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Review 综 述

典型重金属对氯苯类有机物生物转化影响及分子机制研究进展

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GOU Fang, CHEN Hao, XING Zhilin, ZHAO Tiantao. Progress in the effects and molecular mechanisms of typical heavy metals on the biotransformation of chlorobenzenes[J]. Acta Microbiologica Sinica, 2023, 63(10): 3727-3745.

摘 要：重金属和有机物相互作用，形成共污染，是当今面临的重要环境问题之一。明晰重金属作用下氯苯类化合物(chlorobenzenes, CBs)的转化特性以及典型重金属对 CBs 生物降解的影响机制，对有效修复重金属-有机物共污染有重要意义。本文首先对 CBs 生物降解的研究现状进行了总结，明晰了当前 CBs 降解的主要功能菌属类型，包括伯克霍尔德菌(*Burkholderia*)，假单胞菌(*Pseudomonas*)，脱卤球菌(*Dehalobium*)和脱卤拟球菌(*Dehalococcoides*)等；而后概述了重金属与 CBs 的共污染现状，发现绝大多数污染中存在重金属与 CBs 共污染现象；随后系统综述了典型重金属对 CBs 生物转化的影响，表明好氧或厌氧条件下大多数重金属离子对 CBs 生物转化存在抑制作用，受金属离子种类、浓度、价态及 pH 影响显著；另外，对重金属影响下的 CBs 转化机制进行了分析，基于 3 方面影响构建了分子机制模型。最后对目前还存在的问题与局限性进行了分析，并对未来发展方向进行了展望，以期为重金属-有机物共污染的修复提供支撑。

关键词：重金属；氯苯类有机物；生物转化；影响机制模型；多组学

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Progress in the effects and molecular mechanisms of typical heavy metals on the biotransformation of chlorobenzenes

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Abstract: The co-pollution of heavy metals and organic compounds is one of the major environmental issues today. Understanding the degradation and transformation characteristics of chlorobenzenes (CBs) under the influence of heavy metals is of great significance for remediation of the co-pollution. We summarized the current research status of CB biodegradation, clarified the main functional bacterial genera including *Burkholderia*, *Pseudomonas*, *Dehalobium*, and *Dehalococcoides* involved in CB degradation, and then outlined the co-pollution status of heavy metals and CBs. The co-pollution of heavy metals and CBs exists in the vast majority of pollution cases. Further, we systematically reviewed the effects of typical heavy metals on the biotransformation and degradation of CBs. Most heavy metal ions exert inhibitory effects on the biotransformation and degradation of CBs under aerobic or anaerobic conditions, and their inhibitory effects are significantly influenced by pH and the species, concentration, and valence state of heavy metals. In addition, the mechanisms of CB transformation and degradation under the influence of heavy metals were analyzed. A molecular mechanism model was constructed with consideration to three influencing mechanisms. Finally, we analyzed the current problems and limitations and prospected the future development direction, aiming to provide support for the remediation of heavy metal-organic co-pollution.

Keywords: heavy metals; chlorobenzenes; biotransformation; influence mechanism model; multi-omics

氯苯类有机物(chlorobenzenes, CBs)是化工产品中间体、杀虫剂和有机溶剂等的重要组成[1]，已成为制药、印染和有机合成等工业废水普遍存在的持续性有机污染物，工业废水污染物复杂，CBs 去除一直未得到有效解决，非法排放致使环境中广泛存在(图 1)[2-5]。据估计，全球每年由工业废水排放到环境中的 CBs 超过 50 万 t，持续挥发和沉积循环使得 CBs 污染遍布全球，甚至南极大陆和北极积雪中均有检出[6]。最近一项研究发现三氯苯(trichlorobenzenes, TCBs)、四氯苯(tetrachlorobenzenes, TeCBs)、五氯苯(pentachlorobenzene, PeCB)、六氯苯(hexachlorobenzene, HCB)等 8 种 CBs 在废水中广泛存在，原水中 HCB 浓度可达 9.3 μg/L，处理后水中的 CBs 对生态系统依然构成中度风险[2]。CBs 属一级致癌物，被《斯德哥尔摩公约》和美国环保署列为优先污染物，其高毒性、难降解和易生物蓄积等特性严重危及人类健康和生态安全[7-8]。持久性有毒污染物环境暴露与控制问题研究已成为我国优势学科和交叉学科的重要前沿方向。针对国家“十四五”生态环境保护规划里提出包含工业废水在内的各类废水深度超净处理要求，明晰水污染环境中 CBs 的转化特性，采取有效措施消除 CBs 污染已成为急需开展的研究。

随着人类工、农业活动的快速发展，各类污染水体中产生的有毒有害物质越来越复杂多样。

在污染物的交互作用下，极易形成共污染，其中重金属-有机物共污染最为广泛。Arjoon 等[9]总结了氯代有机物-重金属复合污染水体处理面临的挑战，发现几乎所有 CBs 和有机氯农药的污染水体均伴随重金属污染；Lee 等[10]调查了海岸线工业废水排污口近百个沉积物中污染情况，CBs 浓度最高为 290.5 ng/g，重金属主要有 Cu^{2+}、Pb^{2+}、Cd^{2+}、Mn^{2+}和 Cr^{6+}，浓度范围为 0.04–523.8 mg/kg，充分证实了 CBs 类有机物重金属复合污染广泛存在。重金属和有机物与环境之间产生相互作用，对环境的污染从单一变得复杂，不仅增加了处理成本，对生态环境危害更大。近年来，科研工作者逐渐开展了废水中典型重金属对有机物生物转化的影响研究。有研究发现废水中微量 Cr^{6+}、Cd^{2+}和 Pb^{2+}等可显著抑制氯代有机物的转化[11]，重金属作用下有机污染物生物转化研究正成为环境领域关注的重点。

重金属对 CBs 生物转化的影响机制的认知是有效处理重金属-有机物共污染的重要前提。当前，水污染环境中重金属对 CBs 生物转化影响研究才刚刚开始，相关信息还十分有限。有研究表明，重金属影响微生物的分子机制主要包括：重金属作为辅酶因子与酶结合，促进酶活性；重金属与酶的活性部位结合，取代原有的必需金属，抑制酶的活性；重金属与 DNA 的活性或非活性点位结合，抑制转录和翻译过程[12-13]。因此，

