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生物炭对酸性土壤改良效果及机制的研究进展

胡仁, 龙巧玲, 王力敏, 胡红青, 谭文峰, 伍玉鹏, 林杉

华中农业大学资源与环境学院, 武汉 430070

摘要 我国土壤酸化问题普遍, 对农业生产和环境安全造成严重影响。作为一种酸性土壤改良材料, 近年来生物炭受到了广泛关注, 但生物炭对酸性土壤改良的效果及机制研究较少。本文从降低酸度、改良土壤理化性质及生物学特征、促进作物生长3个方面, 综述了生物炭对酸性土壤改良效果的研究现状, 明确了生物炭降低土壤酸度的机制包括生物炭的碱性物质与 H^+ 结合、含氧官能团与土壤交换性 Al^{3+} 发生酯化、吸附及络合等。施用生物炭能够改变土壤环境、促进土壤微生物活动, 进而调控微生物生长; 施用生物炭可以改善作物根系生长环境、提高根际微生物群落丰度, 从而调控根系发育。最后对生物炭改良酸性土壤的研究进行了展望, 旨在为缓解土壤酸化、促进酸性土壤可持续生产提供理论依据。

关键词 生物炭; 酸性土壤改良; 土壤微生物; 铝毒

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土壤酸化是 H^+ 和交换性 Al^{3+} 在土壤中过量积累导致土壤pH下降的过程^[1], 由自然因素和人为因素驱动。自然因素包括母质风化、生物作用(植物根系吸收阳离子时释放 H^+ 、有机质分解产生有机酸等)和降水淋溶(吸附在土壤胶体表面的盐基离子被置换后随雨水淋失); 人为因素包括过量施用氮肥(铵的硝化作用产生 H^+)、酸沉降(燃煤、燃油释放 SO_2 和 NO_x 等, 在大气中转化为 H_2SO_4 和 HNO_3 , 通过降水进入土壤)等^[2]。过去30年间, 我国农业土壤pH约下降0.5个单位, 如不进行人为改良调控, 预计到2050年我国土壤将面临严重的酸化风险^[3]。

目前我国土壤pH值小于6.5的酸化耕地总面积约0.61亿 hm^2 ^[4]。土壤酸化对耕地土壤肥力、生态环境及作物生产等均造成不同程度的危害。在土壤肥力方面, H^+ 的交换能力较强, 使吸附态盐基离子从土壤中释放出来, 表层土壤养分流失严重^[5]; 生态环境方面, 吸附在土壤中的重金属会发生解吸、离解、溶解和氧化还原等物理化学过程, 从而导致生物活性增强^[6], 且土壤中交换态重金属含量与土壤pH呈显著负相关^[7]; 作物生产方面, 酸化土壤中的 Al^{3+} 转变为溶解态, 过多的 Al^{3+} 会对作物细胞结构、根系和光合作用等造成不同程度的损伤, 抑制作物的生长发育^[8]。

Zhu等^[3]通过评估我国1980—2050年小麦、玉米

和水稻产量与土壤pH的关系发现, 如果氮肥投入继续以每年1%的速度增长, 预测土壤pH值可下降约1个单位, 进而导致相对产量损失增加约4%~24%。

为缓解土壤酸化, 我国土壤学者经过30多年的探索, 已研发多种改良酸性土壤的材料, 包括石灰、工业副产品、有机废弃物和作物残渣等。施石灰是改良酸性土壤最常用的方法, Meta分析表明, 施用石灰能显著增加土壤pH, 提高作物产量^[9]。然而, 石灰施入土壤表层后, 在土壤中移动较慢, 土壤中 Ca^{2+} 的浓度过高, 导致黏土颗粒间的结合力增加, 造成土壤板结, 影响土壤质量^[10]。工业副产品的施用会提高土壤pH, 增加阳离子交换量和盐基饱和度, 但某些工业副产品中重金属含量高, 造成土壤污染^[11]。有机废弃物可增加土壤有机质含量, 改变微生物代谢和群落结构, 进而改良酸化土壤^[12], 但部分有机废弃物中也有较高含量重金属, 在施用前需要进行预处理^[13]。作物残渣可以通过分解为植物提供养分, 并直接提高土壤pH值, 但是与土壤原始pH有关, Liang等^[14]研究认为, 旱地和水田的土壤pH值分别低于6.7和5.4时, 秸秆还田将加剧土壤酸化。

