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2000~2020 平尺年
广东茂名主要水系表层沉积物重金属风险评估及源解析
小园 另近极 恢复 对 上
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稻-麦轮作模式下不同钝化材料对镉污染农田土壤的 原位钝化效应

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摘要:为明确大田条件下施用钝化材料对镉(Cd)污染农田土壤的原位钝化效应及其持续性,以秸秆生物炭、YH粉、粉煤灰、海泡石和页岩粉(粒径均<0.2 mm,施用量均为2.25 kg·m²)这5种钝化材料为研究对象,连续监测3 a 稻-麦轮作模式下原位钝化处理对土壤养分、土壤酸碱度、土壤 Cd 污染状况和种植作物籽粒 Cd 含量的影响,探讨其钝化效应及持续性,为有效控制农田土壤 Cd 污染、保证作物安全生产提供理论依据和数据支撑.结果表明:①稻-麦轮作模式下,施用5种钝化材料对土壤养分含量影响较小,但均可提高土壤 pH,促使土壤 Cd 由酸提取态向残渣态转化,降低土壤 Cd 有效性,其中秸秆生物炭与YH粉处理下当季土壤有效 Cd 含量的降幅最大(20.42%~22.53%),是其它钝化处理的1.07~1.84倍.②稻-麦轮作模式下,首年施用5种钝化材料后均显著降低了水稻和小麦籽粒 Cd 含量,降幅分别达 19.88%~48.77%和5.06%~24.00%.施用秸秆生物炭、粉煤灰和YH粉后作物籽粒 Cd 含量显著低于对照和其它钝化材料,该处理条件下的水稻籽粒ω(Cd)(0.195、0.197和0.223 mg·kg⁻¹)达到或接近《食品安全国家标准食品中污染物限量》(GB 2762-2017).③5种钝化材料对农田土壤Cd 的钝化效应随时间的延长均有所减弱,粉煤灰、海泡石和页岩粉在施用后第3a已无明显钝化效应,而秸秆生物炭和YH粉处理下土壤有效 Cd 和作物籽粒 Cd 含量在稻-麦轮作第3a中仍显著低于对照,钝化效果持久性较好.5种纯化材料施用第3a时效果已迅速衰减,但秸秆生物炭和YH粉仍可明显降低土壤有效 Cd 和作物籽粒 Cd 含量,其钝化效果具有较好的持续性,是用于稻-麦轮作模式下 Cd 污染农田土壤安全生产的理想钝化材料.

关键词:钝化材料;镉(Cd);原位钝化;持久性;稻-麦轮作

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In-situ Remediation Effect of Cadmium-polluted Agriculture Land Using Different Amendments Under Rice-wheat Rotation

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Abstract: Exploring the effects of one-time amendment treatments on cadmium (Cd)-contaminated farmland soils is beneficial for providing a theoretical basis to effectively prevent Cd pollution in farmland soils and ensure the safe production of crops. Five amendments, including straw biochar, fly ash, sepiolite, white marble powder, and shale (particle size <0.2 mm, application rate 2.25 kg·m⁻²), were applied to the Cd-contaminated farmland soils. The soil nutrients, pH, soil available Cd, and Cd chemical forms in the soils and grain Cd concentration in the planted crops were determined to investigate the effects and persistence of one-time applications of the five amendments. The results showed that: ① the application of the five amendments had little effect on soil nutrient content, but all of them could increase soil pH. Amendment treatments improved the transfer of Cd from the acid extraction fraction to residue fraction and further reduced the Cd availability in the soil. The decreasing amplitudes of straw biochar and white marble powder soil conditioner were 20.42%-22.53%, which was higher than those in the other treatments. ② The grain Cd concentrations in rice and wheat were significantly decreased under the amendment treatments with the decreasing amplitudes of 19.88%-48.77% and 5.06%-24.00%, respectively. The Cd concentrations in rice grains under the treatments of straw biochar, fly ash, and white marble powder soil conditioner were 0.195, 0.196, and 0.223 mg·kg⁻¹, respectively, which were lower than those under the other treatments and were close to or approached the National Standard of Food Safety (GB 2762-2017) (0.2 mg·kg⁻¹). ③ The immobilization effects on Cd in farmland soils were decreasing with time under one-time application of the amendments. The available Cd concentrations in the soil and Cd concentrations in crop grains were still lower than those in the control after three rounds of rice-wheat rotation. The straw biochar and white marble powder soil conditioner had a good and long-