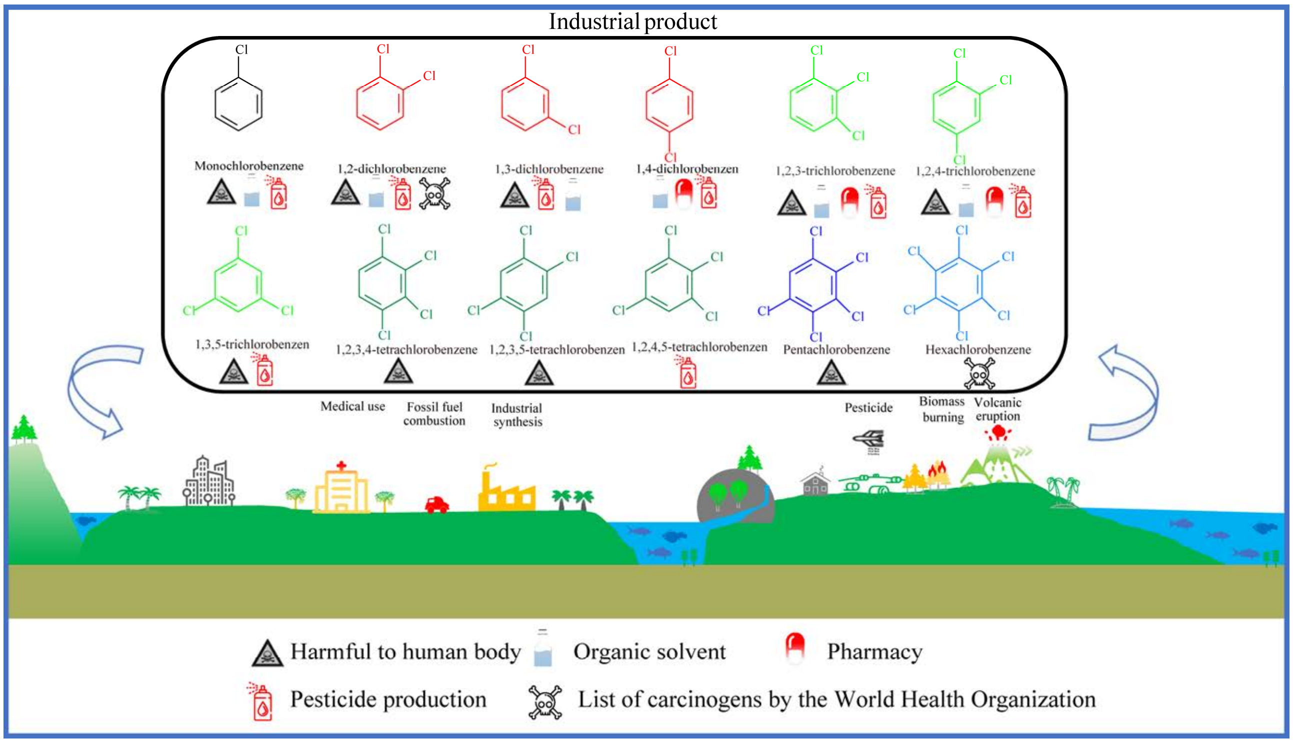

图 1　典型氯苯类有机污染来源及危害[2-5]

Figure 1　Typical chlorobenzene organic pollution sources and hazards[2-5]. CBs are derived from sources such as pharmaceutical intermediates, fossil fuel combustion, pesticide use, volcanic eruptions, and industrial leaks, and after entering the environment, they cycle through the atmosphere, water, and soil media through processes such as volatilization and settling. CBs can accumulate in the bodies of animals and plants, enter the human body through the food chain, and the vast majority of them have teratogenic, carcinogenic, and mutagenic characteristics.

系统认知重金属-有机物共污染的研究现状对进一步探究重金属对 CBs 生物转化的影响机制具有重要指导价值。

据此，本文对 CBs 生物降解的研究现状进行了调研，归纳了重金属与典型 CBs 共污染现状；系统总结了重金属对 CBs 生物转化的影响情况，预测了对 CBs 影响的分子机制。简析了现有研究基础上还存在的问题与局限性，最后对未来发展方向进行了展望，以期为重金属-有机物共污染的修复提供理论指导。

1 CBs 生物转化研究现状

CBs 化学结构稳定，是持续性有毒物质的典型代表。CBs 极易形成氯化有机溶剂，对环境造成污染，该类污染广泛存在于地下水和土壤中。作为重质非水相液体的成分之一，因其化学性质稳定，一旦进入地下，很难将其去除，并且它仍是目前环境中最难修复的污染物之一[14]。通过物化法难以实现 CBs 的高效去除，且极易产生剧毒副产物[4,15]。生物转化技术因具有适用范围广、二次污染小和处理成本低等特点，被认为是 CBs 去除最有前景的方法之一[3,15-16]。生物转化利用生物活性去破坏污染物，将其转化为 CO_2、水等无害产物，可以最大限度地减少残留污染。

自 20 世纪 50 年代发现 CBs 暴露对人体血红素产生严重合成障碍以来，科研工作者开展了广泛的 CBs 生物转化研究[13]，集中在降解菌的分离纯化，生物转化机理解析，环境中生物转化过程模拟等。如表 1 所示，截至目前，所分离的好氧纯菌株主要包括伯克霍尔德菌(*Burkholderia*)，假单胞菌(*Pseudomonas*)，罗尔斯通菌(*Ralstonia*)，鞘氨醇单胞菌(*Sphingomonas*)，红球菌(*Rhodococcus*)，潘多拉菌(*Pandoraea*)等十几种菌属；厌氧纯菌株主要包括脱卤球菌(*Dehalobium*)，脱卤拟球菌(*Dehalococcoides*)，脱卤素杆菌属(*Dehalobacter*)，脱氯梭菌(*Desulfitobacterium*)，脱硫单胞菌(*Desulfomonile*)等菌属[15,17-48]。菌株来源主要为长期受氯苯类污染的土壤或活性污泥，降解率范围大多在 60%–90%，这些菌株的分离为 CBs 降解机制的深入研究提供了保障。基于纯菌株降解过程的系统性分析，CBs 转化机理逐渐被解析，典型 CBs 的生物转化机理如图 2 所示[15,49]。好氧条件下 CBs 作为微生物的唯一碳源和能源，在双加氧酶，二氢二醇脱氢酶，外二醇双氧化酶等系列关键酶的作用下转化为无机物[49]。厌氧条件下，CBs 在脱卤微生物的作用下，脱去氯离子，产生低氯取代烃，脱卤过程受微生物种类和环境的显著影响，不同菌株脱氯可产生不同的同分异构体，完全脱氯后，有机物可进一步被微生物转化，产生有机酸和二氧化碳等产物[15,49]。此外，也有研究发现好氧条件下也可能发生脱氯反应，蒋建东等[50]分离鉴定出一种新型的卤代芳香族化合物水解脱卤酶 *Chd*，它既可以在好氧条件下脱卤，也可以在厌氧条件下脱卤。这些研究为场地 CBs 生物修复提供了理论支撑。

