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Review 综 述

细菌六价铬还原及吸附机制研究进展

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摘 要：六价铬[Hexavalent chromium，Cr(Ⅵ)]是一种致癌物，其毒性远大于三价铬，因此会对人体健康和生态环境造成危害。Cr(Ⅵ)污染场地中的细菌主要通过生物还原和生物吸附降低Cr(Ⅵ)的毒性和迁移能力。Cr(Ⅵ)还原细菌的抗性机制与还原过程已被多次讨论，但现有综述还缺乏细菌类别、铬酸盐还原酶活性与吸附机制的总结。因此，本文通过系统发育树展示常见 Cr(Ⅵ)还原细菌的类别，归纳细菌的 Cr(Ⅵ)还原机制，总结现阶段铬酸盐还原酶的酶活性参数与反应条件，并讨论环境影响因子对细菌 Cr(Ⅵ)还原的影响。其次，本文综述了细菌对 Cr(Ⅵ)的吸附现象与机理。最后，本文对未来细菌修复 Cr(Ⅵ)污染的机理研究进行了展望，以期加深对细菌 Cr(Ⅵ)还原和吸附过程的了解。

关键词：六价铬还原；Cr(Ⅵ)还原细菌；铬酸盐还原酶；生物吸附

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Mechanism of bacterial reduction and biosorption of hexavalent chromium

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Abstract: Hexavalent chromium [Cr(Ⅵ)] is a carcinogen with the toxicity far greater than that of trivalent chromium. The Cr(Ⅵ) discharged by electroplating and tanning have adverse effects on human health and eco-environment. The Cr(Ⅵ) resistance mechanism and reduction process of Cr(Ⅵ)-reducing bacteria have been discussed, whereas there is a lack of summary of the species, chromate reductase activity, and adsorption mechanism of Cr(Ⅵ)-reducing bacteria. In this review, we reviewed the recently reported Cr(Ⅵ)-reducing bacteria via a phylogenetic tree, elaborated the mechanism of Cr(Ⅵ) reduction by bacteria, summarized the enzymatic parameters and reaction conditions of chromate reductase, and expounded the environmental factors affecting the reduction of Cr(Ⅵ) by bacteria. Further, we clarified the adsorption performance and mechanism of Cr(Ⅵ) by bacteria. Finally, we put forward the research prospects on the mechanism of bacterial bioremediation of Cr(Ⅵ) contamination. With this review, we aim to deepen the understanding about the reduction and biosorption processes of Cr(Ⅵ)-reducing bacteria.

Keywords: reduction of hexavalent chromium; Cr(Ⅵ)-reducing bacteria; chromate reductase; biosorption

铬(chromium，Cr)在自然界中的化合价为−2价到+6 价，其中最常见的是六价铬[hexavalent chromium，Cr(Ⅵ)]与三价铬[trivalent chromium，Cr(Ⅲ)][1−2]。Cr(Ⅵ)主要以 CrO_4^{2-}、$HCrO_4^-$与 $Cr_2O_7^{2-}$形态存在[3]。Cr(Ⅲ)在酸性条件下以 Cr^{3+}形态存在，在中性与碱性条件主要以 $Cr(OH)_3$、$Cr(OH)_4^-$与 $Cr(OH)_5^{2-}$形态存在[3]。

Cr(Ⅵ)与 Cr(Ⅲ)的毒性差异由铬的化合价与存在形态决定。对于人体而言，Cr(Ⅵ)属于致癌物质，其致癌机制包括氧化应激反应、DNA损伤与基因组不稳定性[4]。相比于可溶性的Cr(Ⅵ)，Cr(Ⅲ)更容易形成沉淀，其毒性会因生物有效性的降低而减小[4−5]，因此 Cr(Ⅲ)的毒性远小于 Cr(Ⅵ)。而 Cr(Ⅲ)的低毒性体现在对DNA 造成的损伤上，Cr(Ⅲ)进入细胞后会与 S、O 及 N 形成稳定的化学键，进而破坏 DNA[6]。但是吡啶甲酸铬与组氨酸铬等 Cr(Ⅲ)可作为人体的营养补充剂，提供人体所需要的铬元素有利于治疗糖尿病[7−8]。因此高毒性的 Cr(Ⅵ)转化为低毒性的 Cr(Ⅲ)是修复 Cr(Ⅵ)污染的关键，并且 Cr(Ⅵ)来源与污染现状相比于 Cr(Ⅲ)更受研究学者的关注。

环境中 Cr(Ⅵ)的主要来源是人类活动与地质作用。其中人类活动主要包括电镀、化学制造、印刷、制革与冶金等[9]。地质作用会导致地壳中铬铁矿($FeCr_2O_4$)的氧化，从而释放 Cr(Ⅵ)[10]。这些来源可能使得各种环境介质(土壤[11−12]、地下水[13]、地表水[14]等)均受到 Cr(Ⅵ)污染。研究显示，意大利坎帕尼亚平原的农田与索洛弗拉河谷由于制革活动受到了 Cr(Ⅵ)污染[11]。该地 70%的农田土壤与 42%的河谷土壤样品中的 Cr(Ⅵ)含量超过了当地 Cr(Ⅵ)污染限

值(2 μg/g)[11]。在水环境方面，伊朗比尔詹德地下水样品中铬的浓度为0.28–132.34 μg/L，16.66%的样品高于世界卫生组织标准(0.05 mg/L)[13]。我国黄土高原地区的络河与杏子河等流域广泛存在Cr(Ⅵ)，罗江上游更是Cr(Ⅵ)的主要分布区[14]。

环境介质中的Cr(Ⅵ)污染会对生态及人体健康造成危害。研究显示，土壤中高浓度的Cr(Ⅵ)具有生态毒性，可干扰植物生长、养分吸收与光合作用[15]。饮用水中的Cr(Ⅵ)可增加人体胃癌患病的风险[16]。空气中的Cr(Ⅵ)颗粒物也是人体呼吸道癌症的潜在致病因素[17]。因此，近年来如何降低Cr(Ⅵ)污染带来的危害受到了众多研究学者的关注。