生物炭作为酸化土壤改良剂的一种, 由多种原料(作物残体、木材、工业残余物、动物粪便等)在中-低温和限氧条件下热解而成^[15]。尽管生物炭对酸性

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胡仁, E-mail: 1786100126@qq.com

通信作者: 胡红青, E-mail: hqhu@mail.hzau.edu.cn

为进一步提高生物炭对酸性土壤的改良效果,笔者所在课题组将水稻秸秆与碳酸钙混合后烧制生物炭,通过扫描电镜(SEM)和X射线衍射仪(XRD)扫描发现,碳酸钙成功负载在生物炭表面,负载碳酸钙后的生物炭表面含氧官能团的数量增加、自身碱度显著提高。施入酸性土壤后,与普通生物炭相比,负载碳酸钙后的生物炭显著提高了土壤的pH、CEC和有机质含量,同时促进了土壤中交换性 Al^{3+} 向有机络合态Al转化,有效缓解 Al^{3+} 对大豆根系生长的抑制,增加了大豆根瘤数量,显著提高了大豆地上部生物量(数据待发表)。

1.2 改良土壤理化性质及生物学特征

在土壤酸化过程中,大团聚体会向小团聚体转化,抑制土壤微生物活性^[27],而施用生物炭可以显著改善酸化土壤的理化性质。施恩平等^[28]研究发现,施用柚枝生物炭和菌棒生物炭,可使酸性土壤孔隙度增加11.23%,容重降低5.47%。段春燕等^[29]发现,施用不同用量生物炭均可提高土壤毛管孔隙度和总孔隙度,且施用量越高,提升幅度越大。Burrell等^[30]通过3 a定位试验发现,施用不同种类生物炭均能增加酸性土壤中团聚体稳定性。

土壤酸化造成养分流失,因而酸性土壤中养分含量普遍较低^[5],而施用生物炭能有效提高土壤养分含量。段顺霞等^[31]通过Meta分析发现,施用生物炭提高酸性土壤有机质39.35%、硝态氮含量91.23%和速效磷含量89.70%;王响玲等^[32]研究发现,生物炭用量越高,提升酸化土壤中的有机质和养分含量效果越好,与不施生物炭相比,施用2%生物炭后,酸性土壤的有机质和速效钾含量分别显著提高71.25%、59.65%;Wan等^[33]发现,酸性土壤中的养分为生物炭的响应与生物炭的热解温度有关,生物炭的热解温度越高,土壤中交换性盐基离子(Ca^{2+} 、 Mg^{2+} 、 K^{+} 、 Na^{+})含量越高。

土壤pH缓冲能力(pHBC)和阳离子交换量(CEC)是决定土壤酸化速率的关键因素^[34]。生物炭表面含有丰富的弱酸性含氧官能团,这些阴离子与 H^{+} 发生缔合反应,将原吸附的交换性盐基离子释放到溶液中,这一过程是生物炭提高土壤pHBC的主要机制^[35]。研究表明,生物炭表面盐基离子的释放量与 H^{+} 消耗量显著相关,生物炭的施入不仅延缓土壤酸化,而且增加土壤pHBC,从而抑制了土壤的再酸化^[34-37]。而Shi等^[35]认为生物炭的可溶性组分和固体组分均含有弱酸性基团,其中可溶性组分因酚类

对土壤细菌存在毒性,降低了土壤硝化和净矿化作用,抑制土壤酸化,而固体组分表面的羧基是土壤pHBC增加的主要原因。Wang等^[38]认为,在土壤pH值为5.5~6.2时,生物炭中盐基离子与可交换的 $\text{H}^{+}/\text{Al}^{3+}$ 之间的离子交换反应是生物炭增加土壤pHBC的主要原因。对CEC而言,生物炭中的金属氢氧化物或碳酸盐与外源性 H^{+} 发生酸碱中和反应,导致盐基离子释放^[39]。同时随着土壤pH值升高,导致土壤有机质(如腐殖酸)和黏土矿物(如高岭石)表面的一OH基团去质子化($-\text{O}-$)^[40-41],释放更多负电荷位点,增强对阳离子的吸附能力,提高土壤CEC,从而改良酸化土壤^[42]。