近两年，研究者利用功能菌开展了 CBs 生物转化模拟试验。Kurt 等[16]模拟了包气带和地下水界面中 CB，1,2-二氯苯(1,2-DCB)和 1,4-二氯苯(1,4-DCB)的生物转化，证明包气带中微生物促进了地下水中 CBs 的生物转化。Yang 等[51]利用农业短芽孢杆菌(*Brevibacillus agri*) DH-1 强化 1,4-DCB 在生物滤池中的转化，表明该菌株可实现 1,4-DCB 的稳定去除，最高去除率达 100%。Qiao 等[15]连续五年监测旧工业废水管道周边 CBs 的污染和降解情况，发现主要污染物为 1,2,4-三氯苯(1,2,4-TCB)，DCBs 和 CB，其中 1,2,4-TCB 浓度高达 7 300 μg/L，实验室降解模拟研究中发现 1,2,4-TCB 以 2%，10%和 88%的

表 1　功能菌株强化 CBs 降解研究进展

Table 1　Research progress in enhanced degradation of CBs by functional strains

Eubacterium	Strain	Source	Degradation mechanism	Degradation rate constant	References
Lysinibacillus fusiformis	LW13	Mature mud samples of chlorobenzene long-term domestication	Assimilation	97.0 g/(m^3·h)	[17]
Ralstonia pickettii	L2	Bacterial consortium samples collected in biotrickling reactor treating CB contaminated gas streams	Assimilation	117.0 g/(m^3·h)	[18]
Delftia tsuruhatensis	LW26	Biotrickling filter for CB contaminated gas flow	Assimilation	2.5 h^{-1}	[19]
Pseudomonas	FY01, FY04	Activated sludge in sewage treatment aeration tank of Fushun No. 2 petroleum plant		FY04 52.4% FY01 47.2%	[20]
Bacillus	FY02, FY03			FY02 44.8% FY03 42.6%	[20]
Microbacterium	TAS1CB	Gas station, garage and other hydrocarbon contaminated sites	Assimilation	60.0%	[21]
Comamonas testosteroni	KT5	Soil, mud, river sediments, sewage sludge samples and industrial wastewater from several hazardous waste treatment sites in southern Vietnam were thoroughly mixed	Assimilation		[22]
Bacillus subtilis	DKT				
Labrys portucalensis	F11	Sediments collected from contaminated sites	Co-metabolism		[23]
Pandoraea pannomenusa	MCB032	Samples from bioreactors	Assimilation		[24]
Ochrobactrum	ZJUTCB-1	An activated sludge obtained from a Hangzhou wastewater treatment plant	Assimilation	170.9 μmol/(L·h)	[25]
Streptococcus	WCB	Petroleum contaminated soil in Liaohe oilfield	Aerobic	93.2%	[26]
Pseudomonas	LP01	Activated sludge in sewage treatment aeration tank of Fushun No. 2 petroleum plant		93.9%	[27]
Streptococcus	JH02	Activated sludge in sewage treatment aeration tank of Jihua Group sewage treatment workshop		94.7%	[27]
Acinetobacter	CB001	Jilin petrochemical company sewage treatment plant aerobic activated sludge, surface sediment near the sewage outlet and river water			[28]
Ralstonia pickettii	L2	Biofilm on filler surface of biotrickling bed for purifying chlorobenzene waste gas		99.0%	[29]
Lysinibacillus	LW13	Mature sludge of long-term acclimated chlorobenzene		93.8%	[30]
Enterobacter	CB-2	Activated sludge samples from Dalian chemical plant		82.0%	[31]
Flavobacterium	DEB-1	Activated sludge in a sewage treatment aeration tank		94.5%	[32]

(待续)

(续表 1)

Eubacterium	Strain	Source	Degradation mechanism	Degradation rate constant	References
Bacillus cereus	DL-1	Yancheng reed wetland rhizosphere soil		80.3%	[33]
Pseudomonas stutzeri	THSL-1	Soil of chlorobenzene production workshop in Tianjin chemical plant			[34]
Bordetella	E3, F2	chlorobenzene contaminated soil		>90.0%	[35]
Trametes versicolor				91.1% (1,2,3-TCB), 79.6% (1,2,4-TCB)	[36]
Ralstoniapickettii strain	H2	Biotrickling bed filler for purifying chlorobenzene waste gas		97.5%	[37]
Sphingobium fuliginis	HC3	Collection of contaminated soil samples in areas long-term contaminated by PCBs	Aerobic	44.9%	[38]
Delftiatsuruhatensis	LW26	Activated sludge in wastewater treatment tank of a pharmaceutical factory in Zhejiang			[39]
Pseudomonas mosselii	HD-1	Waste pesticide factory soil		59.6%	[40]
Ochrobacterum	ZJUTCB-1	Activated sludge in Hangzhou Qige wastewater treatment plant	Aerobic Anaerobic	19.6 mg/(L·h) 23.6 mg/(L·h)	[41]
Kocuria	KD139	Sludge from sewage outlet of Tianjin chemical plant		39.0%	[42]
Rhodococcus	KD140, KD142			32.0%–40.0%	[42]
Bacillusd	KD178			54.0%	[42]
Arthrobacter	KD230			7.8%–47.0%	[42]
Stentrophomonas	KD237			60.78%	[42]
Paenibacillus	ORNaP1	Obertro Lagoon on the Tyrrhenian coast, central Italy	Aerobic	87.0%	[43]
Pseudomona	ORNaP2		Aerobic	92.0%	[43]
Acinetobacter	WH-L1	River system near Changzhou City, Jiangsu Province		94.1%	[44]
Microbacterium oxydans	WH-L2			72.7%	[44]
Serratia marcescens	WH-L3			67.8%	[44]
Bacillus subtilis	GY1	Water samples collected from Guilin pharmaceutical factory, dye factory, Lijiang River and Taohua River		61.6%	[45]
Bacillus megaterium	GY2			62.7%	[45]
Bacillus anthraci	GY3			60.9%	[45]
Bacillus stratosphericus	GY4			62.5%	[45]
Dehalococcoides	CBDB1	A medium containing 15 μmol/L 1,2,3-trichlorobenzene and 15 μmol/L 1,2,4-trichlorobenzene as electron acceptors	Anaerobic		[46]
Dehalobacter		An industrial pollution site in Liuhe, Nanjing	Anaerobic	(3.2±0.4) μmol/d	[47]
Dehalobium		Homsbush Bay pollution source srea	Anaerobic		[48]