Key words: amendments; Cd; in-situ remediation; persistence; rice-wheat rotation

土壤是人类赖以生存的物质基础,着力解决突出环境问题,强化土壤污染管控与修复是目前我国土壤修复的指导思想. 镉(Cd)是近十年我国土壤中的主要重金属污染元素^[1],Niu等^[2]通过分析发现,我国多数农田表层土壤的 Cd 含量平均值明显高于土壤背景值. 王建乐等^[3]研究显示,我国耕地点位Cd 污染超标率在各污染物中排第一. 由此可见,Cd 污染农田土壤的修复治理已成为保证作物安全生产

的重要课题之一.

目前重金属污染土壤的修复方法可分为物理修 复、化学修复和生物修复这3类,其中原位钝化修 复(化学修复)和植物修复(生物修复)对土壤破坏

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最小[4]. 原位钝化修复技术适用范围广, 可在保证 作物正常生产的前提下进行,对大面积污染土壤的 修复表现出一定的优越性[5]. 当前研究中常用的钝 化材料主要包括以磷酸盐类、黏土矿物类等为主的 无机钝化材料,以生物炭类、有机废弃物类等为主 的有机钝化材料,以及无机-有机复合钝化材料[6,7]. 试验发现不同钝化材料对土壤 Cd 有效性的影响差 异显著[8,9],磷矿粉对土壤有效 Cd 的钝化效果仅为 硅藻土的 49.57% [8], 赤泥和海泡石材料处理后的 根际土壤有效 Cd 含量仅为过磷酸钙、钙镁磷肥材 料处理后的20%~50%[9].因此,选取适宜的钝化材 料是保证原位钝化修复效果的关键[10].目前,已有 研究表明,室内盆栽试验条件下钝化材料对重金属 Cd 的钝化效果与田间试验条件下的钝化效果存在 较大差异[11,12]. 施用黏土矿物和石灰等钝化材料 后,水稻籽粒 Cd 含量降幅在盆栽试验条件下分别 达 44.9% 和 47.7%, 而在大田条件下仅为 33.2% 和 28.8% [13,14]. 由此可见, 钝化材料的田间筛选和验 证是获取具有区域适应性的钝化材料和实现 Cd 污 染农田安全生产的重要手段.

前期室内培养试验发现秸秆生物炭、粉煤灰、YH粉、海泡石和页岩粉对土壤 Cd 具有较好的钝化效果^[15,16],但一次性施用 5 种钝化材料对 Cd 污染农田土壤的钝化效应及持久性尚未明确. 因此,本文以前期筛选出的 5 种钝化材料为研究对象,探讨其在稻-麦轮作模式下一次性施用后连续 3 a 对农田 Cd 污染土壤的原位钝化效应及持续性,以期为修复农田 Cd 污染土壤提供一定的理论依据和数据支撑.

1 材料与方法

1.1 研究区概况

试验田位于成都平原某市,属中纬度亚热带湿润气候,平均海拔为 507 m,年平均气温为 15.2°C. 土壤类型为水稻土,由第四系上更新统钙质黄土状、粉砂质黏土的残积堆积物经水耕熟化后形成,常年水稻-小麦轮作. 土壤基本理化性质为:pH 6.6、CEC 12.21 cmol·kg⁻¹、容重 1.22 g·cm⁻³、 ω (有机质) 34.61 g·kg⁻¹、 ω (全氮) 2.4 g·kg⁻¹、 ω (碱解氮) 100.3 mg·kg⁻¹、 ω (有效磷) 19.0 mg·kg⁻¹、 ω (速效钾) 69.250 mg·kg⁻¹、 ω (砂粒) 44.67%、 ω (粉粒) 25.74%、 ω (黏粒) 29.59%、 ω (全 Cd) 2.68 mg·kg⁻¹和 ω (有效 Cd) 0.49 mg·kg⁻¹.