研究发现,土壤pH值对细菌组成和多样性的影响超过了空间和气候因子,酸化显著改变了土壤的微生物多样性和群落结构^[43]。在酸性土壤中施入生物炭显著提高微生物代谢,增加土壤微生物丰度和多样性^[44]。王义祥等^[45]发现,在酸化茶园中施入生物炭,增加了细菌群落中节杆菌属(*Arthrobacter*)、硝化螺旋菌属(*Nitrospira*)、黄色杆菌科Flavobacteriaceae的相对丰度,降低了嗜酸性细菌如酸杆菌属(*Acidobacterium*)细菌的相对丰度;对于真菌群落,孢霉属(*Mortierella*)、木霉属(*Trichoderma*)、毛壳菌属(*Chaetomium*)的相对丰度增加,黑盘孢属(*Lepidoglyphium*)的相对丰度降低^[46]。Cruz等^[47]发现,在酸性土壤上施用污泥生物炭增加了细菌类梭菌科(Clostridiaceae)和拟杆菌(Bacteroidia),真菌类科毛壳菌科(Chaetomiaceae)和曲霉科(Aspergillaceae)的相对丰度;Geng等^[48]利用树枝生物炭和牛粪生物炭进行酸化改良土壤试验,发现主要增加了酸杆菌(Acidobacteria)和新美菌门(Olpidomycota)的相对丰度,且相比于300℃热解的生物炭,450℃和600℃热解的生物炭改良效果更好。

1.3 提高作物生产力

生物炭在降低土壤酸度的同时,也对作物生长产生积极影响^[49]。El-Desouki等^[50]研究发现,施用花生壳生物炭显著提高了酸性土壤上油菜叶片电子传递速率和光合速率,且叶片中丙二醛含量下降;耿娜等^[51]研究发现,在酸化棕壤上施用以果树枝、花生壳、牛粪为原料的生物炭,油菜的株高、叶面积和产量分别提高了18.09%~44.61%、7.87%~77.13%和37.50%~159.68%;马一博等^[52]发现在酸化土壤上施用玉米秸秆和水稻秸秆生物炭,大豆产量分别提高了7.27%和3.97%。

由表1可知,生物炭用量越高,土壤pH提升幅度越大,交换性 Al^{3+} 含量降低越显著,然而,当生物炭用量增高时,施用成本也增加。生物炭价格随原料类型波动,如秸秆生物炭约1 500~2 000元/t,木材生物炭约为3 500元/t。另外,长期施用生物炭时,由于土壤理化性质改变,导致作物增产效益下降^[53],因此,生物炭的施用量需要根据具体的应用目标(如作物增产、土壤改良、温室气体减排等)、土壤类型、气候条件以及生物炭的性质等因素综合考虑。

2 生物炭改良酸性土壤的机制

2.1 降低酸度的机制

生物炭提高土壤pH主要归因于自身含有较多的碱性物质,如碳酸盐、有机官能团、可溶性有机物和无机碱,前2类是生物炭碱度的主要贡献者^[54]。生物炭表面的有机官能团(如 $\text{R}-\text{COO}-$ 和 $\text{R}-\text{O}-$)是弱酸的共轭碱,可与 H^+ 络合^[55]。He等^[56]用 H_2O_2 和 $\text{HNO}_3/\text{H}_2\text{SO}_4$ 改性稻草生物炭,发现改性生物炭表面的羧基官能团明显增加,显著提高了酸性土壤的缓冲容量,有效增强了酸性土壤的抗酸化能力。可溶性有机碱是可溶性有机酸的共轭碱,如乙酸或甲酸(有机阴离子),其他无机碱包括磷酸盐(PO_4^{3-})、硅酸盐(SiO_4^{4-})和氢氧化铁(图1),这些阴离子可以与 H^+ 结合而消耗质子、降低酸度^[54]。

不同原料的生物炭,自身的碱度以及提升土壤pH的效果不同,Yuan等^[23]研究发现,与谷物秸秆生物炭相比,豆科植物秸秆生物炭施入时,土壤pH高出0.27个单位,可能因为豆科植物吸收了更多的 Ca^{2+} 、 Mg^{2+} 和 K^+ ,其衍生的生物炭中也含有更多的以氯化物、碳酸盐和磷酸盐形式存在的盐基离子^[57]。另外,Hass等^[25]发现,与作物秸秆相比,由畜禽粪便制成的生物炭对土壤pH值的提高效果更明显,且生物炭对土壤pH值的改善效果随其用量的增加而增加。

铝毒是酸性土壤限制植物生长的主要因子^[58],生物炭缓解铝毒主要体现在以下方面:

