贝壳土壤改良剂的应用研究进展

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摘要: 贝类是中国水产动物养殖第一大品种。贝类加工产生的大量下脚料贝壳常作为废弃物丢弃或用于低值饲料的生产, 资源利用率低、污染严重。将贝壳充分利用, 既能减少环境污染, 又可以增加贝类附加值, 对提高中国贝类产业及资源可持续利用的技术水平, 促进海洋生物产业的可持续发展具有重大意义。本文对近年来利用贝壳开发土壤改良剂的研究进展进行了综述, 展望了其发展前景, 为将来贝壳土壤改良剂的应用开发提供参考。

关键词: 贝壳土壤改良剂, 盐碱地改良, 重金属交换, 农作物增产, 微生物丰度

中图分类号: S156.2; P745 **文献标识码**: A **文章编号**: 1000-3096(2023)8-0141-09

DOI: 10.11759/hykx20220716001

中国是水产养殖大国, 贝类产业发展迅速, 海水养殖贝类年产量居世界首位[1-2]。2019 年中国贝类产量达到 1.458×10^4 t, 占世界贝类养殖总量的 60%以上[3]。目前, 中国对贝类资源的利用主要着眼于贝肉, 而对于质量百分比超过 80%的贝壳, 利用措施并不系统、完善[4]。因此, 随着海洋和渔业经济的快速发展、贝类产量的迅猛增加, 废弃贝壳的利用问题也随之出现[5-6]。大量废弃的贝壳, 往往被倾倒堆积, 不仅占用了土地资源, 还会引起蚊虫的孳生, 产生恶臭, 污染水源, 对环境有着巨大的危害[7]。因此, 贝壳的利用是目前制约贝类产业发展的重要因素之一。

中国养殖的贝类主要有文蛤、牡蛎、贻贝、扇贝、海螺等[8-12], 这些贝类的外壳中含有丰富的碳酸钙, 煅烧后可形成多孔结构, 具有良好的吸附能力, 这对调节土壤 pH、培养土壤微生物具有良好的功效[13-15]。同时, 还可使土壤中的重金属离子以碳酸盐的形式沉淀, 从而达到净化土壤的目的[16-17]。此外, Ca^{2+}对抑制盐渍化也有一定的作用, 通过与土壤胶体表面的 Na^+、Mg^{2+}进行交换, 可使土壤由亲水胶体变为疏水胶体, 改善土壤结构和通透性, 达到脱盐和抑制返盐的作用[18-20]。因此, 贝壳以其特殊的物理结构和化学组成, 使其在土壤改良中具有广阔的应用前景。加大贝壳产品的研究与开发, 对促进海洋生物产业的可持续发展具有重大意义。

1 贝壳土壤改良剂可调节土壤 pH, 改善土壤理化性质

中国农业生产规模巨大, 但由于反复浇水、大量使用化肥等不合理的耕作方式, 导致土壤容易形成板结、盐渍化、酸化等问题[21-23]。酸性土壤改良最常用的方法是向土壤中添加石灰, 以便中和土壤中的酸性物质[24-26]。贝壳经煅烧后的产物为生石灰, 可用作实惠的替代品, 用来改良酸性土壤。

国外学者研究表明, 将贻贝壳与牛粪结合使用作为土壤改良剂, 可使改良后土壤生物活性增强, 阳离子交换络合物中铝含量降低, 显著提高土壤 pH, 缓解土壤酸化问题[27]。Yamada 等[28]将粉碎的牡蛎壳加入到土壤中, 发现土壤的 pH 值逐渐升高, 含水量迅速下降。Lee 等[29]为了研究破碎的牡蛎壳粉对土壤

收稿日期: 2022-07-16; 修回日期: 2022-08-26

基金项目: 国家重点研发计划(2019YFD0900705); 山东省自然科学基金(ZR2021QD014)

[Foundation: The National Key R&D Program of China, No. 2019YFD0900705; Shandong Provincial Natural Science, No. ZR2021QD014]

