



基于电活性微生物的芳香烃类污染物转化机制研究进展

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摘要: 芳香烃类化合物(aromatic hydrocarbon compounds)是一类基于苯环结构的有机物, 广泛分布在自然环境中, 难以自然降解、易被生物积累, 且有很大的环境危害性。生物法是有机化合物转化降解的主流工艺, 而电活性微生物(electroactive microorganisms, EAM)因其独特的胞外电子传递(extracellular electron transfer, EET)能力和生理代谢模式在芳香烃类化合物污染修复领域具有巨大的应用潜力。电活性微生物可以通过还原脱卤、脱硝与氧化开环过程相结合的方式, 最终实现芳香烃类污染物的降解矿化。本文重点综述了电活性微生物降解芳香烃类污染物过程中主要还原/氧化反应机理, 归纳了电活性微生物高效还原脱卤、脱硝的关键酶活、代谢途径及转化机理, 分析了不同含氧条件下电活性微生物开环方式及降解代谢途径, 并通过调控微生物胞外聚合物与添加导电材料等途径来提升电活性微生物的胞外电子传递过程, 总结了电极电位、电极材料、电解液性质及温度等环境因子对芳香烃类化合物降解的影响, 探讨了芳香烃类污染物的强化生物降解策略的可行性。最后, 展望了电活性微生物降解技术相关领域未来潜在的研究方向, 以期为加快生物电化学系统的工程化应用提供理论和技术参考。

关键词: 电活性微生物; 胞外电子传递; 转化机制; 芳香烃类污染物

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Transformation mechanism of aromatic hydrocarbon pollutants based on electroactive microorganisms

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Abstract: Aromatic hydrocarbons, a class of organic compounds with one or more benzene rings, are ubiquitous in the natural environment. They are difficult to be degraded naturally and thus easy to be bioaccumulated, posing a huge threat to the environment. Biological degradation seems to be the mainstream method for the transformation of organic compounds, and electroactive microorganisms have great potential in the removal of aromatic hydrocarbons because of their unique extracellular electron transport ability and physiological metabolism mode. They can finally achieve the degradation and mineralization of aromatic hydrocarbon pollutants by combining reductive dehalogenation and denitrification and oxidative ring cleavage. In this paper, we focused on the main reduction/oxidation reaction mechanisms in the degradation of aromatic hydrocarbon pollutants by electroactive microorganisms, summarized the key enzyme activities, metabolic pathways, and transformation mechanism of electroactive microorganisms in the reductive dehalogenation and denitrification, analyzed the ring cleavage modes and metabolic pathways of electroactive microorganisms under different oxygen-containing conditions, and improved the extracellular electron transport process of the microorganisms by regulating microbial extracellular polymers and adding conductive materials. Moreover, we discussed the influence of electrode potential, electrode materials, and environmental factors such as electrolyte properties and temperature on the degradation of aromatic hydrocarbon compounds, and the feasibility of enhanced biodegradation strategies for aromatic hydrocarbon pollutants. Finally, in order to provide theoretical and technical reference for accelerating the engineering application of bioelectrochemical systems, we summed up the directions of future potential research in the related fields of electroactive microbial degradation technology.

Keywords: electroactive microorganism; extracellular electron transport; transformation mechanism; aromatic hydrocarbon pollutant

芳香烃类化合物 (aromatic hydrocarbon compounds) 是一类具有苯环结构的有机物。根据其化学结构的不同, 芳烃类污染物分为单环芳烃、多环芳烃和稠环芳烃 3 类, 而根据其官能团的不同, 常见的芳香烃类污染物又分为硝基芳香烃以及卤代芳香烃等。由于苯环共轭 π

电子云的存在, 芳香烃类污染物往往结构稳定且不易分解, 一旦进入环境, 会对生态环境造成严重污染, 甚至威胁到动植物及人群健康。我国水环境中 68 种优先控制污染物黑名单中, 芳香烃类污染物就占 44 种^[1]。

目前, 芳香烃类污染物的修复方法分为物

理法、化学法和生物法。吸附和萃取等物理法一般局限于污染物的相转移，且使用后的吸附剂或溶剂易产生二次污染^[2]，而高级氧化等化学法处理芳香烃类污染物存在修复成本高、操作难度大等问题^[3]。生物法具有运行成本低和二次污染小等优点，是芳香烃类污染物环境修复的首选^[4]。传统生物修复技术是通过外部添加电子供体(碳源、氢气等)或电子受体(氧气、硫酸盐等)实现污染物的氧化-还原转化。但由于电子供体/受体投加的匹配性和可及性，该法在实际修复应用中仍存在难以精准高效等瓶颈^[5]。

