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秸秆生物炭吸附/钝化土壤重金属的过程机理与影响因素

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摘要: 土壤重金属污染因其隐蔽性、滞后性及对环境和人体健康的危害性, 已引起广泛关注。生物炭因具有较大的孔隙率、比表面积及丰富的表面官能团, 常用来修复重金属污染土壤。秸秆作为农业废弃物, 将其制备为生物炭是其资源化利用和减少环境污染的有效途径。因此, 本文综述不同秸秆生物炭的原料、制备技术和改性方法等对吸附重金属的影响, 探讨其对重金属的吸附机理以及修复重金属污染土壤实际应用效率与影响因素, 包括: (1) 秸秆种类及制备温度对生物炭特性和重金属污染土壤修复效率的影响; (2) 秸秆生物炭吸附/钝化土壤重金属的过程与机理; (3) 可提高生物炭修复重金属污染土壤效率的改性技术及其实际应用效率和影响因素。并结合秸秆生物炭制备和应用中存在的问题提出展望, 以期为提高秸秆生物炭在重金属污染土壤修复效率, 实现农业废弃物资源化回收利用, 减少环境污染提供理论基础和技术参考。

关键词: 秸秆; 生物炭; 重金属; 改性; 修复机制

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Mechanisms and Influencing Factors for Soil Heavy Metals Adsorption/Passivation by Straw Biochar

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Abstract: Soil heavy metal pollution has attracted increasing attention due to its concealment, hysteric and high risk to the environment and human health. Biochar is often used in heavy metals contaminated soils remediation for its large porosity, specific surface area and plenty of surface functional groups. As agricultural waste, transforming straw into biochar is an effective way for resource reutilization and reducing environmental pollution. Therefore, this paper reviews the influence of origin, preparation technology and modification method of different straw biochars on heavy metals adsorption, discusses adsorption mechanism and efficiency and influencing factors during

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their practical application. The content mainly include: (1) effects of straw origin and preparation temperature on biochar characteristics and its remediation efficiency on heavy metals contaminated soils remediation; (2) processes and mechanisms of soil heavy metals adsorption/passivation by straw-based biochar; (3) the modification methods that can improve heavy metals remediation efficiency by straw-based biochar. Based on the problems in preparation and application of straw biochar, prospects are proposed to provide theoretical bases and technical supports to improve heavy metals contaminated soils remediation efficiency by straw-based biochar and promote the reutilization of agricultural wastes thereby to reduce environmental pollution.

Keywords: straw; biochar; heavy metal; modification; remediation mechanism

土壤是人类赖以生存和发展的基石,是保障生态环境和食品安全的重要基础^[1]。随着我国工业化和城镇化进程的加快,人类生产活动对土壤质量的影响日益凸显。近年来,化工产品的广泛生产使用,农药、化肥的大量施用,对土壤造成严重污染与破坏^[2],其中,以重金属污染尤为突出。进入土壤中的重金属被植物吸收后可抑制其生长,且随食物链传递、富集,最终进入人体,危害人类健康^[3]。《全国土壤污染状况调查公报》(2014年)显示,我国土壤重金属总超标率为16.1%,其中重金属污染耕地占比19.4%,主要为铅(Pb)、汞(Hg)、铬(Cr)、铜(Cu)、锌(Zn)、镍(Ni)和砷(As)等^[4]。我国污水灌溉农田土壤达 1.4×10^6 hm²,重金属污染面积占比64.8%,其中Pb、As、Cr、Cd污染耕地面积约 2×10^7 km²,占耕地总面积的20%^[5]。

生物炭作为近年土壤学和环境科学领域的研究热点,被认为是应对气候变化、农业废弃物资源化和环境污染等问题的重要材料。生物炭是以动植物残体或粪便为原料,在200~700℃及限氧条件下,通过热化学转化或热解获得的重金属吸附材料^[6-7]。由于生物炭表面官能团丰富、孔隙率高、具有较大比表面积、较高pH和阳离子交换量,可用于吸附去除水体和土壤中重金属,在改善土壤环境、修复环境污染、降低环境风险等方面具有广阔应用前景^[8-10]。在众多生物炭制备原料中^[11-18],秸秆生物炭表现出突出的重金属吸附效果^[19]。例如,水稻秸秆生物炭对Pb²⁺和Cd²⁺的吸附量(126 mg·g⁻¹和60.6 mg·g⁻¹)显著高于木屑和米糠生物炭(47.6 mg·g⁻¹和6.67 mg·g⁻¹、33 mg·g⁻¹和16.2 mg·g⁻¹),与其较高的无机矿物组分含量(38.8% vs. 17.5%、13.8%)有关^[20]。此外,我国是农业大国,秸秆产量占全球秸秆产量的1/5,秸秆资源丰富易得^[21],为制备生物炭提供丰富原料。通常,秸秆作焚烧处理,易造成环境污染和资源浪费。因此,以秸秆为原料制备生物炭对重金属污

染土壤进行修复,既可实现废弃物资源化利用,降低其二次污染风险,亦可达到吸附稳定/固定土壤重金属的目的,同时降低污染土壤的修复成本。秸秆生物炭具有高芳香化和杂环化结构,表面分布多样微孔结构和多种官能团,对重金属具有极高的吸附/钝化效率。本文通过介绍秸秆生物炭的制备技术、特征性能及其影响因素,重点阐述生物炭对重金属污染土壤的修复机制及实际应用效率和影响因素,并对后续研究提出展望,以期对秸秆废弃物资源化利用及秸秆生物炭吸附/钝化土壤重金属提供理论依据和技术参考。

1 秸秆生物炭制备方法及影响因素 (Preparation methods and influencing factors of straw biochar)

生物炭是有机材料在一定的限氧和高温条件下产生的富碳材料,不同条件制备的生物炭钝化/吸附重金属效率不同,其性能与原料类型、制备技术和改性等因素有关。

1.1 原料类型

秸秆类型不同,其结构特征、元素含量和表面官能团种类等亦不同,故其制备生物炭的性质存在一定差异。邹凡等^[22]对由玉米、水稻和小麦秸秆制备的生物炭吸附Pb²⁺研究后发现,玉米秸秆生物炭结构蓬松,—OH、—C—H和C=C等表面官能团较多,通过表面络合吸附Pb²⁺,吸附量达141 mg·g⁻¹;水稻和小麦秸秆生物炭碳酸盐和磷酸等含量较高,通过化学沉淀吸附Pb²⁺,吸附量达123 mg·g⁻¹和121 mg·g⁻¹。此外,不同原料生物炭的孔隙结构和比表面积存在显著差异。如表1所示,不同生物炭的孔隙体积和比表面积随温度升高而增加,一定温度后降低。水稻和玉米秸秆生物炭制备温度低于500℃时,比表面积和孔隙体积变化不明显;当温度高于500℃时,生物质中纤维素、半纤维素和木质素裂解,秸秆生物炭的孔隙体积和比表面积显著增加。小麦、棉花和烟草秸秆生物炭制备温度为500℃时,

