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生物质炭钝化农田土壤镉的若干研究进展

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摘　要:利用生物质炭治理农田镉污染是农业和环境界关注的热点。本文综述了近年来生物质炭对污染土壤中镉的生物有效性以及对作物镉吸收的影响等方面的研究进展,阐述了生物质炭钝化土壤中镉的多作用机制,分析探讨了影响镉钝化效应的生物质炭性质、土壤和管理因素,提出了提升钝化材料性能并改善管理以提高生物质炭钝化的高效性和持效性机制,建议未来该领域应加强生物质炭大田长期定位试验研究,以进一步为生物质炭污染治理提供科学依据。

关键词:生物质炭; 镉; 多作用机制; 土壤;管理因素

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Several research progresses in Cd inactivation by biochar application in agricultural soil

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Abstract: The application of biochar for Cd pollution remediation in agriculture soil is a hot topic of concern. This paper reviewed the study progress in several aspects, including the impacts of biochar on Cd bioavailability in polluted soil and Cd uptake in plants. Meanwhile, we expounded the multi-mechanism for inactivation of cadmium by biochar and discussed the influencing factors from the aspects of properties of biochar, soil and management factors. The analysis results suggested that the mechanisms for high-efficiency and sustainable inactivation performance of biochar could be realized by improving materials properties and management. Finally, we proposed that long-term location field experiments should be enhanced in this area to provide further scientific evidence for pollution remediation with biochar.

Keywords: biochar; cadmium; multi-mechanism; soil; management factors

随着工业化和城市化的迅猛发展,环境中的重金属污染情况日益严重[1]。采矿、冶炼以及农业生产中磷肥、污泥的施用等活动均加剧了土壤重金属的污染[2-3]。镉在土壤中具有较强的蓄积性、迁移能力和生物可积累性,是最有毒性的无机污染物之一[4-5]。镉主要通过食物摄入的方式进入人体,在人体中的半衰期长达20~40年,对骨骼及肾脏造成严重危害。联合国环境规划署将镉列在优先污染物名单中的首位[6]。据2014年原环保部的数据显示,我国土壤镉污染的点位超标率达7%,远高于汞(1.6%)、砷(2.7%)、铅(1.5%)等其他重金属元素[7]。近年来,由于土壤镉污染造成的粮食作物的镉超标现象引起了极大的关注。Liu 等[8]的研究结果表明,我国稻田的镉污染浓度范围为0.01~5.5 mg·kg^{-1}。其中,南方重金属污染稻田镉污染相对严重,70%的稻米存在镉污染,对我国部分市售大米的抽样检测结果显示,镉超标率达10%[9-10]。针对日益严重的土壤镉污染问题,采取有效的治理措施以保障粮食安全生产一直是相关领域

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的研究热点。

生物质炭是限氧条件下热裂解生物质获得的一种固体材料，含有稳定态有机碳以及可溶性有机及矿质灰分等多组分混合物，生物质炭可明显提高土壤质量和生产力。研究显示，施用生物质炭可改善土壤结构、土壤持水量、提高土壤有机质含量、促进土壤养分循环并提高作物产量[11-17]。同时，生物质炭由于具有高pH、高比表面积、丰富的孔隙及表面官能团等特性，作为重金属污染土壤的修复材料受到环境修复界的广泛关注[18-21]。本文试图总结近十多年来生物质炭对土壤镉钝化并抑制植物吸收的研究进展，期望为农业土壤镉污染治理及污染土壤修复和未来研究问题提供科学参考。

1　生物质炭抑制土壤-作物系统镉迁移转化：多作用机制

大量研究证实，生物质炭对镉在土壤-作物系统中的运移具有较好的钝化效果[20-25]。据广西、湖南、江西等多点野外试验结果表明，施用20~40 t·hm^{-2}的小麦秸秆炭，土壤有效态镉含量降低20%~70%，水稻籽粒镉积累量降低20%~60%[22-24]。Chen等[25]通过整合分析显示，生物质炭处理对土壤有效态镉的平均降幅为52%。Liu等[26]发现施用20 t·hm^{-2}的水稻秸秆和豆秸炭，稻田田面水中的可溶性镉含量分别降低56%~80%和61%~83%。另一研究表明，生物质炭在1%、2%以及4%的施用量下，土壤可交换态镉降低了28.5%~59.4%，对水稻镉积累量的降幅为2.7%~23.8%[25]。类似地，在1.5%、3%以及5%的施用范围内，生物质炭对小麦籽粒镉的降低幅度可分别达到26%、42%以及57%[28]。由此可见，生物质炭在降低土壤镉的生物有效性和抑制作物镉积累方面具有明显的效果。