生物电化学系统(bioelectrochemical system, BES)是一种以电活性微生物(electroactive microorganism, EAM)为核心，能通过低电压输出电流，精确实时输出/摄入电子^[5]，实现污染物还原/氧化转化的生物修复技术^[6]。EAM根据胞外电子传递(extracellular electron transfer, EET)方向，可分为产电菌和嗜电菌^[7]。产电菌可利用芳香烃类污染物作为电子供体，在输出电子的同时实现污染物的矿化^[8]，而嗜电菌则是从固体阴极上摄入电子用于硝基还原或者卤素脱除。一般认为，EAM可利用细胞外膜上的细胞色素 *c* 或纳米导线结构与外界进行直接物理接触^[9]，或通过电子传递介质间接将电子由胞内传递给胞外末端电子受体，有效促进污染物的催化降解，因此，在芳香烃类污染物的修复降解中发挥着越来越重要的作用^[10]。EAM和电极之间电子传递作用使得其对芳香烃类污染物具有独特的降解效果^[11]。可见，集成EAM的电子输出/摄入能力有望实现芳香烃类污染物还原/氧化耦合的低碳绿色修复。

本文就EAM对芳香烃类污染物转化过程中的脱卤、脱硝、开环等关键代谢环节的作用机理展开综述，并从改善EET进程和调控环境因子方面总结了芳香烃类污染物强化降解的研

究进展，最后，展望了EAM降解技术相关领域未来潜在的研究方向，以期为加快生物电化学系统的工程化应用提供理论和技术参考。

1 芳香烃类污染物的还原解毒

卤代芳香烃和硝基芳香烃是2类典型的难降解芳香烃类污染物，大多具有“三致”效应。卤原子和硝基对电子的强吸引力显著降低了苯环的电子云密度，导致其生物降解难度增加，且易形成毒性中间产物。此外，含卤或含硝的化合物往往会抑制微生物活性，从而降低生物降解速率。因此，高效脱卤、脱硝是提高芳香烃类污染物生物降解效率的关键。

还原脱卤是实现卤代芳烃类化合物生物降解的重要手段。学术界认为好氧微生物因缺少脱卤呼吸型还原酶而难以实现卤代芳香烃的好氧降解^[12]，而在氧化还原电位较低的厌氧条件下，卤代芳烃类化合物则表现出较好的生物降解性。据报道，EAM(如 *Geobacter*、*Sulfurospirillum* 和 *Desulfitobacterium*)可通过EET过程进行还原脱卤^[13]。孙世英等^[14]对五氯苯酚(pentachlorophenol, PCP)降解过程的研究表明，EAM首先从H₂中获得电子，随后从邻位到对位再到间位依次将苯环上的氯脱除，最终生成苯酚。Anotai等^[15]用生物发光技术评估PCP还原过程毒性变化，发现PCP转化为氯化程度较低的同系物或苯酚从而实现解毒。顾思文^[16]发现假单胞菌属(*Pseudomonas* sp.)可以利用甲酸盐、乳酸钠等作为电子供体实现2,4,6-三氯酚(2,4,6-trichlorophenol, TCP)的脱氯还原。Souza等^[17]发现TCP由不同降解途径主导，形成不同副产物的残留毒性不同。Jugder等^[18]提到甲萘醌作为电子载体可以吸收电子并参与跨膜转运过程。综上，可以推测在电子传递过程中，脱氢酶可利用电子供体H₂和甲酸盐等获取电子^[19]，

产生的电子以甲萘醌作为电子载体在电子传递链中进行转移, 最终输送到还原脱卤酶^[20], 催化卤素从卤代有机物中脱除^[16], 且脱卤后的芳烃类化合物生物毒性都会不同程度地降低。