比表面积和孔隙体积达到最高,之后随制备温度升高而降低,可能是因其维管束遭到破坏,灰分熔融,孔隙结构坍塌。此外,不同原料生物炭的 pH 值和表面电荷存在显著差异。Nzediegwu 等^[23]利用油菜秸秆和小麦秸秆在 300 ℃、400 ℃和 500 ℃制备生物炭发现,小麦秸秆生物炭 pH 值为 9.4、10.0 和 11.7,油菜秸秆生物炭 pH 值为 8.9、9.6 和 12.1。可见,制备原料对生物炭的特性(表面官能团种类、孔隙结构、比表面积和 pH 等)具有较大影响,进而影响其生物炭对重金属的吸附能力。

1.2 制备技术

制备技术(如热解方式、炭化温度等)影响生物炭的成炭率、比表面积、孔隙结构和表面基团等,秸秆生物炭相比其他生物炭更受制于温度^[29]。通常,重金属吸附量随加热温度和加热速率升高而升高,成炭率随加热温度和加热速率升高而降低^[30]。加热温度对成炭率的影响表现为较低温度(400 ℃)高于较高温度(500 ~ 1 000 ℃),成炭率分别为 35% 和

10% ~ 25%^[31-32],但温度过低(350 ℃)会导致炭化不完全和炭化时间过长,导致成炭率降低^[33]。加热温度对生物炭重金属吸附容量的影响表现为:随制备温度升高,原料中挥发性物质大量流失,使生物炭孔隙度和比表面积增大,但其重金属吸附量降低。例如,Ding 等^[34]发现,炭化温度由 250 ℃升至 600 ℃后,甘蔗渣生物炭比表面积由 0.56 m²·g⁻¹增至 14.1 m²·g⁻¹,但对 Pb 的吸附量由 20.5 mg·g⁻¹降至 6 mg·g⁻¹。类似地,Yang 等^[19]发现,水稻秸秆生物炭制备温度由 500 ℃升至 900 ℃后,对 Ni²⁺的吸附量由 28.6 mg·g⁻¹降至 14.4 mg·g⁻¹,产生这一现象的可能原因是高温炭化过程使 C=O、—OCH₃ 和 C—H 等对重金属具有吸附络合能力的表面官能团减少。

生物炭制备技术有炭化技术、水热炭化、气化和微波热解等^[35-39],对生物炭的结构特性有一定影响,见表 2。综合考虑成炭率和重金属吸附容量,对秸秆进行炭化时,采用慢速(5 ~ 7 ℃·min⁻¹)热裂解(400 ~ 650 ℃)较为合适^[40]。

表 1 不同原料和制备温度生物炭比表面积、孔隙特性和 pH 值
Table 1 Specific surface area, pore property and pH value of biochar prepared by different raw materials and temperatures

秸秆类型 Straw type	制备温度/℃ Preparation temperature/℃	比表面积 (m ² ·g ⁻¹) Surface area (m ² ·g ⁻¹)	孔隙体积 (cm ³ ·g ⁻¹) Pore volume (cm ³ ·g ⁻¹)	平均孔径 /nm Mean pore size /nm	pH 值 pH value	参考文献 References
水稻秸秆 Rice straw	300	5.81	0.0066	5.25	9.5	[24]
	500	6.4	0.0089	9.06	12.3	
	700	185	0.0288	4.71	12.8	
小麦秸秆 Wheat straw	300	3.07	0.005	1.85	—	[25]
	500	6.6	0.01	2.77	—	
	700	3.87	0.005	1.61	—	
玉米秸秆 Corn straw	300	6.8	0.0094	5.53	—	[26]
	400	10.5	0.0117	4.45	—	
	500	13.9	0.0131	3.78	—	
	600	60.5	0.0612	4.05	—	
棉花秸秆 Cotton straw	400	16.4	0.033	80.1	10.5	[27]
	500	107	0.086	32.2	10.7	
	600	31.3	0.052	65.7	12.1	
	700	27.3	0.041	59.5	11.0	
烟草秸秆 Tobacco straw	300	2.88	0.005	1.77	—	[28]
	400	6.07	0.009	2.77	—	
	500	6.85	0.011	4.54	—	
	600	5.27	0.008	3.79	—	

1.3 改性方法

通过直接热解生物质得到的生物炭结构稳定、质地密实、比表面积往往较低、吸附活性位点较少、表面官能团不够丰富,致使生物炭在吸附过程中对污染物的去除效率低、选择性差,阻碍了其在环境领域的实际应用。因此,有必要对生物炭进行改性处理以提高其吸附能力。生物炭改性指通过活化或功能化改变生物炭理化性质。生物炭借此改善其孔隙结构和比表面积并增加表面官能团数量,进而提高其吸附重金属能力^[41]。生物炭改性主要分物理改性、化学改性和生物改性(图1)。

物理改性是通过物理方法,如球磨、紫外线照射、超声波和气体活化等方法处理生物炭,提高生物炭吸附性能。Zhang 等^[42]对玉米秸秆生物炭进行球磨法改性后,生物炭颗粒尺寸变小,其比表面积显著提高($147 \text{ m}^2 \cdot \text{g}^{-1}$ vs. $85.4 \text{ m}^2 \cdot \text{g}^{-1}$),土壤 Cd 可迁移态降低 45.4%。Peng 等^[43]将玉米秸秆、锯末和小麦秸秆生物炭经 365 nm 紫外光照射 24 h 改性,研究后发现紫外线照射增加生物炭的比表面积,并在其表面添加大量的含氧官能团,吸附 Cr^{6+} 能力增加 2 倍~5 倍($14.4 \sim 20 \text{ mg} \cdot \text{g}^{-1}$ vs. $3.6 \sim 8.43 \text{ mg} \cdot \text{g}^{-1}$)。Hu 等^[44]对生物炭超声波改性后发现,改性生物炭的微孔结构和功能性官能团增加,其比表面积上升 249% ($1452 \text{ m}^2 \cdot \text{g}^{-1}$ vs. $416 \text{ m}^2 \cdot \text{g}^{-1}$),吸附能力提高