1.2 供试材料

供试钝化材料:秸秆生物炭、YH 粉(主要成分为 CaCO₃)、粉煤灰、海泡石和页岩粉(基本性质见

表 1); 其全 Cd 含量均在《有机-无机复混肥料国家标准》(GB 18877-2009)、《农用污泥中污染物控制标准》(GB 4284-1984)和《农用粉煤灰中污染物控制标准》(GB 8173-1987)允许值内.

供试作物:水稻(Oryza sativa L.)、小麦(Triticum aestivum L.),品种分别为宜香优 2115 和川麦 104,分别由四川农业大学农学院和四川省农业科学院作物研究所提供.

供试肥料:复合肥,其 N: P_2O_5 : KQ的配比为 25: 5: 10,施用量为 600 kg·hm $^{-2}$,采购自当地农资店.

表 1 供试钝化材料基本性质1)

Table 1	Basic prop	erties of te	sted amendment mate	erials
材料	产地	pН	$\omega(\mathrm{Cd})/\mathrm{mg} \cdot \mathrm{kg}^{-1}$	粒径/mm
秸秆生物炭	四川绵阳	9. 20	0. 17	0. 15
YH 粉	四川成都	8.70	nd	0. 15
粉煤灰	四川成都	10. 20	0.11	0. 15
海泡石	湖南浏阳	8. 40	0. 19	0. 125
页岩粉	四川雅安	8. 50	0. 20	0. 15

1)nd表示未检出

1.3 试验设计与处理

本试验设空自对照、秸秆生物炭、YH粉、粉煤灰、海泡石和页岩粉共计6个钝化处理.每个处理设3次重复,共18个小区,每小区面积为12 m²(4 m×3 m). 钝化材料施用量均为2.25 kg·m⁻². 本试验于2015~2018年开展,采用田间小区试验,所有小区随机区组排列,用塑料薄膜分隔田埂,外设长为1 m、宽为0.4 m 的保护行.于2015年5月水稻移栽前分别将钝化材料均匀撒施于土壤表面,翻耕平整所有小区(深度0~20 cm),之后均不再施用,水肥管理和病虫害防治等均按当地习惯进行,3 a 连续稻-麦轮作.

1.4 样品采集与制备

分别在水稻和小麦成熟期采样穗部样品,每小区采用棋盘式采样法采集长势一致的 30 株作为一个混合样.样品经自然风干后脱粒,按农业部颁布标准(YN122-8)^[17]米质测定方法出糙,将糙米在 75℃烘干至恒重,磨碎过 100 目筛装袋备用.同时收割整个小区籽粒,采用实打实收的方式计算每个小区的产量.采集相应土壤样品,样品经自然风干后研磨过筛后装袋备用.

1.5 测定项目及方法

土壤基本理化性质采用常规方法测定^[18];土壤 Cd 形态采用 BCR 分级提取法测定^[19];土壤 Cd 全量采用 HNO₃-HClO₄-HF(5:1:1,体积比)消化(GB/T 17141-1997);土壤有效态 Cd 采用二乙基三胺五乙酸(DTPA)浸提(GB/T 23739-2009),植株

Cd 采用 HNO_3 - $HClO_4$ (5:1,体积比)进行消化(GB 5009.15-2014). Cd 含量采用原子吸收光谱仪(PinAAcle 900T,Perkin Elmer,USA)测定,以国家标准物质 GBW 10015 和 GBW 07405 为内标控制分析质量. 土壤 Cd 全量、土壤有效态 Cd 含量、土壤 Cd 形态、水稻样品和小麦样品在分析过程中 Cd 的回收率分别为 96% ~ 103%、97% ~ 102%、96% ~ 101%、95%~102%和 97%~104%.