由于纯菌培养困难且纯种的 EAM 脱卤效率低^[21], 因此, 脱卤研究更侧重于生物阴极系统中的混合 EAM 群落^[22]。Aulenta 等^[23]通过实验表明, 与纯菌有限的脱卤性能不同, 混菌可以在几乎相同的条件下实现卤代有机化合物的完全去除, 并推测机理是由于 EAM 间的协同作用^[21]。Chau 等^[24]在研究六氯苯还原脱卤过程中发现, 产甲烷菌的代谢物类胡萝卜素可作为其他脱卤微生物的营养底物, 维持它们的生长、繁殖和新陈代谢, 且一些共底物微生物也可通过消耗抑制性化合物来提高 EAM 的脱卤效率。Li 等^[25]人工构建了 EAM 群落并用于受污染的地下水处理, 实现了 35 d 内 2,4,6-三溴苯酚(2,4,6-tribromophenol, 2,4,6-TBP)的完全厌氧矿化。Yu 等^[26]用 *Geobacter* 与 *Ignavibacterium* 等多种 EAM 共存的反应器对多氯联苯进行厌氧脱氯, 最终转化率达 82%。综上, 推测多种 EAM 协同处理卤代芳烃类污染物效果优良的主要原因为: (1) 不同 EAM 对卤代芳烃类化合物可能具有不同的脱卤代谢途径, 混合菌群带来的脱除效果具有叠加协同效应; (2) 菌群中某些菌种能够利用一些中间代谢产物作为其生长的碳源, 并且可解除中间代谢产物对其他菌种的毒性或抑制作用^[21]。

此外, EAM 在硝基芳烃类化合物(nitro-aromatic compounds, NACs)的高效生物还原方面也具有巨大潜力^[27]。*G. metallireducen* 可在细胞外快速将硝基苯还原为苯胺^[28]。Cabrera 等^[29]分离出一种新的假单胞菌物种, 可在 48 h 内实现 2,4,6-三硝基甲苯(TNT)的完全脱硝转化, 大大降低毒性^[30]。Yin 等^[31]对恶臭假单胞菌降解

4-氯硝基苯过程进行基因特征分析, NACs 经过 EAM 中的硝基还原酶催化生成相应的羟胺芳香化合物, 再由变位酶作用生成开环底物邻氨基苯酚; Wang 等^[32]证明 *Shewanella* 降解 4-硝基甲苯过程, 是硝基经硝基还原酶作用还原成羟胺芳香化合物, 随后由羟胺裂解酶作用水解脱氨基, 形成二羟基芳香化合物进入开环途径。

EAM 还原 NACs 的途径取决于污染物本身性质, 包括范德华体积、极性和分子量等^[33]。范德华体积是还原机理转变的主要因素, 而极化率和分子量也在一定程度上决定了还原机理的选择, 但具体的影响机制报道较少。一种可能的解释是上述因素可以改变 NACs 的性质(如增加分子尺寸和疏水性), 从而导致还原机理的改变^[32]。如硝基芳烃类化合物分子的极性不同, 不仅间接影响 EAM 的还原途径, 还会直接影响其还原发生场所。对于强极性 NACs, 由于较难进入细胞膜, EAM 往往采用胞外还原为主^[34]; 而对于弱极性 NACs, 往往胞内和胞外还原共存。Liu 等^[33]发现 EAM 可在细胞外降解 2,6-二硝基甲苯。而对于小分子污染物(如硝基苯等)的还原, 细胞质中的硝基还原酶和细胞外膜上的蛋白质都参与其中。此外, 有研究表明含较多硝基的 NAC 还原速度更快, 而硝基的位置对还原率几乎没有影响^[32]。笔者认为这可能是因为更多的硝基将导致 NAC 中氮原子更强的电负性, 而氮原子的电负性越强, 还原反应越容易进行。综上所述, 目前对于 NACs 的范德华体积和分子量等具体如何影响 EAM 还原脱硝尚不清楚, 未来深入了解具有不同范德华体积与分子量污染物的 NACs 还原机制对于理解 EAM 的环境污染修复具有重要价值。

2 芳香烃类污染物的氧化降解

苯环是芳香烃类污染物的共性分子结构,

因此,芳香烃类污染物降解的关键步骤是克服稳定环结构的共振能量,故其一般较难开环矿化。前期研究表明,降解芳香烃类污染物的 EAM 主要分布在假单胞菌属(*Pseudomonas*)^[35]、反硝化菌属(*Denitrifying*)^[36]、产甲烷菌属(*Methanogenus*)^[37]、地杆菌属(*Geobacter*)和希瓦氏菌属(*Shewanella*)^[38]等。如 *Geobacter metallireducens* 可降解苯^[39], *Pseudomonas putida* 能高效矿化多环芳烃^[40]等,本文将具有代表性的芳香烃类化合物电活性降解菌及开环底物归纳于表 1 中。