5.3 倍($321 \text{ mg} \cdot \text{g}^{-1}$ vs. $61 \text{ mg} \cdot \text{g}^{-1}$)。Sakhiya 等^[45]对水稻秸秆生物炭空气活化,使其比表面积由 $3.61 \text{ m}^2 \cdot \text{g}^{-1}$ 增至 $105 \text{ m}^2 \cdot \text{g}^{-1}$,表面多孔结构更加分明,吸附 Zn^{2+} 量达 $27.8 \text{ mg} \cdot \text{g}^{-1}$ 。物理改性操作简单,可改善生物炭特征,但物理改性程度有限,对复合污染状况有所限制。

化学改性是指利用强酸、强碱、有机溶剂或负载金属氧化物等改性生物炭,使生物炭表面官能团发生变化,提升其吸附效果。如 Shen 等^[64]对稻壳生物炭进行 KOH 改性处理,使其比表面积提升 12.7 倍 ($1818 \text{ m}^2 \cdot \text{g}^{-1}$ vs. $133 \text{ m}^2 \cdot \text{g}^{-1}$),微孔隙率达 93.3%,吸附性能显著提高。Liatsou 等^[65]使用 2-巯脒嘧啶对丝瓜生物炭纤维进行改性,发现改性生物炭纤维改性后对 Cu^{2+} 吸附性提高至 $487 \text{ mg} \cdot \text{g}^{-1}$,且可对酸性矿山废水中的 Cu^{2+} 进行选择分离。Yang 等^[66]以玉米秸秆为原料,运用还原共沉淀法合成纳米级零价铁生物炭修复 As/Cd 污染土壤,结果表明生物炭表面负载 Fe—O 官能团,并与 As/Cd 络合,使水稻籽粒中 As 和 Cd 含量分别降低 69.3% 和 59.8%。

生物改性是将生物炭与具备某种功能的微生物相结合,从而改善其理化性质的技术。生物炭为微生物提供繁殖生长空间和营养物质的同时,微生物通过代谢转化作用固定污染物,提高改性生物炭吸附性能。Tu 等^[75]以 5% 速率将假单胞菌负载至玉米

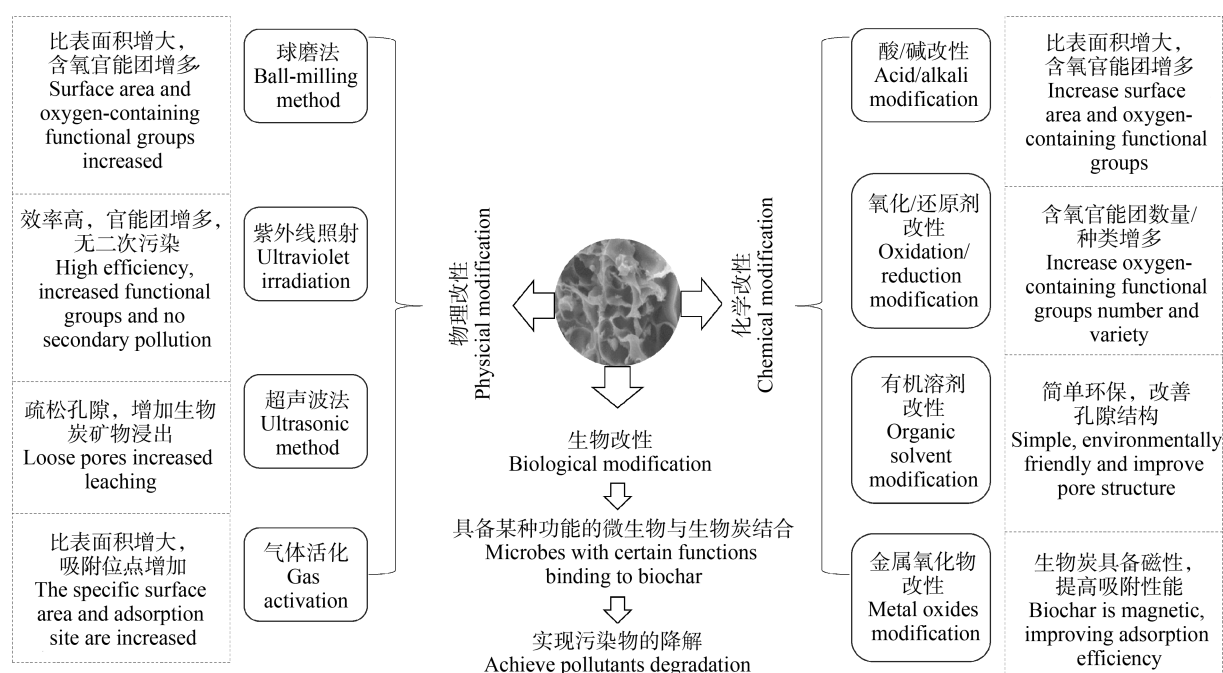


图1 生物炭改性方法及特点^[65,67-74]

Fig. 1 Methods and characteristics of biochar modification^[65,67-74]

表 2 生物炭制备技术及其特点

Table 2 Biochar preparation technology and characteristics

生物炭制备技术 Biochar preparation technique	使用气体 Gas	反应温度/°C Temperature/°C	加热速率 Heating rate	反应时间 Reaction time	成炭率/% Char forming ratio/%	表面积 (m ² ·g ⁻¹) Surface area (m ² ·g ⁻¹)	孔隙度 (cm ³ ·g ⁻¹) Porosity (cm ³ ·g ⁻¹)	生物炭特点 Biochar characteristics	参考文献 References
慢速热裂解 Slow pyrolysis		400 ~ 650	5 ~ 7 °C·min ⁻¹	1 ~ 2 d	35	4.21	0.007	较多 C—C 键和 C—H 键 More C—C and C—H bonds	
中速热裂解 Moderate thermal cracking		400 ~ 550	300 °C·min ⁻¹	10 ~ 20 s	20	13.1	0.026	具有羧基、羟基、酮等结合位点; 孔隙度和表面积较大 It has binding sites for carboxyl and hydroxyl groups and ketone, and large porosity and surface area	[46—50]
炭化技术 Carbonized technology		400 ~ 550	1 000 °C·s ⁻¹	1 ~ 2 s	12	7.02	0.008	孔隙度和表面积较大 Large porosity and surface area	
快速热裂解 Fast pyrolysis		1 000 ~ 1 300	1 000 °C·s ⁻¹	1 s	10 ~ 25	195	0.15	结合位点消失, 表面积降低 The binding site disappears and the surface area decreases	
水热炭化 Hydrothermal carbonization	N ₂	400 ~ 650	-	1 ~ 12 h	37 ~ 60	5.02	0.025	较好保留表面官能团 Better retention of surface functional groups	[51—54]
气化技术 Gasification technology		100 ~ 1 500	100 ~ 200 °C·min ⁻¹	10 ~ 20 min	10	75	0.04	表面积较大 Large surface area	[55—59]
微波热解 Microwave pyrolysis		400 ~ 500	-	0.3 ~ 9 h	35 ~ 50	31.6	0.042	较高芳香度、孔隙度和表面积 High aromaticity, porosity and surface area	[60—63]