生物修复法可以通过不同的方式改变铬的形态、降低其流动性与生物可利用性，使铬污染场地恢复生态功能。生物修复Cr(Ⅵ)主要包括超积累植物富集与微生物修复[18]，其修复原理是通过生物源材料与生物有机体对Cr(Ⅵ)进行还原、吸附、矿化与积累[19]。生物还原(bioreduction)可以将高毒性Cr(Ⅵ)还原成低毒性Cr(Ⅲ)，生物吸附(biosorption)可以限制Cr(Ⅵ)的迁移能力[19–20]。生物矿化是微生物将Cr(Ⅵ)转化为不溶性矿物，或将其固定在微生物合成的矿物晶格中[21]。生物矿化常与生物积累相伴发生，例如，细菌可在胞内将Cr(Ⅵ)还原形成$Cr(OH)_3$与Cr_2O_3晶体，将铬积累在细胞中[22–23]。

生物修复在Cr(Ⅵ)污染环境修复中具有明显的优势。Cr(Ⅵ)还原细菌(Cr(Ⅵ)-reducing bacteria，CRB)分布广泛，与真菌及藻类相比抗性较强且修复效果显著[24]，可应用于土壤[25]、铬矿尾矿坝[26]与地下水[27]的Cr(Ⅵ)污染修复。根际微生物与植物修复常共同作用于Cr(Ⅵ)污染场地土壤的原位修复[28]。其中具有Cr(Ⅵ)抗性的根际微生物对植物生长有益[29]，并且Cr(Ⅵ)还原细菌使铬毒性降低后，可以促进植物积累Cr(Ⅵ)[30–31]。相比于物理化学修复方法(如反渗透、活性炭吸附与电化学法等)，细菌修复Cr(Ⅵ)污染的成本较低[32–33]，且不易造成污染场地的二次污染[34]。此外，在适合细菌生长的条件下，Cr(Ⅵ)还原细菌可以持续地进行修复[35]。所以生物修复是一种经济、安全与可持续的环境友好型修复方式[19,33,36]。

细菌Cr(Ⅵ)还原机理是生物修复领域近5年的研究热点之一。随着研究的推进，越来越多的Cr(Ⅵ)还原细菌被发现[37–39]，我们亟需对Cr(Ⅵ)还原细菌进行系统总结。Cr(Ⅵ)还原细菌可通过还原与吸附作用修复Cr(Ⅵ)污染，其中细菌对Cr(Ⅵ)的还原机制在细胞层面已经较为清晰，但许多文章仅列举铬酸盐还原酶的种类[36,40–41]，并未汇总铬酸盐还原酶活实验参数。此外，由于吸附作用并非主要的修复机制，较少有文章对细菌吸附过程与机制进行深入讨论与总结[19,42]。因此本文在Cr(Ⅵ)还原细菌种类的归纳中增加了系统发育分析，对细菌还原过程的酶活性研究及影响因子进行总结分析，对细菌的铬吸附过程进行更深入的总结，结合环境酸碱性对细菌吸附作用进行了展示。本文可加深读者对细菌Cr(Ⅵ)修复过程的理解，为工程菌的选择及还原条件优化提供参考，并对未来的研究方向进行了展望。

1 细菌Cr(Ⅵ)还原

1.1 Cr(Ⅵ)还原细菌多样性

Cr(Ⅵ)还原细菌在自然界十分丰富。铬污染场地的土壤中，丰度较高的细菌类群包括酸杆菌门(*Acidobacteria*)、放线菌门(*Actinobacteria*)、拟杆菌门(*Bacteroidetes*)、芽单胞菌门(*Gemmatimonadetes*)与变形杆菌门(*Proteobacteria*)等[43–44]。本课题组前期通

过微生物多样性分析发现，天津子牙经济园区铬浓度最高的土壤样品中，变形杆菌门、芽单孢菌门以及酸杆菌门细菌的相对丰度也较高[12,45]。在属水平上，相对丰度最高的是溶杆菌属(*Lysobacter*)。有研究表明，溶杆菌(*Lysobacter*)、黄湿杆菌(*Flavihumibacter*)、黄溶菌(*Flavisolbacter*)与交替赤杆菌(*Altererythrobacter*)的相对丰度与环境中铬的酸溶性(acid-soluble)及可还原组分显著相关[46]。此外，Wang 等[47]发现，在原位修复 Cr(Ⅵ)污染时，氢噬胞菌属(*Hydrogenophaga*)、假单胞菌属(*Pseudomonas*)、微小杆菌属(*Exiguobacterium*)与红杆菌属(*Rhodobacter*)在场地中富集并发挥 Cr(Ⅵ)还原作用。在铬污染场地丰度较高的细菌类群中，包含了许多 Cr(Ⅵ)还原细菌，这些细菌在污染场地的生物修复中起到了重要作用[48–49]。

研究人员已从不同环境中筛选得到了多种 Cr(Ⅵ)还原细菌。图 1 为近年来报道较多的 Cr(Ⅵ)还原细菌 16S rRNA 基因的系统发育树，这些细菌主要集中在变形杆菌门中的 *α*-、*β*-、*γ*-变形杆菌纲、厚壁菌门(*Firmicutes*)与放线菌门[39]，而在蓝细菌门(*Cyanobacteria*)与栖热菌门(*Deinococcus-Thermus*)中分布相对较少。此外，*δ*-变形杆菌纲中的 *Geobacter*[50]与 *Desulfovibrio*[51]等也是被报道较多的 Cr(Ⅵ)还原细菌。

研究显示，Cr(Ⅵ)还原作用在不同菌属中普遍存在，归因于铬酸盐抗性基因(chromate resistance genes)[52]和铬酸盐还原酶基因(chromate reductase genes)[53]在细菌间的水平转移[54]。Huang 等[55]通过基因挖掘技术发现，同时具有铬抗性基因 *chrA* (Cr-resistant gene *chrA*；铬酸盐转运蛋白基因)与铬酸盐还原酶基因的物种有 41 个，其中数量最多的物种依次为产碱杆菌科(*Alcaligenaceae*)、肠杆菌科(*Enterobacteriaceae*)与芽孢杆菌科(*Bacillaceae*)。其中芽孢杆菌是近年来研究较多的 Cr(Ⅵ)还原细菌[21,56–57]，该菌在 Cr(VI)胁迫下具有高耐受性与还原能力。细菌金属抗性基因的水平转移常发生在污水处理过程及自然环境中[58–61]，这有助于提高 Cr(Ⅵ)胁迫下群落结构的稳定性[62]。