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化学、生物特性和作物产量的改善作用，在白菜移栽前分别以 0、4、8、12 和 16 t/ha 施用牡蛎壳粉，采收期时，施用 16 t/ha 牡蛎壳粉的土壤 pH 由 5.8 升高至 7.4，并且明显提高了白菜产量。Alvarez 等[30]采用随机区组设计，在低阳离子交换量和高铝饱和度土壤上，分别添加石灰、细磨贻贝壳、粗磨贻贝壳等处理，比较石灰和贻贝壳添加对土壤阳离子交换量和高铝饱和度的影响。结果表明贻贝壳和石灰的施用导致 pH 和交换性钙含量升高，交换性铝含量降低，这些影响在根际最为明显，此外还发现，改良对植株干重和钙含量也有正向影响。

目前，国内贝壳土壤改良剂的研究多以牡蛎壳为原料，在多种土壤、作物种植中均能有效抑制土壤酸化，提高作物产量。Yang 等通过室内土柱模拟实验，分析了不同配比的牡蛎壳粉对砖红壤养分淋溶特性的影响。实验结果表明，添加牡蛎壳粉后，铵态氮、磷、钾的浸出损失分别降低了 23.90%~57.25%、6.31%~10.07%、17.08%~26.58%。此外，牡蛎壳粉施用于砖红壤具有调酸、保水的作用，土壤 pH 从 4.15 提高到 7.92，水分流失减少了 2.52%[31]。王日新等通过在酸性土壤中增施贝壳粉土壤调理剂，使土壤 pH 由 3.8 升高至 4.1，与有机肥联用时，小麦增产 7.0%[32]。还有研究表明，贝壳粉的粒径是决定其土壤改良效果的因素之一，通常来说，粒径越小，效果越明显。赵晓红等以平邑甜茶幼苗为研究对象，研究不同粒径贝壳粉配制的土壤调理剂对酸化土壤(棕壤土)的改良效果，实验结果表明，采用小粒贝壳粉(100 目)配制的土壤调理剂处理的土壤 pH 升高最多，5.45 升高至 7.13[33]。

2 贝壳土壤改良剂可增加作物产量

近 30 a 来，中国的水田和旱地土壤的 pH 整体呈下降趋势[34]，有研究表明，氮肥的过量使用是造成土壤酸化的主要因素[35]。在全球许多地区，土壤酸化极大地限制了农业产量，许多粮食和饲料作物对酸性土壤的耐受力较低[36]。酸性土壤中钙离子含量低，将会影响根系生长和植物对水分、养分的吸收，最终导致作物的产量下降[37-38]。因此，贝壳土壤改良剂在农业和园艺方面具有很大的应用潜力，国内外已有很多学者对此进行了深入研究。

韩国学者 Lee 等[39]分别采用堆肥牡蛎壳和新鲜牡蛎壳改良土壤，结果表明相比于施用新鲜牡蛎壳，施用堆肥牡蛎壳可将大豆产量提高 21%。Fernandez-Sanjurjo 等将牛粪、木屑和贻贝壳粉混合施用，发现其能够使土壤 pH 和交换性阳离子含量升高，交换性铝含量降低，贻贝壳的加入提高了作物的产量和质量，相较于牛粪处理组，添加贻贝壳粉处理的草地总产量提高了 3 倍，玉米总产量提高了 2 559 kg/ha[40]。Moon 等[41]使用牡蛎壳改良 pH 约为 5 的酸性土壤，处理 1 个月后，土壤中阳离子(Ca^{2+}、Mg^{2+}、K^{+}、Na^{+})的总和显著增加，处理后的玉米长势更好。挪威学者 Sognnes 等[42]将贝壳砂添加到泥炭土中，测定其对草料质量和产量的影响，结果表明，当贝壳砂的添加量为 400 m^3/ha 时，草料的质量和产量最优。