适量氧气可以提高芳烃类污染物的氧化降解速率。Shen 等^[41]发现,存在空气条件下, BES 对对氟硝基苯矿化效率可达到(72.99±5.68)%,而纯氮气与纯氧气条件下降解效率仅为(27.63±1.44)%与(44.76±2.95)%,这是由于对氟硝基苯矿化过程需要耦合还原-氧化协同代谢机制才能实现污染物的最终矿化,而适量氧气有助于矿化过程进行。Silva 等^[42]发现在 5% 的微氧条件下土壤电活性真菌对萘的降解率可达到 46.5%,而在极低氧区域萘的降解率迅速减

少到 22.1%。Mahendran 等^[43]在 3 个不同溶解氧浓度的初始条件下研究假单胞菌的生长模式及其对苯降解率的影响,结果显示菌株在不同溶解氧条件下能以不同模式生长和降解苯,但有氧条件下苯的降解速率远快于缺氧条件。因此,适量氧气有助于 EAM 对芳烃类污染物的矿化。基于此,掌握不同氧气条件下 EAM 对芳烃类污染物的降解机理对实现工程化应用至关重要。

在有氧条件下,芳香烃类污染物通常在氧气的作用下被 EAM 产生的加氧酶攻击,通过外周途径形成儿茶酚、原儿茶酸等具有富电子羟基取代基的中心中间体^[44]。由于电子很难向环转移,因此,这些中间体不容易被还原,只能通过环裂双加氧酶催化中心环裂解。通常情况下,裂解可以发生在 2 个羟基之间的邻位,或与羟基相邻的间位。学者们已经证实了通过儿茶酚或原儿茶酸代谢芳香烃类污染物的一些途径^[45]。然而,当氧气浓度较低或者不太稳定时,芳环的裂解遵循着另一种适应机制。苯甲酰辅酶 A 或苯乙酰辅酶 A 等活性中间体被重排,然

表 1 常见芳香烃类化合物电活性降解菌及开环底物

Table 1 Common aromatic hydrocarbon compounds electroactive degradation bacteria and ring-cleavage substrates

Substrates	Strains	Ring-cleavage substrates	References
Nitrobenzene	<i>Shewanella putrefaciens</i> CN32	2-aminophenol	[53]
2-chloronitrobenzene	<i>Pseudomonas stutzeri</i> ZWLR2-1	3-chlorocatechol	[54]
4-chloronitrobenzene	<i>Pseudomonas putida</i> ZWL73	4-chloro-2-aminophenol	[55]
3-nitrophenol	<i>Pseudomonas</i> sp. B2	Hydroxyquinol	[56]
4-nitrophenol	<i>Bacillus sphaericus</i> JS905	Hydroxyquinol	[57]
Chlorinated phenols pentachlorophenol	<i>Geobacter metallireducens</i> GS-15	Catechol	[58]
2,4,6-tribromophenol	<i>Bacillus</i> sp. GZT	Catechol	[59]
2-nitrobenzoate	<i>Shewanella oneidensis</i> MR-1	Catechol	[60]
3-nitrobenzoate	<i>Pseudomonas</i> sp. JS51	Protocatechuate	[61]
4-nitrobenzoate	<i>Pseudomonas putida</i> TW3	Protocatechuate	[62]
Polychlorinated biphenyls	<i>Shewanella oneidensis</i> MR-1	Catechol	[63]
Naphthalene	<i>Pseudomonas putida</i> BS3701	Benzoyl-CoA	[64]

后通过水解作用使环断裂。此过程所需的关键酶是 I 类二铁蛋白族的单加氧酶, 如细菌多组分单加氧酶^[46]。苯甲酰辅酶 A 还原可以由 I 类苯甲酰辅酶 A 还原酶催化的 ATP 水解来驱动, 而后, 非芳香族二烯酰辅酶 A 产物被苯甲酰辅酶 A 降解途径的酶进一步降解。该途径不同于需氧苯甲酰辅酶 A 氧化途径, 涉及一系列修饰的 β -氧化反应、环的水解裂解和脱羧步骤。使用此方法的电活性菌大多为兼性厌氧菌, 例如 Austin 等^[47]证明 *Rhodospseudomonas palustris* 可代谢甲氧基化芳烃、芳香族酰胺等多种芳香族底物, Mechichi 等^[48]发现 *Thauera aromatica* 多个成员菌株可降解芳香烃类污染物。