1.2 细菌 Cr(Ⅵ)还原机制

Cr(Ⅵ)还原细菌分布范围广泛，且对 Cr(Ⅵ)污染环境的修复效果显著，其 Cr(Ⅵ)还原机制一直是生物修复领域的研究重点[19]。从高效 Cr(Ⅵ)还原细菌的筛选，到关键铬酸盐还原酶基因与铬酸盐还原酶的研究，细菌 Cr(Ⅵ)还原机制的探索已由现象逐步深入到分子机理[63]。如图 2 所示，细菌 Cr(Ⅵ)还原机制包括铬酸盐还原酶还原(chromate reductase reduction)与非酶物质还原(non-enzymatic reduction)[64]。铬酸盐还原酶可分为胞内还原酶(intracellular reductase)、胞外还原酶(extracellular reductase)和膜结合还原酶(membrane bound reductase)[40,42]。由于铬酸盐还原酶并非单独存在于某一细胞组分，不同位点的铬酸盐还原酶在细菌还原过程中均起作用。因此铬酸盐还原酶具有空间位置、还原效果与机制上的差异。而非酶物质还原包括谷胱甘肽、抗坏血酸和半胱氨酸等对 Cr(Ⅵ)的还原[65]。此外，来自铁还原菌与硫酸盐还原菌的厌氧代谢产物 Fe(Ⅱ)和 H_2S 以及环境中的硫化物与有机质也可以对 Cr(Ⅵ)进行还原[2,66]。铬酸盐还原酶与非酶物质都可以单独对 Cr(Ⅵ)进行还原，因此 2 种还原过程相互影响，均起到 Cr(Ⅵ)还原作用。

细菌胞内还原酶的 Cr(Ⅵ)还原作用，普遍高于胞外还原酶和膜结合还原酶的还原作用[67]。例如，*Pseudomonas umsongensis* CY-1

细胞质组分(cytoplasmic fraction)对 Cr(Ⅵ)还原作用远高于细胞膜组分(cell envelope fraction)和细胞外组分(extracellular fraction)[35,68]；*Aeribacillus pallidus* BK1 对 Cr(Ⅵ)的还原也主要依赖胞内还原酶进行[69]。根据蛋白质序列的同源性可以将已鉴别出的多种胞内还原酶分为 2 类[70]：类别一(Class Ⅰ)包括铬酸盐还原酶 ChrR/YieF、N-乙基马来酰亚胺还原酶 NemA、老黄酶 OYE、偶氮还原酶 AzoR 和硝基还原酶 NitR 等。类别二(class Ⅱ)大多为硝基还原酶，包括氧不敏感硝基还原酶 NfsA/NfsB、硝基还原酶 NfrA 和黄素氧化还原酶