根据Ahmad等[29]的研究发现（图1），并结合目前相关研究结果，生物质炭对土壤中重金属离子可能的作用机制大致可表现为以下几个方面：(1)生物质炭较大的表面积使得镉可以通过与生物质炭中的K^+与Na^+等有效态阳离子的交换作用而结合于生物质炭的表面；(2)镉与生物质炭表面官能团相互作用产生的表面络合；(3)生物质炭中较高含量的灰分元素可通过增加土壤pH以及碳酸盐、磷酸盐等无机盐含量而与镉产生沉淀或络合作用[29-33]。

首先，生物质炭由于含有较多的可交换态阳离子以及较大的表面积，可通过离子交换作用将镉固持于表面[21,24]。研究表明，生物质炭表面的H^+、Ca^{2+}以及

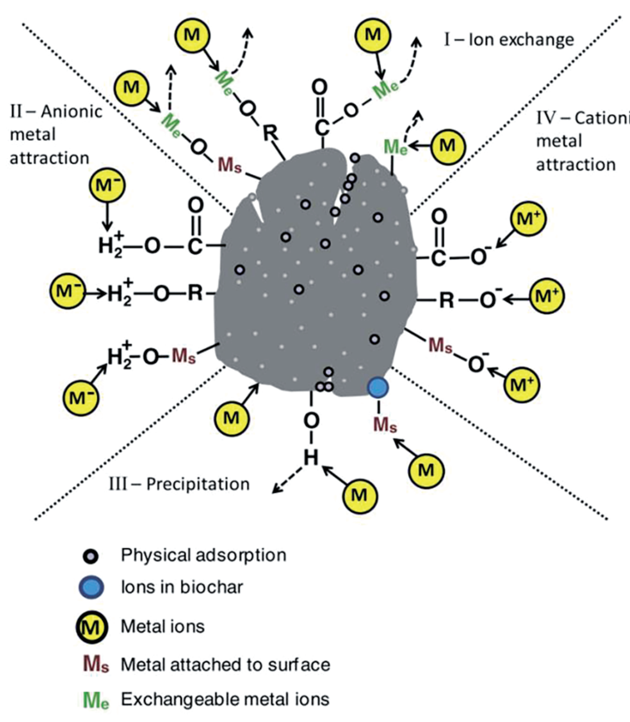

图1　生物质炭对土壤中重金属离子可能的作用机制[29]

Figure 1　Possible mechanisms for the effect of biochar on heavy metals[29]

K^+等可交换态阳离子对镉生物有效性的降低具有重要作用[34–36]。Zhang等[37]研究发现，藻类生物质炭释放出的K^+、Ca^{2+}、Na^+、Mg^{2+}等阳离子的总量几乎与所固持的镉的总当量相等。Harvey等[38]比较松木和灌木生物质炭发现，具有较高CEC的木材生物质炭对镉的吸附机制主要以离子交换作用为主。此外，Xu等[39]发现镉、锌、铅、铜会竞争稻壳炭中质子化的酚羟基官能团结合位点。Mohamed等[40]研究表明，施用1.5%的竹炭后，土壤中DTPA浸提态镉含量从33.32 mg·kg^{-1}降低至12.09 mg·kg^{-1}，这可能是生物质炭表面官能团与土壤中的镉发生了络合作用从而降低了镉的生物有效性[29]。

