稻植株生长, 提高了植株生物量(根、茎、叶和籽粒的干重)和株高, 其中复合材料和铁钙材料对生物量(根、茎、叶和籽粒的干重)的增加达到了显著性水平($P < 0.05$). 在生物质炭添加量为1%和0.5%水平下, 水稻籽粒平均干重较CK分别增加了63.3%和48.5%, 复合材料处理的籽粒干重较CK分别增加142.5%和184.0%, 铁钙材料添加的籽粒干重较CK分别增加119.3%和67.5%; 除FC0.5%处理之外, 其余处理均能显著($P < 0.05$)提升水稻株高(表2). 总体来看, 水稻植株生物量和株高随修复材料用量增加而增加.

2.2.3 修复材料对水稻镉和砷累积的影响

水稻植株体内Cd和As含量如图4所示. 水稻根系中Cd和As积累含量要比水稻茎、叶和糙米高, 这一现象是符合作物对重金属积累的一般规律^[35]. 从图4可看出, 所有修复材料均能降低水稻各部位的Cd含量, 其中复合材料处理效果最佳, 与空白对照相比, 水稻糙米中Cd含量降低了36.9%~42.0%, 不同

修复材料处理下的水稻糙米Cd含量均远低于0.2 mg·kg⁻¹国家标准值(GB 2762-2017). 与空白对照相比, 生物质炭能提高水稻植株各部位的As含量, 而复合材料和铁钙材料均能有效降低水稻各部位As含量. 添加复合材料后水稻糙米As含量比空白对照显著($P < 0.05$)下降了40.4%~44.4%, 铁钙材料也使水稻糙米As含量显著($P < 0.05$)降低了32.9%~36.4%. 复合材料和铁钙材料处理下水稻糙米As含量均低于0.2 mg·kg⁻¹国家标准值(GB 2762-2017).

3 讨论

3.1 修复材料对土壤pH、DOC含量的影响

如图1(a)所示, 生物质炭能提升根际和非根际土壤pH值, 是因为供试生物质炭的pH较高(9.85)且生物质炭中碱性物质(碳酸盐和磷酸盐等)的水解, 会提高土壤中OH⁻含量. 铁钙材料中的铁氧化物会使土壤发生硝化作用, 因此土壤pH值下降^[36]. 而土壤微生物与植物的呼吸作用释放较多的二氧化碳, 同时水稻根系会释放酸性分泌物(有机酸)^[37], 导致成熟期水稻非根际土壤pH高于根际土壤. DOC的主要成分是腐殖质、腐殖酸和黄腐酸, 它们对土壤的结