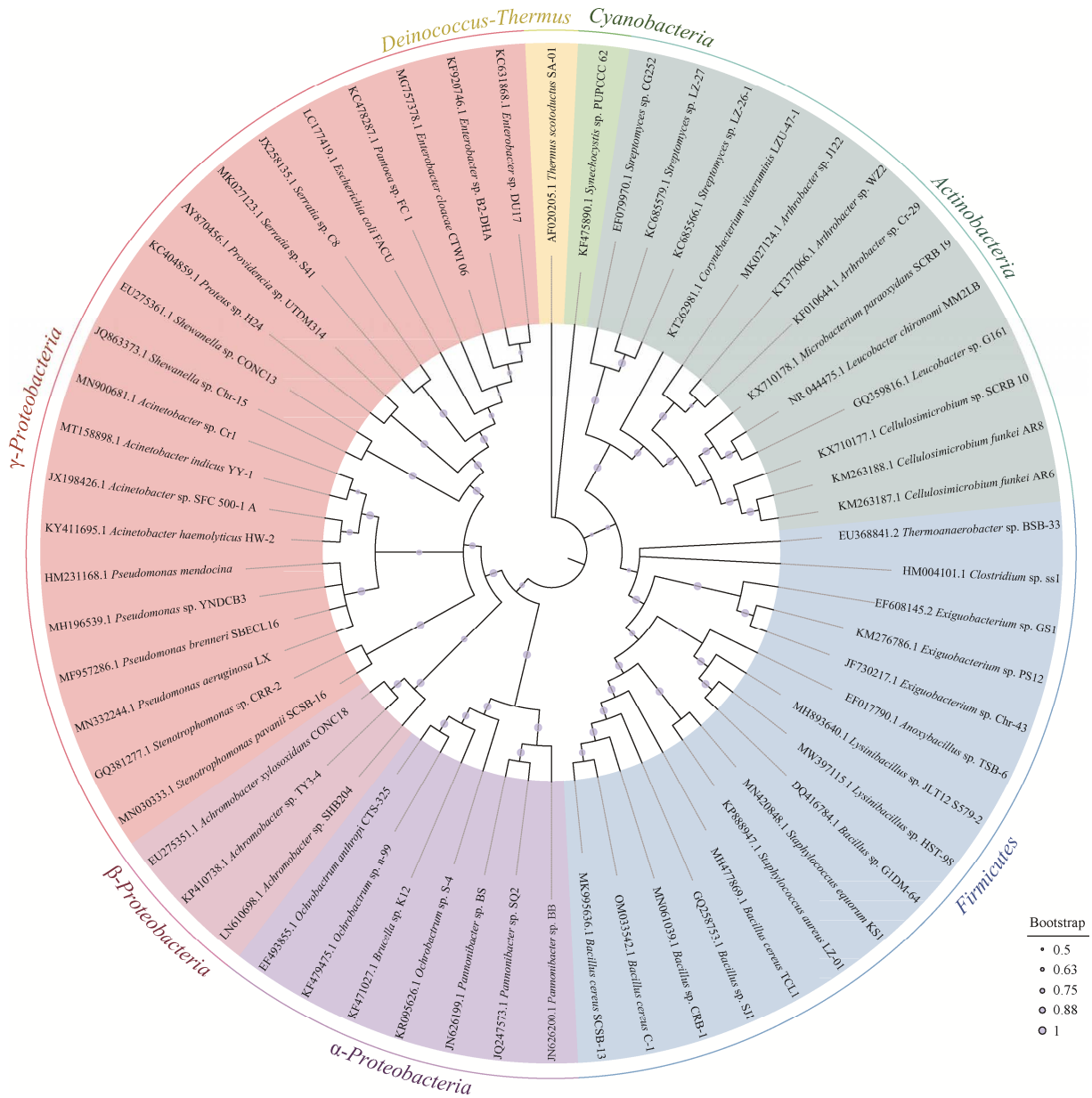

图 1　Cr(Ⅵ)还原细菌 16S rRNA 基因系统发育树

Figure 1　Cr(Ⅵ)-reducing bacteria (CRB) 16S rRNA gene phylogenetic tree. The tree was constructed using neighbor-joining, and the circle on the clade represents the bootstrap of 1 000 repetitions.

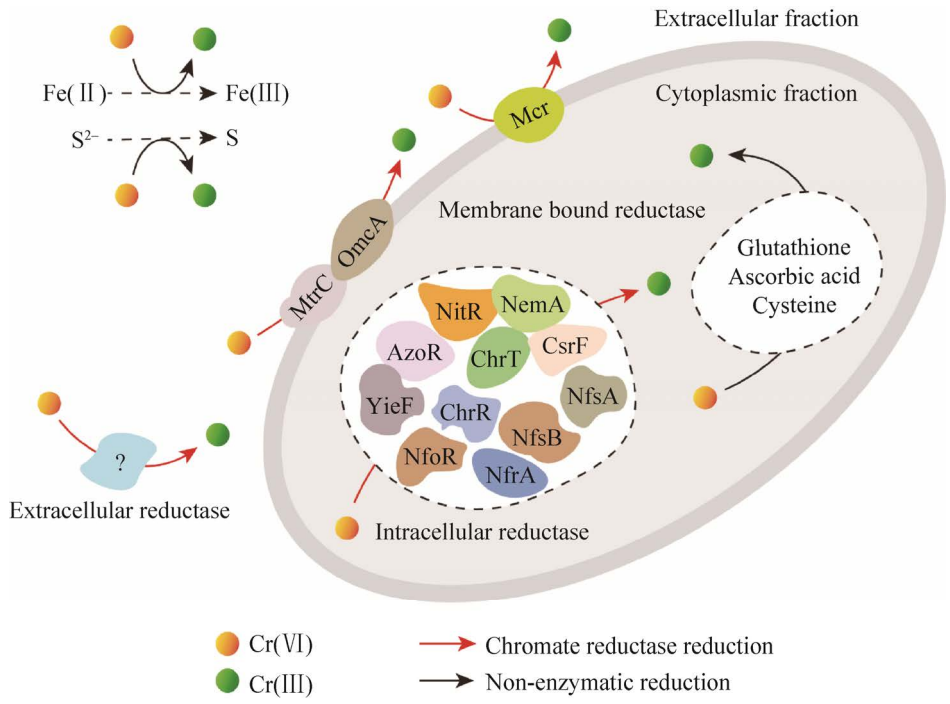

图 2　细菌的 Cr(Ⅵ)还原机制

Figure 2　Mechanism of Cr(Ⅵ) reduction by bacteria. Chromate reductase includes intracellular reductase, membrane bound reductase and extracellular reductase, among which the common intracellular reductases are ChrR, YieF, NfrA, NfsA and NitR, et al. Non-enzymatic substances includes glutathione, ascorbic acid, cysteine, Fe(Ⅱ) and sulfides, et al.

NfoR 等。这些胞内还原酶多以黄素为辅助因子，以 NAD(P)H 为电子供体对 Cr(Ⅵ)进行还原。在细菌 Cr(Ⅵ)还原过程中，电子供体 NAD(P)H 失去氢离子(H^+)及电子形成 $NAD(P)^+$，失去的电子通过铬酸盐还原酶提供给 Cr(Ⅵ)转化为 Cr(Ⅲ)[42]。迄今为止，大部分胞内还原酶的结构、Cr(Ⅵ)结合位点及电子传递机理等尚不明确[71]。

目前，胞外还原酶、膜结合还原酶的研究局限于细胞外组分与细胞膜组分中粗酶还原效果的比较。研究显示，胞外还原酶、膜结合还原酶大多与胞内还原酶共同实现还原作用。例如，*Shewanella loihica* PV-4 利用胞内还原酶与胞外还原酶共同还原 Cr(Ⅵ)[72]，*Bacillus* sp. M6 则利用胞内还原酶与膜结合还原酶共同还原 Cr(Ⅵ)[73]。已知的胞外还原酶与膜结合还原酶较少(图 2)。具有 2 个跨膜螺旋的 Mcr 已被鉴定为膜结合还原酶[74]。此外，Cr(Ⅵ)作为唯一电子受体的条件下，*Shewanella oneidensis* MR-1 的外膜细胞色素 MtrC 与 OmcA 也是胞外末端还原酶[75]。在细胞外和细胞表面 Cr(Ⅵ)还原过程中，细菌可产生纳米导线与电子穿梭体促进胞外电子传递[76]。大部分的细菌的细胞外组分同细胞膜组分均具有 Cr(Ⅵ)还原能力，但其中铬酸盐还原酶并没有经过纯化鉴定，因此缺乏蛋白结构与作用机理等相关信息。胞外还原酶和膜结合还原酶仍是未来研究的重点关注对象。