1.6 数据处理

数据采用 DPS (11.0)进行统计分析,最小显著 差异法(LSD)用于多重比较. 图表制作采用 Excel (2016)和 Origin (9.0).

2 结果与分析

2.1 不同钝化处理对土壤 pH 和土壤养分的影响

稻-麦轮作模式下,5 种钝化材料处理均可提高土壤pH(表2).第1 a(2015年)施用钝化材料后,水稻和小麦季土壤pH 比对照分别增加了0.06~0.57 和0.02~0.54 个单位.其中,YH 粉处理下土壤pH 增幅最大,而页岩粉处理增幅最低.随着施用时间延长,各处理土壤pH 值均逐渐降低,且各钝化处理下土壤pH 与对照差值也逐

渐降低. 在稻-麦轮作第 3 a 时,除 YH 粉外,其余 4 种钝化材料处理对土壤 pH 的提升幅度小于 0.20 个单位.

表 2 稻-麦轮作模式下不同钝化材料对土壤 pH 的影响

Table 2 Effects of different amendments on soil

		pri under	rice-wneat	rotation		
处理		水稻季			小麦季	
处连	2015年	2016年	2017年	2015年	2016年	2017年
对照	6. 54	6. 49	6. 14	6. 52	6. 55	6. 09
秸秆生物炭	6. 91	6. 74	6. 25	6.84	6. 70	6. 18
YH 粉	7. 11	7. 02	6. 36	7.06	6.86	6. 29
粉煤灰	6.85	6.70	6. 11	6.74	6.65	6. 11
海泡石	6.87	6.68	6.31	6.84	6. 69	6. 23
页岩粉	6.82	6.67	6.20	6.71	6.60	6.18

一次性施用不同钝化材料 3 a 后对土壤养分含量的影响见表 3. 施用秸秆生物炭 3 a 后,土壤有机质含量在水稻季和小麦季分别较对照处理提高了17. 48%和11. 20%,且在水稻季差异达到显著. 该处理下土壤全氮、碱解氮、有效磷和速效钾含量与对照处理无显著差异. 另外,与对照处理相比,施用YH粉、粉煤灰、海泡石和页岩粉这 4 种钝化材料对土壤有机质、全氮、碱解氮、有效磷和速效钾含量均无影响.

表 3 稻-麦轮作模式下不同钝化材料对土壤养分含量的影响1)

Table 3	Effects of different	amendments	on soil	nutrient	contents	under	rice-wheat	rotation

	ω(有机质	₹)/g•kg ⁻¹	ω(全氮)	∕g•kg ⁻¹	ω(碱解氮)/mg•kg ⁻¹	ω(有效磷))/mg•kg ⁻¹	ω(速效钾)/mg•kg ⁻¹
处连	水稻季	小麦季	水稻季	小麦季	水稻季	小麦季	水稻季	小麦季	水稻季	小麦季
对照 /	32. 84b	33. 56ab	2. 07 a	1. 96a	109a	109a	13. 85 a	15. 31a	90. 43 a	87. 81a
秸秆生物炭	38. 58a	37. 32a	2. 19a	2. 17a	117a	110a	15. 87a	15. 58a	86. 05 a	85. 70ab
YH 粉	32. 56b	33. 10ab	1.96a	2. 03 a	108a	112a	14. 35 a	15. 42a	81. 24a	82. 56ab
粉煤灰	33. 38b	33. 20ab	1.94a	1. 99a	106a	119a	15. 13a	14. 46a	82. 06a	83. 95ab
海泡石	34. 37 ab	31.87b	2. 03 a	2. 14a	116a	111a	14. 61 a	13. 45a	80. 37 a	79. 23b
页岩粉	31. 11b	30.76b	2. 02a	1.82a	110a	114a	14. 06a	14. 14a	87. 49a	80. 75 ab