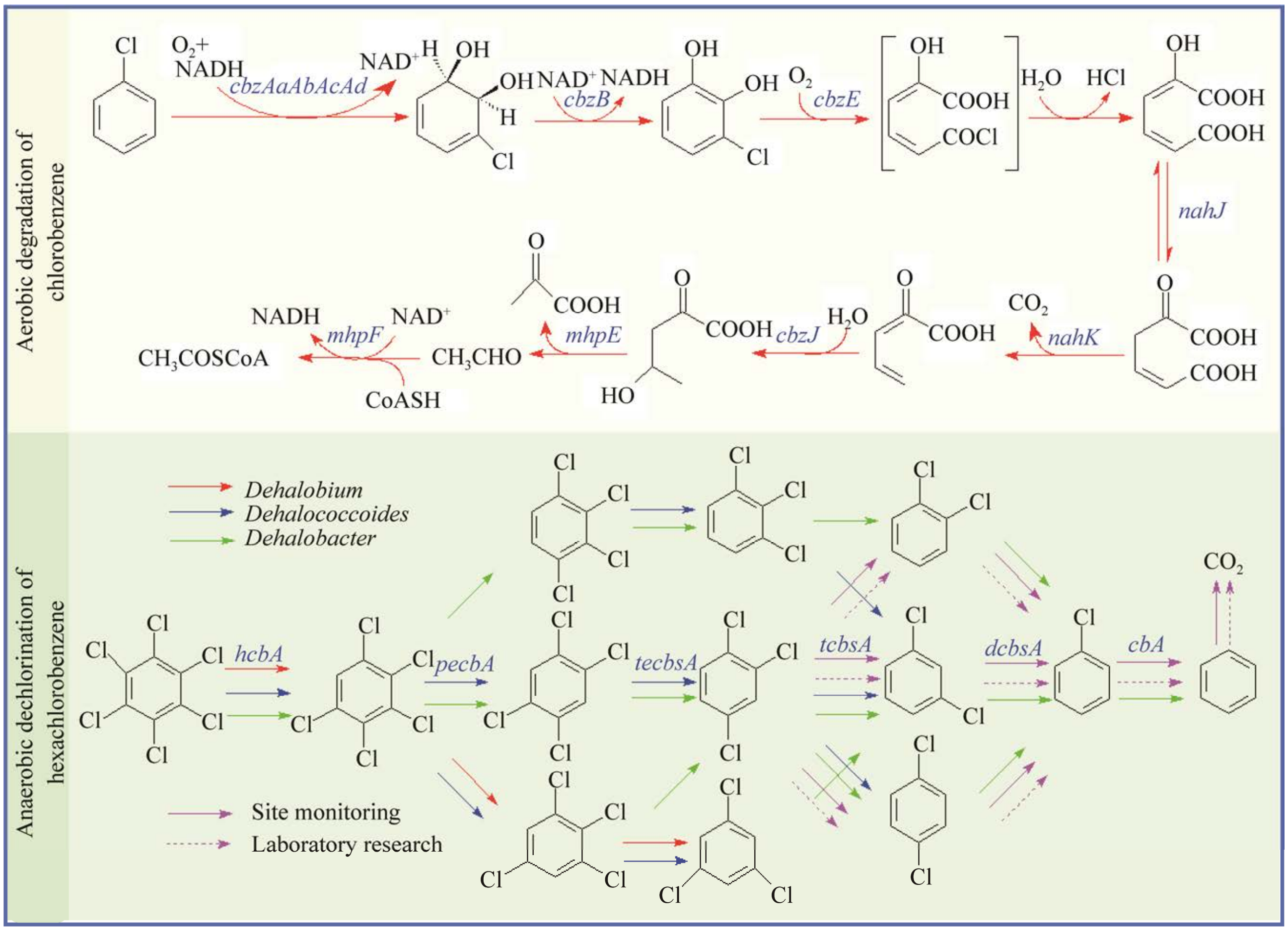

图 2　CBs 生物转化途径及关键酶基因[15,49]

Figure 2　CBs biodegradation pathway and key enzyme genes[15,49]. CB aerobic transformation and degradation occurs gradually under the action of a series of enzymes, such as dioxygenases, dihydroxychlorophenol dehydrogenases, and mutases. The type of microorganisms and experimental conditions have a significant impact on HCB anaerobic dechlorination, and different strains can produce different isomers. *Dehalococcoides*, *Dehalobacter*, and *Dehalobium* are the most typical dechlorinating strains.

摩尔比脱氯成 1,2-DCB、1,3-DCB 和 1,4-DCB。Kurt 等[52]模拟了水体沉积物中 CB 的转化，转化速率为 2–4.2 g/(m^2·d)，表明强化沉积物中生物降解能力可消除 CB 向水中的污染扩散。这些研究充分证明了生物降解是环境中 CBs 去除的有效手段。

已有的 CBs 生物降解研究更多关注于单一污染条件下的转化过程，然而工业发展所导致的环境污染更具复杂性，常常会存在共污染现象[13,53-54]。在多种因子作用下，CBs 降解过程复杂，有研究发现 HCB 在共污染场地中与实验室单一污染条件下的厌氧生物转化途径差异很大[15]。因此，探明影响因子对 CBs 转化的作用机制十分必要，当前开展相关研究已成为 CBs 去除领域的重要方向。

2 重金属与 CBs 共污染现状

就工业废水和环境 CBs 污染而言，重金属-CBs 共污染最为显著[12,43]。美国环境保护署国家优先清单上 40%的危险废物场地都受到有机物和重金属的共同污染。在美国环境保护署超级基金站点最常见的金属分为两类，一类是阳离子金属，以带正电的阳离子形式存在于土壤中，另一类是阴离子化合物，在土壤中存在的形式是与阳离子结合并带负电。对环境造成污染的最常见的阳离子金属包括铜、汞、铅、镉、铬、镍、铜和锌，最常见的阴离子化合物为砷。与此同时，在这些深受重金属污染的地方，常常伴有石油、多环芳烃、氯化溶剂、除草剂和杀虫剂等有机物的共同污染。

Arjoon 等[13]总结了重金属-氯代有机物共污染水体处理面临的挑战，几乎所有 CBs 和有机氯农药等工业污染水体伴随重金属污染，重金属对氯代有机物去除有多重影响。Lee 等[55]调查了台湾南部高雄海岸线工业废水排污口附近 40 个沉积物样品中 CBs 和重金属共污染情况，总 DCBs、TCBs、TeCBs、QCB 和 HCB 的浓度分别为 290.5、117.1、64.5、15.7 和 22.3 ng/g，重金属 Cu^{2+}、Zn^{2+}、Pb^{2+}、Cd^{2+}、Ni^{2+}、Mn^{2+}和Cr^{6+}浓度分别为 1.3–25.0、45.0–127.5、2.5–25.0、0.04–0.42、3.8–42.5、176.3–523.8、12.5–95.0 mg/kg，调研表明重金属-CBs 共污染广泛存在。Sandrin 等[56]调查发现废水处理过程中重金属去除与否可显著影响出水口有机污染物浓度，有机污染物与重金属浓度间存在显著的相关性。重金属-有机物共污染水体处理已成为环境领域关注的重点，有效认知重金属对 CBs 生物转化影响已成为氯代有机污染物去除领域关注的热点。