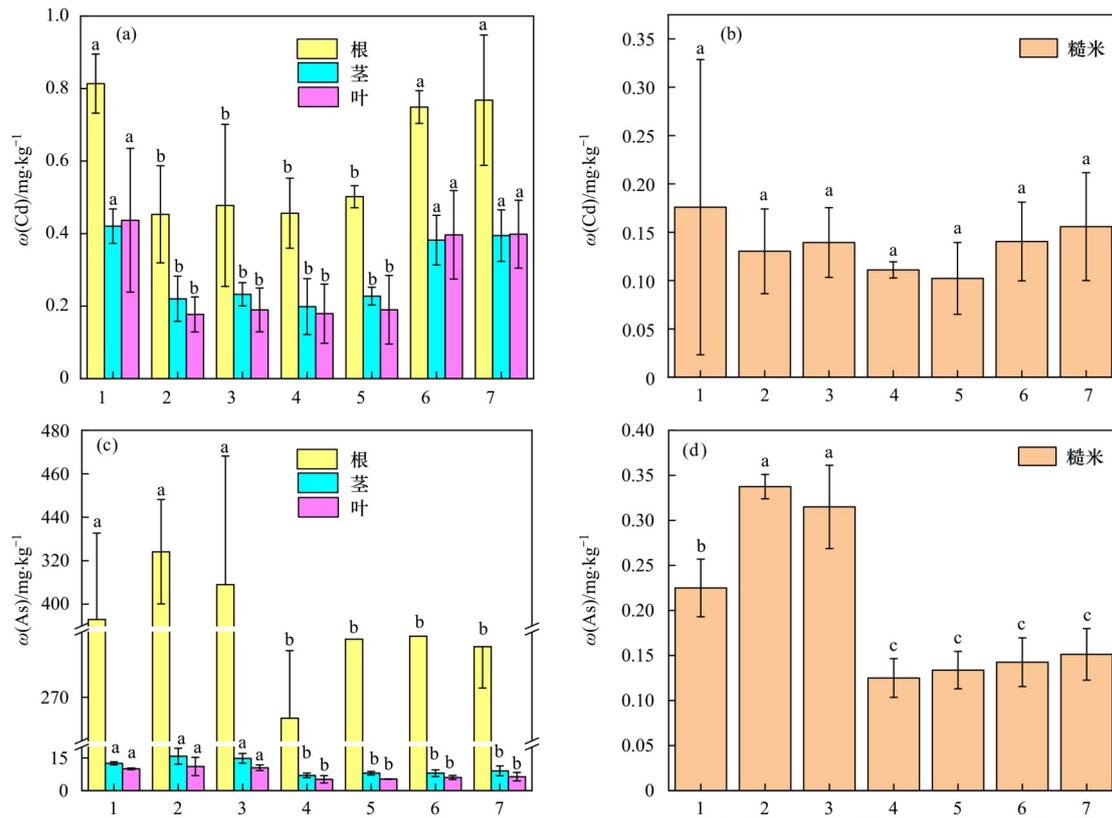


图4 水稻植株各部位Cd和As含量

Fig. 4 Content of Cd and As in various parts of rice plant

合离子、有机分子和固体表面的反应非常活跃^[38]。土壤pH变化会影响DOC含量。例如, Kim等^[39]研究发现, 土壤pH值升高会提升微生物的活性和DOC的溶解性, 在本研究中添加生物质炭后, 土壤pH的增加会导致DOC含量上升。而生物质炭和复合材料中的活性有机碳组分能释放到土壤中, 也会导致土壤DOC含量的增加[图1(b)]。铁钙材料中的Ca²⁺有利于土壤中稳定团聚体的形成, 并促进DOC的凝固^[40], 故使得土壤DOC含量降低[图1(b)]。

3.2 修复材料对土壤孔隙水镉和砷变化的影响

在水稻整个生长期, 不同钝化剂处理的土壤孔隙水中Cd浓度均呈先上升后呈下降趋势, 总体而言, 各处理下土壤孔隙水Cd浓度都处于较低范围。土壤孔隙水Cd浓度上升主要是因为可溶性有机碳能与重金属竞争修复材料表面的吸附点位, 通过共溶效应提升重金属的迁移性。生物炭和复合材料处理中土壤DOC含量均有增加, 导致部分Cd活化, 故提升其迁移性。后期土壤孔隙水Cd浓度下降是由于修复材料中的羧基、羟基等活性官能团发生吸附及螯合作用, 使其在土壤中的移动性及土壤孔隙水中的浓度均低于空白对照组^[41]。在分蘖期和抽穗期水稻生长迅速, 使得水稻根系对水分和养分吸收更加强烈, 土壤孔隙水中具有高浓度营养物质, 特别是磷酸盐, 会导致As从土壤表面释放到溶液中^[42, 43], 因此出

现两个As峰值。张燕等发现水稻在分蘖期和抽穗期体内的砷含量较其他生理期高, 这一结论与本试验结果水稻根系在分蘖期和抽穗期对As具有强烈吸收作用相似^[41]。在生物质炭处理下, 土壤孔隙水As浓度增加的主要原因是修复材料能提高砷还原菌的活性, 使高价态砷还原成低价态砷, 因此更多的砷会进入土壤孔隙水中。铁钙材料和复合材料主要通过铁氧化物表面的电荷吸附和羟基结合形成内表面螯合物, 及含氧官能团上氢键结合来钝化As^[45]。

3.3 修复材料对土壤有效态镉和砷含量的影响

生物质炭和复合材料均使土壤有效态Cd含量显著($P < 0.05$)下降[图3(a)], 由于生物质炭含有丰富的官能团(C—H、C=C和—CH₂等), 而生物质炭上的C—H和C—O对Cd具有吸附作用, 导致土壤中Cd有效性降低。同时, 生物质炭材料施入到土壤中, 会显著($P < 0.05$)提高土壤pH[图1(a)], 进一步增强Cd的水解沉淀, 从而降低了Cd在土壤中的移动性, 是土壤有效态Cd含量降低的另一方面原因。与土壤Cd不同, 生物质炭材料能提升土壤有效态As含量[图3(b)], 因生物质炭表面具有醌基等含氧基团从而使其有电子穿梭等功能, 电子穿梭能将As(V)生化还原为移动性更强的As(III)^[46], 明显提升了土壤有效态As含量、孔隙水As浓度。同时, 因生物质炭添加会提高土壤pH和DOC含量(图1), 土壤中氢氧

根和 DOC 会与阴离子竞争土壤颗粒表面的吸附点位,使得土壤对 As 的吸附能力降低,导致更多 As 由土壤颗粒向土壤溶液的释放,从而增强了 As 的有效性^[47]. 铁钙材料具有粒径小和反应活性较高的特征,在土壤中可以通过电化学腐蚀释放出游离的 Fe^{3+} ,并快速形成铁氧化物例如水铁矿^[48,49],新生成的铁氧化物可以为 Cd 和 As 提供更多的吸附点位,或将其吸收到矿物体内,从而降低土壤 Cd 和 As 的有效性(图 3). 同时, Fe^{3+} 在水解时生成的次级氧化物会与三价砷或五价砷离子发生表面共沉淀反应,生成稳定性更强的砷酸铁矿物 $[\text{Fe}_3(\text{AsO}_4)_2 \text{ 或 } \text{Fe}_3(\text{AsO}_4)_2]$ ^[50]. 复合材料中生物质炭的电子穿梭功能促进铁钙材料的电化学腐蚀,从而提升了铁氧化物的生成速率^[51,52],另外生物质炭的巨大比表面积和众多的吸附点位有利于铁氧化物附着其表面,进而形成较为均匀的生物物质炭负载铁氧化物的复合物^[53,54],从而增强对土壤 Cd 和 As 的吸附能力,使复合材料处理的土壤有效态 Cd 和 As 含量比生物质炭、铁钙材料处理更低(图 3).