秸秆生物炭,研究其固化土壤 Cd 和 Cu 的效果后发现,可交换态 Cd 降低 12.8%,Fe-Mn 氧化物结合 Cd 和残留 Cd 分别增加 8.17% 和 5.49%;碳酸盐结合 Cu 降低 26.6%,残留 Cu 增加 11.5%。同时改善了培养结束时的土壤微生物群落,使金属稳定后的土壤功能得到恢复。生物改性将微生物的某种功能赋予生物炭,使其有效吸附污染物,但局限于微生物培养困难,难以推广,且细菌和真菌存在一定生态风险^[76]。

2 秸秆生物炭修复重金属污染土壤的机制 (Mechanisms of straw biochar in heavy metal contaminated soils remediation)

秸秆生物炭利用其表面富含的官能团和矿物质成分等吸附重金属离子涉及多种作用机理,主要包括静电吸引、离子交换、物理吸附、络合、沉淀和氧化还原(图 2)。

2.1 静电吸引

静电吸引指生物炭利用其表面的正负电荷与重金属离子发生静电吸引从而吸附固定重金属^[77]。Tong 等^[78]研究发现,提高 pH 可增加生物炭对 Cu^{2+} 的吸附。当土壤 pH 值 > 零电荷点 (pH_{PZC}) 时,生物炭表面呈负电性,通过静电吸引重金属阳离子,同时也可与 H^+ 结合提高土壤碱度,增强吸附作用;反之,生物炭表面携带正电荷,通过静电吸引类金属阴离子^[79-81]。因此,秸秆生物炭的高电负性可促进其与正电离子的静电吸引^[82],吸附强度取决于生物炭的 pH_{PZC} 与土壤 pH 值的大小关系。

2.2 离子交换

生物炭表面存在大量 K^+ 、 Ca^{2+} 和 Na^+ 等碱金属离子,能够与重金属离子发生离子交换,从而吸附重金属离子^[83]。研究表明,土壤中的 Cd^{2+} 可与生物炭中碱金属离子选择性置换^[84],其反应式为: $\text{C}-\text{X}^{n+} + \text{Cd}^{2+} \rightarrow \text{C}-\text{Cd}^{2+} + \text{X}^{n+}$ (X^{n+} 表示盐基离子),这是因为 Cd^{2+} 的离子半径、电荷量和键合特性等与盐基离子相似^[85]。此外,生物炭中 K^+ 和 Ca^{2+} 等阳离子与 Cd^{2+} ^[86]、 Al^{3+} ^[87] 发生离子交换作用,进而提高生物炭对 Cd^{2+} 、 Al^{3+} 的吸附效率。可见,生物炭表面存在的碱金属离子可通过离子交换过程对土壤中重金属离子进行固定。

2.3 物理吸附

物理吸附由生物炭表面范德华力产生,受生物炭孔隙结构和比表面积影响^[88]。研究表明,生物炭表面存在的不同大小的孔隙为 Cd^{2+} 和可穿透络合物等提供吸附位点^[89-90]。生物炭比表面积和孔隙体

积随制备温度升高而增大,制备温度为 500 ~ 700 °C 时,生物炭比表面积和孔隙体积较大。Sui 等^[91]研究发现用硼酸改性玉米秸秆生物炭使比表面积提高至 898 $\text{m}^2 \cdot \text{g}^{-1}$,且随生物炭制备温度升高,其对 Fe^{2+} 的吸附性能增强,800 °C 制备的改性生物炭对 Fe^{2+} 的吸附量达 133 $\text{mg} \cdot \text{g}^{-1}$,且吸附过程符合伪二阶动力学方程,表明生物炭对 Fe^{2+} 的吸附过程为表面吸附。因此,生物炭比表面积和孔隙体积越大,对重金属的吸附能力越强。

2.4 络合作用

生物炭表面富含 $-\text{COOH}$ 、 $-\text{OH}$ 和 $-\text{NH}_2$ 等官能团,可与重金属离子发生络合,从而固定重金属^[6],其中以 $-\text{COOH}$ 和 $-\text{OH}$ 络合作用最为突出^[92]。王棋等^[93]通过傅里叶红外光谱法分析生物炭吸附重金属离子前后生物炭表面官能团的变化,结果表明,生物炭的 $-\text{OH}$ 伸缩振动峰 (3 422 cm^{-1}) 在吸附 Cu^{2+} 、 Pb^{2+} 、 Cd^{2+} 和 Ni^{2+} 后位移均发生明显变化,表明 $-\text{OH}$ 与重金属离子发生络合。相较于 $-\text{OH}$,高硫生物炭表面的 $-\text{SH}$ 对 Hg^{2+} 、 Cd^{2+} 等的络合能力更强^[94-95],这是由于其能与 Hg^{2+} 、 Cd^{2+} 等形成更稳定的络合物。此外,生物炭表面官能团亦可通过间接方式与重金属离子发生络合,进而改变重金属形态。例如,生物炭表面丰富的含氧官能团可先与土壤中 Fe、Mn 结合形成铁锰氧化态物质,再与 As 发生络合作用^[96]。综上,生物炭表面官能团 ($-\text{OH}$ 、 $-\text{SH}$ 等) 通过直接或间接过程络合金属离子。

2.5 沉淀作用

生物炭灰分中的矿物成分可与重金属发生沉淀反应,从而实现重金属的固定。由于生物炭制备原料的不同导致其矿物质成分不同,生成的重金属氧化物、氯化物、碳酸盐和硫酸盐等沉淀物亦不同^[6]。水稻秸秆生物炭中 $\text{C}_2\text{O}_4^{2-}$ 和 CO_3^{2-} 可与 Pb^{2+} 分别形成 PbC_2O_4 和 $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ 沉淀,是固定 Pb 的主要机制^[97]。 OH^- 、 CO_3^{2-} 、 PO_4^{3-} 和 SO_4^{2-} 等阴离子可与 Pb^{2+} 生成 PbCO_3 、 $\text{Pb}_3(\text{PO}_4)_3\text{OH}$ 等沉淀^[98],与 Cd^{2+} 生成 $\text{Cd}_3(\text{PO}_4)_2$,与 Zn^{2+} 生成 $\text{Zn}_3(\text{PO}_4)_2$ 沉淀。因此,针对不同重金属种类,可通过特定的阴离子对生物炭进行改性,增强生物炭对重金属的沉淀效率,提高重金属吸附效率。