研究者在重金属和有机物的共污染场地成功分离出了一些具有重金属耐受性和氯代有机物转化功能的微生物。这些微生物包括红球菌(*Rhodococcus ruber*) C1、沙雷氏菌(*Serratia marcescans*) TF-1 和贪铜菌(*Cupriavidus* sp.) SWA1，它们都表现出了惊人的适应性和强大的降解能力。红球菌不仅能够耐高浓度苯酚和重金属，还能在低温环境下生存并保持活性[57]。沙雷氏菌既可以利用氯苯作为唯一的碳源和能源，又可以通过共代谢作用来降解 CB[58]。这意味着它可以与其他微生物合作，通过相互作用来降解污染物，这种合作对于复合污染场地的治理尤为重要。贪铜菌能够以氯代烯烃等难降解毒性有机物为唯一碳源和能源生长，并且可以在贫养环境中保持较高活性[59]。这些微生物的强大能力和适应性使得它们在复合污染场地中保持着高活性，进一步明晰复合环境中重金属对 CBs 生物转化的影响特性极为重要，可以为有效修复重金属和有机物的共污染场地提供理论基础。

3 重金属对 CBs 生物转化的影响特性

大量研究表明废水中微量重金属即可对有机物的生物转化产生影响。Garg 等[8]研究发现制革废水中汞对五氯苯酚抑制作用最强，而钴的抑制作用最小。Sandrin 等[60]总结发现有机物生物转化机理受重金属种类、浓度和价态影响极大。

好氧和厌氧条件下重金属对氯代芳烃生物转化影响情况如表 2 和表 3 所示[11,61-75]。好氧条件下复合污染的重金属主要有 Cu^{2+}、Cd^{2+}、Hg^{+}、Mn^{2+}、Ni^{2+}、Pb^{2+}和 Zn^{2+}等，它们对氯代芳烃生物转化产生影响的最低浓度范围分别在 0.01–71.6 mg/L、0.000 06–50.6 mg/L、0.002–226 mg/L、28.2–317 mg/L、5.18–20 mg/L、1.41–2.8 mg/L 和 0.006–736 mg/L。厌氧条件下复合污染的重金属主要有 Cd^{2+}、Cr^{6+}、Pb^{2+}和 Zn^{2+}等，它们对氯代芳烃生物转化产生影响

表 2 好氧条件下重金属对氯代芳烃生物降解影响

Table 2 Effects of heavy metals on biodegradation of chlorinated aromatic hydrocarbons under aerobic conditions

Metal	Organic	Lowest metal concentration	Microbe	pH	References
As^{3+}	DDT	5 mg/L^{a}	Indigenous community	NR	[61]
Cu^{2+}	2,4-DME	0.027 mg/L^{a}	Indigenous community	5.0	[62]
Cu^{2+}	2,4-DME	0.076 mg/L^{a}	Indigenous community	6.1	[62]
Cu^{2+}	4-CP, 3-CB, 2,4-D, XYL, IPB, NAPH, BP	<14.3–71.6 mg/L^{a,b}	*Alcaligenes* sp., *Pseudomonas* sp., *Moraxella* sp.	7.0	[63]
Cu^{2+}	PHB	8 mg/L^{d}	*Acidovorax delafieldii*	6.9	[64]
Cu^{2+}	Crude oil	6.30 mg/L^{a}	*Pseudomonas* sp.	7.2	[65]
Cu^{2+}	Crude oil	11.25 mg/L^{a}	*Micrococcus* sp.	7.2	[65]
Cu^{2+}	PH	0.01 mg/L^{a}	*Acinetobacter calcoaceticus* AH	7.8	[66]
Cd^{2+}	2,4-D	24 mg/L^{a}	*Alcaligenes eutrophus* JMP134	6.0	[67]
Cd^{2+}	2,4-D	0.000 06 mg/L^{a}	*Alcaligenes eutrophus* JMP134	8.2	[67]
Cd^{2+}	2,4-D	0.000 06 mg/L^{a}	*Alcaligenes eutrophus* JMP134	8.2	[67]
Cd^{2+}	2,4-DME	0.100 mg/L^{a}	Indigenous community	6.5	[62]
Cd^{2+}	2,4-DME	0.629 mg/L^{a}	Indigenous community	5.6	[62]
Cd^{2+}	2,4-D	>3 mg/L^{a}	*Alcaligenes eutrophus* JMP134	6.0	[67]
Cd^{2+}	2,4-D	24 mg/L^{a}	*Alcaligenes eutrophus* JMP134	6.0	[67]
Cd^{2+}	4-CP, 3-CB, 2,4-D	<25.3–50.6 mg/L ^{a,b}	*Alcaligenes* spp., *Pseudomonas* spp., *Moraxella* sp.	7.0	[62]
Cd^{2+}	PHEN	1 mg/L^{d}	Indigenous community	7.6	[68]
Cd^{2+}	TOL	37 mg/L^{a}	*Bacillus* sp.	5.9	[69]
Co^{2+}	4-CP, 3-CB, 2,4-D, XYL, IPB, NAPH, BP	<13.3–1.330 mg/L ^{a,b}	*Alcaligenes* spp., *Pseudomonas* spp., *Moraxella* sp.	7.0	[64]
Cr^{3+}	2,4-DME	0.177 mg/L^{a}	Indigenous community	6.1	[62]
Cr^{6+}	4-CP, 3-CB, 2,4-D, XYL, IPB, NAPH, BP	<131 mg/L ^{a,b}	*Alcaligenes* spp., *Pseudomonas* spp., *Moraxella* sp.	7.0	[62]
Hg^{2+}	2,4-DME	0.002 mg/L^{a}	Indigenous community	6.8	[62]
Hg^{2+}	4-CP, 3-CB, 2,4-D, XYL, IPB, NAPH, BP	<45.2–226 mg/L ^{a,b}	*Alcaligenes* spp., *Pseudomonas* spp., *Moraxella* sp.	7.0	[62]
Mn^{2+}	Crude oil	317.0 mg/L^{a}	*Pseudomonas* sp.	7.2	[65]
Mn^{2+}	Crude oil	28.2 mg/L^{a}	*Micrococcus* sp.	7.2	[65]
Ni^{2+}	4-CP, 3-CB, 2,4-D, XYL, IPB, NAPH, BP	5.18–10.3 mg/L^{a,b}	*Alcaligenes* spp., *Pseudomonas* spp., *Moraxella* sp.	7.0	[63]
Ni^{2+}	TOL	20 mg/L^{a}	*Bacillus* sp.	5.9	[69]
Pb^{2+}	Crude oil	2.8mg/L^{a}	*Pseudomonas* sp.	7.2	[65]
Pb^{2+}	Crude oil	1.41 mg/L^{a}	*Micrococcus* sp.	7.2	[65]
Zn^{2+}	2,4-DME	0.006 mg/L^{a}	Indigenous community	6.4	[63]
Zn^{2+}	2,4-DME	0.041 mg/L^{a}	Indigenous community	5.6	[63]
Zn^{2+}	4-CP, 3-CB, 2,4-D, XYL, IPB, NAPH, BP	<29.5–736 mg/L^{a,b}	*Alcaligenes* spp., *Pseudomonas* spp., *Moraxella* sp.	7.0	[63]
Zn^{2+}	pH	10 mg/L^{a}	*Acinetobacter calcoaceticus*, AH	7.8	[66]
Zn^{2+}	Crude oil	0.43 mg/L^{a}	*Pseudomonas* sp.	7.2	[65]
Zn^{2+}	Crude oil	0.46 mg/L^{a}	*Micrococcus* sp.	7.2	[70]
Zn^{2+}	TOL	2.8 mg/L^{a}	*Bacillus* sp.	5.9	[69]

