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土壤中铬价态转化的影响因素与作用机制研究进展

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摘要: 土壤中铬(Cr)污染是全球性环境问题, 六价铬 Cr(VI) 因其高毒性及致癌性而成为关注焦点。土壤中的 Cr 主要以 Cr(III) 和 Cr(VI) 的形式存在, 两者之间的转化受到诸如土壤 pH 值、氧化还原电位(Eh)、天然氧化还原剂、有机质和微生物的影响。随着工农业活动的增多, 土壤中的 Cr 浓度不断增加, 并通过植物吸收进入食物链等多种途径, 对生态系统和人体健康构成威胁。本文对 Cr 在全球范围内的污染现状及来源、土壤中 Cr 的不同价态及其毒性特征进行了评述, 并分析了 pH、Eh 对土壤中 Cr 的具体存在形态与价态的影响, 及天然氧化还原剂、有机质等因素利用自身化学性质充当电子供体或受体的角色对土壤中 Cr 价态进行转化的氧化还原机理, 以及不同影响因素之间的相互作用关系, 从而可以全面理解土壤中 Cr 价态转化的行为机制。此外, 在对 Cr 价态影响因素深入了解的基础上, 总结了以生物炭和纳米材料为代表的先进修复技术方法, 这些材料和方法由于能够将 Cr(VI) 有效地还原为毒性较小的 Cr(III), 从而降低生态环境风险, 因而是一类具有巨大潜在应用价值的修复材料和修复方法, 但大规模应用的可行性及其修复效果仍需要进一步验证。

关键词: Cr 污染; Cr 价态; 天然氧化还原剂; 有机质; 修复技术

要点:

- (1) 土壤中的 Cr(VI) 主要以铬酸盐(CrO_4^{2-})、氢铬酸盐(HCrO_4^-)和重铬酸盐($\text{Cr}_2\text{O}_7^{2-}$)等氧化离子的形式存在, 是土壤中毒性最大的 Cr 价态。
- (2) 土壤中 Cr 价态受 Eh、有机质等多种因素影响, 这些因素可以促进或抑制 Cr(VI) 的还原。
- (3) 生物炭和纳米材料等新型修复技术能够将 Cr(VI) 有效地还原为低毒性的 Cr(III), 是治理 Cr(VI) 污染的一种可行技术方案。

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铬(Cr)属于天然存在的过渡元素, 是一种显著影响土壤环境的潜在有毒重金属, 随着人类活动的加剧, 土壤中 Cr 的浓度在不断上升^[1-3], 植物对 Cr 的吸收也随之增加, 从而导致人类通过食物链摄入的 Cr 也会增多, 此外, 人类还会通过吸入和皮肤接触等方式摄入环境中的 Cr, 当 Cr 在人体内积累到

一定水平时, 会对人体健康产生严重影响^[4-6]。随着土壤中 Cr 浓度的增加, Cr 造成的土壤环境污染问题已经引起了广泛的关注。

Cr 在自然界中有 Cr(II) 到 Cr(VI) 等多种价态^[7], 在土壤中主要以 Cr(III) 和 Cr(VI) 的价态存在。这两种价态的 Cr 具有不同的毒理学特征, Cr(VI) 比

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Cr(Ⅲ) 更具危险性, 毒性更高^[8], 可造成 DNA 突变和染色体损失^[9], 已被确认为致癌和致突变物质^[10]。土壤中的 Cr(Ⅲ) 和 Cr(VI) 会受到土壤酸碱度 (pH)、氧化还原电位 (Eh)、天然氧化还原剂、有机质、微生物的作用, 从而发生相互转化^[11-16]。这些因素在 Cr 价态转化的过程中也存在复杂的相互作用。

对于受 Cr 污染的土壤, 通常将 Cr(VI) 还原为 Cr(Ⅲ)^[17], 以降低其毒性, 从而获得更好的环境效益。生物炭作为一种有机质, 由于其丰富的官能团, 可实现土壤中 Cr(VI) 的还原, 被作为修复 Cr(VI) 污染土壤的优先选择^[18]。除此之外, 纳米材料也常搭配生物炭, 用于修复 Cr(VI) 污染的土壤。

由于不同价态的 Cr 在毒性和化学行为上存在显著差异, 本文阐述了国内外土壤中 Cr 污染现状、主要来源以及土壤中不同价态 Cr 的毒性, 总结了关于土壤 pH、Eh、天然氧化还原剂、有机质、微生物对土壤中 Cr 价态转变的作用机制以及不同因素之间的相互作用关系, 并在此基础上探讨了 Cr 污染土壤绿色经济的新型修复方法。

1 国内外土壤中 Cr 的污染现状

随着全球工业化的迅速发展, 土壤 Cr 污染已成为一个国际性问题。由表 1 可知, 不同国家位于工业区附近的土壤样品出现了不同程度的总 Cr 或 Cr(VI) 污染情况, 有的甚至造成了地下水污染。中国关于工业区土壤的 Cr 污染现象值得关注, 具体数据显示, 中国工业用地中总 Cr 浓度跨度极大, 从 0.74 ~ 37967.33mg/kg 不等, 其中 4.15% 的土壤样本

Cr 含量超标 (筛选参考值为 2500mg/kg)^[25]。在 2002—2009 年期间, 工业区土壤中总 Cr 浓度整体呈上升趋势, 而在 2009—2021 年间则有所下降^[25], 重污染地区主要集中在中国东部的长三角、环渤海地区、南部的珠三角, 以及沿长江和黄河的流域, 包括浙江省^[26]、安徽省^[27]和黑龙江省^[28]等工业密集区域。与此同时, 中国农田土壤中总 Cr 的浓度范围为 1.48 ~ 820.24mg/kg, 其中大约有 4.31% 和 0.12% 监测点的 Cr 浓度分别超过了中国《土壤环境质量标准》(GB15618—2018) 筛选值 (150mg/kg) 和控制值 (800mg/kg)。值得注意的是, 2011—2016 年, 农业土壤中总 Cr 的累积速率相对减缓, 这可能是由于中国政府采取了一系列措施调整产业结构, 并严格限制了工业废料的排放, 从而有效地缓解了农业土壤中 Cr 污染的程度^[29]。

2 土壤中 Cr 的来源

自然活动会为土壤带来重金属 Cr。土壤中 Cr 的浓度增加通常与自然界中某些类型的岩石有关, 例如蛇纹岩、玄武岩及花岗岩等, 这些岩石中的 Cr 浓度分别可达大约 2400mg/kg、200mg/kg 和 10mg/kg。同时, 由于风化作用会导致岩石中 Mg 等可溶性元素元素的浸出和流失, 而 Cr 和 Fe 等较难溶解的元素则留在土壤中, 从而导致土壤中 Cr 的浓度升高 (平均浓度达到了 2650mg/kg)。此外, 富含 Cr₂O₃ 的矿物, 如铬铁矿 (Cr 含量大于 35%) 和磁铁矿 (Cr 含量小于 15%), 也是土壤中 Cr 的重要来源^[30-31]。其他自然活动, 如火山喷发也会给土壤引入新的 Cr, 例如

表 1 不同国家土壤 Cr 污染现状

Table 1 Current situation of Cr pollution in different countries.