1)不同小写字母表示同一收获时间下不同钝化处理间差异显著(P<0.05),下同

2.2 不同钝化处理对土壤 Cd 有效性的影响

稻-麦轮作模式下,5 种钝化材料处理均可显著降低土壤有效 Cd 含量(表 4). 与对照相比,施用钝化材料第 1a(2015 年)水稻季和小麦季土壤有效 Cd 含量 分 别 下 降 12.21% ~ 22.53% 和 8.40% ~ 20.08%.5 种钝化材料中,页岩粉处理下土壤有效

Cd 含量显著高于其它钝化材料. 随时间延长,各钝化处理土壤有效 Cd 含量在水稻季逐年增高,而在小麦季则无明显变化. 5 种钝化材料中,仅有秸秆生物炭和 YH 粉处理下土壤有效 Cd 含量连续 3 a 显著低于对照,分别为对照的 77.47%~87.97% 和79.55%~86.61%.

表 4 稻-麦轮作模式下施用不同钝化材料对土壤有效镉含量的影响1)

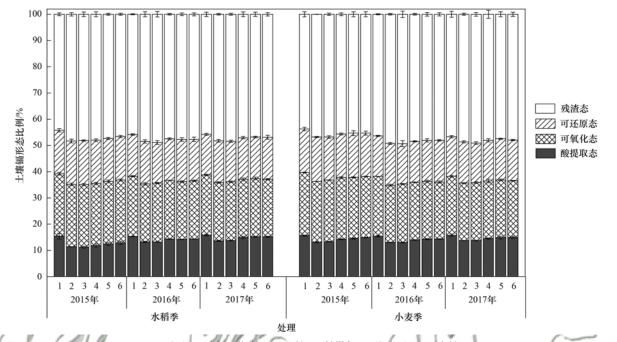
Table 4 Effects of different amendments on soil available Cd concentration under rice-wheat rotation

AL TH		水稻季			小麦季	
处理	2015 年	2016 年	2017 年	2015 年	2016 年	2017 年
对照	0. 475aA	0. 478aA	0. 482aA	0. 488aA	0. 486aA	0. 489aA
秸秆生物炭	0. 368cB	0. 414bA	0. 424cA	0. 390cB	0. 395bB	0. 395bB
YH 粉	0. 378cB	0. 414bB	$0.421 \mathrm{cA}$	0. 395 cB	0. 389bB	0. 389bB
粉煤灰	0. 375 cB	0. 435abA	0. 434abA	0. 410bB	0. 408bB	0.408bB
海泡石	0. 392cB	0. 436abA	0. 442abA	0. 427bcA	0. 411bB	0.411bB
页岩粉	0. 417bB	0. 443 abA	0. 457abA	0. 447bA	0. 412bB	0.412bB

¹⁾不同小写字母表示同一收获时间下不同钝化处理间差异显著 (P < 0.05);不同大写字母表示同一钝化处理在不同收获时间差异显著 (P < 0.05),下同

各钝化处理条件下,土壤不同形态 Cd 所占比例均表现为:残渣态 > 可氧化态 > 可还原态、酸提取态(图1). 施用 5 种钝化处理均降低了土壤中的酸提取态 Cd 占比,其中秸秆生物炭和 YH 粉处理对酸提取态 Cd 的降低效果更佳,与对照相比分别降

低了 26.13% 和 16.45%.此外,与对照处理相比,钝化处理下土壤残渣态 Cd 占比增大,但可还原态和可氧化态 Cd 占比变化不明显.随着施用时间的延长,各处理下土壤酸提取态 Cd 占比有所上升,但始终低于对照.



1. 对照, 2. 秸秆生物炭, 3. YH 粉, 4. 粉煤灰, 5. 海泡石, 6. 页岩粉

图 1 稻-麦轮作模式下施用不同钝化材料后土壤各形态 Cd 所占比例

Fig. 1 Percentages of Cd forms in soil treated with different amendments under rice-wheat rotation