DDT: 1,1,1-trichloro-2,2-bis (4-chlorophenyl)ethane; 2,4-DME: 2,4-dichloro-phenoxyacetic acid methyl ester; 4-CP: 4-chlorophenol; 3-CB, 3-chlorobenzoate; 2,4-D: 2,4-dichlorophenoxyacetic acid; XYL: Xylene; IPB: Isopropyl benzene; NAPH: Naphthalene; BP: Biphenyl; PHB: Polyhydroxy butyrate; PH: Phenol; PHEN: Phenanthrene; TOL: Toluene; MTC: Maximum total concentration; NR: Not reported; ^{a}: Value represents total metal added to system; ^{b}: Value represents MIC calculated by multiplying MTC by a factor of 2.25.

表 3　厌氧条件下重金属对氯代芳烃生物降解的影响

Table 3　Effects of heavy metals on biodegradation of chlorinated aromatic hydrocarbons under anaerobic conditions

Metal	Organic	Lowest metal concentration	Microbe	pH	References
Cd^{2+}	2-CP, PH, BEN, 3-CB	0.5–1.0 mg/L^b	Indigenous community	7.0	[71]
Cd^{2+}	2-CP, 3-CP	20 mg/L^b	Indigenous community	7.0	[72]
Cd^{2+}	TCA	0.01 mg/L^a	Indigenous community	6.9–7.4	[73]
Cd^{2+}	TCA	0.2 mg/L^a	Indigenous community	6.8	[73]
Cd^{2+}	HCB	0.75 mg/L ^{a}	Indigenous community	NR	[11]
Cr^{6+}	2-CP, 3-CP	20 mg/L^b	Indigenous community	7.0	[72]
Cr^{6+}	2-CP, PH, BEN, 3-CB	0.01–0.5 mg/L^b	Indigenous community	7.0	[71]
Cu^{2+}	2-CP, PH, BEN, 3-CB	0.1–1.0 mg/L^b	Indigenous community	7.0	[71]
Cu^{2+}	2,4-DANT, RDX	4 mg/L^b	Indigenous community	6.5	[74]
Cu^{2+}	4-ADNT	8 mg/L^b	Indigenous community	6.5	[74]
Cu^{2+}	2-CP, 3-CP	20 mg/L^b	Indigenous community	7.0	[72]
Cr^{6+}	2-CP, 3-CP	20 mg/L^b	Indigenous community	7.0	[72]
Pb^{2+}	HCB	0.75 mg/L^b	Indigenous community	NR	[11]
Pb^{2+}	2,4-DANT, RDX	>0.001 mg/L^b	Indigenous community	6.5	[74]
Hg^{2+}	2-CP, PH, BEN, 3-CB	0.1–1.0 mg/L^b	Indigenous community	7.0	[71]
Zn^{2+}	PCP	2 mg/L^b	Indigenous community	NR	[75]
Zn^{2+}	2,4-DANT	0.001 mg/L	Indigenous community	6.5	[74]

2-CP: 2-chlorophenol; BEN: Benzoate; 3-CP: 3-chlorophenol; TCA: Trichloroaniline; HCB: Hexachlorobenzene; 2,4-DANT: 2,4-dinitroanisole; RDX: Cyclonite; 4-ADNT: 4-amino-3,5-dinitrotoluene; PCP: Pentachlorophenol; NR: Not reported; ^{a}: Value represents solution-phase concentration of metal present in system; ^{b}: Value represents total metal added to system.

的最低浓度范围分别在 0.01–20 mg/L、0.01–20 mg/L、0.001–0.75 mg/L、0.001–2 mg/L。不同重金属种类和金属离子形式对氯代烃生物转化的影响不同，且能够产生影响的最低金属浓度也有差异。重金属离子形式受环境条件影响，如 pH、水相的氧化还原电位、土壤特性等，其中土壤特性包括离子交换能力、黏土的类型和含量以及有机物的含量等[47]。Hoffman 等[76]用最低盐培养基分离出睾丸酮丛毛单胞菌(*Comamonas testosterone*)，评估了镉对该菌株降解萘的影响，采用了 3 种培养基 Tris-buffered MSM、PIPES-buffered MSM 和 Bushnell-Haas，每种培养基的抑制程度不同，PIPES-buffered MSM 抑制最大，Bushnell-Haas 抑制最小，结果表明介质类型决定了金属抑制生物降解的模式和程度。无论是好氧条件还是厌氧条件下，重金属对氯代芳烃生物转化产生影响的环境大多在中性或者酸性，其中好氧条件下 pH 值在 5.0–8.2 之间，厌氧条件下在 6.5–7.4 之间。Sandrin 等[60]将微生物培养基的 pH 值从 7 降低到 4，研究了 pH 对萘生物转化过程中镉的毒性、形态和积累的影响。发现，随着 pH 下降，镉的积累减少，镉的毒性减小，对萘生物降解的抑制作用减小。

用于表征金属毒性的方法目前最常用的是

生物利用度，重金属的化学和物理形态不同，其金属形态和生物利用度也不同。生物利用度是指特定环境中、一定时间内，全部金属里能够产生作用的一部分，另一部分可以被微生物直接吸收。重金属的生物利用度决定了金属对生物的毒性影响作用，一般生物利用度越小，说明金属对生物的毒性作用越小。但是目前很少有研究提供生物利用度的具体数据[70]。Arjoon[13]等使用无机处理添加剂，碳酸钙($CaCO_3$)、石膏($CaSO_4{\cdot}2H_2O$)和磷酸二钠(Na_2HPO_4)来改善 1,2-二氯乙烷(1,2-DCA)共污染土壤的修复。结果表明无机处理添加剂可用于减少土壤中金属的生物利用度，从而限制这些金属对氯代烃生物降解的毒性作用。