研究场地	Cr(Ⅲ) 含量 (mg/kg)	Cr(VI) 含量 (mg/kg)	总 Cr 含量 (mg/kg)	对照标准	是否污染 地下水
埃塞俄比亚某制革厂周边 污染区域土壤 ^[19]	791.5 ~ 1811.4	0.621 ~ 0.973	792.47 ~ 1812.21	制革厂 90 公里外某处未受污染土壤 样品: Cr(Ⅲ) 浓度 0.18mg/kg, Cr(VI) 未检出, 总 Cr 浓度 0.18mg/kg	是
意大利南部一处往年被长期非法 掩埋皮革工业废物的农田 ^[20]	—	0.15 ~ 11.18	48 ~ 6831	意大利议会制定的关于土壤中 Cr(VI) 筛选值 2mg/kg, 总 Cr 筛选值 150mg/kg	未评估
中国重庆某铬盐生产场地 遗留旧址 ^[21]	—	168.8 ~ 203.4	—	《土壤环境质量标准》 (GB 36600—2018) 限值 5.7mg/kg	未评估
中国天津原同生化工厂残渣垃圾 堆放场地及周边表层土壤 ^[22]	—	—	8571.4 ~ 10711.4	《土壤环境质量标准》 (GB 15618—2018) 限值 250mg/kg	是
中国宁夏回族自治区某煤化 化工厂周边土壤 ^[23]	—	6.480 ~ 11.750	73.800 ~ 107.080 ^[24]	中国土壤 Cr(VI) 背景值 6.100mg/kg; 宁夏土壤 Cr(VI) 背景值 6.000mg/kg	未评估

注: “—”表示数据缺失。

1991年菲律宾皮纳图博火山喷发,释放了大约 5.5km^3 的火山灰,为土壤环境带来约55万吨Cr^[32]。

工业生产是土壤中Cr的主要人为来源之一^[33]。随着现代工业的发展,Cr在土壤中的浓度不断积累和上升^[1]。铬铁作为一种重要的合金,是由铬铁矿($\text{FeO}\cdot\text{Cr}_2\text{O}_3$)通过高温还原法制备的,在这个过程中不仅产生铬铁合金,还会生成大量含Cr的炉渣和高浓度Cr粉尘。这些炉渣含有2%~12%的以氧化物和金属形式存在的Cr,由于炉渣经常被随意废弃,导致Cr浸出进入土壤。铬铁粉尘中可浸出Cr(VI)浓度超过多个国家饮用水中Cr(VI)的标准限值(0.05mg/L)^[34]。此外,制革工业通常可以产生多达 75000m^3 的含Cr废水(Cr含量为 $2000\sim 5000\text{mg/L}$),远超世界卫生组织对于工业废水中Cr含量的规定值(2.0mg/L),这些未经妥善处理的含Cr废水一旦排入环境中,将对土壤产生严重污染^[35]。

农业活动中使用的农药和化肥也会造成土壤Cr污染^[36]。例如,一些落叶剂的有效成分中含有重铬酸钠($\text{Na}_2\text{Cr}_2\text{O}_7$),可能会在过量使用的情况下造成土壤Cr(VI)污染^[3]。此外,磷肥是农业活动中重金属污染的另一个主要来源,例如过磷酸钙肥料中含有Cd、Cu、Cr等多种重金属。据估测,每公顷土壤每年施用 20kg 磷肥可引入约 25g 的Cr^[37]。

3 土壤中Cr的主要存在价态与毒性

Cr是自然界中价态较为丰富的金属元素之一,在土壤环境中主要以Cr(III)和Cr(VI)两种形式存在,这两种形式因其化学性质差异大而展现出不同的生态毒理学特征,Cr(VI)以其显著的毒性成为环境科学关注的重点。

3.1 土壤中Cr的主要存在价态

在过去的多项研究中,土壤中的Cr根据其在固体颗粒中的赋存状态,通常被划分为酸溶态、可氧化态、残渣态等几种形态,以此来评估其潜在的毒性和生态风险^[38-39]。然而,Cr的环境行为与其氧化态密切相关,因此,明确土壤中Cr的具体价态及其各自的毒性相比研究其物理形态更加关键。尽管Cr有多种存在价态——Cr(II)到Cr(VI),但在土壤环境中,Cr(III)和Cr(VI)是最普遍和稳定的价态,其他价态如Cr(IV)和Cr(V),通常是Cr(III)和Cr(VI)氧化还原过程中的中间产物。土壤中的Cr(III)主要以铬铁矿($\text{FeO}\cdot\text{Cr}_2\text{O}_3$)、氢氧化铬 $[\text{Cr}(\text{OH})_3]$ 或氧化铬(Cr_2O_3)的形态存在,具有较低的毒性和迁移性;而土壤中的Cr(VI)主要以铬酸盐(CrO_4^{2-})、氢铬酸盐

(HCrO_4^-)和重铬酸盐($\text{Cr}_2\text{O}_7^{2-}$)等氧化离子的形式存在,毒性和迁移性较高^[40]。

3.2 Cr(III)的毒性与危害

Cr(III)在自然环境中的生态毒性较为复杂。对于植物而言,Cr(III)没有已知的基本营养功能,在低浓度Cr(III)存在的环境下植物也可以正常生存,不会对其生长构成直接威胁。而在动物体内,尤其是哺乳动物中,Cr(III)作为一种微量营养元素参与脂类和糖类的代谢过程^[41]。世界卫生组织推荐的人体每日Cr(III)的理想摄入量为 $50\sim 200\mu\text{g}$,过量摄入可能对生物体造成损害^[1],这是因为Cr(III)虽然不能轻易穿过细胞膜,但可积聚在细胞周围,破坏细胞膜脂质,改变细胞表面形态,进而破坏细胞的完整性和正常功能^[35]。不过,相比于Cr(VI),Cr(III)的毒性要低得多。