其次，生物质炭灰分中可溶性盐、可溶性有机成分的溶解以及炭表面官能团的解离均能够增加土壤pH[41–45]，这也是生物质炭降低土壤镉生物有效性的重要机制之一[38]。Rees等[46]研究显示，生物质炭能够同时增加酸性和碱性土壤的pH。同时，生物质炭中的矿质组分可通过与镉产生的共沉淀及内部络合作用降低镉的生物有效性[19–20]。Trakal等[47]通过FTIR图谱发现葡萄秸秆炭以及稻壳炭对镉的吸附会引起CO_3^{2-}峰的改变，这表明镉可能与CO_3^{2-}在生物质炭表面形成了共沉淀。Zhang等[37]利用X射线衍射仪发现，藻类生物质炭对镉的吸附伴随着碳酸镉及磷酸镉矿物的形成。Xu等[39]的研究表明低温畜禽粪便炭（350 ℃）中磷酸根及碳酸根对镉的吸附贡献分别为<10%及>90%，而通过酚羟基的结合产生的表面吸附所占比例<25%。此外，生物质炭对土壤pH的增加还可增加土壤胶体表面的负电荷，从而进一步降低重金属的运移风险[48]。多年定位试验发现，生物质炭对土壤pH的增幅会逐年降低，但对镉的钝化效应却具有一定的持效性。这可能是由于土壤的生物及非生物氧化作用增加了老化生物质炭表面的含氧官能团，进而促进了生物质炭对镉的吸附作用[41–43]。Bian等[49]的田间试验证实，田间老化三年的生物质炭颗粒表面的含氧官能团有所增加。

生物质炭抑制作物镉吸收的效应与土壤中镉的钝化有直接关系[38, 45–47]。研究显示，生物质炭处理下水稻籽粒镉的降低量与土壤中$CaCl_2$浸提态镉的降低量存在显著正相关关系[50–51]。Xu等[52]的研究结果显示，5%（*W*/*W*）的花生壳炭能够显著降低土壤中$MgCl_2$浸提态镉的含量，对水稻籽粒镉含量的降低幅度达22.9%。此外，生物质炭还可通过元素的相互作用来抑制作物对镉的吸收。整合分析结果显示，生物质炭对镉在土壤–作物体系中运移的抑制效果均高于锌[11, 25]。通常情况下，施用锌肥可抑制作物对镉的吸收[53–55]。施用含锌量高的生物质炭（如畜禽粪便炭）可提高作物对锌的吸收从而降低镉的积累[11, 56]。此外，水稻秸秆类生物质炭还可增加土壤中有效态的硅含量，而硅可通过在水稻和小麦的根部内皮层形成沉淀来阻隔镉从根部向地上部的运移[57–58]。因此，施用含硅量较高的生物质炭可进一步抑制作物对镉的吸收和积累。

2 生物质炭的土壤镉钝化效应：多因素影响

2.1 原料和热裂解温度

生物质炭的性质是由原料和制备工艺共同决定的。不同原料及工艺制备的生物质炭对重金属的钝化效应存在一定的差异[41, 59]。与秸秆、木材等原料相比，畜禽粪便类生物质炭对镉的钝化效果相对较好，这是由于畜禽粪便炭的灰分含量及阳离子交换量较高，可与土壤中的镉形成共沉淀或者通过离子交换作用抑制镉的运移[29, 41, 60–62]。Xu等[39]研究显示牛粪炭对镉、锌、铅、铜的作用主要以碳酸根以及磷酸根的沉淀作用为主。

热裂解温度也是影响生物质炭对镉钝化效果的重要因素。在一定范围内，生物质炭的灰分含量随着热裂解温度的增加而增加，pH也随之增加[29]。Xu等[39]的研究显示当热裂解温度从200 ℃升高至350 ℃时，生物质炭的pH由7.63上升到9.98，对镉的吸附量从31.9 mg·g^{-1}提高到51.4 mg·g^{-1}，其中可溶性CO_3^{2-}组分具有重要贡献。此外，生物质炭的挥发分、含氧组分以及电荷零点等均能影响其表面官能团的形成[29]，较高热裂解温度（>600℃）制备的生物质炭会出现CEC下降、挥发性组分损失、比表面积增加以及表面含氧官能团数量和电荷密度下降等现象，生物质炭表面官能团数量也随之下降[63]。因此，从生物质炭的结构特性来看，在200~450 ℃的热裂解温度范围内制备的生物质炭具有相对丰富的含氧官能团、较高的静电引力以及较高的可溶性无机盐含量，从而对土壤中的镉具有较好的钝化效果[11, 29]。