在无氧条件下, 亚硫酸铁与零价铁(常见的还有还原型铁氧还蛋白)作为还原剂与芳香烃类污染物作用, 形成具有吸电子效应取代基的不同中心中间体, 促进电子向环转移。芳香烃类污染物厌氧降解中最常见的中间产物同样为苯甲酰辅酶 A, 其中羧基硫酸酯基团为吸电子取代基。EAM 分泌的芳构化还原酶作用于苯甲酰辅酶 A 可将其还原为环状共轭化合物环己烷-1,5-二烯-1-羧基辅酶 A。除苯甲酰辅酶 A 外, 其他中间产物如 3-羟基苯甲酰辅酶 A、4-甲基苯甲酰辅酶 A 和 3-甲基苯甲酰辅酶 A 也可通过还原酶还原, 过程类似于苯甲酰辅酶 A^[49]。对于那些在间位有 2 个或 2 个以上羟基的中间产物, 羟基会使环极化, 非芳香性的中间相结构导致其也很容易被还原^[50]。Kleemann 等^[51]使用厌氧萘分解培养物(N49)在厌氧条件下将萘完全氧化成 CO_2 , 该培养物还能够在 1-甲基萘、2-萘甲酸等芳烃类化合物上生长。基因序列分析显示, 培养物的微生物群落由一种细菌微生物主导, 该群落与另一组铁还原、苯降解富集培养物中的主要生物体密切相关, 最终被证实为是一种罕见的电活性革兰氏阳性菌(99% 16S

rRNA 基因序列相似性)^[52]。

3 芳香烃类污染物修复的强化调控

电活性微生物可以通过还原脱卤脱硝与氧化开环过程相结合的方式, 最终实现芳香烃类污染物的降解矿化(图 1)。然而如何进一步提高修复效率, 满足工程化应用需求, 则是当前电活性微生物修复芳香烃类污染物的研究重点和方向。本节通过已有文献报道, 归纳总结了通过 EET 强化和环境因子调控等方式强化芳香烃类污染物修复的研究进展。

3.1 EET 强化

通过改善 EET 进程来强化芳香烃类污染物修复的途径大致可分为通过微生物胞外聚合物(extracellular polymeric substances, EPS)调控与添加导电材料 2 种强化途径。

EPS 在 EET 过程中起着至关重要的作用。EPS 中的细胞色素 *c* 和核黄素是负责跨膜和跨细胞外基质电子转移的重要电子穿梭体^[65]。Schwarzenbach 等^[66]研究了细胞色素 *c* 的辅基存在对单取代硝基苯和硝基酚还原反应动力学的影响, 确定了细胞色素 *c* 在硝基苯还原过程中的电子传递能力。EET 过程的顺利进行必须要 EPS 充当电子介质组分的协助^[67], 电子介质的作用机制是增强还原型烟酰胺腺嘌呤二核苷酸与酶之间的电子传递, 而芳香烃类污染物降解的增强与电子介质的分泌有关^[68]。Amézquita-García 等^[69]将外生电子介质固定在活性炭纤维上, 显著提升了硝基苯酚向氨基苯酚的转化。电子介质可能还具有物种特异性, 不同电子介质的电子传递效率不同, 从而影响生物电化学和污染物降解过程。除此之外, 腐殖质(humic substances, HS)对于 EPS 的生物降解性、吸附能力和电子传递能力具有较大影响。HS 中醌的