2.6 氧化还原作用

生物炭可作为电子供体或受体诱导重金属发生氧化还原反应,达到吸附和钝化重金属的目的。如生物炭表面 $\text{C}_6\text{H}_5-\text{OH}$ 等官能团拥有转移电子的能

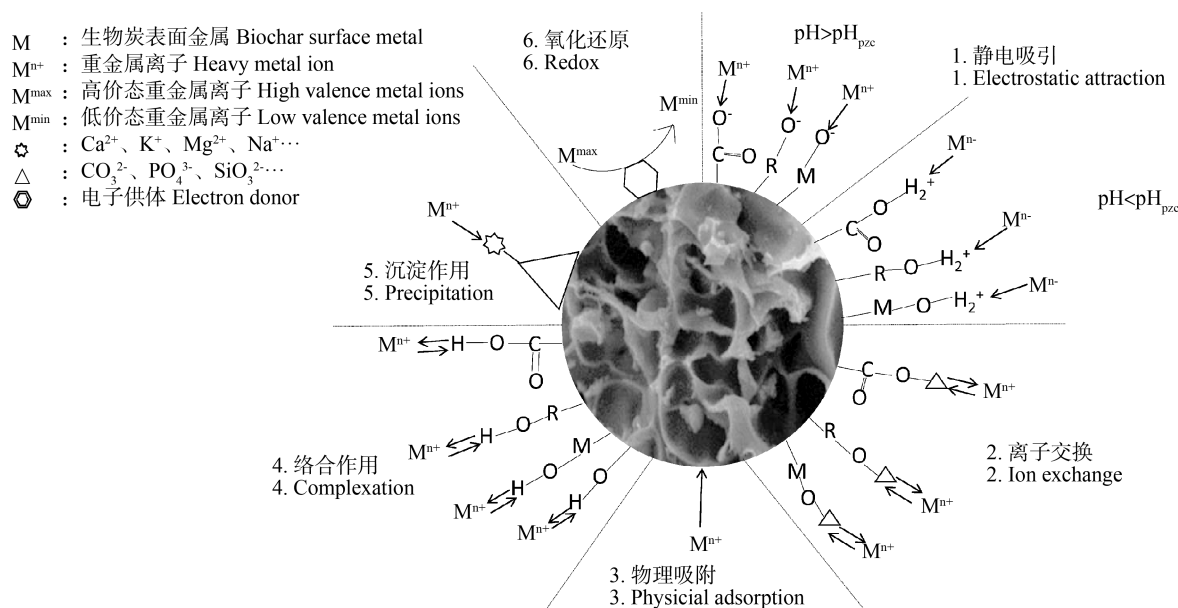


图2 秸秆生物炭吸附土壤重金属机制示意图

Fig. 2 Mechanisms for heavy metals adsorption by straw-based biochar

力,可将 As^{3+} 氧化为 As^{5+} 或还原 Cr^{6+} 为 Cr^{3+} [99]。Lyu 等[100]预磁化生物炭后,将其与 $Ca-Mg-Al$ 三元层状金属氧化物交联得到磁性生物炭交联金属复合材料,其对 As 的最大吸附容量达 $265 \text{ mg} \cdot \text{g}^{-1}$,其涉及的机制为改性生物炭表面的 Fe_2O_3 将 As^{3+} 氧化为 As^{5+} ,而后 As^{5+} 与生物炭表面金属官能团配位,生成 $M-O-As$ 配体。

综上,秸秆生物炭通过表面富含的碱金属离子(K^+ 、 Ca^{2+} 和 Na^+ 等)、官能团($-COOH$ 、 $-OH$ 和 $-NH_2$ 等)和矿物质成分等,通过及吸附、络合、沉淀、氧化还原等过程,对重金属离子进行吸附钝化。

3 秸秆生物炭修复重金属污染土壤的效率与影响因素 (Efficiency and influencing factors of straw biochar in heavy metals-contaminated soils remediation)

生物炭修复重金属污染土壤过程中,修复效率主要受土壤 pH 值、土壤类型、生物炭改性方式、重金属种类和田间管理方式等因素的影响(表3)。

3.1 土壤 pH 值

通常,生物炭吸附重金属的效率随土壤 pH 值升高而升高,但同时受生物炭制备温度和土壤阳离子强度的影响。例如,安增莉等[101]在不同温度下制备水稻秸秆生物炭,研究其在不同 pH 值下对 Pb 的吸附特性,结果表明, $pH=3.5$ 时,300 °C 和 400 °C 制备生物炭对 Pb 的吸附量较大($6.82 \text{ mg} \cdot \text{g}^{-1}$ 和 5.90

$\text{mg} \cdot \text{g}^{-1}$), $pH=6$ 和 6.5 时,500 °C 和 600 °C 制备的生物炭吸附量较大($3.57 \text{ mg} \cdot \text{g}^{-1}$ 和 $1.69 \text{ mg} \cdot \text{g}^{-1}$),表明环境 pH 值和制备温度影响水稻秸秆生物炭对 Pb 的吸附效率。此外,梁程等[102]于 500 °C 制备水稻秸秆生物炭,研究其对土壤 Pb 的吸附机制,发现适当提高 pH 可促进生物炭吸附 Pb^{2+} ,当 $pH=6$ 时吸附率可达 92.6%,而较高的 Na^+ 和 Ca^{2+} 离子强度使 Pb^{2+} 吸附率降低,当离子强度由 $10 \text{ mmol} \cdot \text{L}^{-1}$ 增至 $50 \text{ mmol} \cdot \text{L}^{-1}$ 时,吸附率由 97.6% 降至 92.5%,可见提高 pH 值可提高生物炭对 Pb 的吸附率,但较高的阳离子浓度可抑制重金属吸附。董丽佳等[103]研究水稻秸秆生物炭对 Eu^{3+} 的吸附行为和机理时发现,土壤 pH 值对水稻秸秆生物炭吸附 Eu^{3+} 具有重要影响,当 $pH=1.9 \sim 8.4$ 时,随 pH 值升高吸附率由 9% 提高至 97%,并在 $pH=8.4$ 时达到最大吸附量 $40.7 \text{ mg} \cdot \text{kg}^{-1}$,可见生物炭吸附 Eu^{3+} 效率随 pH 值的升高而提高。因此,合适的 pH 值和生物炭制备温度可提高生物炭对重金属的吸附/钝化效率。