1.3　铬酸盐还原酶活性研究

铬酸盐还原酶活性(chromate reductase activity)的检测可以用于分析细菌对 Cr(Ⅵ)的还原作用机制[77]，例如，通过对粗酶和纯化的铬

酸盐还原酶进行活性检测，可判断细菌 Cr(Ⅵ)还原是否为生物作用。虽然铬酸盐还原酶活性的定义不尽相同[63,77−78]，但基本定义均为“一个单位的酶活性为 1 min 还原 1 nmol Cr(Ⅵ)的酶量”。细菌还原 Cr(Ⅵ)的具体位点可以通过不同组分的铬酸盐还原酶活性比较确定[63]。例如，Huang 等[65]利用 *Sporosarcina saromensis* W5 各组分的粗酶进行 Cr(Ⅵ)还原实验发现，胞内还原酶和膜结合还原酶的还原作用比胞外还原酶更强；Elmeihy 等[79]利用链酶蛋白酶消化 *Geobacter sulfurreducens* 的胞外还原酶，确定了细菌 Cr(Ⅵ)还原主要发生在胞外。

迄今为止，铬酸盐还原酶的酶学实验(enzyme assays)数据相对较少。表 1 总结了近年来铬酸盐还原酶的酶动力学参数，其中米氏常数 K_m 表示铬酸盐还原酶与 Cr(Ⅵ)的亲和力，K_m 越小则亲和力越强[80]。最大反应速率 V_{max} 代表一定铬酸盐还原酶量下 Cr(Ⅵ)饱和的反应速率。多数铬酸盐还原酶对 Cr(Ⅵ)的还原不具有专一性，而是行使其他生理功能的同时展现 Cr(Ⅵ)还原特性[71]，例如 NitR 的硝基还原酶活性[77]与 YhdA 的偶氮还原酶活性[81]等。此外，铬酸盐还原酶还原 Cr(Ⅵ)的酶学实验中，基本以 NADPH 或 NADH 作为电子供体[82]。

虽然许多具有铬酸盐还原酶活性的蛋白已被报道，但目前我们对铬酸盐还原酶的 Cr(Ⅵ)结合位点及还原过程的了解还十分有限。未来需要进一步探究铬酸盐还原酶的结构与功能。

表 1　铬酸盐还原酶的动力学参数与反应条件

Table 1　Kinetic parameters and reaction conditions of chromate reductase in enzyme assays

Chromate reductase	Strain	K_m/(μmol/L)	V_{max}/(μmol/(min·mg))	T/℃	Time	Electron donor	Buffer (pH)	References
NitR	*Pannonibacter phragmitetus* BB	14.55	34.46	35	30 min	NADPH	Phosphate buffer (pH 7.0)	[63]
GST-EcNfsA	*Escherichia coli* DH5α	11.8	3.8×10^{-3}	55	1 h	1 mmol/L NADH	10 mmol/L Tris-HCl (pH 7.0)	[77]
GST-EcNfsB	*Escherichia coli* DH5α	23.5	3.9×10^{-3}	30	1 h	1 mmol/L NADH	10 mmol/L Tris-HCl (pH 7.0)	[77]
GST-VhNfsA	*Vibrio harveyi* KCTC 2720	5.4	10.7×10^{-3}	30	1 h	1 mmol/L NADH	10 mmol/L Tris-HCl (pH 7.0)	[77]
NemA	*Enterobacter* sp. Z1	212.1±63.6	37.7±3.9	Room temperature	20 min	1 mmol/L NADPH	Borate saline buffer	[80]
YhdA	*Bacillus subtilis*	7 260	26.8	30	30 min	10 mmol/L NADPH	100 mmol/L Tris-HCl (pH 7.5)	[81]
ChrR	*Pseudomonas putida*	260	8.8	70	/	/	0.05 mol/L citrate buffer(pH 5.0)	[83]
YieF	*Escherichia coli*	200	5	35	/	/	0.05 mol/L citrate buffer (pH 5.0)	[83]
NfoR	*Staphylococcus aureus* LZ-01	120.84	16.30	37	5 min	0.3 mmol/L NADH	50 mmol/L Tris-HCl buffer (pH 7.0)	[84]
OYE	*Thermus scotoductus* SA-01	3.5/8.4 mol/L	6.2 /16.0	65	5 min	0.3 mmol/L NADH/NADPH	20 mmol/L MOPS-NaOH buffer, 10 mmol/L $CaCl_2$ (pH 6.5)	[85]

/: not mentioned.

1.4 细菌 Cr(Ⅵ)修复过程的影响因子

多种环境因子均能影响细菌 Cr(Ⅵ)还原与吸附的效果，如 pH、温度、Cr(Ⅵ)初始浓度、共存离子与电子供体等[37,86]。这些环境因子主要以改变铬酸盐酶活性影响 Cr(Ⅵ)修复效果，而其中 pH 可以改变细菌表面与 Cr(Ⅵ)之间的静电斥力而影响细菌对铬的吸附。

环境 pH 可以改变 Cr(Ⅵ)吸附作用与细菌生长进而影响细菌 Cr(Ⅵ)修复效果。由于 Cr(Ⅵ)在 pH 为 1–6 时以 $HCrO_4^-$与 $Cr_2O_7^{2-}$的形态存在，在碱性条件下以 CrO_4^{2-}的形态存在，因此铬酸根始终带负电荷存在于溶液之中。而一般情况下细菌表面呈负电荷，所以当 pH 升高时细菌表面与 Cr(Ⅵ)的静电斥力增强，细菌对 Cr(Ⅵ)的吸附作用会减弱[87]。此外，pH 的极端变化也会改变细菌的生长，进而影响铬酸盐还原酶活性[86]。研究发现，细菌可以在宽范围的 pH 条件下生存，其中弱碱性条件更有利于 Cr(Ⅵ)的还原效果[88]。例如，在 pH 为 4–10 的环境中，*Bacillus* sp. CRB-7 能够生长并且还原 Cr(Ⅵ)，其中在 pH 为 7–9 时具有较高的生长活性与还原效果[89]。同样的现象也出现在 *Stenotrophomonas pavanii* WY601 中[35]。此外，*Pannonibacter phragmitetus* BB 在还原的过程中可以将 pH 为 6.5 的培养基调节至 pH 为 8.4，通过产碱来应对 Cr(Ⅵ)的胁迫[90]。但也存在一些适宜在酸性条件下进行 Cr(Ⅵ)还原的细菌，例如，*Pseudomonas brenneri* 能在 pH 为 1–7 的环境中生存，其 Cr(Ⅵ)还原的最适 pH 为 6[91]。虽然 Cr(Ⅵ)还原细菌的最适酸碱条件具有差异，但 pH 为 6–8 是大多数细菌还原 Cr(Ⅵ)的最佳条件。