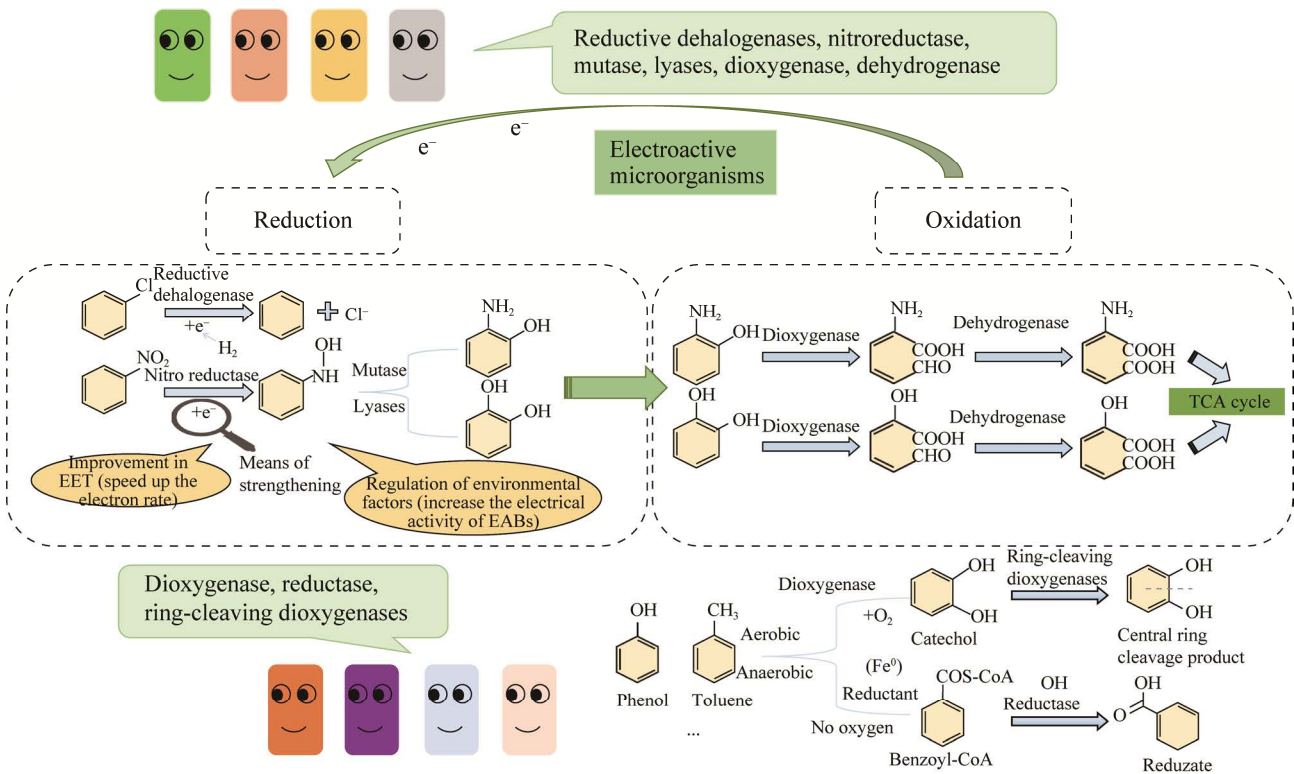


图 1 电活性微生物降解芳香烃类污染物的机制与强化途径^[19,31,44,49,71,82]

Figure 1 Mechanism and enhancement pathway of degradation of aromatic hydrocarbon contaminants by electroactive microorganisms^[19,31,44,49,71,82]. This figure depicts the key degradation and metabolic pathways of aromatic hydrocarbon compounds based on the action of electroactive microorganisms, such as dehalogenation, denitrification, and ring cleavage. Electroactive microorganisms accelerate the reduction/oxidation process of halogenated/nitro-substituted aromatic hydrocarbon compounds by regulating environmental factors and enhancing extracellular electron transport, and finally convert pollutants into CO₂ and H₂O through the tricarboxylic acid cycle (TCA cycle), and the electrons lost by oxidation cleavage can also be transferred for the reducing dehalogenation/denitrification process.

氧化还原部分可增强远距离电子转移进而协助 EET 加速代谢活动，因而其对于芳香烃类污染物的生物降解具有重要作用。有研究表明，将 HS 固化在石墨电极上，通过生物电化学手段可以显著提高五氯苯酚的降解效率^[70]。

导电材料或氧化还原介质可改善 EET 进程，从而加速有机污染物的 EAM 降解^[71]。例如，含铁生物炭促进了 EET 对芳香烃类化合物的还原。Yu 等^[72]发现生物炭显著增强了从 *Geobacter sulfurreducens* 到五氯苯酚的电子转移，从而促进了五氯苯酚还原，其最大降解效

率可达到 85.1%^[73]。通常认为，吸附在生物炭上的有机污染物对化学和生物转化不起作用。然而，最新研究表明，生物炭可以加速污染物的化学催化转化^[74]。生物炭表面含氧官能团是其催化反应活性中心，且芳香烃类污染物化学还原的速率常数随着炭黑表面上活性含氧官能团的数量呈线性增加^[75]。生物炭中的凝聚芳香结构区可将电子从电子供体直接转移到芳烃类污染物，其介导的电子转移过程在生物系统中引起了广泛关注^[76]。相关研究发现，生物炭还可以起到电子穿梭体的作用，促进电子从