2.3 不同钝化处理对籽粒 Cd 积累的影响

稻-麦轮作模式下,5 种钝化材料处理均可降低作物籽粒 Cd 含量(图 2). 施用钝化材料第 1 a(2015年)的水稻和小麦籽粒 Cd 含量比对照分别降低了 19.88%~48.77%和 5.06%~24.00%. 其中,秸秆生物炭、粉煤灰和 YH 粉处理下水稻籽粒 ω (Cd)分别为 0.195、0.197和 0.223 mg·kg⁻¹,达到或接近《食品安全国家标准食品中污染物限量》(GB 2762-2017)(0.2 mg·kg⁻¹),显著低于海泡石和页岩粉处理. 秸秆生物炭和 YH 粉处理下小麦籽粒 Cd 含量显著低于粉煤灰、海泡石、页岩粉和对照处理,但所有处理下小麦籽粒 ω (Cd)均高于食品安全国家标准的 0.1 mg·kg⁻¹.

随着施用时间延长,同一钝化材料处理下的水稻籽粒 Cd 含量显著增加,但在钝化施用第 3 a 时仍显著低于对照.在不同年份小麦季,除 YH 粉处理下小麦籽粒 Cd 含量呈显著增加趋势外,其余各处理小麦籽粒 Cd 含量随时间延长无显著差异.在施用钝化材料第 3 a 时,仅有秸秆生物炭和 YH 粉处理下小麦籽粒 Cd 含量仍显著低于对照.

2.4 不同钝化处理对作物产量的影响

稻-麦轮作模式下,5种钝化材料处理后,水稻

和小麦产量与对照相比均无显著变化(图 3). 且随着施用时间延长,同一钝化材料处理下的水稻和小麦产量也均无显著变化. 以上结果表明,不同钝化处理未对水稻和小麦的正常生长造成影响.

3 讨论

施用钝化材料主要通过降低土壤中 Cd 的有效性来实现 Cd 污染农田的安全生产. 土壤中 Cd 的有效性受土壤酸碱度和 Cd 形态的影响. 其中,土壤 pH 直接影响 Cd 在土壤中迁移转化,在高 pH 环境下,土壤中游离的 Cd²+会以 Cd(OH)2 的形式被固定,Cd 的迁移能力和生物、化学有效性均降低[20,21]. Cd 在生态系统中的迁移性和生物毒性的高低也受到 Cd 形态特征的影响[22]. 土壤可利用态 Cd 向难利用态 Cd 转化可降低大白菜对 Cd 的吸收[23]. 本研究中,施用 5 种钝化材料均提高了当季土壤 pH 值,且促使土壤 Cd 由酸提取态向残渣态转化,降低了土壤 Cd 有效性和种植作物的籽粒 Cd 含量. 其中,YH 粉与秸秆生物炭处理对水稻和小麦籽粒 Cd 水平的降低效果最佳,粉煤灰和海泡石次之,这与高瑞丽等[24]和崔红标等[25]研究的结果相似.

稻麦轮作体系下,钝化材料主要通过降低土壤

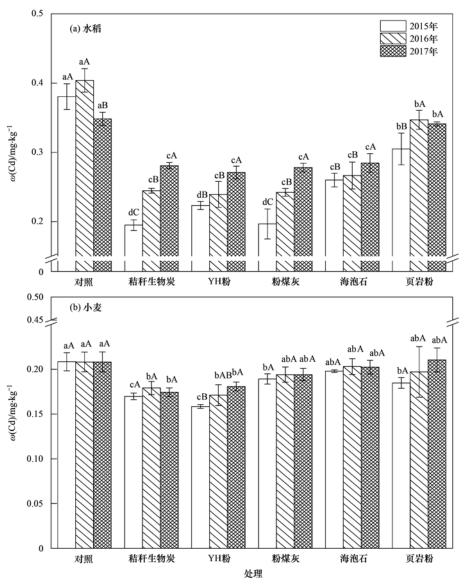


图 2 稻麦轮作模式下施用不同钝化材料对水稻和小麦籽粒 Cd 含量的影响

Fig. 2 Effects of different amendments on the Cd concentration of rice and wheat in rice-wheat rotation