温度是影响铬酸盐还原酶活性的另一个重要因素。大多数细菌的最适生长与 Cr(Ⅵ)还原的温度在 30–37 °C 之间，这与铬酸盐还原酶的最佳酶活性温度接近。研究显示，铬酸盐还原酶 YieF 酶活性的最佳温度为 35 °C[83]，YhdA 最佳温度为 30 °C[81]。高温与低温均会抑制酶的活性，温度过高会使得铬酸盐还原酶变性[89]。但也存在一些嗜热菌，能够在高温下发挥 Cr(Ⅵ)还原作用。例如，*Aeribacillus pallidus* BK1 的最佳生长温度为 60 °C，可耐受的温度甚至达到 70 °C[69]。针对冶金等行业的高温废物处理，此类嗜热 Cr(Ⅵ)还原细菌具有较高的应用价值[92]。而低温一般不利于细菌生长[89]，会限制生物吸附剂的产量，降低对 Cr(Ⅵ)的吸附量。

Cr(Ⅵ)的初始浓度也会影响细菌的还原作用，这与不同细菌的 Cr(Ⅵ)最低抑菌浓度 MIC 紧密相关[93]。当 Cr(Ⅵ)浓度低于最低抑菌浓度时，细菌能保证基本生长活性，从而持续地对 Cr(Ⅵ)进行还原[21]：*Stenotrophomonas pavanii* WY601 在达到生长稳定期后，菌株对 Cr(Ⅵ)的还原率仍可以进一步提高[35]。Cr(Ⅵ)浓度越高，细菌生长越受抑制，还原效率就越低。Cr(Ⅵ)浓度也会影响细菌的基因表达，包括铬酸盐抗性基因与铬酸盐还原酶基因[94]。研究发现，在 100–1 000 mg/L Cr(Ⅵ)的浓度区间中，*Pannonibacter phragmitetus* BB 的铬抗性基因 *chrA* 与硝基还原酶基因 *nitR* 的相对表达量呈下降趋势[63]。综上，细菌在低浓度 Cr(Ⅵ)区间中保持较强的生长活性，其铬酸盐抗性基因与铬酸盐还原基因表达水平较高，Cr(Ⅵ)还原能力增强；高浓度 Cr(Ⅵ)条件下，细菌为维持其他生理功能而降低 Cr(Ⅵ)还原能力，同时 Cr(Ⅵ)对细菌产生毒性作用[23]。

环境中的共存离子也会影响细菌对 Cr(Ⅵ)的还原，包括金属离子与无机酸根离子。金属离子的作用主要体现在对细菌生长的影响上。研究发现，Cu^{2+}能促进细菌对 Cr(Ⅵ)的还原[95]。Cu^{2+}与黄素氧化还原酶 NfoR 的非特异性结合，

可以促进 Cr(Ⅵ)还原中的电子转移[96]。Cu^{2+}除了作为辅酶外，还能够在细胞氧化呼吸系统中协助电子转移[86]。由于许多硝基还原酶具有铬酸盐还原酶活性，硝酸盐离子(NO_3^-)对 Cr(Ⅵ)还原的影响备受关注[97]。研究发现，NO_3^-浓度提高可促使细菌 *Pseudomonas aeruginosa* G12 产生多种还原酶，增强细菌的 Cr(Ⅵ)还原能力[98]。共存离子促进细菌对 Cr(Ⅵ)的还原，彰显了细菌在复合污染环境修复的优势。

此外，由于 Cr(Ⅵ)作为还原过程中的电子受体，研究者也需要考虑电子供体(electron donors)本身对 Cr(Ⅵ)的还原作用。不同细菌对电子供体的代谢途径具有差异，因此电子供体对 Cr(VI)还原的影响取决于细菌种属。常见的有机电子供体有葡萄糖、果糖、乳糖、乳酸、柠檬酸、甘油、醋酸与 NADH/NADPH 等[86,99]。现阶段未发现仅利用无机电子供体的 Cr(Ⅵ)还原细菌[100]。但在细菌群落中，无机与有机电子供体可作为联合电子供体(例如 H_2 与 CH_4[101]、单质硫与有机硫[102])起到共同促进 Cr(Ⅵ)还原的作用。细菌群落也可以利用无机电子供体 S(0)或 Fe(0)，产生挥发性脂肪酸以促进 Cr(Ⅵ)还原细菌对 Cr(Ⅵ)的还原[103]。具备还原能力的电子供体，可以对 Cr(Ⅵ)进行直接还原。例如，LB 培养基可以缓慢地还原 Cr(Ⅵ)[104]。电子供体还可通过提高菌量促进 Cr(Ⅵ)还原效果。本课题组研究发现，在单一有机污染物作为碳源的条件下，*Acinetobacter haemolyticus* HW-2 还原 0.7 mg/L 的 Cr(Ⅵ)需 12 h，而添加 2%的 LB 培养基后，还原相同浓度 Cr(VI)仅需 2 h[105]。因此，在选择最佳的电子供体时，应考虑在最高细菌生物量下进行[86]。

细菌 Cr(Ⅵ)还原过程不仅受到以上环境因子的影响，还受到细菌的营养方式、溶解氧和共存有机污染物等因素的影响，未来还需要进一步探究不同影响因子与细菌 Cr(Ⅵ)还原的相互关系。