Shewanella oneidensis MR-1 转移到 Fe (III) 矿物, 进而提高 Fe (III) 的微生物还原速率和还原程度。Tong 等^[77]证明, 在水稻土中添加生物炭可提高 PCP 的微生物转化率, 在没有生物炭的情况下培养 PCP 15 d 后转化百分比为 12.5%, 而含 1% 生物炭的土壤中 PCP 15 d 转化的五氯苯酚达到 60.7%。此外, 在生物炭用量为 2%、5% 和 10% 的 3 个高剂量条件下, 加入反应器的 PCP 在培养 15 d 后被完全转化。这是由于生物炭可促进土壤中 EAM 的生长和代谢速率, 进而改善 EET 进程, 显著加速了电子从细胞向 PCP 的转移, 从而增强了还原脱氯。上述工作表明, 生物炭是芳烃类污染物脱卤的有效电子媒介, 并且生物炭的缩聚芳香结构在电子转移的过程中起着重要作用^[78]。

除此之外, 研究人员还通过添加石墨烯或碳纳米管等纳米材料来改善 NACs 的生物还原。林小秋^[79]发现纳米钨铁和生物电化学阳极可以显著强化四溴双酚 A 的 EAM 降解。顾思文^[16]还通过制备电气石复合功能生物载体和铁碳微电极复合功能生物载体发现, 2 种复合功能生物载体均可强化 2,4,6-三氯酚还原。另外, 有研究表明, 部分金属离子可在很大程度上影响细菌活性和 EPS 合成, 进而影响胞外电子传递活性的差异, 最终影响芳香烃类化合物的生物降解。例如, Fe³⁺ 的存在可提高氧化还原酶活性并加速 EET 过程, 进而增强芳香烃类污染物的生物降解^[80]。综上所述, 通过增强的 EET 过程, 很多有机污染物(如酚类、染料和石油烃等) 能够被 EAM 高效降解^[81]。

3.2 环境因子调控强化

改变 BES 阳极或阴极的电位可以调控 EAM 的群落结构, 进而控制污染物的转化。电活性生物膜的富集受外加偏压或微生物自身形成的电场强度调控, 较高的阳极电位或较低的

阴极电位可强化电活性生物膜的形成和电活性还原能力^[82], 从而增强芳烃类污染物的转化。Friman 等^[83]在阳极电位为 +275 mV 至 +700 mV 的情况下使用纯种假单胞菌 (*Pseudomonas putida*) F1 对甲苯进行降解, 发现电流随着阳极电位的增加而增加。Aulenta 等^[84]在阴极电位 -250 mV 至 -750 mV 条件下研究了生物电化学反应器处理有机污染物的性能, 发现污染物的脱卤速度和程度以及对可用电子的竞争高度依赖于设定的阴极电位, 在阴极电位低于 -450 mV 的情况下可实现较高污染物的脱氯速率。通过调整特定的电极电位可以富集 EAM, 一定厚度的阳极生物膜可以实现高库仑效率和功率输出。王鑫^[85]研究了污水中电活性生物膜的成膜过程, 发现 *Geobacter* 含量随电场强度增大而升高。因此, 优化电极电位是未来 EAM 强化修复芳香烃类污染物的重要研究方向。

对电极而言, 导电性、表面积、电化学稳定性、孔隙率、毒性和生物相容性等一些固有特征也会影响其与 EAM 的相互作用^[86], 进而影响芳烃类污染物的转化。尤其是导电性和生物相容性对于 EAM 的粘附和后续生长以及通过电极材料的电子转移或储存至关重要^[87]。葛志鹏^[88]研究了钛、不锈钢和石墨 3 种不同的阴极材料对卤代硝基苯还原性能的影响, 发现石墨和不锈钢的脱卤效率要显著高于钛电极, 这可能是因为不同电极材料的过电势影响了脱卤效率。电极材料或电极表面改性一直是改善 EAM 与电极相互作用的主要途径, 而此类工作集中在修饰阳极材料及其表面, 主要包括: 使用功能化学物质或聚合物涂层进行表面修饰, 以改善生物相容性和耐腐蚀性^[89]; 使用纳米材料涂层增加表面积, 以促进更多 EAM 的生长, 提高电导率和 EET, 从而提高芳烃类污染物的转化速率^[89]; 提供更多孔径结构或改善孔隙率