1)生物炭通过提高土壤pH,促使具有生物毒性的交换性 Al^{3+} 转化成低毒和无毒的羟基Al或 $\text{Al}(\text{OH})_3$,从而缓解Al毒害^[59]。Xia等^[60]发现,在酸性土壤中施入3%的花生壳生物炭后,土壤交换性 Al^{3+} 的含量从748.66 mg/kg降低到60.04 mg/kg,降幅高于90%。

2)生物炭中丰富的交换性盐基离子与土壤固相 Al^{3+} 竞争吸附位点,促使交换性 Al^{3+} 从土壤固相向土壤溶液释放,有利于土壤 Al^{3+} 与碱性生物炭的反应。豆科植物生物炭由于盐基离子的含量较高,掺入酸性土壤后,土壤可交换性 Al^{3+} 的降低程度大于非豆科植物。

3)生物炭表面的含氧官能团(如 $-\text{COOH}$ 、 $-\text{OH}$)与 Al^{3+} 发生表面吸附及络合反应等,使 Al^{3+} 形成沉淀,减少其游离态含量^[58]。值得注意的是,这些官能团受生物炭热解温度的影响,温度越高,官能团的数量会显著减少^[61]。

2.2 改善酸性土壤理化性质及生物学特征的机制

酸性土壤常质地黏重、结构不良,影响土壤通气和透水性。生物炭的结构疏松多孔,施用后可降低土壤容重,提高土壤孔隙度,从而增强土壤对小分子物质的吸附。同时,生物炭通过存储氧气和水分,提高土壤通气性和持水性,与外部环境形成良好的物质交换与流通体系。生物炭的施用量增加显著促进土壤田间持水量和毛管孔隙度的提高^[62]。就团聚体而言,生物炭的施用刺激了土壤微生物生长,从而产生更多胞外聚合物作为胶结剂,将较小的土壤颗粒粘结在一起,进一步促进土壤团聚体的形成^[63]。另外,生物炭内部孔隙较多,形状不规则,可有效增加粗骨土的储水量^[64]。

生物炭中含有丰富的营养元素(N、P、K、Ca、Mg和S等),施入酸性土壤后,直接提高了土壤养分含量,但是其提高土壤养分含量的机制有所不同。Yuan等^[65]研究认为,生物炭作为“电子穿梭体”,显著提高了硝酸盐异化还原成铵功能微生物丰度和该功能基因的表达水平,进而增加酸性水稻土 NH_4^+-N 的产生速率,生物炭施用不仅缓解了水稻土的酸化,还增强了氮素利用率。

含 phoD 基因微生物是一类解磷微生物,可通过分泌磷酸酶提高土壤磷素有效性。杨文娜等^[66]发现,pH是影响含 phoD 基因微生物的关键环境因子,在酸性土壤上施入生物炭,可通过改变含 phoD 基因微生物群落组成来提高土壤磷素生物有效性,进而促进作物对磷素的吸收^[67]。对钾素而言,施用生物炭可促进溶钾细菌的生长,进而促进矿物钾的释放^[68],因此,在酸化土壤上施用生物炭可显著增加交换性钾和速效钾含量^[69]。

生物炭对酸性土壤微生物的影响较复杂,其机制是一种“环境改良-资源供给-功能激活-定向调控”

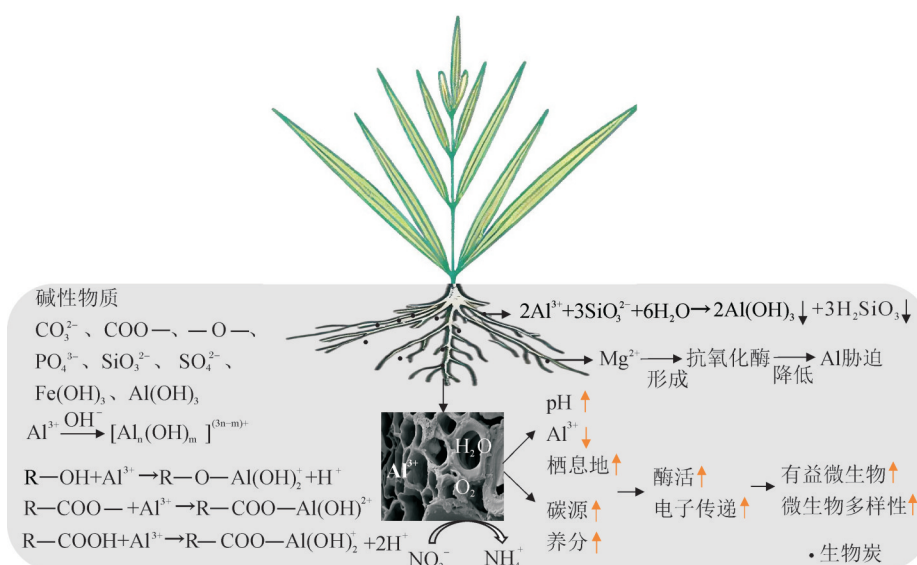


图1 生物炭改良酸性土壤理化性质及生物学特征的机制

Fig.1 Mechanism of biochar for improving properties and biological characteristics of acidic soils