2 细菌 Cr(Ⅵ)吸附现象与机理

2.1 细菌对 Cr(Ⅵ)的吸附

由于细菌对 Cr(Ⅵ)的还原作用十分显著，因此现阶段已有研究大多关注细菌的还原过程与机制。而报道相对较少的吸附作用在细菌 Cr(Ⅵ)修复中也具有重要意义。生物吸附指具有活性或非活性的生物质表面吸附金属离子的物理化学过程[19]。这一过程并不涉及微生物的能量消耗，无论是活细菌还是死细菌都能实现[19]，因此生物吸附具有成本低、化学成分少的优点[106]。

细菌可以通过菌体、细胞产物与胞外聚合物(EPS)对 Cr(Ⅵ)进行吸附[107−108]。例如，阚洪媛等[109]发现 *Bacillus cereus* MZ-11 灭活菌株可以对 1 600 mg/L 的 Cr(Ⅵ)保持良好的吸附效果。硫酸盐还原菌降解碳源后产生的硫化物和乙酸盐可诱导金属离子沉淀(FeS_2 和 Cr_2S_3)，该沉淀物可以对铬进行吸附[110]。细菌胞外聚合物中−OH、−NH 及 C−O 等官能团在吸附过程中起重要作用[111−112]。如表 2 所示，许多 Cr(Ⅵ)还原细菌也具有 Cr(Ⅵ)吸附能力，但多数菌株的吸附作用在微生物修复作用中占比较低[99]。细菌进行固定化后可以提高对 Cr(Ⅵ)的吸附作用[113]。此外，细菌也可以通过固定化提高海藻酸钠对 Cr(Ⅵ)的吸附量[114]。

在 Cr(Ⅵ)污染修复过程中，细菌对 Cr(Ⅵ)的吸附作用不可或缺。细菌还原与吸附 Cr(Ⅵ)的时间次序和空间差异，与细菌主要的 Cr(Ⅵ)还原机制有关。Cr(Ⅵ)的吸附主要发生在细胞表面与胞外聚合物中，也可能发生在相应的还原酶中。当细菌利用胞外还原酶还原时，还原作用与细胞表面及胞外聚合物的吸附作用同时发生，吸附于胞外还原酶的 Cr(Ⅵ)进而被还原[86]。

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表 2　具有吸附作用的 Cr(Ⅵ)还原细菌总结

Table 2　Summary of Cr(Ⅵ)-reducing bacteria with bioadsorption function

Strain	Cr(Ⅵ) concentration /(mg/L)	Time	pH/ *T*/℃	Percentage of bioremediation/%	Percentage of biosorption/%	Adsorption mechanism	Dynamic fitting	Reference
Enterobacter sp. SL, *Acinetobacter* sp. SL-1	87	168 h	7/35	98.48	9.33	Function of –NH_2, –OH, –COOH and other functional groups on the surface of bacteria	Pseudo-second-order kinetics model (R^2> 0.94)	[117]
Bacillus sp. CRB-B1	150	24 h	7/37	89.64	2.76–7.71	–NH_2, –OH, –COOH on the surface of bacteria	Exponential decay model (R^2≥0.914 3)	[86]
Parapedobacter sp. ISTM3 (EPS)	20	15 min	5/30	95.10	95.10	–CH_2, C=O, S=O on the EPS	Langmuir adsorption isotherms (R^2=0.994 6)	[118]
Pseudochrobactrum saccharolyticum W1	200	60 h	9/30	53.70	5.00	C–H, C–C, C=O, C–OH and C–O–C on the surface of bacteria	/	[115]
Bacillus sp. CRB-7	120	48 h	7/37	100	3.63	–COOH, –CO-NH_2, –OH, C–$PO(OH)_2$ and C=O on the surface of bacteria	/	[89]
Strain H (*Bacillus cereus*)	40	20 h	7/30	50.6±1.8	8±0.5	/	/	[119]
Bacillus sp. M6	200	72 h	9/30	45.90	Negligible	–COOH, –OH on the surface of bacteria	/	[73]

/: not mentioned.

此时吸附与还原均在胞外进行。当细菌利用膜结合还原酶还原时，Cr(Ⅵ)吸附在无膜结合还原酶的细胞表面，可被胞外还原酶还原或被固定在细胞表面。吸附在膜结合还原酶表面的 Cr(Ⅵ)可进一步被还原。此时吸附作用与膜结合还原酶的还原作用发生在细胞表面及胞外[91]。当细菌利用胞内还原酶还原时，吸附在细胞表面的 Cr(Ⅵ)可被转运至细胞内还原。此时，2 种作用在不同空间上独立进行[115]。由于细菌的 Cr(Ⅵ)还原并非某一种还原酶独立作用，因此吸附作用与还原作用在时间与空间上相对独立[116]。例如，*Geobacter sulfurreducens* PCA 细胞表面的总铬含量与胞内总铬含量分别随时间增加而增加[50]。因此根据 Cr(Ⅵ)的浓度变化拟合的动力学模型也通常是 2 种作用的结果。

2.2 细菌的 Cr(Ⅵ)吸附机理

细菌 Cr(Ⅵ)吸附过程中的物理吸附依靠 Cr(Ⅵ)与细菌表面较弱的范德华力，而化学吸附则依靠不可逆的化学键[120]。细菌吸附 Cr(Ⅵ)的机理包括络合、沉淀及静电作用[42]。环境 pH、细菌表面官能团及细胞壁的主要成分都会影响 Cr(Ⅵ)的吸附过程。

环境 pH 影响细菌对 Cr(Ⅵ)的静电吸附。在溶液中，Cr(Ⅵ)主要以带负电的含氧酸根形态存在，因此 Cr(Ⅵ)易吸附在细菌表面的正电物质上。培养环境的 pH 会影响细菌对 Cr(Ⅵ)的吸附，当 pH 较低时，细菌表面质子化后带正电荷，容易吸附 $HCrO_4^-$与 $Cr_2O_7^{2-}$。例如，胺(−NH−)可质子化成−NH_3^+，通过静电吸附 Cr(Ⅵ)[121]。当 pH 上升后，细菌表面释放质子带负电，对 Cr(Ⅵ)的静电斥力增强，则吸附作用减弱[87]。因此在碱性条件下，OH^-与 CrO_4^{2-}存在吸附竞争[87]。