3.3 Cr(VI)的毒性与危害

Cr(VI)是土壤中毒性最高的Cr价态,它不仅对植物生长造成严重影响,还对动物和人体健康构成重大威胁。作为一种强氧化剂,Cr(VI)可溶于水并穿透细菌和真核细胞的细胞膜,其毒性可达Cr(III)的 $10\sim 100$ 倍。当土壤中Cr(VI)浓度超过 5mg/kg 时,便对植物产生严重危害^[42],会降低种子萌发率,阻碍蛋白质和核酸合成,并引发植物细胞膜过氧化反应^[43],导致植物不同器官超微结构畸形和叶肉细胞损伤,甚者造成植物的死亡^[44]。对于人类而言,Cr(VI)可通过硫酸盐和磷酸盐离子通道进入细胞内部,经还原形成Cr(V)、Cr(IV)等一系列中间产物,这些中间产物会攻击细胞和其他重要生物分析,诱导活性氧(ROS)的生成,如超氧化物(O_2^-)、过氧化氢(H_2O_2)和羟基自由基($\cdot\text{OH}$)等,进而引发细胞损伤甚至癌变,是A类致癌物之一^[45]。此外,Cr(VI)还能在母体胎盘组织中积累,造成氧化应激,增加细胞凋亡,影响胎儿发育,导致新生儿出现各种健康问题,如呼吸困难、黄疸及其他先天性疾病^[46]。

4 土壤中Cr价态的影响因素

Cr(III)和Cr(VI)是土壤中最常见的两种Cr价态,其中,Cr(VI)因其较高的毒性及较强的迁移性而成为环境修复的重点对象。Cr(VI)向Cr(III)的转变不仅降低了Cr的环境风险,还减少了其在生态系统中的迁移性。这一转化过程受到多种因素的影响,包括土壤pH、Eh、天然氧化还原剂、有机质以及微生物活动等^[47]。

4.1 土壤 pH 和 Eh 对土壤 Cr 形态和价态的影响

土壤 pH 和 Eh 作为土壤的基础理化特性,直接影响土壤中 Cr 的存在形态与价态转化过程。

4.1.1 土壤 pH 对土壤 Cr 形态的影响

由于 H^+ 和 OH^- 离子浓度不同,决定了 Cr(III) 在不同的 pH 区间呈现出不同的存在形态^[48]。在 pH 0~4 的酸性条件下, Cr(III) 倾向于与氨、硫酸盐、尿素、水以及有机酸等形成各种不溶的六配位复合物。当 pH 值升高至 4~6 时, Cr(III) 会形成诸如 $Cr(OH)_2^+$ 、 $Cr(OH)_2^{2+}$ 以及 $Cr(OH)_3$ 等水解产物,这些产物不易溶解,并且对有机物质表现出一定的亲和力。若进一步提高 pH 值,当 $pH > 6$ 时, Cr(III) 会形成稳定的 $Cr(OH)_3$ 沉淀。而当 pH 值继续上升至 9 以上, $Cr(OH)_3$ 沉淀则会转变为可溶的 $Cr(OH)_4^-$ 络合物^[49]。

对于 Cr(VI), 其形态同样受到 pH 值的严格控制。当 pH 值在 6.5~12 之间时, Cr(VI) 主要以 CrO_4^{2-} 的形式存在; 而 pH 值在 0.7~6.5 之间时, Cr(VI) 则表现为 $Cr_2O_7^{2-}$ 和 $HCrO_4^-$ 的形式; 当 $pH < 0.7$ 时, Cr(VI) 将以 H_2CrO_4 的形式出现^[49]。

4.1.2 土壤 Eh 对土壤 Cr 价态的影响

土壤 Eh 是衡量其提供或接受电子能力的一个重要指标,它直接影响着土壤的氧化还原状态,进而影响 Cr 的价态^[50]。通常情况下,土壤中的氧化过程在高 Eh 条件下占据主导地位,而还原过程则在低 Eh 条件下更加活跃。随着土壤 Eh 值的降低,还原性条件得以增强,从而促进 Cr(VI) 向 Cr(III) 的转化。这种转化导致 Cr(VI) 的浓度减少,通过还原形成的 Cr(III) 往往以铬酸盐的形式被土壤胶体所固定。例如,在热带地区高度风化的 Oxisols 类型土壤中,实施了连续淹水处理,使得土壤表面保持 3cm 深的水位。在这种条件下,土壤的 Eh 值从 342mV 降至 -370mV,土壤呈现出强烈的还原性特征。观察发现,随着灌溉周期的延长,土壤中 Cr(VI) 浓度显著下降。经过 114 天的处理后, Cr(VI) 浓度减少了约 46%。这表明,在持续的还原条件下, Cr(VI) 可以被有效地还原为 Cr(III)。相比之下,采用 2~3 天灌溉周期且水位保持在土壤表面以上 0~2cm 处的干湿交替处理,则显示出不同的结果。在这种处理方式下,土壤的 Eh 值在每次淹水后迅速下降,而在下次灌溉前随着土壤的干燥而逐渐回升, Eh 值范围在 -291~142mV 之间变化,因此,土壤在还原状态与氧化状态之间不断切换,导致 Cr(VI) 的浓度随灌溉周期的变化而呈现出下降的趋势,然后又因氧化条件的恢复其浓度升高^[51]。

以上实例清晰地表明,土壤 Eh 可以影响土壤中 Cr 的存在价态,在还原性条件下, Cr(VI) 更容易被还原为毒性较低的 Cr(III),而在氧化条件下, Cr(III) 可能会被重新氧化为 Cr(VI)。因此,理解和调控土壤的氧化还原状态是有效地管理 Cr 污染土壤的关键策略之一。

4.1.3 土壤中的天然氧化还原剂对土壤 Cr 价态的影响

土壤中的天然氧化还原剂,如锰氧化物 (MnO_x)、过氧化氢 (H_2O_2) 等,都具有一定的氧化或还原特性,能够与土壤中的 Cr 发生一系列复杂的氧化还原反应^[52]。

锰氧化物被认为是土壤中一种主要的天然氧化剂,各种类型的锰氧化物均具有显著氧化 Cr(III) 的能力,特别是在土壤的好氧区,各类锰氧化物主导了 Cr(III) 的氧化过程。锰氧化物可以通过溶解氧化、催化氧化和吸附氧化的方式将 Cr(III) 氧化为 Cr(VI)。具体而言,在酸性条件下 ($pH < 6.0$), 溶解氧化占据了主导地位;而在碱性条件下 ($pH > 8.0$), 吸附氧化和催化氧化则更加显著^[53]。这种氧化作用有助于提高土壤中 Cr(VI) 的比例,从而增加 Cr(VI) 的迁移性和毒性。