中国学者罗华汉等研究发现在稻田中施加牡蛎壳粉可以明显提高水稻的产量和质量，相较于空白组增产 14.8%~22.9%[43]。代小青等采用贝壳粉修复砷污染的稻田，发现施加贝壳粉可是土壤有效 As 含量降低 2.72%，水稻籽粒中 As 含量降低 6.3%，水稻产量提高 17%[44]。除了粮食作物外，国内学者也将贝壳粉应用在蔬菜、水果等经济作物的种植当中，并取得了较好的成效。周红梅等研究了麦饭石、牡蛎壳、蒙脱石、硅钙矿和有机肥对大蒜产量的影响，结果指出 5 种改良剂均能提高大蒜产量[45]。为了探明牡蛎壳土壤调节剂施用量与黄泥田花生产量的关系，严建辉设计了施用量 2 250 kg/hm^2 和 1 500 kg/hm^2 两个实验组以及空白对照组，结果表明在实验范围内，花生的产量与牡蛎壳土壤调节剂的施用量呈正相关关系，土壤的氮、磷、钾、钙、pH 等指标也均有提高[46]。周恩生研究指出在土壤中施用贝壳粉可有效降低花生空秕率，每亩收益增加 180.1 元[47]。许玲玲等[48]测定了煅烧牡蛎壳对玉菇甜瓜品质的影响，结果表明当施用量为 2 250 kg/hm^2 时，玉菇甜瓜单果质量增长 12.66%，果实脆度提高 39.93%，果实硬度提高 46.10%，维生素 C 含量增加 47.97%，口感及品质提升明显。春桃番茄的种植中也有类似发现，当牡蛎壳土壤调理剂的施用量达到 3 000 kg/hm^2 时，单果重、出汁率和维生素 C 含量相较于空白对照组分别提高了 8.39%、11.61%和 18.44%[49]。罗军元等[50]比较了空白、石灰粉和贝壳粉对蜜橘生长的影响，发现施贝壳粉或石灰粉均能有效提高蜜橘的产量和品质，且贝壳粉的效果要略好于石灰粉。

3 贝壳土壤改良剂可钝化土壤重金属，减少作物胁迫

重金属污染在世界范围内的耕地土壤中普遍存

在, 耕地土壤的重金属污染是经过长时间积累所导致的, 随着矿产冶炼、机械加工等产业的快速发展, 不可避免地将重金属带入到农田生态系统中[51-52]。重金属污染不仅会导致农作物减产, 还会威胁食品安全, 影响中国居民的生活水平和身体健康[53-54]。

当前, 镉(Cd)、铬(Cr)、铅(Pb)是土壤重金属污染的主要元素类型, 其中 Cd 污染的影响是最严重的[55-57]。Cd 能够破坏植物组织细胞, 影响光合作用, 降低作物产量[58]。贝壳粉由于其多孔、碱性等特征, 能够通过吸附、络合等多种方法钝化土壤中的重金属, 降低其毒性和迁移性, 达到净化土壤的目的[59-61]。张曦比较了麦饭石、蒙脱石、牡蛎壳和硅钙类矿物 4 种土壤改良剂对土壤中镉形态及毒性的影响, 结果表明牡蛎壳的吸附效果最好[62]。大量研究表明, 在土壤中添加贝壳粉, 可以有效降低土壤中可交换性 Cd[63], 使其钝化形成 $CdCO_3$[64-66]; 降低 Cd 的迁移性, 将白菜叶中的 Cd 含量减少 98%[67]; 降低水稻根际 Cd 含量, 促进水稻生长[16, 68]; 减少水稻及油菜籽的 Cd 吸收量[69], 大幅降低莴苣可食部分的 Cd 含量[70], 对食用苋菜的生长有积极影响, 显著抑制其对 Cd 的吸收[71]。

同 Cd 类似, Pb 也会显著影响植物生长, 其作用机理是能够进入根部, 降低根细胞分裂速度, 导致植物生长缓慢; 而且其在植物体内的积累会破坏代谢酶系统, 浓度过高时还会引起组织坏死及植物死亡。Moon 等[72]利用牡蛎壳等废弃物对污染土壤中的 Pb 进行了固定化研究, 结果表明, 这种改良剂可在 28 d 的养护期内降低 99%以上的 Pb 浸出性。韩国学者采用牡蛎壳粉对矿山土壤进行改良, 30 d 后, Pb 的提取率降低了 95%[73]。郝春莉等[74]发现采用贝壳粉钝化土壤中的 Pb, 可使水溶态 Pb 和可交换态 Pb 含量分别降低 22.3%和 67.0%。张琢等指出, 在铅蓄电池污染土壤中添加 2%~10%质量分数的贝壳粉后, 可使土壤中 Pb 的浸出浓度降低 22%~62%[65]。