中 Cd 的有效性,减少水稻和小麦对 Cd 的吸收,继 而达到钝化的目的. 不同钝化材料对土壤 Cd 的钝 化机制不同,导致其对土壤 Cd 的修复效果存在差 异[26]. YH 粉中的 CaCO, 可在土壤中发生水解作用 产生 OH-,增强土壤碱性,较其余 4 种材料相比,施 入土壤后可为土壤营造更高的 pH 环境,因此其对 土壤 pH 值的提升最强. YH 粉的添加还可以通过增 加土壤颗粒表面的负电荷数,增强对 Cd2+的吸附, 利于形成氢氧化物或碳酸盐沉淀[27]. 另外,土壤中 Ca2+的增加,会促进土壤中矿物如铁矿物表面胶体 的形成,进而增强对土壤中 Cd 的吸附[28],有效降低 土壤中 Cd 的有效性,降低水稻和小麦对 Cd 的吸收 积累. 生物炭进入土壤后, 其灰分中以氧化物或碳酸 盐形式存在的矿物质元素溶于水后可呈碱性,间接 提高了土壤环境的 pH,促使土壤 Cd 生成 Cd(OH), 以及其它难溶沉淀[29],另外其具有丰富的蜂窝孔状 结构和较大的比表面积,为 Cd 提供了丰富的吸附 位点[30,31], 可通过羧基、羟基和酚基与 Cd 络 合[32,33],有效降低水稻和小麦籽粒 Cd 含量.此外, 粉煤灰的表面积及孔隙较大,且含有多种金属氧化 物如SiO₂、Fe₂O₃和Al₂O₃等,铁铝氧化物对Cd具 有一定的吸附作用,可将 Cd 由水溶性交换组分转 化为与铁锰氧化物结合的组分,调节土壤中 Cd 的 有效性[34,35],海泡石属于黏土矿物,是一种层链状 纤维形态多孔的含镁硅酸盐矿物,具有两层硅氧四 面体,中间一层为镁氧八面体,水分子和可交换的阳 离子存在于其形成的上下层相间排列孔道中,可通 过离子交换吸附 Cd[36]. 值得注意的是, 秸秆生物 炭、粉煤灰、海泡石和页岩4种钝化材料对土壤pH 的提升效果相当,但页岩粉对土壤 Cd 的降低效果 最差. 页岩粉是一种黏土物质微小颗粒, Cd 可被黏 粒微孔结构固持,降低 Cd 在土壤中的有效性[37],可

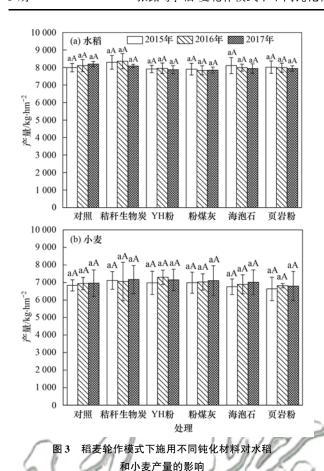


Fig. 3 Effects of different amendments on the yield of rice and wheat in rice-wheat rotation

能由于页岩粉的黏粒微孔结构较少,对 Cd 的固持能力有限,导致其对土壤 Cd 的钝化效果劣于其他钝化材料.