土壤中的过氧化氢 (H_2O_2) 在酸性条件下 ($pH < 7.5$) 表现出还原性,特别是在 $pH < 3$ 时, H_2O_2 可以还原土壤中的 Cr(VI)。然而,在碱性条件下 ($pH > 7.5$), H_2O_2 不仅能够直接地氧化 Cr(III), 还能在氧化 Mn^{2+} 的过程中生成 Mn^{3+} 和羟基自由基 ($\cdot OH$)。 Mn^{3+} 和 $\cdot OH$ 均具有较强的氧化能力,能够进一步将 Cr(III) 氧化为 Cr(VI)。这种机制促进了 Cr(VI) 的生成,从而提高了 Cr 在土壤中的毒性^[53]。

在富含 Fe 的土壤中,由于风化作用,表层土壤中的 Fe 主要以 Fe^{3+} 的形式存在。在太阳光的照射下, Fe^{3+} 可以被还原为 Fe^{2+} , 并参与 Cr(VI) 的还原过程。然而,对于普通土壤而言, Fe^{2+} 在好氧环境中较为罕见,因此其对 Cr(VI) 的还原作用较小^[54], 这意味着在普通土壤中, Cr(VI) 的还原可能更多地依赖于有机质或微生物的生化反应^[55]。此外,土壤中的 $Fe(OH)_2^+$ 在 pH 2.5~5.5 酸性条件下通过光解能够产生大量的羟基自由基 ($\cdot OH$), 这些羟基自由基能够直接氧化 Cr(III), 促使其转变为 Cr(VI)。然而,在高 pH 值条件下, $Fe(OH)_2^+$ 光解过程中生成的 Fe^{2+} 能够迅速还原 Cr(VI), 从而降低 Cr(VI) 的浓度。

通过这些机制可以发现,土壤中的天然氧化还原剂在调节 Cr 的价态方面发挥着重要作用。了解

这些过程有助于人们更好地理解 Cr 在土壤中的行为模式,并为开发有效的 Cr 污染治理策略提供科学依据。

4.2 有机质对土壤 Cr 价态的影响

有机质 (OM) 是土壤的关键组成成分,具有复杂的化学性质,土壤有机质在 Cr 价态转化中发挥着重要作用。如图 1 所示,有机质基于“吸附-还原-络合”机理,可将土壤中毒性较大的 Cr(VI) 还原为毒性较小的 Cr(III),并形成稳定的络合物^[56-58],因此目前也被作为修复受 Cr 污染土壤的有效方法之一。此外,有机质还影响着微生物对 Cr(VI) 的还原过程。然而,有机质与 Cr(III) 形成的络合物毒性如何,是否比游离的 Cr(III) 毒性更小,还有待进一步验证。

4.2.1 有机质对 Cr 价态的影响与机理

土壤中的有机质作为一种重要的电子供体,可以直接还原 Cr(VI)。其对 Cr(VI) 的还原通常遵循“吸附—还原—络合”机制^[59]。首先,Cr(VI) 通过静电吸附或离子交换吸附在有机质表面;接着,有机质利用羟基 (—OH) 等官能团完成对 Cr(VI) 的还原;最后,还原生成的 Cr(III) 通过羰基 (—C=O) 等官能团进行络合作用,形成稳定的配合物并保留在其表面^[60-61]。具体来说,有机质中的苯酚和羟基是还原 Cr(VI) 的主要电子供体 (如图 2 所示)^[62],而羧基和羰基则更可能参与 Cr 的络合。例如,土壤中普遍存在的腐植酸 (HA) 和胡敏酸 (HM) 在还原 Cr(VI) 的过程中,利用傅里叶变换红外光谱 (FTIR) 分析发现,在 1708、1626、1226 和 1078 cm^{-1} 处的吸光度峰随着时间的推移而显著下降,这些峰分别对应羧基的 C=O 拉伸振动、羰基的 C=O 拉伸振动、苯

酚的 C—O 拉伸振动和羟基的 C—O 拉伸振动。进一步利用 X 射线光电子能谱 (XPS) 分析表明,在 286.1eV 处的峰代表为 C—O,在与 Cr(VI) 反应 60 天后,腐植酸和胡敏酸表面苯酚和羟基官能团中的 C—O 几乎消失,而其他官能团则保持相对不变^[63]。

除了作为直接的电子供体,有机质还能作为电子穿梭体间接地还原 Cr(VI)。例如,乳酸虽然其本身作为电子供体单独还原 Cr(VI) 的效果不佳,但与生物炭共同存在时,生物炭中的含氧官能团 (如羰基) 起到“电子载体”的作用,增强了乳酸与 Cr(VI) 间的电子传递,使得两者共存时的还原效率显著提高 (分别是单独使用乳酸和生物炭的 345 倍和 16.3 倍),这表明生物炭作为电子穿梭体的作用比作为电子供体的作用更为显著^[64]。此外,磁性灰长石 (Fe_3S_4) 改性的生物炭产生的以碳为中心原子的持久性自由基 (EPFRs) 也可作为电子穿梭体,促进 Fe(III)/Fe(II) 循环,进而利用 Fe(II) 还原 Cr(VI) (如图 3 所示)^[65-66]。由于有机质的电子穿梭性质,它还可用作稳定剂,间接地提升土壤中 Fe 对 Cr(VI) 的化学还原效率^[67-68]。例如,在利用 FeSO_4 还原 Cr(VI) 时,当 FeSO_4 用量为理论值的 2.5 倍,玉米秸秆改性的生物炭添加量为 8%,水土比为 50%,土壤停留 7 天后,Cr(VI) 含量从 1000.00 mg/kg 降至 18.909 mg/kg ^[17]。

此外,有机质因其光敏特性^[69],亦可通过光催化途径还原土壤中的 Cr(VI)。在紫外光照射下,有机质 (OM) 会促进持久性自由基 (EPFRs) 的生成 (如图 4 所示)^[70],这些自由基将电子转移给 O_2 ,生成 $\text{O}_2^{\cdot-}$,从而将 Cr(VI) 还原为 Cr(III)^[71-72]。Zn Fe_2O_4 改性的生物炭含有的 B—H 基团同样有助于光催化