除镉和铅外, 还有许多研究表明贝壳粉对土壤中的砷(As)、铜(Cu)、锑(Sb)、铬(Cr)和汞(Hg)具有良好的吸附作用。Moon 等施用的贝壳改良剂可显著降低 As 和 Cu 的浸出性, 效果分别为 93%和 99%, 采用扫描电镜-能量色散 X 射线能谱分析表明, As 的固定可能与 Ca-As 和 Fe-As 相的形成有关, 而 Cu 的固定可能与水合硅酸钙和水合铝钙相的形成有关[72]。Garrido-Rodriguez[75]研究了在富铜酸性土壤中添加贻贝壳粉对 Cu 释放速度的影响, 结果表明在 pH 为 3 的土壤中, 添加贝壳粉可使铜的解吸率下降 86%, 在 pH 为 5 时, 铜的释放速度降低了 98%, 而在 pH 为 7 时, 贝壳粉的添加则对铜的释放速度无显著影响, 这表明贝壳粉是通过调节 pH 来起到改变铜释放速度的作用。Ahmad 等[76]指出废牡蛎壳引起的土壤 pH 值变化对 Sb 浸出性有显著影响, Sb 被贝壳粉固定最可能的原因是形成锑酸钙沉淀。Rivas-Perez 等针对 As 和 Cr 同时污染的问题, 采用贻贝壳对森林和葡萄园土壤进行了 As 和 Cr 的竞争吸附实验, 实验发现在森林土壤中, 贻贝壳可同时提高对 As 和 Cr 的吸附, 而在葡萄园土壤中, 贻贝壳可提高对 As 的吸附[77]。Pena-Rodriguez 等[78]测定了汞在煅烧和研磨贻贝壳上的滞留量, 结果证明煅烧过的贻贝壳对汞的吸附量更高, 符合 Freundlich 方程, 磷酸盐可以增加贻贝壳对汞的吸附, 使汞的解吸率由 13%下降到 2%。此外还发现煅烧贻贝壳对汞的吸附量与贝壳中方解石和白云石的浓度有关, 当磷酸盐存在时, 汞-磷酸盐相互作用会导致汞吸附量增加, 且该吸附不可逆。贝壳粉的广谱吸附特点使得其在处理重金属污染土壤时的作用范围大大增加, 为其推广应用奠定了良好的基础。

4 贝壳土壤改良剂可改善土壤微生物群落, 减少土传病害

土壤微生物主导着土壤生态, 通过调节养分循环、分解有机质、构建土壤结构、抑制植物病害和促进植物生长来发挥一系列重要的土壤功能[79]。微生物的存在及其活性可以通过多种方式影响土壤, 一方面, 土壤微生物是土壤生态系统变化的促进者, 另一方面, 微生物群落结构和多样性也可以作为土壤健康的指标, 因此, 土壤微生物对土壤有机污染物的代谢、土传病害防治具有重要作用[80]。

Fernandez-Calvino 等[17]用贻贝壳粉对铜污染的极酸矿区土壤进行了改良, 结果表明土壤中的细菌和真菌群落经改良后均明显增多, 同时, 贻贝壳粉还可以防止土壤酸化, 避免了过低 pH 对细菌生长的抑制。Zheng 等[55]对金属污染土壤中贝壳改良剂施用后的细菌群落进行了定量和定性分析后指出, 在培养 108 d 后, 优势菌群逐渐向缓解土壤金属离子再溶解和促进土壤养分循环的方向转变。Wang 等[70]的研究表明经贝壳粉改良后土壤细菌丰富度和多样性增加, 细菌群落中的耐金属菌增加, 变形菌、酸菌和芽单胞菌减少。沈桂花等研究发现牡蛎壳粉土壤改良剂可以通过提高土壤 pH, 提高微生物的碳源利用