原位钝化修复技术主要是通过改变 Cd 在土壤 中的赋存形态进而降低 Cd 在土壤中的移动性,但 并不能达到清除土壤 Cd 的目的,因此钝化剂对重 金属 Cd 钝化效果的持久性是一个值得探讨的问 题. 本研究在稻麦轮作体系下连续 3a 监测了 5 种钝 化材料对 Cd 的修复效果,结果表明,土壤有效态 Cd 含量和水稻、小麦籽粒 Cd 含量随钝化时间的延长 而提高,5种钝化材料的钝化效果随时间的延长而 减弱,这与裴楠等[36]的研究结果一致. 这主要是由 于土壤环境较为复杂且具有较强的缓冲调节能力、 钝化材料自身形态结构以及钝化材料与 Cd 的结合 均会受到环境的影响而发生改变,因此钝化剂对土 壤 Cd 的钝化效果会随时间的延长而减弱[5]. 本研 究中钝化效果的减弱可能受到农艺管理措施、灌 水、施肥、钝化剂本身特征和作物种类等因素的影 响^[38]. 土壤 pH 是影响土壤 Cd 形态的重要因素之 一,本试验区由于长期单一施用化肥,未施用有机 肥,导致土壤酸化,土壤 pH 值降低,Cd 在土壤中的 有效性增加. 另外,水旱轮作下土壤有较长的排水 期,耕层土壤中大量亚铁离子被氧化,氧化过程中质 子的释放会进一步导致土壤酸化,pH 值降低^[39],减 弱了钝化剂对 Cd 的钝化效应. 在稻麦轮作体系下, 农田灌溉会带入新的 Cl⁻,土壤中 Cl⁻与 Cd²⁺的配 位可以促进土壤 Cd 的释放,土壤 Cd 的溶解度增 加,随灌水次数的增加,其钝化效应会逐渐减弱[40]. 对于钝化剂自身形态结构特征而言,如海泡石和页 岩等均属于黏土矿物,具有层链结构和纤维状形态, 对 Cd 具有吸附能力,随着海泡石与土壤组分之间 进行充分的物理化学反应,可能存在土壤中与 Cd2+ 相似的金属离子(Ca2+、Zn2+和Cu2+)与土壤稳定 态 Cd 呈现竞争吸附关系,导致土壤稳定态 Cd 再释 放[41,42]. 任心豪等[43] 通过探讨小麦根系环境对生 物炭吸附态 Cd 的影响研究发现,小麦根系分泌的 苹果酸和草酸可通过酸溶作用和络合作用促进生物 炭上 Cd 的解析,增强 Cd 的土壤中的活性.

本研究表明,5种钝化材料中,YH 粉和生物炭 在施用3a后其钝化后效明显高于其余3种钝化材 料. 对于 YH 粉而言, YH 粉施用后土壤 pH 在前两 年均趋于中性,可能是该材料钝化效果较为持久的 主要原因. 就生物炭而言,土壤干湿交替与定期施肥 过程中,阳离子、阴离子和有机复合物首次进入潮 湿的土壤环境后会发生解析,促进土壤形成有机矿 质层[44]. 无论是在碳晶格中还是在微米级矿物相中 的水溶性有机物质和 K、Ca、P、N、S 和 Cl 等物质 会溶解并扩散到周围土壤中,改变土壤 pH 和 Eh,进 而改变生物炭表面结构及化学特性,导致其老化,增 加其表面含氧官能团含量[45],形成新的重金属吸附 位点,保证生物炭表面可以常年保持活性,持续吸附 重金属[29,46]. 此外,随着施用时间的延长,5 种钝化 材料处理下种植作物的籽粒 Cd 含量逐年增高,仅 YH 粉和秸秆生物炭材料在施用后第 3a 仍可显著 降低水稻和小麦籽粒 Cd 含量. 由此可见, YH 粉和 秸秆生物炭材料对作物籽粒 Cd 含量的降低效果可 持续3 a,是 Cd 污染农田土壤原位钝化修复的较为 理想的材料.

4 结论

- (1)稻-麦轮作模式下,一次性施用 5 种钝化材料后对土壤养分含量影响较小,但可有效提高土壤pH,促使土壤酸提取态 Cd 向残渣态 Cd 转化,降低农田土壤有效 Cd 含量及作物籽粒 Cd 含量.
- (2)稻-麦轮作模式下,当季施用 YH 粉、秸秆生物炭和粉煤灰对作物籽粒 Cd 含量的降低效果最明显.随钝化处理时间的延长各材料的钝化效果逐渐减弱,施用海泡石、粉煤灰和页岩第 3a 时钝化效

果迅速衰减,YH 粉和秸秆生物炭处理在施用后第3a仍可有效降低土壤有效 Cd 及作物籽粒 Cd 含量,是 Cd 污染农田土壤原位钝化修复的理想材料.参考文献:

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