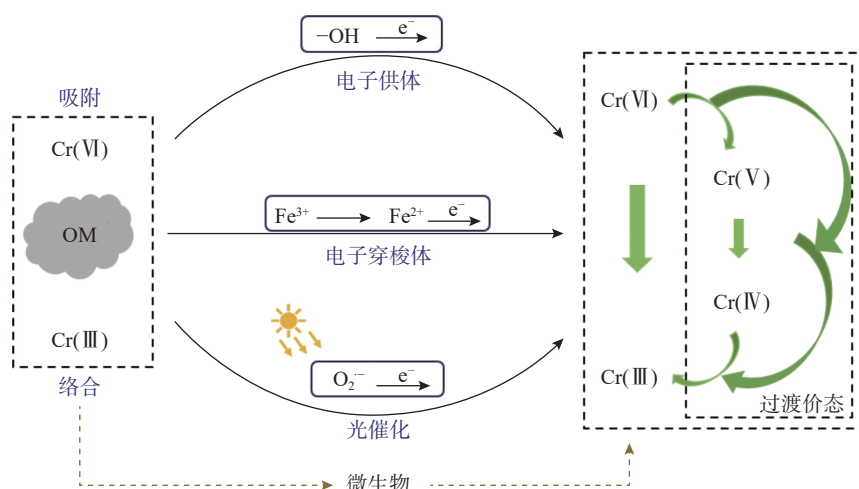


图1 土壤中的有机质对 Cr 的“吸附—还原—络合”机理

Fig. 1 The mechanism of “adsorption—reduction—complexation” of Cr by organic matter in soil.

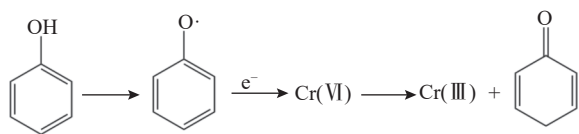


图2 酚羟基对 Cr(VI) 的还原作用

Fig. 2 The reduction effect of phenolic hydroxyl groups on Cr(VI).

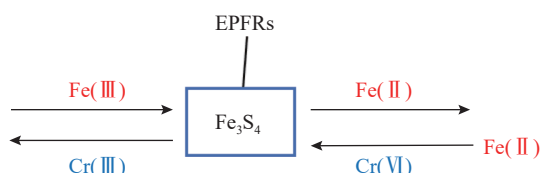


图3 Fe(III)/Fe(II) 通过 Fe_3S_4 改性的生物炭完成对 Cr(VI) 的还原

Fig. 3 The reduction of Cr(VI) by Fe(III)/Fe(II) modified biochar with Fe_3S_4 .

过程中电子的供给,实现 Cr(VI) 的还原^[73]。有机质还可以作为提高光催化剂性能的优良载体^[74]。例如,将钨酸铋 (Bi_2WO_6) 负载到尿素改性的生物炭上,可改变生物炭的导电性,提高光电生成的电子空穴对在可见光激发下的分离和迁移,加快光生电子向 Cr(VI) 的转移,从而提高 Cr(VI) 的还原效率^[75]。在传统光催化剂二氧化钛 (TiO_2) 中添加 10%(质量分数) 的红枣籽衍生生物炭制备新型光催化剂,并加入 2.5mmol/L 柠檬酸,结果显示,在光照 25min 后 Cr(VI) 的还原效率提升至 94.7%,而纯 TiO_2 的转化率仅为 72.10%,其中柠檬酸在防止 Cr(III) 向 Cr(VI) 的再氧化过程中起到了关键作用^[76]。

4.2.2 有机质对 Cr 生物还原的影响

土壤中的微生物种类繁多,能够通过直接或间接的途径还原土壤中的 Cr(VI)。直接途径主要依靠铬酸盐还原酶的作用,而间接途径则是通过微生物代谢产生的还原物质,如硫化氢 (H_2S) 和 Fe^{2+} , 来还

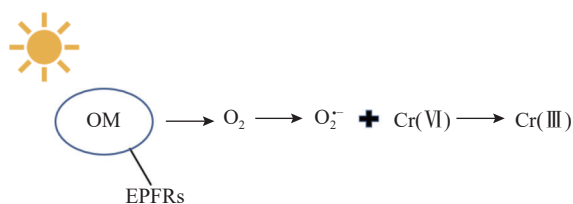


图4 有机质 (OM) 中的持久性自由基在光照条件下对 Cr(VI) 的还原作用

Fig. 4 The reduction effect of persistent free radicals in organic matter (OM) on Cr(VI) under light conditions.

原 Cr(VI)^[52]。微生物在自然环境中广泛存在,由于其生长条件易于控制且具有快速修复环境污染的能力,不会对环境造成二次污染,因此被认为是治理环境污染的有效手段之一。一些长期生活在含 Cr 环境中的细菌、真菌等微生物对 Cr(VI) 的修复更为有效^[77],如铜绿假单胞菌^[78]、金黄色葡萄球菌^[79]和阴沟球菌^[80]等都可以实现 Cr(VI) 的还原,从而被应用于环境修复治理中。

微生物对 Cr(VI) 的还原过程会受到土壤有机质的影响。有机质能够改变土壤中微生物的丰度^[81],优化群落结构^[82],还可以提高微生物对 Cr(VI) 的还原效率。例如,葡萄糖、果糖、乳糖等有机质是 Cr(VI) 生物还原过程中常用的电子供体,这些电子供体的加入可以提高异养微生物可溶性还原酶的活性,从而加速 Cr(VI) 的生物还原^[83]。例如,腐臭链球菌 CN32(*S. putrefaciens* CN32) 作为一种能够还原 Cr(VI) 的菌种,在土壤腐殖质存在的情况下,能够利用腐殖质作为电子供体,实现微生物对 Cr(VI) 的有效还原^[84]。此外,蜡样芽孢杆菌 WHX-1 在浒苔制成的生物炭存在的情况下,其对 Cr(VI) 的还原活性也得到了显著提升^[85]。研究表明,当添加 2mg/L 腐植酸时,嗜水杆菌 ATCC 7966 对 Cr(VI) 的还原速度明显加快,比对照组提高了 338%^[86]。

因此,更多的学者选择在土壤中加入活性炭、海藻酸钠等有机质,以促进微生物的代谢,提高生物降解效率^[87]。有机质的存在不仅为微生物提供了必要的营养物质和电子供体,还优化了微生物的生存环境,从而增强了微生物对 Cr(VI) 的还原能力。通过这种方式,有机质成为促进微生物活性、提高 Cr(VI) 生物还原效率的重要因素之一。