多级联合效应(图1)。施用生物炭能够改善酸性土壤中微生物的生存环境,如提高土壤pH、缓解铝毒和锰毒,同时,生物炭的孔隙结构可为土壤微生物提供栖息地^[70]。生物炭施入土壤后,除了所含的营养物质可以提高土壤养分含量,其表面的多孔结构也可增加对 NH_4^+ 、 NO_3^- 、 PO_4^{3-} 等养分的吸附,减少土壤养分流失^[71]。同时,生物炭含稳定有机碳和少量易分解碳,为异养微生物提供能量来源,Li等^[72]发现,生物炭为酸性土壤中异养微生物提供了额外的能源,从而促进了微生物的代谢活动和土壤碳循环。

在酸性土壤中施入生物炭,可促进土壤微生物代谢。一方面,可提高土壤蔗糖酶、脲酶、磷酸酶、脱氢酶等酶活性^[73],改变多种胞外酶和胞内酶的活性,从而增加土壤微生物生物量^[74]。另一方面,生物炭含有丰富且具氧化还原活性的官能团,介导土壤微生物电子传递,促进微生物生长代谢^[75-76]。

大部分微生物更适应于中性环境下生长^[77],因此在酸性土壤上施用生物炭,可进一步提高有益微生物丰度,促进酸性土壤中放线菌门细菌增殖^[78],加快功能微生物如固氮菌、解磷菌等生长^[79-80],同时抑制酸性土传病原微生物的生长,降低病害发生率^[80]。生物炭的孔隙结构能够为微生物的生长提供更好的保护,减少微生物之间的直接竞争,从而提高微生物群落的多样性^[81]。

2.3 提高作物生产力的机制

在酸性土壤中由于 Al^{3+} 胁迫的影响,常常使作物根系生长受限,而根系发育不良将进一步影响其

对土壤养分和水分的吸收^[82]。施用生物炭通过提高酸性土壤的pH值和孔隙度,为根系生长提供更加良好的土壤环境,从而促进根长的增加^[83]。

一方面,生物炭的施入缓解了 Al^{3+} 胁迫对根系的影响(图1)。生物炭中含有大量 Mg^{2+} ,在酸性土壤中能够持续释放进入土壤中^[84],可有效减轻受 Al^{3+} 诱导的玉米植株根系伸长抑制、Al积累和氧化应激反应^[85]。Shetty等^[86]发现,硅(Si)在水稻根尖可形成Al-Si化合物来降低 Al^{3+} 对水稻根系的毒害,富Si生物炭的施入可以显著促进水稻根系伸长,使根系获取更多的养分。

另一方面,生物炭添加能够提高根际土壤微生物群落的丰度,调控根际土壤微生物群落结构^[87]。根际微生物(如丛枝菌根真菌、根瘤菌等植物根际促生菌和微生物群落)通过产生激素、释放挥发性有机物、固氮、溶磷和改善根际土壤结构等机制,影响根系生物量、根系分支、侧根和根毛的生长,调控根系生长发育^[88]。

3 改性生物炭在酸性土壤改良中的应用

生物炭表面官能团和碱性阳离子浓度都可以通过化学试剂来改性^[89]。为进一步提高生物炭对酸性土壤的改良效果,科研工作者对生物炭进行了众多改性研究。生物炭的改性方法有物理方法和化学方法。物理改性主要包括球磨、蒸汽、紫外线照射等,Zhang等^[90]发现,通过紫外照射后的油菜和黑麦草生

物炭的比表面积和羧基官能团增加,土壤pH和电导率显著提高。

化学法主要包括碱改性、有机改性、金属改性等,Liu等^[91]通过盐酸结合超声波改性椰子壳生物炭,发现改性生物炭具有更多的活性官能团(—OH、—COOH、—C—O),表面带负电荷,在提高土壤pH的同时,能够增加土壤对阳离子的吸附力;He等^[92]发现,壳聚糖和海藻酸钠的引入有效扩增了生物炭的官能团量,并提高了土壤的抗酸化能力;Liu等^[93]通过氯化镁改性玉米秸秆生物炭发现,与未改性生物炭相比,氯化镁改性生物炭不仅提高了土壤pH,其速效钾、速效磷、有机质等养分含量也显著增加。