3.4 修复材料对水稻植株镉和砷含量的影响

所有修复材料均能降低水稻各部位的 Cd 含量,复合材料和铁钙材料均能有效降低水稻各部位 As 含量,而生物质炭提高了水稻植株各部位的 As 含量(图 4). 水稻中 Cd 和 As 含量可能受到了土壤有效态 Cd 和 As 及根表铁膜的影响. 生物质炭的添加提高了土壤有效态 As 含量和孔隙水 As 浓度(图 2 和图 3),促使其有效性和移动性增加,从而提高水稻体内的 As 含量;铁钙材料和复合材料添加降低了土壤有效态 As 含量和孔隙水 As 浓度,不同修复材料添加均降低了土壤有效态 Cd 含量和孔隙水 Cd 浓度(图 2 和图 3),从而降低了水稻中 Cd 和 As 含量. 同时,修复材料添加也促进了水稻根表铁膜的形成(表 2),已有研究表明,根表铁膜在一定程度上作为土壤重金属进入水稻根系的屏障,因此能够有效地抑制水稻根系对土壤重金属的吸收^[55],进一步降低了水稻体内 Cd 和 As 的积累量. 在不同修复材料处理中,复合材料降低土壤有效态含量和孔隙水 Cd 和 As 浓度效果最好,导致水稻中 Cd 和 As 含量最低.

3.5 修复材料对水稻生长影响

所有修复材料均能提高水稻根、茎、叶和籽粒的干重. 李婧菲^[55]向砷污染(全量 $85.2 \text{ mg} \cdot \text{kg}^{-1}$)土壤中施入外外源性铁能使水稻增产超 100%,王贺东^[56]研究发现,1% 的小麦秸秆生物质炭能显著提升 143.7% 的水稻生物量,这与本试验的研究结果相似. 生物质炭是一种高效天然的肥料,有作物生长所需的营养元素 Ca、K 和 N 等,当施入土壤中,不仅能增加土壤养分元素含量还能改善土壤结构和微生物

群落^[57]. 在 BC1% 处理下籽粒干重显著 ($P < 0.05$) 增加 63.3% (表 2),黄雁飞等^[58]施用 3% 的桑树枝干和甘蔗废渣生物质炭,可使水稻籽粒干重显著提高 38.1% 和 32.8%,与本研究结果一致. 本试验结果表明,在生物质炭、复合材料和铁钙材料处理下,水稻植株中 Cd 和 As 含量总体上均下降,根表铁膜的含量均较空白对照上升,而根表铁膜在一定程度上会抑制水稻对重金属吸收,进一步降低水稻中 Cd 和 As 含量,减少 Cd 和 As 对水稻生长的毒害作用,从而提高水稻的生物量.

4 结论

(1) 生物质炭材料能显著 ($P < 0.05$) 提高土壤 pH,且能提升土壤 DOC 含量;铁钙材料能显著 ($P < 0.05$) 降低土壤 pH,同时降低土壤 DOC 含量;复合材料的添加未能使土壤 pH 有显著变化,但能提升土壤 DOC 含量. 非根际土壤 pH 高于根际土壤,而 DOC 含量低于根际土壤.

(2) 复合材料和铁钙材料能够同时降低土壤孔隙水 Cd 和 As 浓度及有效态 Cd 和 As 含量,而生物质炭能够有效降低土壤孔隙水 Cd 浓度和有效态 Cd 含量,却提升了土壤孔隙水 As 浓度和有效态 As 含量,在不同修复材料中,复合材料对土壤孔隙水和有效态重金属降低效果最佳.

(3) 生物质炭、铁钙材料和复合材料均能促进水稻植株生长,提高植株生物量(根、茎、叶和籽粒的干重),并增加根表铁膜含量. 复合材料和铁钙材料能同时降低水稻各部位的 Cd 和 As 含量,使水稻糙米中 Cd 和 As 含量均低于国家标准值(GB 2762-2017).

(4) 在本研究的几种修复材料中,以复合材料对土壤 Cd 和 As 污染修复效果最好,不仅能提高水稻产量,且通过增加根表铁膜、降低土壤 Cd 和 As 生物有效性(孔隙水浓度和有效态含量),从而实现水稻安全生产.

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