4.2.3 有机质对 Cr 价态转化的影响因素

有机质作为土壤中影响 Cr 价态的重要因素之一,在其还原 Cr(VI) 的过程中,会受到土壤 pH 值、铁氧化物等因素的影响。

(1) 土壤 pH 值

有机质在酸性条件下对 Cr(VI) 的吸附效果更好。这是因为,在酸性条件下,土壤中的 Cr(VI) 主要以 HCrO_4^- 的形式存在,其吸附自由能较低^[88]。同时,有机质在酸性条件下表面具有更多的 H^+ ,发生高度质子化,有利于通过静电力吸附阴离子,增强对 HCrO_4^- 的静电吸引力^[89]。而在碱性环境下,Cr(VI) 以 CrO_4^{2-} 的形式存在,由于 OH^- 的浓度较高,有机质表面的负电荷增加,导致有机质表面的活性位点与 CrO_4^{2-} 之间产生静电斥力^[90]。

此外, 有机质对 Cr(VI) 的还原速率随着 pH 值的降低而增加。在 pH 值较低条件下, 带正电的生物质表面减少了 OH⁻阴离子的竞争性吸附, 并且 H⁺的增加可以通过中和 Cr(VI) 和有机质之间的负电荷来增强它们之间的键合^[91]。例如, 在利用纳米零价铁辅助生物炭去除 Cr(VI) 的过程中, 随着 pH 值从 2 增加至 8, Cr(VI) 的去除率由 99.8% 下降至 60.2%, 再次证明了在酸性条件下有机质对 Cr(VI) 的还原效果更佳^[92]。

土壤中有有机质与 Cr(III) 的络合在不同 pH 条件下也有所不同。单体络合物普遍存在于 pH 值较低的酸性有机土壤中, 而在 pH 值较高的碱性有机土壤中, 主要是以二聚体或四聚体组成的多核络合物为主^[93]。

(2) 铁氧化物

铁氧化物的存在对有机质还原 Cr(VI) 的过程有两方面的影响。一方面, 铁氧化物的存在可能会抑制有机质对 Cr(VI) 的还原速率。当外源电子穿梭体蒽醌-2, 6-二磺酸盐 (AQDS) 存在时, 腐殖质对 Cr(VI) 的还原程度增强^[94]。然而, 在 AH₂DS(AQDS 的还原形态) 与铁氢氧化物 [如针铁矿, α-FeO(OH)] 共同存在的情况下, Cr(VI) 的还原会受到抑制。当两者比例为 1 : 1 时, 抑制效果最为明显, 这可能是由于在 Fe³⁺的还原过程中产生了半醌自由基, 导致 AH₂DS 与 AQDS 之间的交叉反应迅速发生, 从而减少了 AH₂DS 与 Fe³⁺和 Cr(VI) 之间的电子转移, 降低了 Cr(III) 的产率^[95]。此外, 在中性 pH 的条件下, 零价铁存在时, 腐植酸不与 Cr(VI) 发生相互作用, 这可能是由于 Cr(VI) 与零价铁之间发生了快速反应^[96]。

另一方面, 铁氧化物也可能促进有机质对 Cr(VI) 的还原速率。例如, 腐殖质在酸性条件下还原 Cr(VI) 时, 会先将 Fe³⁺还原为 Fe²⁺, 再利用 Fe²⁺还原 Cr(VI)。腐殖质还原 Cr(VI) 的速度在 pH≈2 时相对较慢, 而 Fe²⁺还原 Cr(VI) 的速度很快, 可以在不到 5min 的时间内完成^[97]。

(3) 有机质种类和初始 Cr(VI) 浓度

有机质对 Cr(VI) 的降解速率还会受到有机质种类和初始 Cr(VI) 浓度的影响。土壤中有有机质种类繁多, 如腐殖质可分为腐植酸 (HA)、黄腐酸 (FA) 和胡敏酸 (HM)^[91], 其中黄腐酸含有最为丰富的官能团^[98]。因此, 腐殖质对 Cr(VI) 的还原速率会随着黄腐酸的浓度和初始 Cr(VI) 浓度的增加而增加。

通过以上分析可以看出, 土壤中有有机质对 Cr 价态的影响受到多种因素的共同作用, 包括土壤 pH 值、铁氧化物以及其他环境条件。理解这些因素是如何相互作用的, 对于设计有效的土壤修复策略至关重要。

5 Cr 污染土壤新型修复方法

Cr 污染土壤的修复方法众多, 总体上可以分为物理法 (客土法等)、化学法 (化学还原法等) 和生物修复法。然而, 一些传统的修复方法已不能满足现代修复需求。例如, 客土法等物理法存在成本高、适用性差等问题; 化学还原法则容易造成二次污染; 生物修复法虽然环保, 但也存在成本高、耗时长等不足。因此, 基于可持续发展理念, 目前已开发了一些环境友好、成本低廉且修复效果良好的新型修复技术, 如生物炭修复和纳米修复^[99-101], 均展示了广阔的应用前景。

生物炭修复, 是利用生物炭独特的物理化学性质, 以修复受 Cr 污染的土壤。生物炭具有低成本、来源广泛、结构多孔隙、表面积大、官能团丰富且相对稳定等优点, 其表面的羧基、羟基和酚类官能团能够有效地吸附和还原 Cr(VI)^[102]。然而, 未经预处理或改性的原始生物炭的吸附位点较少、功能有限且去除性能较差, 难以从环境基质中分离出来, 降低了利用的可行性。为了弥补这些不足, 进一步提高生物炭的可利用性, 通常是将生物炭利用物理、化学、生物等方法进行改性后再运用于 Cr 污染土壤的修复。例如, 使用磷酸 (H₃PO₄) 对生物炭进行改性时, 可以通过产生水蒸气增加羧基和羟基含量 (见式 1),

表 2 Cr 污染土壤新型修复方法经典案例

Table 2 Classic cases of new remediation methods for Cr-contaminated soil.