4 重金属对 CBs 生物转化的影响机制分析

系统总结发现，重金属对有机物生物转化影响主要表现有：污水中微量重金属[(0.001–0.002) mg/mL]即可影响有机物转化；重金属既能抑制又能促进有机物转化，同一体系中不同有机物生物转化过程对重金属响应差异很大，不同重金属的抑制浓度可相差数十倍，有机物转化过程对同一种金属的不同价态敏感程度不同，有机物转化过程添加某些重金属可使降解速率提高 133%–168%[12-13,77]。Xu 等[78]利用纯菌株同步去除废水中 1,2-DCB 和 Cr^{6+}研究时发现 Cr^{6+}与 1,2-DCB 的去除速率呈显著负相关。随后，Jackson 等[11]评估了沉积物中重金属对 HCB 还原脱氯的影响。发现 Cd^{2+}、Cu^{2+}、Zn^{2+}和 Pb^{2+}对 HCB 还原脱氯均有抑制作用。这些研究证实了重金属是 CBs 生物转化的重要影响因子。

分子水平上，重金属对水体污染物代谢影响的分子机制解析正受到关注。在基因组方面，研究发现 Cu^{2+}、Zn^{2+}、As^{3+}等可对微生物 DNA 造成严重损伤，最高损伤比例超过 90%[79]；考察了 Cu^{2+}作用下关键酶基因的表达及活性变化规律，结果表明 Cu^{2+}浓度不同，关键酶基因表达量和酶活性均发生变化，重金属对功能基因表达和酶活性具有显著的调控作用[80]。在转录组方面，研究发现 Cu^{2+}可抑制 *amoA* 和 *nxrB* 基因表达[22]；Cr^{3+}抑制 *amoA* 和 *hao* 的表达，Cr^{6+}也抑制 *amoA* 的表达，而当浓度高于 30 mg/L 时，促进 *hao* 的表达[81]；Ni^{2+}抑制 *amoA* 和 *hao* 的表达，而 0.33 mg/L 的 Zn^{2+}促进 *amoA*、*hao* 和 *nirK* 表达[77]；Feng 等[82]的研究发现 Cr^{6+}能显著抑制四溴双酚 A 代谢相关酶细胞色素 p450、谷胱甘肽 s 转移酶和五氯酚 4-单加氧酶基因表达。在酶活性方面，研究发现 Pb^{2+}可显著降低水处理系统脲酶、过氧化氢酶、转化酶和酸性磷酸酶的活性[83-84]，As^{3+}显著降低芳基硫酸酯酶的活性，但对转化酶，蛋白酶和碱性磷酸酶无影响。这些研究证实了在分子水平上重金属对基因组，关键酶基因表达及酶活性产生影响进而影响污染物转化。

生物转化可发生在胞外、间膜以及胞内，研究表明胞内转化更容易受到重金属的抑制作用[85]。CBs 转化主要在微生物细胞内进行，重金属可以干扰酶的活性，影响转化过程。微生物细胞对重金属响应机制研究的系统性总结表明，在分子水平上，影响机制主要包括：(1) 外源重金属离子与酶的活性位点结合取代原有必需金属离子，抑制酶活性；(2) 重金属可作为辅酶因子，成为结构蛋白的组成部分，促进降解酶活性；(3) 重金属胁迫下，微生物产生活性氧(reactive oxygen species, ROS)，破坏细胞中所有生物大分子，抑制转录、翻译、酶催化过程(图 3)[12-13,86]。

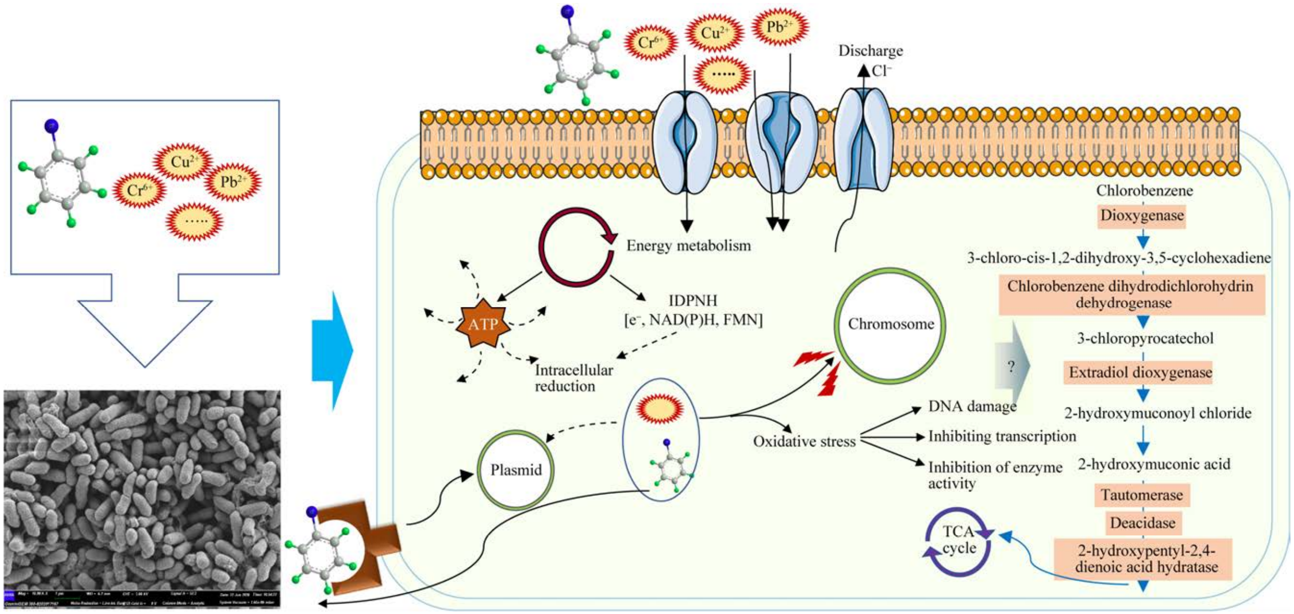

图 3　重金属对 CBs 生物转化影响的分子机制预测模型

Figure 3　Molecular mechanism prediction model for the effect of heavy metals on CBs biodegradation. Heavy metals can bind to the active site of the enzyme, hinder the binding between the enzyme and the substrate, or interfere with the metal ions required for the enzyme-catalyzed reaction. Heavy metals can also bind to substrates or reaction products, thereby changing the reaction equilibrium and further inhibiting the conversion process. Or form stable complexes to inhibit the catalytic activity of the enzyme by competitively inhibiting the binding of metal ions to the enzyme.