细菌表面的蛋白质与多糖等物质的官能团可以吸附 Cr(Ⅵ)[112,115](表 2)。羟基(−OH)和羧基(−COOH)是吸附 Cr(Ⅵ)的常见官能团[86]，可以通过化学结合力与静电作用吸附 Cr(Ⅵ)。氨基(−NH_2)作为细胞膜中蛋白质、碳水化合物及己糖胺的主要成分，可以通过静电作用与氢键作用吸附 Cr(Ⅵ)[42]。

细胞壁成分也会导致 Cr(Ⅵ)吸附差异。革兰氏阴性菌表面肽聚糖层外的脂多糖，可作为 Cr(Ⅵ)的金属螯合剂[36]；革兰氏阳性菌表面众多的负电荷基团可发挥 Cr(Ⅵ)吸附作用，包括硫酸基团、羧基与氨基等[36]。

如图 3 所示，细菌表面上存在 Cr(Ⅵ)的吸

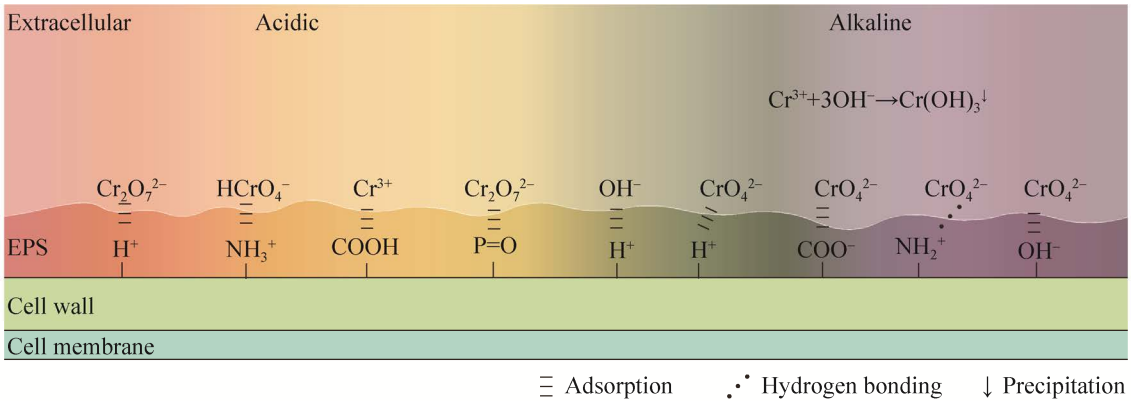

图 3 细菌表面 Cr(Ⅵ)的吸附与 Cr(Ⅲ)的沉淀过程

Figure 3 Adsorption of Cr(Ⅵ) and precipitation of Cr(Ⅲ) on bacterial surface. The three horizontal bars (≡) represent the adsorption of the functional groups with chromium, three dots (…) represent hydrogen binding, and the down arrow (↓) represents the Cr(Ⅲ) precipitation.

附与 Cr(Ⅲ)的沉淀过程[36,106,120−121]。在酸性条件下，细胞表面质子化后，H^+或$-NH_3^+$通过静电吸附 Cr(Ⅵ)[121]，羟基与羧基可静电吸附 Cr(Ⅲ)[36]，含磷基团(−P=O)也可对 Cr(Ⅵ)进行吸附[42]。碱性环境中，Cr(Ⅲ)由离子态沉淀为 $Cr(OH)_3$，羟基与羧基可吸附 Cr(Ⅵ)[86]，氨基($-NH_2^+$)通过氢键与 Cr(Ⅵ)结合[42]，Cr(Ⅵ)与带负电荷的 OH−存在吸附竞争[87]。

3 总结与展望

细菌修复 Cr(Ⅵ)污染主要依靠还原与吸附作用，自然界中的 Cr(Ⅵ)还原细菌的种类十分丰富，但均具有相似的还原或吸附机制。还原过程中涉及到细菌的胞内还原酶、胞外还原酶及膜结合还原酶的作用。胞内还原酶还原是细菌 Cr(Ⅵ)还原的主要方式；细胞外组分与膜组分也具有 Cr(Ⅵ)还原作用，但缺乏相应铬酸盐还原酶种类与结构的信息。环境因子可通过改变细菌的生长活性、相关基因的表达及酶活性来影响细菌的 Cr(Ⅵ)还原能力。细菌修复 Cr(Ⅵ)以还原作用为主；吸附作用主要涉及铬的络合、沉淀及静电吸引，细菌表面官能团在其中发挥主要作用。

目前，研究者不断深入探索细菌对 Cr(Ⅵ)还原与吸附机制，但现阶段的研究仍存在许多问题：(1) 许多研究停留在 Cr(Ⅵ)污染修复效果的展示，对还原过程中分子机制与电子转移关注较少；(2) 铬酸盐转运蛋白 ChrA 及膜结合还原酶的结构尚未得到解析；(3) 细菌的吸附过程多与还原过程相耦合，因此单独研究细菌对 Cr(Ⅵ)的吸附是一大难点，许多研究仅依靠官能团种类推测吸附过程。

因此，细菌的 Cr(Ⅵ)还原与吸附机制可从以下方面深入探究：(1) 从分子生物学水平上，发掘更多与 Cr(Ⅵ)还原过程相关的基因与蛋白，并对铬酸盐还原酶种类进行更加严谨有效的分类。同时探究 Cr(Ⅵ)与铬酸盐还原酶的结合位点及电子转移过程，明晰铬酸盐还原酶在还原过程中的作用机制；(2) 利用 X-射线晶体衍射法、核磁共振等方法解析铬酸盐转运蛋白 ChrA 的结构；(3) 利用新的方法与检测手段对吸附微过程进行研究与定量，确定铬在吸附过程中的动态变化。综上所述，未来需要综合利用分子生物学与酶动力学方法探究 Cr(Ⅵ)的还原过程，厘清细菌对 Cr(Ⅵ)的吸附作用，阐明细菌的 Cr(Ⅵ)修复过程。

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