修复材料	初始 Cr(VI) 浓度 (mg/kg)	反应时间 (d)	Cr(VI) 去除率 (%)
案例 1: 以动物粪便为原料的改性生物炭 ^[104]	100	30	55.0
案例 2: 以花生壳为原理的改性生物炭 ^[105]	212.88	45	79.35
案例 3: 纳米零价铁 ^[106]	300	60	84.6
案例 4: 生物炭负载纳米零价铁 ^[107]	320	15	100.0

从而扩大孔隙结构^[103]。且由表2中的案例1和案例2可知,不同的原料及改性方式生产的生物炭,其对Cr(VI)的去除率也有所不同,因此,可从原料和改性方法入手,进一步优化生物炭对Cr(VI)的去除效率。



纳米修复,是利用纳米颗粒(NPs)吸附重金属,并可将其有害价态还原到稳定的金属状态,具有成本较低、处理安全、耗时较短且不会对环境造成二次污染等优点,是一种绿色高效的修复方法^[108-109]。目前,以纳米零价铁(Nano zero-valent iron, nZVI)为代表的纳米材料已被应用于Cr污染土壤的修复中。由于nZVI具有纳米级颗粒,因此具有较大的比表面积(25~35m²/g)和表面能,表现出极强的还原和反应活性。当nZVI快速吸附并固定在铁表面的Cr(VI)时,可通过氧化还原反应将其还原。然而,nZVI的化学稳定性较差,容易被氧化并出现结块现象,导致其化学活性较低。为了改善这一现象,通常会选择将纳米零价铁负载到生物炭上,由表2中的案例3和案例4比较可知,纳米零价铁不仅可以提高其稳定性,也可提高Cr(VI)去除率^[110]。

通过上述新型修复技术的应用,不仅能够有效地解决传统修复方法中存在的问题,还能提高修复效率,减少修复成本,并且对环境更加友好。这些技术的发展为Cr污染土壤的治理提供了新的思路和方向。

6 结论与展望

土壤中Cr(III)和Cr(VI)之间的价态转化受到多种因素的影响。土壤pH值不仅影响Cr的具体存在形态,还影响天然氧化还原剂和有机质对Cr的氧化还原效率,Cr(VI)在低Eh的土壤条件下,更倾向

于被还原为Cr(III)。土壤中的天然氧化还原剂可以充当电子供体或受体的角色,影响Cr的价态。有机质由于其复杂的物理化学性质,既可以通过“吸附-还原-络合”的方式直接还原固定土壤中的Cr(VI),还可以促进Fe(II)和Fe(III)之间的循环,间接地还原Cr(VI),此外,有机质还可以利用自身的光敏特性或作为光催化剂的优良载体,参与到Cr(VI)的还原中。有机质在微生物还原Cr(VI)的过程中,可以促进可溶性还原酶的活性,提高生物还原的效率。由于Cr(VI)的高毒性,绝大多数修复方法选择将Cr(VI)还原为毒性较低的Cr(III),并在原有修复方法的基础上进行改进,形成了以生物炭、纳米材料为代表的多种新型绿色高效的修复方法。

关于土壤中Cr污染的研究,未来需要关注以下几个问题:①探究有机质和Cr(III)形成的络合物的生态毒性及其在土壤-植物系统中的影响。目前,对于有机质与Cr(III)形成的络合物的生态毒性及其在土壤-植物系统中的影响研究较少,这些络合物的稳定性、迁移性和生物可利用性如何,是否比游离的Cr(III)毒性更小等问题仍需深入研究。②新型修复方法的实际应用效果和生态影响。目前关于新型土壤中Cr(VI)修复方法的研究与试验大多停留在实验室阶段,实际场地的运用效果和可能产生的生态影响还有待进一步研究。特别是在大规模应用时,这些修复技术的长期效果、经济可行性和环境安全性都需要进行全面评估。③优化现有修复技术和开发新方法。未来需要进一步优化现有的生物炭修复、纳米修复等技术,并探索更多高效、低成本且环境友好的新型修复方法。通过这些研究,可以更好地理解Cr在土壤中的行为,并为开发更加高效、环保的修复技术提供科学依据,从而保障土壤生态系统的健康和可持续发展。

Research Progress on Influencing Factors and Mechanisms of Chromium Valence State Transformation in Soil

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HIGHLIGHTS

- (1) Cr(VI) in soil mainly exists in the form of oxidized ions such as chromate (CrO_4^{2-}), hydrogen chromate (HCrO_4^-), and dichromate ($\text{Cr}_2\text{O}_7^{2-}$), and is the most toxic Cr valence state in soil.
- (2) The valence state of Cr in soil is affected by Eh, organic matter and other factors, which can promote or inhibit the reduction of Cr(VI).
- (3) New remediation technologies such as biochar and nanomaterials can effectively reduce Cr(VI) to low toxicity Cr(III), which is a feasible technical solution for treating Cr(VI) pollution.

ABSTRACT: Chromium (Cr) pollution in soil is a global environmental problem, and hexavalent chromium [Cr(VI)] has become a focus of attention due to its high toxicity and carcinogenicity. Cr in soil mainly exists in the form of Cr(III) and Cr(VI), and the transformation between the two is influenced by factors such as soil pH, redox potential (Eh), natural redox agents, organic matter, and microorganisms. This article provides an overview of the global pollution status and sources of Cr in soil, as well as the different valence states and toxicity characteristics of Cr in soil. It also analyzes the redox mechanisms of chromium valence state transformation in soil affected by different factors, as well as the interactions between different factors. In addition, through a deep understanding of the factors affecting the valence state of Cr, advanced remediation techniques represented by biochar and nanomaterials have emerged. These methods can effectively reduce Cr(VI) to less toxic Cr(III), thereby reducing ecological and environmental risks. Therefore, they are a potentially valuable remediation material and technique. However, the feasibility and effectiveness of large-scale applications still need further verification. The BRIEF REPORT is available for this paper at <http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202401180007>.

KEY WORDS: chromium pollution; chromium valence state; natural redox agent; organic matter; remediation technology

BRIEF REPORT

Chromium (Cr) is a potentially toxic heavy metal that significantly affects the soil environment. Humans can ingest Cr through the food chain, inhalation, skin contact, and other means. When it accumulates to a certain level in the body, it can have serious effects on human health^[4-6]. Cr has multiple valence states ranging from Cr(II) to Cr(VI)^[7]. In soil, Cr mainly exists in the valence states of Cr(III) and Cr(VI). Cr(VI) is more dangerous and toxic than Cr(III)^[8], and can cause DNA mutations and chromosome loss^[9]. It has been confirmed as a carcinogenic and mutagenic substance^[10]. Cr(III) and Cr(VI) in soil can undergo interconversion due to the effects of soil pH, Eh value, natural redox agents, organic matter, and microorganisms^[11-16]. There are also complex interactions between these factors in the conversion process of Cr valence states. In the face of soil contaminated with Cr, Cr(VI) is usually reduced to Cr(III) to reduce its toxicity and achieve better environmental benefits^[17-18].