3.2 土壤类型

我国土壤类型多样[104],不同土壤对重金属的吸附能力存在差异,如碱性土壤(灰漠土、褐土和黑土等)对 Cd 的吸附量($55.6 \sim 58.8 \text{ mg} \cdot \text{L}^{-1}$)高于酸性土壤(棕壤、黄棕壤和红壤等)($37.2 \sim 54.5 \text{ mg} \cdot \text{L}^{-1}$)[105]。因此,利用生物炭修复重金属污染土壤时需考虑土壤类型对吸附效率的影响。Wang 等[106]以 400 °C 制

备玉米秸秆生物炭修复 Cd 污染红壤和黄棕壤时发现,添加 3% 生物炭后,红壤和黄棕壤 pH 值分别提高 2.71 和 0.83,使红壤和黄棕壤中有效态 Cd 含量分别降低 79.2% 和 49.2%,表明生物炭可通过改变不同类型土壤的理化性质进而影响重金属固定效率。张家康等^[107]研究水稻秸秆生物炭对不同类型土壤中有效态 Cd 含量的影响,结果表明,添加 5% 生物炭使黄壤和水稻土 pH 值分别提高至 5.22 和 7.79,土壤溶液电导率提高至 $590 \mu\text{s}\cdot\text{m}^{-1}$ 和 $916 \mu\text{s}\cdot\text{m}^{-1}$,有机质含量分别为 $5.67 \text{ g}\cdot\text{kg}^{-1}$ 和 $32.8 \text{ g}\cdot\text{kg}^{-1}$,使有效态 Cd 含量分别降低 17.3% 和 56.3%。因此,相较于酸性黄壤,秸秆生物炭对碱性水稻土中 Cd 的钝化效率更高,且与土壤 pH 值、溶液电导率和有机质含量有关。

3.3 生物炭改性方式

为提高生物炭对重金属的吸附效率,通常采用物理、化学过程等对生物炭进行改性。例如,Liu 等^[108]利用水稻秸秆生物炭修复 Zn 污染土壤时发现,生物炭使土壤 pH 值提高 0.7 ~ 2.0,土壤中 Zn^{2+} 溶出量降低 18.4% ~ 36.9%,而 KOH 改性后生物炭比表面积和孔隙体积较未改性分别提高 1.74 倍和 1.68 倍,使 Zn 吸附效率提高 12.6%,表明改性可通过提高生物炭比表面积和孔隙体积进而提高对重金属的吸附效率。何璇等^[109]探究铁改性水稻秸秆生物炭对土壤中 As 吸附效率的影响,发现铁改性水稻秸秆生物炭使土壤中有效态 As 含量降低 63.1%,可归因于改性后生物炭抑制 As^{5+} 向 As^{3+} 的还原,进而降低土壤中 As 的活动性。梁欣冉等^[110]对水稻秸秆生物炭进行锰改性,探究其对 Cd-As 复合污染土壤的修复效率,结果表明,添加 3% 改性生物炭使土壤 Cd 和 As 的毒性淋溶(TCLP)提取态分别降低 75.5% ~ 84.2% 和 43.3% ~ 49.9%,通过降低酸溶态和可还原态 Cd 和 As 含量,增加残渣态 Cd 和 As 含量使其钝化。Li 等^[111]以小麦秸秆为原料制备生物炭并用有机气凝胶进行改性,研究其对铅锌尾矿中多种重金属的钝化效率,发现改性后生物炭 pH 提高,对 Cd^{2+} 、 Pb^{2+} 和 Zn^{2+} 的吸附率较未改性生物炭提高 124%、83.3% 和 109%。综上,生物炭改性后可提高其 pH、比表面积和孔隙体积等进而提高生物炭对重金属的吸附效率。

3.4 重金属种类

秸秆生物炭对 Cd、Pb 和 Cu 等重金属污染土壤具有较好的吸附钝化效果。张华纬等^[112]采集矿区

周边土壤,以 400 °C 制备水稻秸秆生物炭作为修复剂,探究其对 Cd 污染土壤中有效态 Cd(二乙基三胺五乙酸提取态 Cd,DTPA-Cd)含量的影响,发现添加 3% 水稻秸秆生物炭 10 d 后土壤中 DTPA-Cd 含量降低 17.5% 并达到平衡,然而,由于土壤 Cd 总量($31.8 \text{ mg}\cdot\text{kg}^{-1}$)和 DTPA-Cd 含量($25.1 \text{ mg}\cdot\text{kg}^{-1}$)较高,虽通过生物炭可固定土壤 Cd,使玉米地上部 Cd 含量降低 60.6%,但其含量($22.5 \text{ mg}\cdot\text{kg}^{-1}$)仍高于食品安全标准限值($0.1 \text{ mg}\cdot\text{kg}^{-1}$),因此,对于重金属含量严重超标的土壤,可通过生物炭与其他技术联用以保障土壤的种植安全和农作物的食品安全。Wang 等^[113]研究不同生物炭对 Cu 的吸附效果,发现水稻秸秆生物炭对土壤中 Cu 的吸附效率最高,施用量为 $100 \text{ g}\cdot\text{kg}^{-1}$ 时使毛竹根系对 Cu 的吸收降低 35%,显著高于核桃壳等农业废弃物生物炭,表明秸秆生物炭相比其他农林废弃物生物炭具有更好的重金属吸附效果。谢亚萍等^[114]研究水稻生物炭与肥料配施对 Cr 的钝化效果发现,生物炭与氮磷钾复合肥配施后,使土壤 Cr 有效性降低,并使水稻根系对 Cr 的富集系数降低 68.8%,表明生物炭联合其他技术共同修复重金属污染土壤可使修复效率进一步提高。Ali 等^[115]研究水稻秸秆生物炭对 Ni 的吸附效率,发现 Ni 的可交换态随生物炭施用量增加(由 1% 增至 2%)而降低(由 70.9% 降至 59%),促进 Ni 与 Fe/Mn 和碳酸盐结合,形成难溶性稳定复合物,降低 Ni 在土壤中的活动性和迁移性,可见生物炭修复重金属污染土壤效率随施用量增加而提高。