5　总结与展望

复合污染问题日益严重，对生态环境危害极大且治理极具挑战。“有机物-重金属复合污染治理”已成为各类环境政策中关注的重点，仅针对单一污染的治理策略已无法满足严格保护生态环境、有效控制环境污染的需求。面向解决复杂环境中持续性有机污染物的高效去除，针对实现重金属作用下功能菌株对 CBs 高效转化，重金属作用下 CBs 转化机理和系统的代谢分子机制亟待探索与解析。未来研究中需要关注以下几个方面的研究：

(1) 多组学技术解析重金属对生物转化的影响机制。为准确解析重金属对 CBs 生物转化影响的分子机制，宏基因组学、宏转录组学、蛋白组学和代谢组学等组学技术为解析 CBs 降解机制及环境因子对微生物行为的影响提供了有力手段[87]。CBs 等有机物生物降解过程受多种基因控制，宏基因组可识别单一菌株或环境微生物中的全部潜在功能基因，该技术已经广泛应用于氯代有机污染降解菌的基因组分析[49]。

环境中有毒物质存在对暴露微生物的基因表达水平产生影响，形成转录调控，宏转录组学技术已被应用于各种微生物系统，以探索全基因组的转录活性，Cheng 等[88]首次利用宏转录组解析了红串红球菌(*Rhodococcus erythropolis*) D310-1 对氯嘧磺隆降解过程的基因表达，发现了 500 个基因的表达上调。蛋白质组学分析可以了解外源物质刺激下微生物蛋白质谱图的变化以及蛋白质功能和相互作用，是解析重金属作用下微生物转化关键酶变化的有效手段。Liu 等[89]利用蛋白组学解析了吐温 80 强化鞘脂单胞菌属

(*Sphingomonas* sp.) GY2B 降解菲过程蛋白表达，获得了 23 个高表达蛋白和 19 个低表达蛋白信息。因此，在重金属-CBs 共污染体系中，应用该技术可全面解析 CBs 降解基因、转录信息及酶活性变化规律(图 4)，为补充和完善重金属-有机物共污染水体中 CBs 代谢规律信息，明晰复杂环境介质持续性有毒污染物归趋规律提供理论支撑。

(2) 不仅限于单一重金属对微生物降解 CBs 的影响特性研究，而要扩展研究多类重金属混合作用下 CBs 的微生物降解机理，以及不同重金属间的协同、拮抗、加和等作用机制。在实际污染场地，多种重金属并存的复合污染更为普遍，李晓曼等[90]分析了上海市 3 类典型工业用地土壤和地下水中有毒有害 6 种重金属的污染程度，发现 3 类工业用地 30 个潜在污染区域土壤和地下水均受到重金属污染，Cd、Cr、Pb、Hg 和 Ni 在表层土壤中存在明显累积，As、Cr、Pb 和 Ni 在地下水中存在明显累积，重金属 Cr、Pb 和 Ni 存在明显的水土复合污染现象。多种重金属相互作用下对微生物转化 CBs 的影响并非单一重金属作用的简单加和，其相互作用机制会更为复杂，再加上外界环境中 CBs 种类繁多，对复合污染的响应存在差异性，因此，扩展重金属复合污染的研究深度与范围，将更全面系统的解析重金属对 CBs 生物转化的机理。

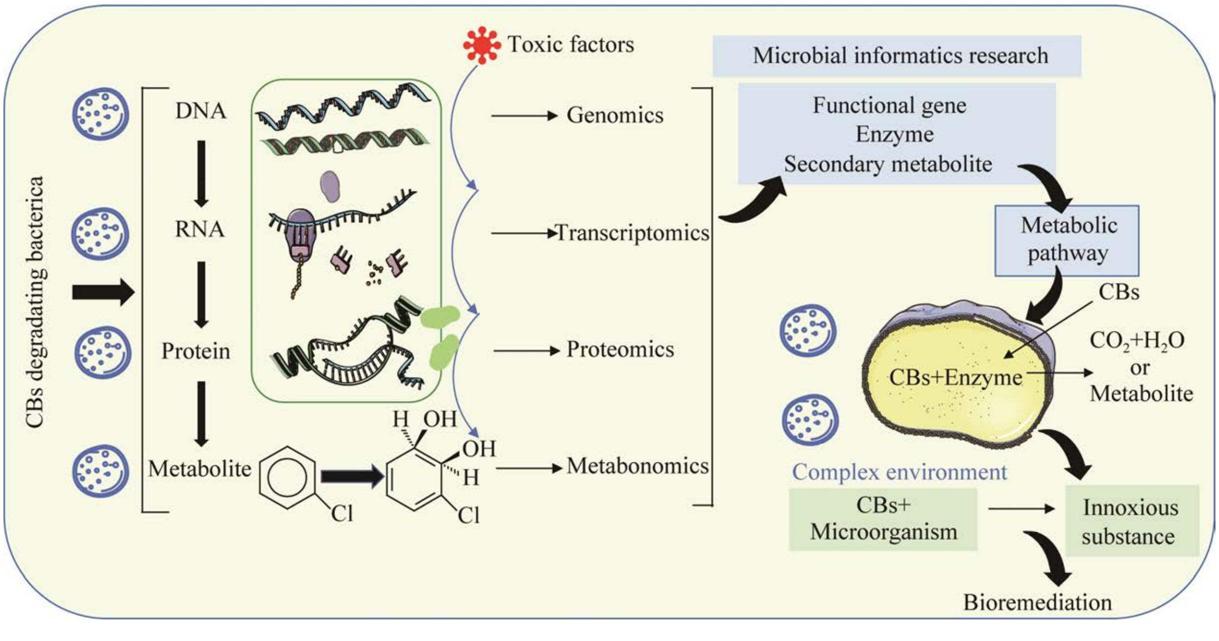

图 4　多组学技术解析有毒物质对微生物影响的分子机制

Figure 4　Multi-omit techniques analyzes the molecular mechanism of the effect of toxic substances on microorganisms. By combining genomics, transcriptomics, proteomics, and metabolomics, the analysis of the DNA, RNA, proteins, and metabolites of functional microorganisms under the influence of toxic factors reveals the composition of functional genomes, differences in gene expression, secondary metabolites and their metabolic pathways, ultimately elucidating the transformation pathways of CBs in complex environments.

(3) 基于重金属和有机物共污染的复杂性，以及传统检测污染物方法的局限性，可考虑利用人工神经网络-深度学习法，结合传统测定污染物的方法预测该类污染归趋，以期为重金属作用下 CBs 生物降解机理的探究提供理论基础。曹文琪[91]将目前常用于数据预测的最优人工神经网络与最优群智能优化算法深度结合，有效预测了土壤重金属含量。因此，在重金属-CBs 共污染体系中应用该技术可以更有效的明晰重金属作用下的生物转化机制。

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