1. The pollution status and sources of Cr

Soil Cr pollution has become an international issue, and the phenomenon of soil Cr pollution in China is particularly prominent. The total Cr concentration in industrial land in China varies greatly, ranging from 0.74mg/kg to 37967.33mg/kg. Among them, 4.15% of soil samples have Cr content exceeding the standard (with a screening reference value of 2500mg/kg)^[19]. Heavy pollution areas are mainly concentrated in the Yangtze River Delta and Bohai Rim regions in eastern China, the Pearl River Delta in the south, and the basins along the Yangtze River and Yellow River, including industrial intensive areas such as Zhejiang Province^[20], Anhui Province^[21], and Heilongjiang Province^[22]. These areas not only have high total Cr concentration, but also have serious Cr(VI) pollution problems. At the same time, the concentration range of total Cr in Chinese farmland soil is 1.48–820.24mg/kg, with approximately 4.31% and 0.12% of monitoring points exceeding the screening value (150mg/kg) and control value (800mg/kg) of China's Soil Environmental Quality Standards (GB15618—2018), respectively^[23].

The main sources of Cr in soil are both natural and from human activities, among which human activities include industrial production and agricultural activities. The weathering and volcanic eruptions of rocks rich in Cr in nature^[32], the mining of chromite in industrial production^[34], and the use of phosphate fertilizers in agricultural activities all contribute a large amount of Cr to the soil^[35].

2. Toxicity of Cr in different valence states

Cr(III) has no known basic nutritional function for plants and does not pose a direct threat to plant growth in environments with low concentrations of Cr(III). In animal bodies, especially mammals, Cr(III) participates in lipid and carbohydrate metabolism as a micronutrient^[41]. However, although Cr(III) cannot easily penetrate the cell membrane, it can accumulate around cells, destroy cell membrane lipids, change cell surface morphology, and thus damage cell integrity and normal function^[35]. High concentrations of Cr(III) may still cause damage to organisms^[1].

Cr(VI) is the most toxic Cr valence state in soil, soluble in water and penetrating the cell membranes of bacteria and eukaryotic cells. Its toxicity can reach 10–100 times that of Cr(III). When the concentration of Cr(VI) in the soil exceeds 5mg/kg, it poses a serious threat to plants^[42], reducing seed germination rate, hindering protein and nucleic acid synthesis, and triggering plant cell membrane peroxidation^[43], and even causing plant death^[44]. For humans, Cr(VI) can enter the interior of cells through sulfate and phosphate ion channels and be reduced to form a series of intermediate products such as Cr(V) and Cr(IV). These intermediate products can attack cells and other important biological analyses, induce the generation of reactive oxygen species (ROS), and lead to cell damage and even cancer^[45].

3. Factors affecting the valence state of Cr

(1) The influence of soil pH and Eh on the valence state of soil Cr. Soil pH and Eh values, as the basic physicochemical properties of soil, directly affect the forms and valence state transformation of Cr in soil (Fig. E.1). Due to the different concentrations of H^+ and OH^- ions, soil pH determines that Cr(III) and Cr(VI) exhibit different

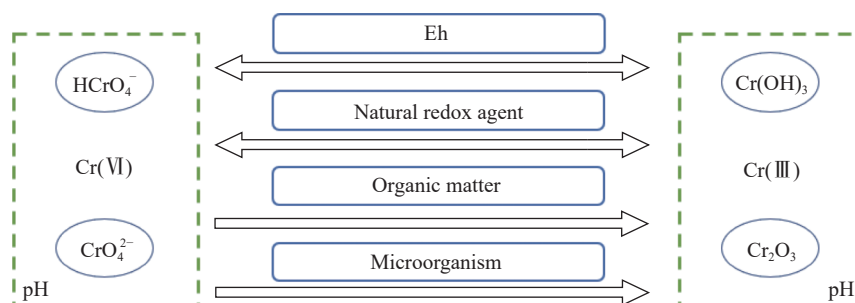


Fig. E.1 Factors affecting the valence state of Cr in soil.

forms in different pH ranges^[48]. The Eh value of soil is an important indicator of its ability to provide or accept electrons, which directly affects the redox state of soil. Under reducing conditions, Cr(VI) is more easily reduced to less toxic Cr(III), while under oxidizing conditions, Cr(III) may be re oxidized to Cr(VI)^[51].

(2) The effect of natural redox agents in soil on the valence state of soil Cr. Natural redox agents in soil, such as manganese oxide (MnO_x), hydrogen peroxide (H_2O_2), and Fe^{2+} , all have certain redox characteristics and can undergo a series of complex redox reactions with Cr in soil^[52].

(3) The influence of organic matter on the valence state of soil Cr. Due to its complex physical and chemical properties, soil organic matter can use its own functional groups as electron donors. Based on the “adsorption reduction complexation” mechanism, it can reduce Cr(VI), which is more toxic in soil, to Cr(III), which is less toxic, and form stable complexes^[56]. It can also act as an electron shuttle to indirectly reduce Cr(VI)^[65-66], and can also use its photosensitivity to catalyze Cr(VI) in soil^[69]. However, the reduction process of Cr(VI) by organic matter is influenced by soil pH, iron oxides, types of organic matter, and initial Cr(VI) concentration. In addition, organic matter can also alter the abundance of microorganisms in soil^[81], optimize community structure^[82], and improve the reduction efficiency of microorganisms towards Cr(VI).

4. New remediation methods for Cr contaminated soil

Based on the concept of sustainable development, some environmentally friendly, low-cost, and effective new remediation technologies have been developed, such as biochar remediation and nano remediation, both of which utilize the physical and chemical properties of their own materials to achieve the adsorption and reduction of Cr(VI)^[99-101].

5. Concluding remarks

The valence state transformation between Cr(III) and Cr(VI) in soil is influenced by various factors. The soil pH value not only affects the specific forms of Cr, but also affects the redox efficiency of natural redox agents and organic matter on Cr. Under acidic conditions, Cr(VI) mainly exists in the form of HCrO_4^- , and organic matter is more likely to adsorb Cr(VI) and reduce it to Cr(III) under these conditions; under alkaline conditions, Cr(VI) mainly exists in the form of CrO_4^{2-} , and the negative charge on the surface of organic matter increases, leading to a weakened adsorption effect. Natural redox agents in soil can act as electron donors or acceptors, affecting the valence state of Cr. Organic matter can directly reduce and fix Cr(VI) in soil through adsorption reduction complexation; it can also indirectly reduce Cr(VI), and in addition, organic matter can promote the biological reduction of Cr(VI). At present, new remediation technologies represented by biochar and nanomaterials have emerged, which are not only low-cost and efficient, but also environmentally friendly, demonstrating broad application prospects.

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