硅酸根是铝的重要吸附位点,这为缓解酸性土壤中Al毒提供了新的思路。笔者所在课题组采用硅酸钾对生物炭进行改性,通过SEM观察发现,硅酸钾颗粒附着在生物炭的表面和孔隙中,FTIR和XRD观察发现,硅酸钾改性后的生物炭表面含氧官能团数量增加,且在生物炭表面形成稳定的晶形结构。施入土壤后,与未改性生物炭相比,显著降低了土壤交换性酸和 Al^{3+} 的含量,显著提高pH值、pH缓冲容量和CEC,同时显著提高了小麦株高、百粒重和产量。与此相似,张传峰等^[94]以硅灰石、油菜秸秆与硅酸钠同时煅烧,形成硅灰石-硅酸钠-生物炭复合材料,施入后发现,酸性土壤的pH值增加1.4个单位,酸缓冲容量增加了1.15 cmol/kg,表明针对酸性土壤的特征对生物炭进行改性,可使酸性土壤改良的效果更明显。

4 展 望

施用生物炭在改善酸性土壤和提高作物产量方面具有明显潜力,是实现可持续农业和减缓气候变化的有效途径。然而,关于生物炭对酸性土壤的改良在实际应用过程中仍有一些亟待深入研究的问题。

1)生物炭的老化及中长期效果。生物炭施入土壤后,其自身碱性物质会通过淋溶和 H^+ 输出而逐渐消耗,其表面因吸附 Al^{3+} 而导致土壤矿物附着在生物炭表面,而其含氧官能团中酸性官能团比例会持续增加,土壤pH再次下降,如何延缓生物炭老化、防止土壤pH再次下降值得进一步探讨。

2)影响生物炭降酸效果的环境因素及田间应用。生物炭的施用受多种因素的影响(包括原料、热解条件、土壤性质、栽培作物养分吸收和根系代谢

等),为了推进生物炭在酸性土壤改良中的开发应用,必须针对具体情况,考虑多种因素,且其改良效果和机制仍需长期的田间试验验证。

3)降酸生物炭的改性方法及环境影响。改性生物炭对酸化土壤的改良效果显著,但是其制作工艺更复杂,并引入了新的化合物,可能抑制部分土壤微生物活性,造成土壤阴阳离子滞留或者二次释放。因此,在制备生物炭时应权衡制作成本与改良效果,同时改良制作工艺,避免造成新的环境问题。

总之,生物炭能够改良酸性土壤,提高土壤肥力,促进作物生产,这是一个长期的过程。为充分发挥生物炭的改良效能,需要建立综合的调控技术,如调整施用方法、种植耐酸作物和加强土壤监测评估,及时了解土壤理化性质变化,达到长期、高效阻控土壤酸化的目的。

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Progress on effects and mechanism of biochar on amelioration of acidified soils

HU Ren, LONG Qiaoling, WANG Limin, HU Hongqing, TAN Wenfeng, WU Yupeng, LIN Shan
College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China

Abstract The problem of acidification in soil is widespread in China, causing serious impacts on the agricultural production and environmental safety. Biochar, as an excellent material for ameliorating acidic soils, has received extensive attention in recent years. However, there is relatively few studies on the effects and mechanism of biochar on ameliorating acidic soils. This article reviewed the research status of biochar in ameliorating acidic soil from three aspects including reducing acidity, improving the physical and chemical properties and biological characteristics of soil, and promoting the growth of crops. The mechanism of biochar reducing the acidity in soil including the binding of alkaline substances in biochar with H^+ , the esterification, adsorption and complexation of oxygen-containing function groups with exchangeable Al^{3+} in soil was clarified. The activities of microorganisms in soil were promoted by changing the environment in soil to regulate the growth of microorganisms in soil. The environment for the growth of crop roots was improved to increase the abundance of microbial communities of rhizosphere and regulate the development of root. The studies on the effects and mechanism of biochar on the amelioration of acidified soils were prospected to provide theoretical basis for alleviating the acidification in soils and promoting sustainable utilization of acidic soils.

Keywords biochar; amelioration of acidic soils; microorganisms in soil; toxicity of aluminum

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