率、代谢多样性以及群落物种均匀度，并且，较高的pH 还可抑制烟草青枯病的传播，实验组较对照组发病率降低了 43.33%[81]。张小远等[82]研究发现，采用贝壳砂改良过的土壤中具有较高的微生物多样性。赵晓红等[33]分析了经贝壳粉土壤调理剂改良后土壤中的微生物丰富度、多样性及群落结构，结果表明调理剂可显著提高细菌丰富度和多样性指数，但却能够降低真菌的多样性。

贝壳粉对土传病害的防治主要是通过提高 pH 实现的，目前，在烟草种植中的应用研究较多。单晓鹏研究发现在烤烟土壤中施用牡蛎壳粉可降低黑胫病、青枯病、花叶病的发生及流行[83]。龚杰等[84]在长期种植烟草的酸化土壤中分别添加了草木灰和牡蛎壳粉，发现两者皆可对烟草青枯病起到防治效果。除烟草外，也有研究发现施用牡蛎壳粉可以使榨菜(茎瘤芥)根肿病的发病率降低 26%，并且能够提高根际土壤微生物的碳代谢能力[85]。

5 展望

作为常见的酸性土壤改良剂和钙补充剂，石灰已在农业生产中使用多年，然而，石灰的开采和加工会带来环境污染、能源消耗等问题，其替代产品的研发，符合当今“绿色农业”理念的要求。贝壳是水产加工产业的副产品，具有资源丰富，成本低廉等优点。贝壳是一种天然的纳米复合材料，由砖状碳酸钙层和薄蛋白质层组成，其丰富的天然多孔表面使其具有很强的吸附能力[86]。因此，粉碎的贝壳粉可作为石灰的替代材料，以恢复土壤的化学性质和微生物特性，并提高作物产量。但是，贝壳土壤改良剂在应用中仍存在一些问题需要被进一步改进或阐明。

1)贝壳中含有大量的氯化钠，土壤中添加过多的钠会引起黏土颗粒分散，堵塞土壤孔隙，降低土壤的渗透性、孔隙度和导流能力，进一步引起土壤盐渍化[29]。同时，贝类生物在生长过程中也会富集海水中的重金属元素，这些重金属元素会随着贝壳粉一同被施用在土壤之中，造成污染[87]。因此，贝壳粉在使用时必须注意用量以及土壤本身的性质，提前做好评估，避免在碱性土壤中使用。

2)大量研究表明，未经煅烧的贝壳粉对于土壤的改良效果有限，这是因为碳酸钙的化学性质稳定，无法与土壤中的重金属、NaCl 相互作用所导致的[39]。因此，必须将贝壳在炉中加热至 600 ℃以上煅烧，方可使碳酸钙发生分解[88]，为了进行这种高温处理，会导致大量燃料消耗以及温室气体的排放，存在环境污染和能源消耗等问题。

综上所述，贝壳土壤改良剂的研究与开发仍处于起步阶段，需要加大投入力度，使贝壳变废为宝，这对水产养殖产业的可持续发展、“绿色农业”的推广具有重要意义。

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Study and application of a shell soil conditioner

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Received: Jul. 16, 2022
Key words: shell soil conditioner; saline-alkali soil improvement; heavy metal exchange; increased production; microbial abundance

Abstract: Shellfish are the most common part of aquaculture in China. Shells are often discarded as waste or used in low-value feed production, which results in a waste of resources and serious environmental pollution. Thus, effective use of shell resources can not only lessen pollution but also increase the value of shellfish, which is of great significance for improving the technical level of sustainable utilization of the shellfish industry and promoting sustainable development of the marine biological industry. In this paper, the research progress of the development of soil conditioners that utilize seashells as raw materials in recent years is reviewed. In addition, potential risks are identified, and future research directions of shell soil conditioners are presented. Thus, this work offers a guide for future application and development of marine shellfish wastes.

(本文编辑: 杨　悦)