此外,重金属污染土壤一般为多金属复合污染^[116],生物炭通过对多种重金属的吸附、离子交换和氧化还原等,使重金属形成沉淀以降低其迁移性^[117]。周雷等^[118]以水稻秸秆生物炭为土壤吸附/钝化剂研究其修复 Cd-Pb 复合污染土壤效果,通过元素分析和 FTIR 等方法分析得出,添加生物炭后,土壤中 Cd 和 Pb 有效态和酸溶态含量显著降低($47.6 \text{ mg}\cdot\text{kg}^{-1}$ vs. $20.4 \text{ mg}\cdot\text{kg}^{-1}$, $32.9 \text{ mg}\cdot\text{kg}^{-1}$ vs. $15.4 \text{ mg}\cdot\text{kg}^{-1}$; $89.5 \text{ mg}\cdot\text{kg}^{-1}$ vs. $22.73 \text{ mg}\cdot\text{kg}^{-1}$, $36.6 \text{ mg}\cdot\text{kg}^{-1}$ vs. $9.47 \text{ mg}\cdot\text{kg}^{-1}$)。同时,Cd 和 Pb 残渣态含量提高($2.62 \text{ mg}\cdot\text{kg}^{-1}$ vs. $18.7 \text{ mg}\cdot\text{kg}^{-1}$, $10.3 \text{ mg}\cdot\text{kg}^{-1}$ vs. $49.3 \text{ mg}\cdot\text{kg}^{-1}$),使土壤中 Cd 和 Pb 固化稳定化,表明生物炭可通过络合沉淀作用修复 Cd-Pb 复合污染土壤。综上,生物炭对重金属污染土壤的修复包括物理吸附、络合和沉淀等多种机制共同作用,且受重金属种类和含量的影响。

表 3 秸秆生物炭对重金属污染土壤的修复效率
Table 3 Remediation efficiency of straw biochar towards heavy metals-contaminated soils

秸秆类型 Straw type	土壤类型及重金属含量 Soil type and heavy metal content		制备条件 Preparation condition		施用量 (g·kg ⁻¹) Dosage (g·kg ⁻¹)	土壤 pH 值 变化 Soil pH changes	重金属 吸附率/% Adsorption efficiency/%	应用影响因素 Application influencing factors	参考文献 References
	土壤类型 Soil type	重金属种类 Heavy metal	重金属含量 (mg·kg ⁻¹) Heavy metal content/(mg·kg ⁻¹)	温度/℃ Temperature/℃	时间/h Time/h				
水稻土 Paddy soil	-	Zn	38	500	2	4.8 升至 6.3 ~ 6.8 Increase from 4.8 to 6.3 ~ 6.8	18.4 ~ 29	碱性后吸附效率由 18.4% ~ 29% 提高至 26.2% ~ 36.9%, 使有效态 Zn 含量降低 After alkali modification, the adsorption efficiency was increased from 18.4% ~ 29% to 26.2% ~ 36.9% and reduced Zn bioavailability	[108]
	水稻土 Paddy soil	As	141	300	1	7.2 升至 -(文中未提及加入 生物炭后的土壤 pH, 下同) Increase from 7.2 to - (soil pH after biochar application is not mentioned; the same below)	63.1	水稻秸秆生物炭降低 As 还原释放, 铁改性后吸附效率由 110 μg·L ⁻¹ 提 高至 384 μg·L ⁻¹ Rice straw biochar reduced As reduc- tion release and the adsorption efficien- cy was improved from 110 μg·L ⁻¹ to 384 μg·L ⁻¹ after iron modification	[109]
	黄棕壤 Yellow brown soil	Cd	31.8	400	-	4.3 升至 4.5 ~ 5.4 Increase from 4.3 to 4.5 ~ 5.4	17.5	生物炭施用量、土壤 pH 值和有机碳 的提高显著降低 Cd 生物有效性 Increasing biochar application, soil pH value and organic carbon significantly decreased Cd bioavailability	[112]
水稻土 Paddy soil		Pb	527	500	0.5	5.7 升至 6.1 ~ 6.5 Increase from 5.7 to 6.1 ~ 6.5	48.1 ~ 97.9	Pb 吸附率(48.1%、97.9%)随生物炭施 加量升高(1%、5%)而升高 The adsorption of Pb (48.1%, 97.9%) was increased with the increasing bio- char application (1%, 5%)	[119]
	-	Cu	667	500	2	7.16 降至 7.06 Decrease from 7.16 to 7.06	35	生物炭对 Cu 吸附率随 pH 升高(4.01、 4.25、4.33)依次降低(13.6%、6.57%、 4.36%), 故在酸性土壤中效果较好 Biochar-adsorbed Cu (13.6%, 6.57%, 4.36%) was decreased with increasing pH (4.01, 4.25, 4.33), which performs better in acidic soils	[113]

续表3

秸秆类型 Straw type	土壤类型及重金属含量 Soil type and heavy metal content			制备条件 Preparation condition		施用量 (g·kg ⁻¹) Dosage (g·kg ⁻¹)	土壤 pH 值 变化 Soil pH changes	重金属 吸附率/% Adsorption efficiency/%	应用影响因素 Application influencing factors	参考文献 References
	土壤类型 Soil type	重金属种类 Heavy metal	重金属含量 (mg·kg ⁻¹) Heavy metal content/(mg·kg ⁻¹)	温度/℃ Temperature/℃	时间/h Time/h					
水稻秸秆 Rice straw	-	Cu	667	500	2	100	7.16 降至 7.06 Decrease from 7.16 to 7.06	35	生物炭对 Cu 吸附率随 pH 升高(4.01、4.25、4.33)依次降低(13.6%、6.57%、4.36%),故在酸性土壤中效果较好 Biochar-adsorbed Cu (13.6%, 6.57%, 4.36%) was decreased with increasing pH (4.01, 4.25, 4.33), which performs better in acidic soils	[113]
	水稻土 Paddy soil	Cr	67	500	-	-	7.2 升至- Increase from 7.2 to -	14.7	生物炭与氮磷钾复合肥配施提高 Cr 吸附率 Cr adsorption efficiency was improved by combining biochar with N-P-K fertilizer	[114]
	红壤 Red soil	Ni	35	500	2	-	5.3 升至 6.4 Increase from 5.3 to 6.4	59 ~ 70.9	添加生物炭使土壤 pH 值升高 Biochar increased soil pH	[115]
	高山土 Alpine soil	Cd Pb	50 100	500	2	50	7.6 升至 8.4 Increase from 7.6 to 8.4	57.1 74.6	水稻秸秆生物炭 H/C 物质的量比为 0.52,不易降解 The H/C content ratio of rice straw biochar is 0.52, which is not easy to degrade	[118]
	红壤 Red soil	Cd As	4.55 70.1	500	2	30	7.7 降至 7.6 Decrease from 7.7 to 7.6	75.5 ~ 84.2 43.3 ~ 49.9	改性生物炭提高土壤阳离子交换量,促进对 Cd、As 固定 Modified biochar improved cation exchange capacity and promoted Cd and As fixation	[110]
小麦秸秆 Wheat straw	-	Cd	58.3				50	生物炭提高土壤溶解有机物丰度和种类,提高微生物群落多样性和种类 Biochar increased dissolved organic matter abundance and species and increased microbial diversity and species	[111]	
		Pb	3 074	900	2	30	7.4 升至 8.7 Increase from 7.4 to 8.7	94.8		
		Zn	4 234					22.3		
		Co	26	550	2	50	4.6 升至- Increase from 4.6 to -	7.1	表面—OH 和—COOH 促进 Co ²⁺ 络合 Surface —OH and —COOH promote Co ²⁺ complexation	[120]