2.2 土壤pH和有机质

土壤的pH和有机质等性质可通过影响土壤的酸碱性、吸附性以及氧化还原状态而对生物质炭的钝化效果产生一定的影响[64–71]。通常，实际应用的生物质炭大多呈碱性[72]，这是由于生物质炭对土壤pH的增加可以抑制重金属在土壤中的运移[50, 73–74]。当石灰

效应较弱时，生物质炭对镉可能无显著的钝化效果。Qi等[75]的研究发现，酸性刨木炭（pH=3.25）对偏酸性（pH=6.14）及偏中性（pH=7.87）土壤中的镉均无明显钝化作用。另一盆栽试验结果显示，5%（*W/W*）生物质炭（pH=9.46）的施用增加了碱性土壤（pH=8.0）中超积累作物天蓝遏蓝菜（*Noccaea caerulescens*）对镉的积累量[76]。在长期定位试验中，碱性生物质炭在酸性土壤中对镉的钝化效果比在碱性土壤明显。Bian等[77]在太湖地区进行的大田(pH=5.36)试验结果表明，小麦秸秆炭（pH=10.4）能够连续三年显著增加土壤的pH，同时显著降低土壤可提取态镉含量及水稻籽粒镉积累量。而Sui等[78]在我国北方碱性土壤（pH=8.07）连续三年的定位试验结果表明，生物质炭（pH=10.4）的施用并未显著提高土壤的pH，且仅在第一年表现出对小麦镉吸收的抑制效果。由此可见，石灰效应是生物质炭降低酸性土壤镉的生物有效性、抑制作物镉吸收的重要机制[44, 59-79]。

土壤的有机质含量对生物质炭的镉钝化效应也有一定的影响。通常，土壤中较高的有机质含量会促进重金属的钝化[79-82]。研究表明，生物质炭对可溶性有机质的吸附能够增加其表面官能团数量，从而增加生物质炭的吸附能力[83]。Chen等[25]的研究结果表明，当土壤有机质的含量较高时（>15 $g\cdot kg^{-1}$），生物质炭对作物镉积累量的降低幅度较高。这可能是由于较高的土壤有机质含量可以在增加生物质炭表面官能团数量的同时提供更多的镉结合位点。此外，相关研究还表明，土壤中的无机、有机组分以及微生物可以与生物质炭相互作用，在生物质炭表面形成有机-矿质-生物覆膜，增加生物质炭表面官能团数量[86-87]，这也可能会进一步促进生物质炭对镉的钝化。

2.3 管理方式

除生物质炭制备条件及自身性质外，生物质炭的施用量以及施用深度也会影响生物质炭对土壤中镉的钝化效果。在10~40 $t\cdot hm^{-2}$施用量范围内，生物质炭对土壤中镉的钝化效应随着施用量的增加而提高[49-51,77-78]。据统计，实际应用过程中生物质炭一般通过表层撒施、机械点施等方式将生物质炭翻耕于15 cm土层内，但也有至25 cm甚至更深的土层[79]。研究显示,增加施用深度可显著提高作物产量，但作物对镉的积累量也有提高[52, 79]。这可能是由于深耕使生物质炭改善了作物根系区域的pH环境以及养分条件，促进了作物的生长，但由深耕带来的重金属下移也会增加作物根部对重金属的吸收[79, 86]。

3 结语

目前为止，生物质炭对土壤镉钝化机制的认识还未深入到纳米或分子的水平，特别是关于生物质炭施用下土壤中矿物与有机质的相互作用的影响研究不多，这也是不同土壤治理效果产生较大差异的原因。另外，大量研究都提示，并不是所有生物质炭对镉都有显著的钝化效果，因此从生物质炭材料学角度加强性质与钝化功效研究，筛选最优材料或最优工艺在环境修复产业上显得尤为重要。最后，生物质炭镉污染治理技术还需要更多的大田定位长期试验研究，从而为生物质炭污染治理的生态系统服务功能和人类福祉的改善提供依据。

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