以增强传质^[90]；改善活性阳极生物膜形成的表面亲水性^[87]等。Kokulnathan 等^[91]报道了氧化石墨烯/氧化镁纳米复合电极用于水样中硝基苯(NBZ)的电化学分析,发现此电极与其他电极相比显示出了优异的 NBZ 传感性能。运用此电极的反应器可以很好地测定较低浓度的 NBZ,且具有良好的选择性、重复性和稳定性。此外,氧化石墨烯/氧化镁纳米复合电极运用到水样中 NBZ 的定量测定,加标回收率可以达到 99.35%–99.80%之间。Zhang 等^[92]使用碳纳米管和镍纳米线修饰的阴极可以增强其导电性、生物相容性和静电相互作用,从而提高芳烃类污染物的转化率。人工介质(单体、低聚物和聚合物)的使用也是改善阳极和阴极微生物电子转移过程的重要方法之一^[93]。综上所述,材料表面改性或修饰是强化芳烃类污染物降解的又一有效途径。

操作温度通过对微生物代谢反应和动力学的影响,最终会影响电活性微生物的生长和性能^[94]。Zhang 等^[95]发现 BES 系统能提供电活性微生物代谢所需的能量,并促进了具有耐低温性质的 *Pseudomonas* 富集,从而缓解低温对微生物代谢的抑制。而在之后的研究中发现高温 BES 具有更优越的芳香烃类化合物去除性能,55 °C 高温 BES 中芳香烃类化合物总有机碳(total organic carbon, TOC)去除率为(91.96±5.70)%,远大于 30 °C 中温 BES 中的(75.83±4.21)%。这可能是因为高温 BES 系统中富集了具备高温催化酶系的特殊功能电活性微生物^[96]。因此,电活性微生物在不同温度下都能在一定程度上强化芳烃类化合物的强化修复。

电解质溶液的 pH 值会影响 EAM 微生物群落的生长、膜电位、质子净产生和消耗量以及细胞内细胞质电化学梯度,最终会影响芳烃类化合物的生物利用性。在阳极生物膜区域中,

由于质子浓度差的原因,局部生物膜 pH 值较低有助于芳香烃污染物的还原解毒。此外,pH 值较低时,可以促进 NADH 的分泌,提高微生物的还原能力^[97],然而过低的 pH 也会影响微生物的活性,从而造成系统崩溃^[98]。大多数微生物在 pH 中性附近活性最佳,但受污染的地方可能会出现过酸或过碱条件,因此,改变 pH 值可能是强化生物修复过程的一种调控方法。

此外,添加乙酸盐、葡萄糖或甲醇等有机底物可以提供电子供体和能源,有助于沉积物中卤代芳烃类污染物的脱卤过程。本课题组发现电子供体的投加有利于电活性微生物还原去除对氟硝基苯,其中投加葡萄糖产生的还原效果优于乙酸钠;而电子受体也在对氟硝基苯脱氟过程中起关键作用,氧气是唯一可用的电子受体,硝酸盐和硫酸盐却无法作为对氟硝基苯氧化的有效电子受体^[99]。因此,投加合适的电子供体/受体可以有效调控芳烃类污染物的矿化。

上述研究表明,环境因子的调控,如适当调整电极电位、改变电极材料和调节 pH 值等对 EAM 降解芳烃类化合物都至关重要。

4 总结与展望

目前,基于 EAM 修复芳香烃类污染物的研究已取得了一定进展。本文针对相关研究进行梳理总结,如探究 EAM 对芳香烃类污染物的还原解毒、氧化开环机制以及改善 EET 进程、调控环境因子的强化策略,但仍有许多未知的调控强化技术以及芳烃类污染物降解机制需进一步探明,以期对未来实际工程化应用建立基础。

(1) 多种 EAM 协同处理卤代芳烃类污染物效果优异,且不同 EAM 对卤代芳烃类化合物可能具有不同的脱卤代谢途径,今后应细化不同 EAM 代谢卤代芳烃类污染物的各阶段途径,探

明代谢中间产物与各 EAB 的相互作用网络, 实现对其降解过程的有效调控;

(2) NACs 分子结构和性质对电活性微生物还原 NACs 过程中电子传递通路和功能酶的影响仍有待系统研究;

(3) NACs 溶解度较小, 大部分的 NACs 以非水相的固体和液体存在于体系中, 微生物能否还原这部分 NACs 有待进一步探讨;

(4) 相较于 EPS 强化手段可控性较低以及环境因子调控技术开发程度不高的特点, 以生物炭为主的材料强化技术可控性较佳且具有良好的实际应用前景, 但现有研究尚未建立生物炭结构与其强化微生物反应活性之间的构效关系, 特别是生物炭的表面官能团、自由基以及大分子骨架结构在生物还原氧化反应中的作用机制仍有待阐明。

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