续表3

秸秆类型 Straw type	土壤类型及重金属含量		制备条件		施用量 /(g·kg ⁻¹) Dosage /(g·kg ⁻¹)	土壤 pH 值 变化 Soil pH changes	重金属 吸附率/% Adsorption efficiency/%	应用影响因素 Application influencing factors	参考文献 References
	Soil type and heavy metal content		Preparation condition						
	土壤类型 Soil type	重金属种类 Heavy metal	重金属含量 /(mg·kg ⁻¹) Heavy metal content/(mg·kg ⁻¹)	温度/℃ Temperature/℃					
玉米秸秆 Corn straw		Hg	675	350	1	20	99.9	ZnCl ₂ 和 S 共改性生物炭稳定化效果 显著高于单独改性生物炭 The stabilization effect of ZnCl ₂ and S co-modified biochar is significantly higher than that of the single modified biochar	[121]
		Hg	4						
	-	Cd	3	400	10	30	10.1		
		Pb	800				11		
						5.4 升至 6.4 ~6.7 Increase from 5.4 to 6.4 ~6.7			[122]
棉花秸秆 Cotton straw	棕壤 Brown soil	Cd	10	650	2	40	57.4	生物炭使土壤 pH 升高, 使土壤可交 换态 Cd 含量降低 Biochar increased soil pH and de- creased exchangeable Cd content in soil	[123]
烟草秸秆 Tobacco straw	-	Cd	5	400	2	4.5	44	生物炭降低土壤可交换态 Cd 含量, 降低 Cd 生物有效性 Biochar reduced Cd exchangeable con- tent and bioavailability	[124]
	褐土 Cinnamon soil	Cd	11.7				52.9	生物炭经纳米羟基磷灰石改性后表 面磷基和羧基官能团数量增加, Cd 和 Cu 钝化效率提高 Phosphorus and carboxyl functional groups on nano-hydroxyapatite modi- fied biochar surface were increased, im- proving the passivation efficiency of Cd and Cu	[125]
	Cu	239	400	2	30	-	53.8		

3.5 田间管理方式

生物炭对重金属的钝化效率易受水分条件等的影响,淹水和干旱过程导致土壤氧化还原反应呈周期性交替变化,影响土壤 pH 值、有机质含量和矿物转化,进而影响重金属的形态分布^[126]。水分条件和生物炭的协同效应与土壤理化性质及生物炭对重金属的吸附能力高度相关。例如,李富荣等^[127]研究水作和旱作栽培方式下,水稻秸秆生物炭对土壤中有有效态 Cd 和 Pb 含量的影响,发现施用 6 g·kg⁻¹ 生物炭后水作和旱作土壤 pH 值分别提高 0.3 和 0.1,有机质含量提高 68.9% 和 45.9%,从而使水作和旱作土壤中有有效态 Cd、Pb 含量分别降低 7.05%、6.4% 和 6.55%、6.2%,表明施用生物炭对水作条件下土壤中 Cd 和 Pb 的钝化效率更高。汤家庆等^[128]研究淹水和干湿交替条件下水稻秸秆生物炭对 Cd-Pb 复合污染钝化效率的影响,发现施用 1% 水稻秸秆生物炭后,淹水和干湿交替条件下土壤 pH 值分别提高 1.09 和 1.04,可溶性有机碳分别提高 19.8% 和 31.5%,淹水和干湿交替条件下毒性淋溶(TCLP)提取态 Cd、Pb 含量分别降低 25.4%、31.9% 和 16.1%、20.3%,表明生物炭可通过提高土壤 pH 值和可溶性有机碳实现 Pb 和 Cd 的有效钝化,且对淹水条件下 Cd、Pb 钝化效率更高。因此,生物炭对重金属污染土壤的修复效率受田间管理方式的影响,且在淹水条件下对重金属的钝化效率较高。

4 结论与展望 (Conclusions and prospects)

由于经济性和原料丰富易得,秸秆被广泛用作生物炭制备原料。本文基于秸秆生物炭原料类型的选择、制备技术和改性方法,总结了生物炭修复重金属污染土壤的机制及其实际应用效率与影响因素。分析得出:利用慢速热裂解制备秸秆生物炭可安全有效吸附土壤重金属;秸秆生物炭吸附重金属效率随制备温度升高而提高,但温度过高可抑制其吸附性能;秸秆生物炭改性后可进一步提高其吸附性能;秸秆生物炭主要通过络合和沉淀作用吸附固定重金属,该过程受其表面官能团种类和含量影响。

虽然秸秆生物炭在重金属污染土壤治理方面具有良好的应用前景,但目前研究仍存在一定局限性。为提高秸秆生物炭修复重金属污染土壤效率,未来可加强以下方面研究:(1)目前研究大多停留在生物炭修复单种重金属污染土壤,对复合重金属污染土壤修复效率及是否受共存元素(其他重金属和无机盐离子)影响有待深究;(2)秸秆生物炭具有多环芳

烃、Pb 和 As 等有毒有害物质,施加后生物炭与土壤难以分离,随土壤环境变化和时间延长,其本身含有的毒害物质和吸附固定的重金属是否会释放到环境中,即是否会产生二次释放及影响二次释放的关键环境因子值得研究;(3)秸秆生物炭多用来修复酸性和中性污染土壤,修复碱性污染土壤研究较少,因此需加深秸秆生物炭修复碱性污染土壤的作用机理及效率的研究。

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